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Complex molecules in the laboratory and star forming regions

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Complex Molecules in the Laboratory and Star Forming Regions

Proefschrift

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Aan mijn ouders

Front cover: “Stars dancing on ice” made by Wouter Bisschop.

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Chapter 1

Introduction

“Chemistry everywhere” (Chemie overal) is one of the most used chemistry books in secondary education. This title is highly appropriate on earth and far beyond. Up to the 1920’s no chemistry was expected to occur in “diffuse molecular clouds”, because of their low densities (~ 100 hydrogen nuclei cm^{-3}) and temperatures of 50 K (-223°C) (Snow & McCall 2006). However, in 1937 the first gas phase molecules CH and CN were detected in space (Swings & Rosenfeld 1937), so “Chemistry everywhere” also includes these environments. Since then the number of detected interstellar species in both the gas phase and the solid state has increased tremendously. As of August 2007 there are 149 known interstellar species¹ and several new ones are detected each year. Some of those are common on Earth like H_2O and CO_2 (Cheung et al. 1969). Others contain very long chains of carbon-atoms, like C_6H_2 (Cernicharo et al. 2001). Furthermore, “complex organics”² such as CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ and CH_3OCHO are detected prominently in warm gas phase regions (e.g., Ball et al. 1970; Zuckerman et al. 1975). Even positive ions, such as N_2H^+ and HCO^+ (Turner 1974; Green et al. 1974; Buhl & Snyder 1970), and very recently the negative ions C_6H^- , C_4H^- and C_8H^- (e.g., McCarthy et al. 2006), have been detected in space.

Another interesting fact is that molecules are not only detected in the gas phase, but also in the solid state frozen out onto interstellar dust particles. H_2O was the first molecule to be detected in “interstellar ices” by Gillett & Forrest (1973) and a number of other solid state species such as CO_2 , CO , CH_4 and HCOOH have been observed as well (see e.g., Gibb et al. 2004, for an overview). The tiny dust grains with diameters of $\sim 0.1 \mu\text{m}$ consist mainly of heavier atoms such as Si (silicon) and Fe (iron) and are detected through their infrared absorption. It is not clear what the exact composition of amorphous interstellar dust is, but the infrared absorption features toward star forming regions point to olivine and pyroxene silicates, amorphous carbonaceous material, poly-cyclic aromatic hydrocarbons (PAHs) and potentially even small diamonds (Draine 2003). This plethora of species requires a scientific discipline that studies the formation and behavior of molecules under exotic conditions and the importance of chemistry on astrophysical processes. This discipline is known as “astrochemistry”.

¹ http://www.astrochymist.org/astrochymist_ism.html

² “Complex organics” are organic molecules consisting of more than 4 atoms. They are thus complex from an astronomical, but not from a chemical viewpoint.

1.1 The cycle of gas and dust

In astrochemistry the evolution of gas and dust can be presented in a cyclic fashion (see Fig. 1.1 and for an overview of the physical and chemical processes of star formation see Evans 1999 or van Dishoeck 2004). Figure 1.1a shows that much of the interstellar material is present in clumps with relatively high densities. This material collapses, due to its own gravity or external forces (Fig 1.1b). As the star formation process continues, material accretes through a circumstellar disk and no longer directly from the surrounding envelope. At the same time outflows from the poles expel material from the protostellar system and sweep up the surrounding cloud (Fig. 1.1c). Eventually both the envelope and the circumstellar disk are dispersed and a solar system with planets, formed from the disk, emerges (Fig. 1.1d). The cycle of star formation will start over after the star dies and expels much of its material into space (Fig. 1.1e). Matter is not perfectly recycled in this system, because stars will continually enrich the interstellar medium with heavier atoms due to the process of nuclear fusion in their center. Furthermore, when stars die they leave very compact objects behind, e.g. neutron stars or even black holes in the case of the most massive stars. Indeed, the above scenario applies primarily to the formation of single isolated low-mass stars. The formation of high-mass stars is much less understood, although it is known to occur in clustered environments. The focus of this thesis is on the chemistry during the embedded phase of star formation (Fig. 1.1b & c), specifically on the origin of widely observed complex organics toward low- and high-mass star forming regions.

1.2 Chemical processes during star formation

1.2.1 Scenario

The physical and chemical processes that occur during star formation are subdivided into four distinct phases that are shortly listed below (see for a review e.g. van der Tak 2005):

- I. At low temperatures and low densities mainly ion-molecule gas phase reactions take place in interstellar clouds.
- II. When the densities increase molecules freeze out onto dust grains and surface reactions of atoms and molecules will occur. Atomic hydrogen is the most mobile species on surface of the ice, triggering hydrogenation reactions. This results in the formation of many hydrogen-rich species.
- III. The ices warm up as a result of the luminosity of the star and are irradiated by UV-light. Atomic hydrogen no longer sticks to the grain-surface and some complex molecules dissociate. Simultaneously, heavier atoms and radicals become mobile and more complex solid state species form, which are less saturated with hydrogen.

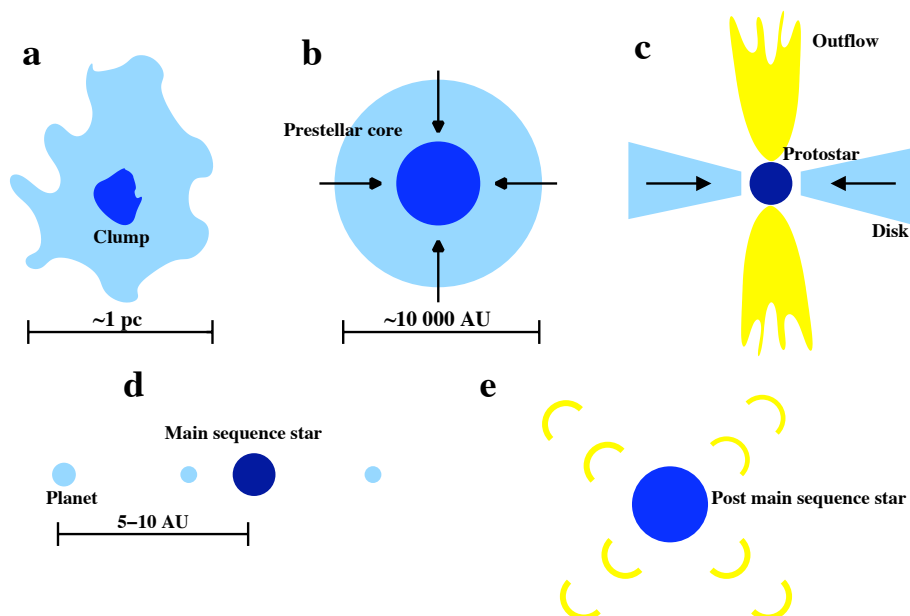


Figure 1.1. Overview of the cycle of star formation and star death with a) interstellar gas and dust located in clumpy material, so-called clouds, b) the material in the clumps collapses onto a central object (prestellar core), c) further accretion occurs through a circumstellar disk and at the same time material is expelled from the protostar through outflows, d) from the disk a new solar system is formed and finally e) the star dies expelling much of its mass into the interstellar medium.

- IV. When the temperature increases above 90 K the ice mantles totally evaporate and “warm gas phase” reactions occur. This leads to the destruction of grain-surface chemistry products and the formation of so-called “second generation” molecules.

In the first phase, gas phase chemical reactions occur in cold dense clouds, although at a very low speed. These are very different from the chemical reactions commonly occurring on our planet. At the low temperatures (10 K) in interstellar clouds, atoms and molecules have very little kinetic energy. Reactions are only possible if there is no energy barrier. In contrast, at the relatively high temperatures encountered on our planet some barriers can be overcome. Furthermore, atmospheric densities on Earth are so high (3×10^{19} molecules cm^{-3}) that collisions between three or four species simultaneously are not uncommon. In interstellar clouds, however, different atoms and molecules may collide with another species only once a month. Only two-body reactions are possible, so no third body is available to absorb the excess bond energy. The result of this is that the molecules that form under these conditions are often very different

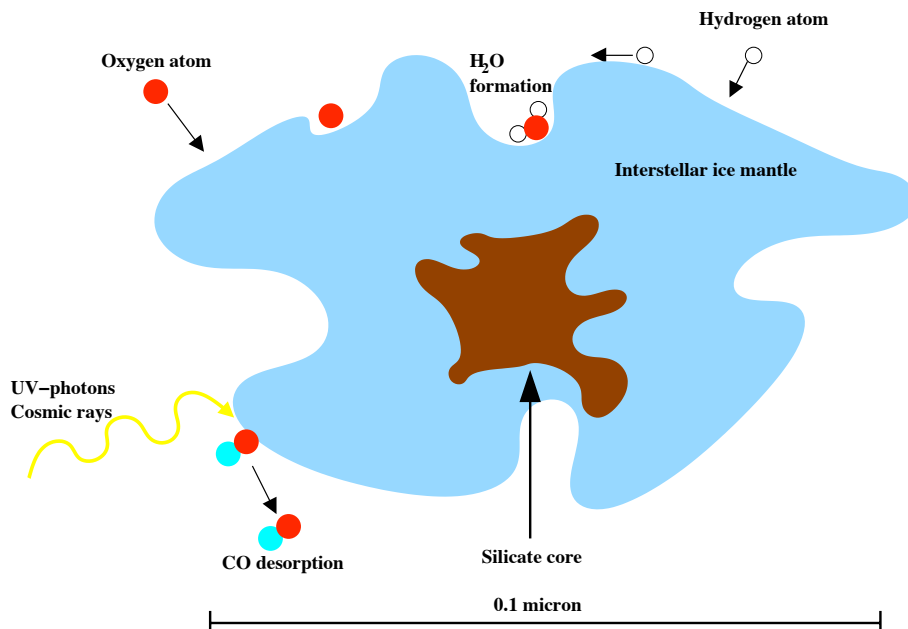


Figure 1.2. Schematic picture of an interstellar dust grain. Oxygen atoms are depicted in dark grey and hydrogen atoms in white. The oxygen atoms accrete onto the surface and then remain in the same site bound to the surface by long range van der Waals forces. Hydrogen atoms on the other hand are able to move over the surface and find the oxygen atoms. This can lead to the formation of H_2O . Solid state molecules can desorb thermally or due to radiation as depicted in the lower left corner for CO.

from those commonly found on Earth.

In the second phase, the densities increase when a cold cloud starts to collapse due to its own gravity or external pressure. The result is that molecules and atoms collide with each other and with microscopic grains more frequently. Since the temperatures are still very low, all molecules and most atoms that collide with a dust grain will stop and stick. Through this mechanism, small icy mantles accrete onto grains (see Fig. 1.2). This leads to an entirely different kind of chemistry, in particular, of heavier atoms with atomic hydrogen. Hydrogen is by far the most mobile species at a temperature of 10 K and can quickly scan the surface of a dust grain (this mechanism is shown in Fig. 1.2 for O and H which react to form H_2O). The result is that mainly hydrogenation reactions, i.e., reactions with H-atoms, occur. This results in the formation of H_2 , CH_4 , H_2O and NH_3 (Tielens & Hagen 1982; Tielens & Charnley 1997). These ices are dominated by H_2O and are so-called polar ices Tielens et al. (1991), although hydrogen-bonded ices would be a better term. Apolar ices dominated by CO, and CO_2 can also form at high densities due to freeze-out of gas phase CO. All

of these species have been detected in ices toward high- and low-mass star forming regions (Ehrenfreund & Schutte 2000; Gibb et al. 2004). Both polar and apolar ices are expected to be amorphous although crystallization may occur at high temperatures. These ices are exposed to interstellar radiation in particular cosmic rays (Léger et al. 1985). This may result in the destruction of some hydrogen-rich species. The resulting radicals cannot travel far through bulk ice, but they can travel far over the surface if they carry excess energy (e.g. for OH radicals see Andersson et al. 2006). Reactions with resulting radical fragments, forming other less hydrogen-rich species, are thus possible. Furthermore, cosmic rays can spot-heat grains, which causes local grain-mantle evaporation as shown in Fig. 1.2 for CO (Hasegawa & Herbst 1993; Herbst & Cuppen 2006). The newly evaporated species can take part in gas phase reactions. Chemistry in the solid state and in the gas phase are thus not separate processes, but interact and influence each other strongly.

In the third phase, the luminosity of the young stellar object increases. Initially, this luminosity will be due to the accretion of gas and dust onto the protostar, but eventually it evolves to become a young star in which nuclear fusion takes place. The gas and dust that has not accreted onto the star will be heated and irradiated by UV-light. At these higher temperatures radical species and heavier atoms become mobile on the surfaces of dust grains and the UV-photons cause some solid-state molecules to dissociate (Garrod & Herbst 2006). This is expected to lead to the formation of more “complex” ice species. Furthermore, some volatile species may desorb from the ices thermally or induced by photons (e.g., Sandford & Allamandola 1988; Collings et al. 2004; Bisschop et al. 2006). Thus the balance between solid state chemistry and gas phase reactions will change.

Not all solid state species evaporate at the same temperature/time due to different binding energy to the ices, but eventually in the fourth phase when the temperature has increased beyond ~ 90 K all species have evaporated initiating high temperature gas phase reactions (e.g., Charnley et al. 1992). This will lead to the destruction of grain-surface products and the formation of new molecules such as $\text{C}_2\text{H}_5\text{CN}$. Part of the solid state and gas phase molecules may be incorporated into a disk which has higher densities than the surrounding envelope. Indeed the molecular content of meteorites and comets is very similar to that of star forming regions (Ehrenfreund & Charnley 2000). It is not yet clear whether meteoritic and cometary species are formed at the earlier stages or whether the chemistry in the protoplanetary disks is just very similar to that in the envelope. In either case these complex species are possibly incorporated into planets to be the first building blocks of prebiotic species.

1.2.2 Open questions

In Table 1.1 the solid state and gas phase abundances are given for the molecules studied in this thesis. Clearly, the solid state abundances for most molecules are much higher than those for the gas phase. However, the detection limit is lower for gas phase species. Furthermore, the abundances of complex molecules

Table 1.1. *Overview of solid state and gas phase abundances in high-mass YSOs.*

	NGC 7538 IRS9 ^a	NGC 6334 IRS1 ^b
	Ice ^c	Gas
H ₂ CO	2×10^{-6}	5×10^{-7}
CH ₃ OH	4×10^{-6}	4×10^{-6}
HCOOH	1×10^{-6}	2×10^{-10}
CH ₂ CO	—	3×10^{-10}
CH ₃ CHO	$< 4 \times 10^{-7}$	$< 5 \times 10^{-11}$
C ₂ H ₅ OH	$< 1 \times 10^{-6}$	8×10^{-8}
OCN ⁻ /HNCO ^d	2×10^{-6}	2×10^{-8}
NH ₂ CHO	—	3×10^{-9}

^aFrom Gibb et al. (2004) except C₂H₅OH which is taken from Boudin et al. (1998). ^bFrom Bisschop et al. (2007c). ^cThe abundances are given with respect to H₂, assuming for the solid state that H₂O has an abundance of 10^{-4} compared to H₂. ^dAssuming that HNCO is the solid state counterpart of OCN⁻.

vary by a few orders of magnitude. These abundances and other observational constraints on complex organics lead to a number of open questions regarding the chemistry of star forming regions:

- ▷ Which molecules form on the surfaces of grains and which after grain-mantle evaporation in the gas phase?
- ▷ What is the structure of interstellar ices and how does it affect the chemistry?
- ▷ How do impinging H-atoms and UV-photons affect the ices? Can complex molecules survive in the ices until they evaporate from the grain-surfaces?
- ▷ How complex are the molecules that are formed, i.e., do amino acids form in space?

In this thesis a number of these questions will be addressed, focusing on low temperature solid state chemistry, ice evaporation, and gas phase species after ice evaporation (see Sect. 1.3 and 1.4). The method used in this thesis is a combination of laboratory experiments in which the interstellar ice environment is simulated as well as submillimeter observations of gas phase molecules after ice evaporation.

1.3 Solid state experiments of astrophysical ice analogues

Molecules can be formed both by reactions with atoms arriving from the gas, or by energetic processing. Here the term “processing” refers to an increase of

the ice temperature, bombardment by cosmic rays or exposure to UV-radiation. So far, very few of the proposed formation routes to complex organics have been studied in the laboratory under controlled conditions. In this section experiments in the “*Raymond and Beverly Sackler Laboratory for Astrophysics*” are presented: i) reactions of molecules with H-atoms in the ices (Sect. 1.3.1, phase 2), ii) the spectroscopy and thermal behavior of pure, layered and mixed ices (Sect. 1.3.2, phase 3) and iii) the desorption, mixing and segregation of ices (Sect. 1.3.3, end of phase 3).

1.3.1 Hydrogenation experiments with SURFRESIDE

Reactions of H-atoms with CO molecules that have accreted from the gas phase onto grains form H_2CO and CH_3OH as shown in laboratory experiments (Watanabe et al. 2004; Hiraoka et al. 2002; Fuchs et al. 2007). In the hydrogenation scheme by Tielens & Charnley (1997) reactions of H-atoms with HCOOH and CH_3CHO are predicted to result in the formation of $\text{CH}_2(\text{OH})_2$ and $\text{C}_2\text{H}_5\text{OH}$, respectively. HCOOH has previously been detected in ices of star forming regions with abundances of a few percent and CH_3CHO is tentatively detected as well (Schutte et al. 1997; Keane et al. 2001). The importance of hydrogenation reactions for CO_2 , HCOOH and CH_3CHO have been studied in this thesis (see Chapter 2).

For these kind of experiments an Ultra High Vacuum (UHV) setup SURFace REaction SIMulation DEvice (SURFRESIDE) is used with pressures of $\sim 10^{-10}$ Torr (see Fig. 1.3). These low pressures are needed because then the main contaminant of the gas phase is H_2 , similar to that in interstellar space, and the pressures are close to those of dense star forming regions (3×10^6 vs. $100 \text{ molecules cm}^{-3}$). Furthermore at most one monolayer of background gas accretes onto interstellar ice analogues during an experiment so that the behavior and reactivity of the ices is not strongly influenced. The substrate is mounted on top of a helium cryostat, which cools it down to ~ 12 K. Additionally, two thermal couples which measure the temperature are connected to the substrate and a heating element regulates the temperature between 10 and 300 K. Gas phase molecules are deposited onto the cold substrate by flowing gas through a deposition tube. Pure ices containing one specific species as well as mixed ices containing multiple different components are grown with thicknesses of a few monolayers up to ~ 100 ML. The ices are monitored by Reflection Absorption Infrared Spectroscopy (RAIRS). In this technique infrared light is shone onto the ice and substrate with an angle. The reflected light is monitored by a detector. All molecular species have specific frequencies for their vibrational transitions and RAIRS is a very sensitive technique that monitors these modes down to sub-monolayer coverages. The H-atoms are produced by thermally dissociating molecular hydrogen, H_2 , and flowing it through a quartz capillary. The ices are exposed to the incoming hydrogen and are continuously monitored with RAIRS. When the hydrogen exposure is terminated the ices are slowly heated ($\sim 2 \text{ K min}^{-1}$) and the gas phase products are detected mass selectively with a mass spectrometer. This technique is called Temperature Pro-

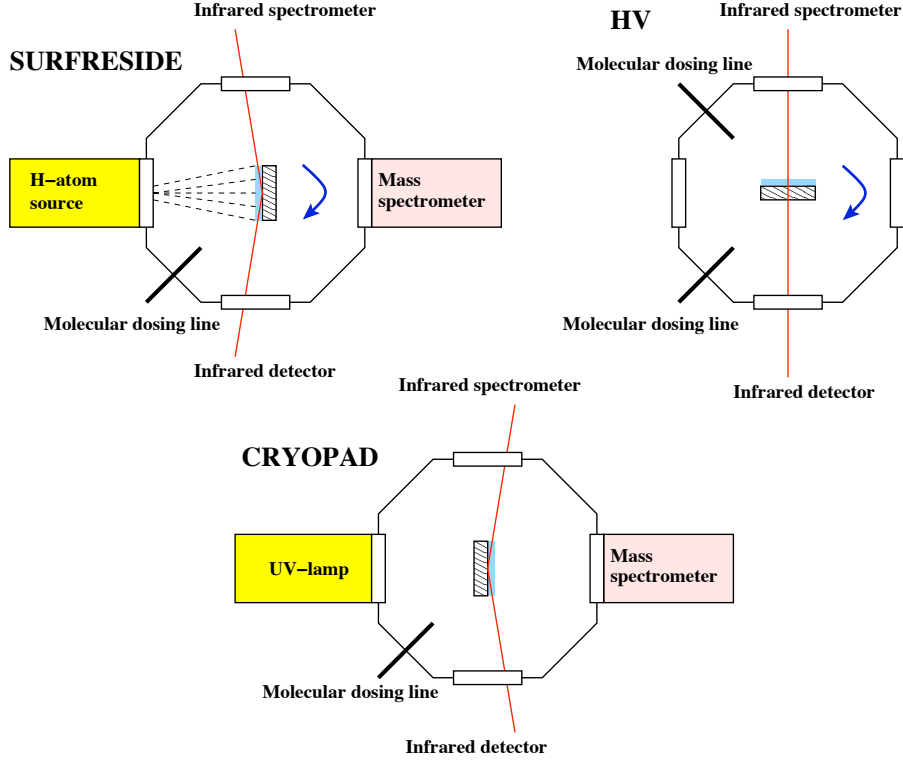


Figure 1.3. Schematic overview of three solid-state experimental setups in the “Raymond and Beverly Sackler Laboratory for Astrophysics” used in this thesis for the research of interstellar ice analogues, the SURFace REaction SIMulation DEvice (SURFRESIDE), the High Vacuum setup (HV) and the CRYOgenic Photoproduct Analysis DEvice (CRYOPAD). In SURFRESIDE the ices are bombarded with H-atoms depicted with dashed lines. The aim of CRYOPAD is to study the interaction of ices with UV-radiation. In this thesis it is only used to study the thermal behavior of ices and hence only the relevant parts of the experiment are shown (see van Broekhuizen 2005, for the complete UV setup). The analysis techniques used for SURFRESIDE and CRYOPAD are Reflection Absorption Infrared Spectroscopy (RAIRS) (the approximate beams are shown and have a small angle (6°) with respect to the ice) as well as Temperature Programmed Desorption (TPD) measured with the mass spectrometer. In the HV setup Fourier Transform Infrared Transmission spectroscopy is used, where the infrared beam travels along the surface normal through the ice. The arrows indicate that the samples can be turned. Experiments with SURFRESIDE are presented in Chapter 2, with the HV experiment in Chapters 3 & 4 and with CRYOPAD in Chapter 5.

grammed Desorption (TPD). In summary, the RAIRS data give time-resolved information about the destruction of the initial ice species and the formation of new products. The TPD data give information on low abundance products as well as supply yields of newly formed species with uncertainties of $\sim 20\%$. The combination of these two techniques is crucial for the understanding of the hydrogenation reactions.

It is important to separate the effects of ice temperature and thickness (Watanabe et al. 2004; Hiraoka et al. 2002; Fuchs et al. 2007, see also Chapter 2). The ice temperature determines how mobile H-atoms are through thermal hopping on the ice surface and thus how quickly they can find a reaction partner. At higher temperatures reaction rates are therefore expected to increase. However, at higher ice temperatures the evaporation rate increases as well. This decreases the time that the atoms spend on the grain-surface. Due to the competition of these two processes there is an optimum temperature for hydrogenation reactions. Ice thickness can also affect production yields, because H-atoms have a certain penetration depth in the ice, which means that not all ice species are accessible for the incoming H-atoms. This effect becomes more pronounced for thicker ices. Furthermore, the reaction rates depend strongly on energy barriers to the entrance channel. Some species such as CO_2 and HCOOH do not react with the cold H-atoms even when the end product is energetically favorable (Chapter 2).

1.3.2 Infrared spectroscopy experiments of ices with the HV set-up

The mid-infrared spectra of interstellar ices contain many absorption features due to molecular vibrational transitions (see Fig. 1.4). The strengths and line shapes of these features depend on the structure, temperature, and composition of the ice, which makes these spectra a powerful tool to study interstellar solid state chemistry. Additionally, ices are expected to have layered morphologies, because of different freeze-out temperatures, i.e., CO and N_2 require temperatures of ~ 15 K for freeze-out, whereas H_2O already freezes out at ≤ 80 K. The presence of layered ices may affect the spectra, because molecules can interact with each other at the interface and potentially mix at higher temperatures.

Two species for which the spectroscopy has been studied in detail in this thesis are CO and HCOOH (see Chapters 3 & 4). CO is one of the most abundant ice species and it is the starting point for the formation of complex molecules in the ice (Tielens & Hagen 1982; Tielens & Charnley 1997). Recently, Pontopidan et al. (2003a) performed a survey of low-mass star forming regions and found that the CO absorption band could be decomposed into three Gaussians with the same frequency and width for all sources. Only the relative intensities varied between the different sources. The question that arises from this analysis is what could cause this similarity between all lines-of-sight. HCOOH has been detected in interstellar ices with abundances of a few percent with respect to H_2O with the Infrared Space Observatory (ISO) (Schutte et al. 1999, 1997) and more recently with the “Spitzer Space Telescope” (Knez et al. 2005, Boogert et

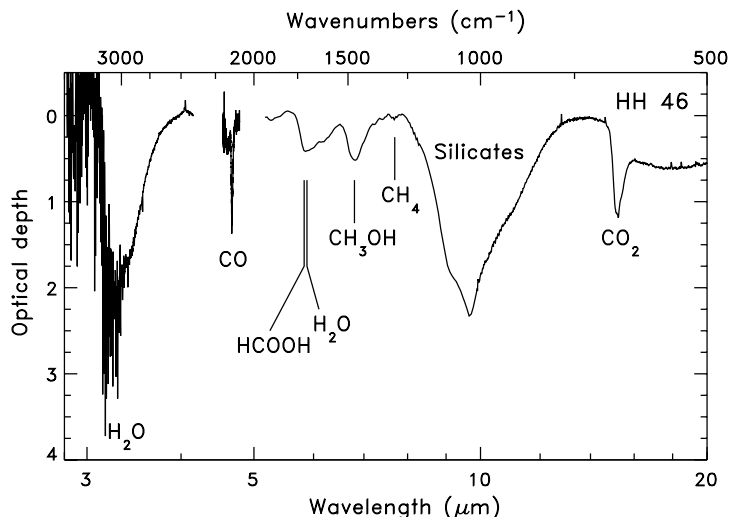


Figure 1.4. Mid-infrared absorption spectrum of the ice composition toward the low-mass star *HH 46* observed with the Very Large Telescope below $5\ \mu\text{m}$ (Moorwood et al. 1999) and with the Spitzer Space Telescope above $5\ \mu\text{m}$ (Boogert et al. 2004).

al. in prep.). Its most intense transitions overlap with those of other molecules, but one of its weaker bands is also commonly detected. The ice composition, however, strongly affects the infrared absorption profiles of these bands for both CO and HCOOH. In Figure 1.5 it can be seen that a tertiary mixture fits much better than any binary mixture (see Chapter 4).

To study the spectroscopy of “simple” organic species the experiment is equipped with a High Vacuum (HV) setup with a transmission infrared spectrometer (depicted in Fig. 1.3). The ice temperatures, purity and thickness are varied systematically. In contrast to the transmission spectra obtained here are directly comparable to observations for minor ice species. A grain-shape model needs to be applied to some major ice constituents to derive the astrophysically relevant spectrum. Such spectroscopic studies are presented in Chapters 3 and 4 for CO and HCOOH for pure, mixed and layered ice morphologies, respectively.

1.3.3 Ice evaporation experiments with CRYOPAD

The aim of the experiments described below is to determine the desorption kinetics of CO and N₂ in pure, mixed and layered ices. These properties affect interstellar chemistry strongly. When ices species evaporate, they instigate warm gas phase reactions. The desorption temperatures vary strongly (Sandford & Allamandola 1993; Collings et al. 2004; Fuchs et al. 2006). Some molecules are more strongly bound on grain surfaces than others, and consequently desorb

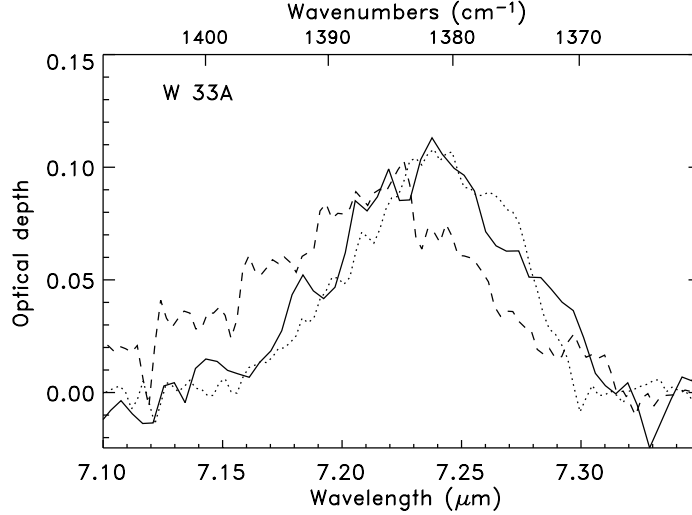


Figure 1.5. The infrared absorption spectrum observed toward the high-mass star forming region W 33A with the Infrared Space Observatory by Gibb et al. (2000b) is indicated with the solid line. Over-plotted on the observation with a dotted line is the laboratory spectrum of the $\text{HCOOH}:\text{H}_2\text{O}:\text{CH}_3\text{OH}$ 6:68:26% mixture, the best-fitting ice mixture for the observed $7.2\ \mu\text{m}$ band and with a dashed line the $\text{HCOOH}:\text{H}_2\text{O}$ 9:91% mixture (Bisschop et al. 2007a, see Chapter 4).

later. In some cases desorption can be delayed because a molecule is trapped by less volatile species. Furthermore, the exact ice thickness and underlying or overlying ice layers are crucial for the desorption temperature. For example, a larger fraction of carbon monoxide ice is trapped when it is present underneath H_2O than when it is deposited as an overlayer (Collings et al. 2003b). In the latter case some CO molecules can migrate into the H_2O ice where they become more strongly bound. In conclusion, desorption kinetics of molecular species are very sensitive to their microscopic environment.

The desorption kinetics of two of the most abundant species CO and N_2 are expected to be similar. N_2 cannot be detected in the solid state and gas phase due to its lack of a dipole moment, but its presence in the gas is deduced from the detection of N_2H^+ . In pre- and protostellar regions N_2H^+ and CO are often found to have anti-coincidences, i.e. their abundances peak at different locations in the cloud (e.g. Bergin et al. 2001; Jørgensen et al. 2004b). This was assumed to be due to the much lower binding energy for N_2 to icy grain surfaces compared to CO. From a chemical perspective this big difference in binding energy is not expected because both species are iso-electronic, i.e. have the same electronic structure. To determine whether the difference in binding energies is indeed large, desorption experiments of pure, layered and mixed ices

of CO and N₂ have been undertaken (Öberg et al. 2005; Fuchs et al. 2006; Bisschop et al. 2006, see also Chapter 5).

The experiments are performed in a setup very similar to that described in Sect. 1.3.1. The CRYOgenic Photoproduct Analysis Device (CRYOPAD) is shown in Fig. 1.3. The difference between CRYOPAD and SURFRESIDE is that the latter is designed to focus on chemical reactions between gas phase atoms and ice species, whereas the first is designed to study photo-induced processes (van Broekhuizen 2005; Öberg et al. 2007). In this thesis, however, CRYOPAD is used to study thermal processes only. Here the ices are deposited at ~ 14 K, and the temperature is subsequently increased by 0.1 K min^{-1} . The ice and gas phase are furthermore continuously monitored with RAIRS and mass spectrometry, respectively. In this manner both the ice structure plus desorption behavior can be accurately determined.

During thermal processing several processes compete. First, evaporation takes place through which molecules desorb from the substrate. Second, when ices are initially frozen out in separate layers, mixing can occur as soon as the species become mobile in the ice. Conversely in mixtures, segregation may also occur. All of these processes may strongly depend on the ice temperature as well as ice thickness.

1.4 Submillimeter observations of complex organics toward star forming regions

The molecular species present in interstellar ices will eventually evaporate from interstellar grains when the temperature increases. As described previously this may not happen simultaneously for all species, but above ~ 90 K almost all ice species will have evaporated (e.g. Viti et al. 2004). Infrared observations of the ices are able to detect solid state species only up to abundances of 10^{-3} with respect to H₂O, because the absorption bands are relatively broad and superposed on a strong continuum. Additionally, the overlap of bands of the same functional groups (i.e., CH, OH, CC, etc) makes it difficult to identify less abundant molecules uniquely. No such problems exist for submillimeter observations of gas phase species. Molecular emission in this frequency range is due to rotational relaxation of molecules. Submillimeter observations are very suitable to detect molecules with low abundances that have evaporated from the ices. Naturally, the grain-surface products will react and can be destroyed after evaporation leading to so-called “second generation” organics. In this section submillimeter observations of both “first” and “second” generation are discussed with the aim to determine chemical relations between complex organics.

1.4.1 Single dish observations of high-mass star forming regions

Many complex organics are thought to be related through successive H-, C-, O- and N-addition to CO (Tielens & Charnley 1997). A few of these reactions have

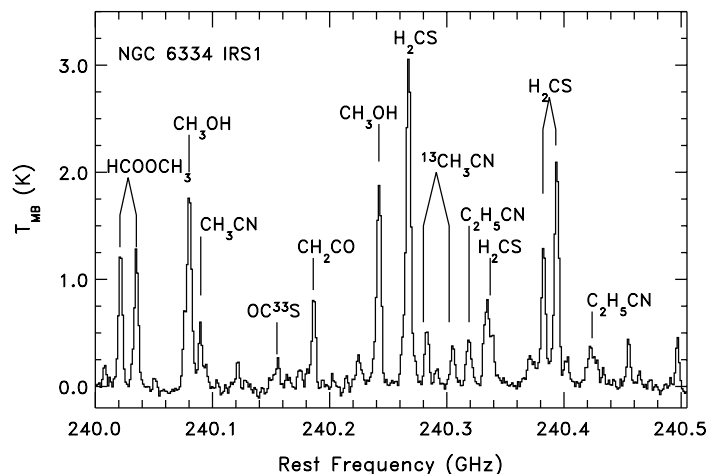


Figure 1.6. Submillimeter emission spectrum observed with the ground-based James Clerk Maxwell Telescope toward the high-mass young stellar object NGC 6334 IRS1 (Bisschop et al. 2007c, see Chapter 6).

been discussed in Sect. 1.3.1 (see Fig. 6.1). Another way to check empirically whether molecular species are related is through a gas phase submillimeter survey targeted at emission lines of “first generation” molecules (Chapter 6). Figure 1.6 shows an example of how rich some submillimeter spectra of star forming regions are. The strengths of the transitions and the exact frequency are different for each molecule, i.e., some molecules have much stronger lines than others. The line intensities can be used to determine the molecular column density (molecules cm^{-2}) and abundances as well as the rotation temperature, if the emission spans a large range of excitation energies. In thermodynamic equilibrium (high densities), the rotation temperature is equal to the kinetic temperature. Some assumptions have to be made for this kind of analysis, for example that the emission is optically thin and that it arises from a region with a single temperature only. Even if these conditions are not always fulfilled, a good indication of the temperature of the gas can still be obtained.

1.4.2 Interferometric observations of a low-mass star forming region

Additional information about the exact location and relation between molecules is obtained through interferometry. Chandler et al. (2005), for example, show that toward the low-mass protostar IRAS 16293-2422 all molecules have their own distinct emission location (with separations of $\approx 0.1''$) and is often slightly offset from the continuum peak for the source. Through the analysis of maps

it is possible to determine whether molecules are present in a cold extended envelope or hot compact emission.

The location of submillimeter emission is very informative about the chemical origin of a molecule. Molecular species may have extended emission because they are formed in a cold gas phase environment or because they evaporate due to non-thermal processes, e.g., cosmic rays, from the grains. Emission from a warm compact component can be due to “first generation” species that have evaporated or “second generation” species that are newly formed in the gas phase. Spatial coincidences, in which two molecules are always detected in the same location, are a strong indication for a common origin. In contrast, anti-coincidences indicate that species are not related at all. One study that uses this kind of analysis of interferometric observations with the SubMillimeter Array is presented in Chapter 7.

1.5 Main conclusions of this thesis

This thesis seeks to improve the understanding of the formation mechanisms of complex organics in interstellar ices through a combination of solid state experiments and observations of gas phase molecules. The main conclusions are as follows:

Chapter 2: Hydrogenation experiments have been performed for CO₂, HCOOH and CH₃CHO-containing ices. It is clear that hydrogenation of CO₂ and HCOOH in interstellar ice analogues is not very efficient. In contrast, CH₃CHO reacts with H to form C₂H₅OH ($\leq 20\%$), but also dissociates to form CH₄, H₂CO and CH₃OH. This is the first time that this pathway for C₂H₅OH formation in the hydrogenation scheme by Tielens & Charnley (1997) is experimentally confirmed.

Chapter 3: The infrared spectroscopy of pure, layered and mixed ices of CO with CH₃OH, CH₄, CO₂ and HCOOH has been studied under high vacuum conditions. The interstellar 2140 cm⁻¹ band of CO in pure and layered ices can be explained by the same three components. The interstellar CO feature at 2136 cm⁻¹ commonly assigned to CO in mixtures with H₂O, is also observed when it is mixed with other hydrogen-bonding species such as CH₃OH. This similarity in line-profile explains the universality of the observed CO components even in slightly different chemical environments. Furthermore, CO can be trapped in other ice components, in particular CH₃OH and HCOOH, up to 100 K in the laboratory, making high temperature solid state reactions with carbon monoxide in those ices possible under interstellar conditions.

Chapter 4: The infrared spectroscopy of pure and mixed HCOOH ices with H₂O, CO, CO₂ and CH₃OH has been studied under high vacuum conditions. The HCOOH vibrational modes and band strengths are strongly influenced by ice composition. The observed 5.9, 7.2, and 8.1 μm features toward the low-mass young stellar object HH 46 and the high-mass young

stellar object W 33A are not reproduced by pure HCOOH ice and binary mixtures of HCOOH. In contrast the tertiary mixtures, in particular HCOOH:H₂O:CH₃OH $\sim$ 7:67:26%, match the observations the best. This suggests that HCOOH is present in complex mixtures in interstellar ices, consistent with its possible solid state formation mechanisms.

Chapter 5: Thermal desorption and sticking experiments of pure, layered and mixed ices of CO and N₂ have been performed. A kinetic model describing the desorption, mixing and segregation of the ice species has been constructed to fit the experimental TPD data. The results show that the ratio for the binding energies of N₂ and CO is $\sim$ 0.94 for pure ices and 1.0 for ice mixtures. The desorption temperature of N₂ is thus much more similar to CO than was previously assumed in astronomical literature. Additional sticking probability experiments show that the sticking behavior is very similar as well and close to unity at low temperatures. The observed anti-coincidences of CO and N₂H⁺, the daughter species of N₂, are thus not due to a difference in desorption temperature or sticking probability. It is the freeze-out of CO which results in a significant decrease of the N₂H⁺ destruction rate and causes the anti-correlation.

Chapter 6: Submillimeter observations with the James Clerk Maxwell Telescope of complex organics that are thought to have originated from grain-surface chemistry are presented in this chapter. Additionally, lines are detected from some supposed “second generation” species. Molecules are classified to be either cold (<100 K): CH₂CO, CH₃CHO and CH₃CCH or hot (H₂CO, CH₃OH, C₂H₅OH, CH₃CN, C₂H₅CN, HCOOCH₃ and CH₃OCH₃) (>100 K). The relative abundances of some “hot” molecules are similar for all sources. This is the case for a group of oxygen-bearing species as well as for the nitrogen-bearing species: HNCO and NH₂CHO. The relative abundances of the nitrogen-bearing species compared to the oxygen-bearing species, however, varies strongly. The organics detected in hot gas are most likely due grain-surface reactions followed by evaporation. The relatively constant abundance ratios suggest that the conditions for ice formation are rather similar for all sources. The formation of the cold molecules can be assigned to gas phase reactions or non-thermal, cosmic ray stimulated grain-surface desorption.

Chapter 7: Toward the proto-binary source IRAS 16293-2422 interferometric submillimeter observations with the SubMillimeter Array have been analyzed. The two binary components are called “A” and “B”. The nitrogen-bearing species HNCO and CH₃CN show compact emission toward both sources with a significantly lower flux from source B. In contrast CH₃CHO only shows compact emission toward source B, whereas for CH₂CO and C₂H₅OH similar fluxes arise from both sources. Evaporation of HNCO from grains and formation of CH₃CN in the gas phase may lead to the enhanced abundances toward source A. Their relatively low signal in source B may be explained by higher initial ice abundances of NH₃ or OCN[−]

for source A compared to B. The $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{CHO}$ and $\text{CH}_3\text{OH}/\text{H}_2\text{CO}$ abundance ratios differ by an order of magnitude which cannot be explained by successive hydrogenation reactions on grains. It is possible that an additional destruction mechanism for CH_3CHO is present in source A, but not in source B that causes this large difference between both sources for both sets of molecules.

The aim of this work is to test the grain-surface hydrogenation scheme shown in Fig. 6.1. It is clear that some of these reactions like $\text{CH}_3\text{CHO} + \text{H}$ indeed occur, whereas others such as $\text{CO}_2 + \text{H}$ do not take place. From the observations on the other hand it can be deduced that CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ are likely chemically related. These experimental and observational data show the importance of testing these reaction schemes both experimentally and observationally to increase our knowledge of grain-surface chemistry.

1.6 Future directions

To take the next step in understanding the formation of complex organics, a few possible directions are presented.

Laboratory experiments:

- To test the grain surface chemistry scheme shown in Fig. 6.1 it is necessary to move from a single hydrogen source to double atom-beam experiments. Then reactions of e.g. CO with H- and N-atoms can be tested simultaneously. Not only the relative reactivities of the atoms can be determined but also the resulting ice composition. Infrared transmission spectra of such mixtures can then be measured in the laboratory and directly be compared with infrared observations of star forming regions to discern the likelihood of such reactions occurring in interstellar space.
- One key question about complex organics in space is exactly how complex they become and whether potential prebiotic species can be formed. To be able to answer this question, laboratory submillimeter spectroscopy of complex organics is required. Also the measurement of many isotopomers is needed to get rid off the so-called interstellar “weeds” (i.e., lines of vibrationally excited levels or isotopes of common molecules like CH_3OH and CH_3OCH_3) that are responsible for many of the observed weaker emission lines. Only when the “weeds” are removed it becomes possible to search for previously undetected complex molecules with very low abundances to answer the question about molecular complexity.

Observations:

- Parallel to the measurement of the submillimeter spectra in the laboratory, deep unbiased surveys are needed to create inventories of the molecular complexity in star forming regions. Recently, the new single dish telescope

the Atacama Pathfinder EXperiment (APEX) has come online, which for the first time makes these studies possible at high frequencies (≥ 300 GHz) on the Southern Hemisphere. Since these surveys span large frequency ranges, there is a large potential for detecting more complex species than has been possible so far. Furthermore the detection of many emission lines from one particular species gives good insight in the excitation conditions and the environment from which the emission is arises.

- To be able to determine the chemical relationship between molecules the exact location of their emission is crucial. The next step is therefore to perform interferometric observations of star forming regions, in particular with the new Atacama Large Millimeter Array in ≥ 2010 . Observations of complex molecules should preferably span a large range in excitation energies so that the presence of hot compact and cold extended emission can easily be distinguished.

Part I

Laboratory experiments

Chapter 2

H-atom bombardment of CO₂, HCOOH and CH₃CHO containing ices

Abstract

Context: Hydrogenation reactions are expected to be among the most important surface reactions on interstellar ices. However, solid state astrochemical laboratory data on reactions of H-atoms with common interstellar ice constituents are largely lacking.

Aims: The goal of our laboratory work is to determine whether and how carbon dioxide (CO₂), formic acid (HCOOH) and acetaldehyde (CH₃CHO) react with H-atoms in the solid state at low temperatures and to derive reaction rates and production yields.

Methods: Pure CO₂, HCOOH and CH₃CHO interstellar ice analogues are bombarded by H-atoms in an ultra-high vacuum experiment. The experimental conditions are varied systematically. The ices are monitored by reflection absorption infrared spectroscopy and the reaction products are detected in the gas phase through temperature programmed desorption. These techniques are used to determine the resulting destruction and formation yields as well as the corresponding reaction rates.

Results: Within the sensitivity of our set-up we conclude that H-atom bombardment of pure CO₂ and HCOOH ice does not result in detectable reaction products. The upper limits on the reaction rates are $\leq 7 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$ which make it unlikely that these species play a major role in the formation of more complex organics in interstellar ices due to reactions with H-atoms. In contrast, CH₃CHO does react with H-atoms. At most 20% is hydrogenated to ethanol (C₂H₅OH) and a second reaction route leads to the break-up of the C–C bond to form solid state CH₄ (~20%) as well as H₂CO and CH₃OH (15–50%). The methane production yield is expected to be equal to the summed yield of H₂CO and CH₃OH and therefore CH₄ most likely evaporates partly after formation due to the high exothermicity of the reaction. The reaction rates for CH₃CHO destruction depend on ice temperature and not on ice thickness. The results are discussed in an astrophysical context.

Bisschop, Fuchs, van Dishoeck & Linnartz, 2007, submitted to A&A

2.1 Introduction

It is generally assumed that at the low temperatures in interstellar clouds, thermal hydrogenation of molecules on icy grain surfaces is the main mechanism to form more complex saturated species (Tielens & Charnley 1997). This is due to the relatively high abundance of H-atoms in the interstellar medium as well as their high mobility even on cold grains. However, most of the reactions in the

proposed reaction schemes have not yet been measured experimentally. Hiraoka et al. (1994, 2002), Watanabe et al. (2004), Hidaka et al. (2004) and Fuchs et al. (2007) have studied reactions of thermal H-atoms with CO ice in the laboratory, and shown that H₂CO, and at higher fluxes also CH₃OH, are readily formed at temperatures as low as 12 K. It thus seems likely that other species will also be able to react with H-atoms to form saturated grain-surface products. These species may be the starting point for an even more complex chemistry that occurs at higher temperatures or by energetic processing due to UV or cosmic rays in the ice. Eventually, the ices will evaporate when heated by a protostar, leading to the complex organics seen in hot cores (e.g., Blake et al. 1987; Ikeda et al. 2001). The aim of this paper is to study the reactivity of a number of astrophysically relevant molecules with H-atoms in interstellar ice analogues at low temperatures to test the proposed thermal hydrogenation reaction scheme and to characterize which products are formed and which mechanism is involved.

Interstellar ices contain both simple and complex species (see Ehrenfreund et al. 1999). The most abundant ice molecules are H₂O, CO and CO₂, which have very strong vibrational modes. The spectroscopic identification of other less abundant ices, such as HCOOH and CH₃CHO studied here, relies on weaker bands i.e. the OH and CH bending modes, $\nu_B(\text{OH/CH})$, of HCOOH at 7.25 μm and the CH₃ deformation, $\nu_D(\text{CH}_3)$, of CH₃CHO at 7.41 μm . Solid state abundances of HCOOH are 1–5% in both low and high mass star forming regions with respect to H₂O (Schutte et al. 1997, 1999; Gibb et al. 2004; Boogert et al. 2004). The detection of CH₃CHO is less certain, but abundances up to 10% have been reported (Gibb et al. 2004; Keane et al. 2001).

The specific species studied in this paper are CO₂, HCOOH and CH₃CHO, molecules that take a central place in inter- and circumstellar hydrogenation reaction schemes (Fig. 2.1). CO₂, HCOOH and CH₂(OH)₂ differ only in their number of hydrogen atoms. It is therefore possible that they are related through successive hydrogenation reactions. Previous laboratory experiments of H₂ and CO₂ have resulted in the formation of HCOOH on ruthenium surfaces (Ogo et al. 2006), but this reaction may have been mediated by the catalytic surface.

Another series of organics that are thought to be linked through successive hydrogenation are CH₂CO, CH₃CHO and C₂H₅OH (Fig. 2.1). Ethanol is indeed detected in warm gas phase environments in star-forming regions but CH₂CO and CH₃CHO are found mostly in colder gas (Ikeda et al. 2001; Bisschop et al. 2007c). This may be either due to very efficient conversion of CH₃CHO into C₂H₅OH or because the latter species may be formed through another route. In particular, astronomical observations show a constant CH₃OH/C₂H₅OH ratio which indicates that these two species are chemically linked (Bisschop et al. 2007c).

H-addition reactions in astrophysically relevant ices have been studied previously through UV photolysis experiments, where the hydrogen atoms are produced by dissociation of a suitable precursor molecule, often H₂O ice (e.g., Ewing et al. 1960; Milligan & Jacox 1964, 1971; Van Ijzendoorn et al. 1983; Allamandola et al. 1988; Gerakines et al. 2000; Moore et al. 2001; Wu et al. 2002). Although these experiments give a useful indication whether certain hy-

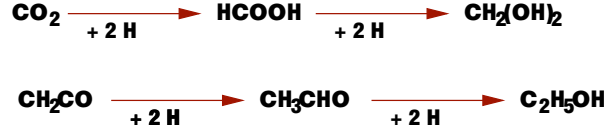


Figure 2.1. *Potential reaction routes for hydrogenation of CO₂ and CH₂CO ice. Only stable products are shown.*

drogenation reactions may or may not occur, their results cannot be compared directly with those obtained from the laboratory studies mentioned above, nor can they be used to quantitatively test reaction schemes such as those in Fig. 2.1 (see § 2.2.2 for details).

This paper is organized as follows: § 2.2 explains the experimental method, § 2.3 focuses on the data reduction and analysis, § 2.4–2.6 discuss the results, derived reaction rates and chemical physical mechanisms for hydrogenation reactions with HCOOH, CO₂ and CH₃CHO, § 2.7 presents the astrophysical implications and finally § 2.8 summarizes the main conclusions of this study.

2.2 Experiments

2.2.1 Our experiment

The experiments are performed using a new ultra-high vacuum set-up that comprises a main chamber and an atomic line unit. The details of the operation and performance of the set-up are described by Fuchs et al. (2007). The main chamber contains a gold coated copper substrate (2.5×2.5 cm²) that is mounted on top of the cold finger of a He cryostat. Temperatures can be varied between 12 and 300 K with 0.5 K precision using a Lakeshore 340 temperature control unit and are monitored with two thermocouples (0.07% Au in Fe versus chromel) that are mounted on the substrate face and close to the heater element. The typical pressure in the main chamber during operation is better than 5×10^{−10} mbar.

Pure ices of ¹³C¹⁸O₂ (97% purity, Icon), ¹²C¹⁸O₂ (97% purity, Icon), HCOOH (98% purity, J. T. Baker) and CH₃CHO (99% purity, Aldrich) as well as mixed ices of ¹³C¹⁸O₂ with H₂O (deionized) and CO (99.997% purity, Praxair) are studied (see Table 2.1, for an overview of the mixture ratios, ice thicknesses and ice temperatures). The two isotopologues of CO₂ are used to distinguish between atmospheric CO₂ and solid CO₂ processed by H-atoms. The ices are grown at 45° with a flow of 1.0×10^{−7} mbar s^{−1} where 1.3×10^{−6} mbar s^{−1} corresponds to 1 monolayer (ML) s^{−1}. The temperatures of the ices range from 12 to 20 K and their thicknesses are chosen between 8 and 60 ML.

H-atoms are produced in a well-studied thermal-cracking device (Tschersich & von Bonin 1998; Tschersich 2000). The dissociation rate and resulting H-atom flux depend on the temperature and pressure which are both kept constant during a single experiment. The temperature of the heated Tungsten filament, T_W is ~2300 K in all experiments and the H+H₂ flow through the

capillary in the atom line is either 1.0×10^{-4} or 1.0×10^{-5} mbar s⁻¹. For the latter pressure the calculated dissociation rate, α_{dis} , in the atomic line is 0.45. The atoms that exit the source are hot. Before the H-atoms enter the main chamber, they pass through a quartz pipe and equilibrate to ~ 300 K. The minimum number of collisions of H-atoms with the quartz pipe is 4 due to the nose-shaped form of the pipe. Since H-atoms are thermalized with the surface after only 2–3 collisions, it is expected that most H-atoms will have temperatures equal to the quartz pipe of 300 K. Due to collisions with the walls of the pipe and with each other, a fraction of the atoms recombines to H₂. The effective dissociation fraction, $\alpha_{\text{dis}}^{\text{eff}}$, and H-atom flux on the sample surface are therefore calculated to be lower than given by Tschersich (2000), i.e. 0.13 and 5.0×10^{14} cm⁻² s⁻¹, or 0.20 and 7.8×10^{13} cm⁻² s⁻¹ for the chosen flow-rates of 1.0×10^{-4} and 1.0×10^{-5} mbar s⁻¹, respectively (Fuchs et al. 2007). Note also that, the absolute number of H-atoms on the surface at a given time is not equal to the surface flux, because processes such as scattering and recombination take place on the surface. Theoretical simulations show that a steady-state H-atom coverage of 5.0×10^{14} cm⁻² s⁻¹ with an error of a factor 2 is quickly reached in this regime independent of the exact H-atom flux (Cuppen, private communication). A more extensive discussion of the derivation of these steady-state numbers is given by Fuchs et al. (2007). The time and H-fluence, i.e. the total number of atoms cm⁻² integrated over time in each experiment are listed in Table 2.1. At the temperatures and fluxes used in our experiment, the substrate surface will be covered with H₂ in a few seconds. Since H₂ molecules do not stick to other H₂ molecules, the maximum coverage with H₂ will only be a few monolayers. H-atoms therefore have to diffuse through the cold H₂ layer before reaching the ice and will be completely thermalized with the surface at the moment they encounter the ice sample. Experiments with only H₂ molecules have been performed for comparison by setting the source temperature T_{W} to ~ 600 K as an additional check to confirm that reactions are due to H-atoms and not to H₂ molecules (see Table 2.1).

The ices are monitored by Reflection Absorption InfraRed Spectroscopy (RAIRS) using a Fourier Transform InfraRed (FTIR) spectrometer, covering 4000–700 cm⁻¹ with a spectral resolution of 4 cm⁻¹. The infrared path length is the same for all experiments. Typically 512 scans are co-added. An experiment starts with a background RAIR scan and subsequently an ice is deposited onto the substrate surface. Another RAIR spectrum is taken after deposition to determine the initial number of molecules in the ice. An additional background spectrum is recorded afterward such that subsequently recorded spectra yield difference spectra between ices before and after H-atom bombardment. The next step in the experiments is the continuous H-atom bombardment of the ice during which a RAIR scan is taken every 10 minutes. After 3 hrs the experiment is stopped and a Temperature Programmed Desorption (TPD) spectrum is obtained using a quadrupole mass spectrometer. The ramp speed is 2 K min⁻¹ and is continued until the temperature reaches 200 K. Control experiments with pure ices of CO₂, C₂H₅OH, CH₄ and CH₃OH are studied to determine RAIR band strengths and to calibrate the production yields that are measured using

the mass spectrometer (see § 2.3.3). In those cases RAIR spectra are taken right after deposition and subsequently TPD spectra are recorded as described here for the other experiments.

2.2.2 Comparison with other hydrogenation experiments

A large number of photolysis experiments of astrophysically relevant ices exist where H-atoms are produced through photo dissociation of H₂O or other precursors (e.g., Ewing et al. 1960; Milligan & Jacox 1964, 1971; Van Ijzendoorn et al. 1983; Allamandola et al. 1988; Gerakines et al. 2000; Moore et al. 2001; Wu et al. 2002). These give useful information on potential hydrogenation reactions schemes, but do not give specific information about reaction rates (see for example § 2.4.3 & 2.6.3). Also the question whether thermal hydrogenation reactions can be responsible for newly formed species is not answered, for several reasons. First, the hydrogen atoms resulting from photolysis are produced *in situ* inside the ice with an excess energy of several eV; such atoms can travel significant distances through the ice (e.g., Andersson et al. 2006) and a reaction may take place before thermalization is achieved. Thus, activation energy barriers can be overcome, in contrast to thermal hydrogenation reactions where this is less probable. Second, although dilution in an inert Ar matrix can stabilize the H-atoms, the H-atom flux on the reactants remains poorly characterized. Third, other reactive products such as OH are also formed by photolysis of H₂O which makes it hard to discriminate the different effects. It is not possible to study pure ices through this method since H₂O or another precursor is always needed to provide a source of H-atoms. Finally, the photolysis experiments reported so far have been carried out under high vacuum conditions (typically 10⁻⁷ mbar) in which several monolayers of background gases (mostly H₂O) are accreted in less than a minute, providing additional molecules that can be photolyzed during the experiments. This may affect the outcome. In contrast, our experiments and the previously mentioned surface science experiments on CO hydrogenation are performed under ultra-high vacuum conditions (typically 10⁻¹⁰ mbar) in which less than a monolayer of background gas (mostly H₂) is accreted during the time-scale of the experiments (a few hours). Here the H-atoms are formed by a microwave source or by thermal cracking and are thermalized to room temperature or less before striking the ice surface, rather than being produced inside the ice.

2.3 Data analysis

2.3.1 RAIR analysis

Different frequency ranges are selected for baseline subtraction that depend on the species under study. Fourth order polynomial baselines are fitted to the recorded RAIR spectrum. Additionally, local third order polynomial baselines are subtracted around the features of interest to accurately determine the integrated absorption. The frequency ranges are given per ice morphology in

Table 2.1. Summary of all H-atom bombardment experiments for pure CO₂, HCOOH and CH₃CHO ices, as well as the mixed morphologies. The total time that the ices are exposed to H-atoms are indicated with t and the temperature of the tungsten filament with T_W . A value T_W of 2300 K refers to an experiment in which H₂ is dissociated and of 600 K to control experiments of ices bombarded with H₂-molecules.

Thickness (ML)	T_{ice} (K)	t (min)	T_W (K)	H-fluence (molecules cm ⁻²)
CO ₂				
15	12.5	180	2300	5.4(18)
15	14.5	180	2300	5.4(18)
15	14.5	180	600	—
CO ₂ :H ₂ O				
15 ^a	14.5	180	2300	5.4(18)
15 ^b	14.5	180	2300	5.4(18)
15 ^c	14.5	180	2300	5.4(18)
15 ^a	14.5	120	2300	3.6(18)
15 ^a	14.5	180	600	—
CO: ¹³ C ¹⁸ O ₂				
30 ^d	14.6	180	2300	5.4(18)
15 ^d	14.6	180	2300	5.4(18)
30 ^d	14.6	180	2300	5.4(18)
45 ^d	14.6	180	2300	5.4(18)
15 ^e	14.6	180	2300	5.4(18)
30 ^e	14.6	180	2300	5.4(18)
HCOOH				
20	12.5	240	2300	7.2(18)
20	40.0	240	2300	7.2(18)
20	12.5	240	600	—
HCOOH:H ₂ O ^f				
40	12.5	180	2300	5.4(18)
CH ₃ CHO				
16.2	14.5	180	2300	5.4(18)
7.8	14.5	180	2300	5.4(18)
11.4	14.5	180	2300	5.4(18)
13.5	14.5	180	2300	5.4(18)
18.8	14.5	180	2300	5.4(18)
21.2	14.5	180	2300	5.4(18)
22.1	14.5	180	2300	5.4(18)
56.0	14.5	180	2300	5.4(18)
45.8	14.5	180	2300	5.4(18)
11.4	12.4	180	2300	5.4(18)
11.3	17.4	180	2300	5.4(18)
11.2	19.3	180	2300	5.4(18)
11.7	14.5	180	600	—

^a39:61% ¹³C¹⁸O₂:H₂O, ^b22:78% ¹³C¹⁸O₂:H₂O, ^c48:52% ¹³C¹⁸O₂:H₂O, ^d45:55% ¹³C¹⁸O₂:CO, ^e80:20% ¹³C¹⁸O₂:CO, ^fHCOOH:H₂O 20:80%.

Table 2.2. From the integrated intensity of the infrared bands, the column density of species X in the ice is calculated through a modified Lambert-Beer equation:

$$N_X = \frac{\ln 10 \int A \, d\nu}{S_X^{\text{ref}}}, \quad (2.1)$$

where the $\ln 10$ is needed to convert the integrated absorbance, A , to optical depth and S_X^{ref} is the experimental RAIR band strength of species X. Transmission band strengths available from the literature cannot be used, because the total number of molecules probed with RAIRS cannot directly be related to a value probed in a transmission absorption experiment. This is because the incident beam goes through the ice layer twice with an angle to the surface. Instead, values of S_X^{ref} have been calculated from a calibration experiment without hydrogenation where the deposition rate is 1.0×10^{-7} mbar s $^{-1}$ to grow a layer of typically 10 to 20 ML and where the sticking probability is assumed to be 1. It should be noted that these experimental values can differ between different experimental set-ups and even for the same set-up over time, because they are determined by intrinsic properties such as the alignment of the system. They should therefore not be used to compare directly with observations of interstellar ices and even a comparison between different experiments should be made with caution. The values for S_X^{ref} as well as the spectral assignments of the vibrational modes are summarized for all species in Table 2.2.

There are several contributions to the uncertainty in the experimentally measured band strengths. The largest fraction comes from the actual deposition and sticking onto the surface. Since our experiment does not contain a microbalance, the absolute number of molecules on the surface is not known and the possibility that some molecules freeze out on other surfaces than the Au substrate cannot be ruled out. This leads to systematic errors for S_X^{ref} but there is no effect on the relative error for S_X^{ref} between different experiments with the same ice morphology. Based on experiments aimed at the same ice thickness, inaccuracies in the deposition flow are estimated to be $\sim 30\%$. Since the integrated area of the absorption band is determined very precisely for the deposited species, the column densities can be accurately normalized, but the derived band strengths cannot. Another source of uncertainty for ice mixtures is the precision of the mixing ratio, which is of the order of 10% (see also Öberg et al. 2007; Bisschop et al. 2007a). In summary, the actual uncertainty on the band strengths is substantial and ranges from 30–40%, but the relative uncertainty for ices with the same morphology is less than 5%.

2.3.2 Reaction rate calculations

The method for calculating reaction rates is described in detail by Fuchs et al. (2007). In short, a species X can react with H-atoms to form species Z through: $X + H \xrightarrow{k_0} Z$. The column density of X that has reacted, $N_X(t)$, is given by:

Table 2.2. Overview of the integrated frequency ranges with corresponding spectral assignment and band strength. The error on S_X^{ref} amounts to $\sim 30\text{--}40\%$.

Species	Mode	Integration range (cm ⁻¹)	S_X^{ref} (cm molecule ⁻¹)
¹³ C ¹⁸ O ₂ ^a	ν_3	2265–2245	1.3(-17)
¹³ C ¹⁸ O ₂ ^b		2265–2245	8.8(-17)
¹³ C ¹⁸ O ₂ ^c		2265–2245	4.8(-17)
¹³ C ¹⁸ O ₂ ^d		2265–2245	4.3(-17)
¹³ C ¹⁸ O ₂ ^e		2265–2245	3.2(-17)
¹³ C ¹⁸ O ₂ ^f		2265–2245	2.7(-17)
CO ^e	ν_1	2160–2120	9.5(-18)
CO ^f		2160–2120	6.4(-18)
HCOOH	ν_3	1800–1550	1.3(-16)
CH ₃ CHO	ν_7	1745–1719	8.0(-18)
CH ₃ CHO		1365–1330	2.8(-18)
CH ₃ OH	ν_8	1060– 990	1.1(-17)
CH ₄	ν_4	1320–1290	8.2(-18)

^apure ¹³C¹⁸O₂, ^b22:78% ¹³C¹⁸O₂:H₂O, ^c39:61% ¹³C¹⁸O₂:H₂O, ^d48:52% ¹³C¹⁸O₂:H₂O, ^e45:55% ¹³C¹⁸O₂:CO, ^f80:20% ¹³C¹⁸O₂:CO.

$$\frac{dN_X(t)}{dt} = -k_0 N_H N_X, \quad (2.2)$$

where k_0 stands for the reaction constant and N_H for the surface density of H-atoms. In our experiment the H-atom flux is kept constant and corresponds to 7.8×10^{13} or 5.0×10^{14} cm⁻² s⁻¹. Furthermore, the atoms have a certain penetration depth as observed in experiments of H-atom reactions with CO (Watanabe et al. 2004; Fuchs et al. 2007) which means that not all of the deposited parent species are available for the reaction. Consequently, $N_X(t)$ is calculated via:

$$N_X(t) = N_X(0) \alpha_0 (1 - e^{-\beta_0 t}), \quad (2.3)$$

where α_0 is the fraction of $N_X(0)$ that is available to react and β_0 (in min⁻¹) corresponds to $k_0 N_H / 60$ (the factor 60 comes from the conversion of seconds to minutes). In specific cases only upper limits on reaction rates are calculated and then it is assumed that α_0 only includes the uppermost ice layer. Limits based on the column density decrease after 1 minute give the most conservative upper limit on β_0 . Similar to the cases described by Fuchs et al. (2007), fits to the reaction rate differ when they are made over the complete time-period of the experiment (hrs) or only over a shorter period (minutes).

2.3.3 TPD analysis and calculation of the production yield

The TPD data provide complementary information on the reaction yields and are important, in particular, for those molecules that are not accurately determined by RAIRS. The TPD data are fitted by second order polynomial baselines. The temperature range over which a baseline is fitted depends on the desorption temperature of a specific species. Calibration experiments of pure ices with a known number of molecules have been performed by measuring the corresponding integrated area of the mass spectrometer signal. The number of molecules N_Z in other experiments has been determined by comparison of the integrated signal to the number of molecules in the calibration experiments. Since pure ices are needed for the calibration, no accurate yields can be calculated for H₂CO which is not readily available as a pure ice due to polymerization (see § 2.6.1). The yield, Y_Z , of the newly formed species Z in % can then be calculated through:

$$Y_Z = \frac{N_Z}{\alpha_0 N_X(0)}, \quad (2.4)$$

where N_Z is the column density as derived from the TPD data, α_0 is taken from the fit of the RAIRS data and $N_X(0)$ is the initial column density of the precursor species as derived from the RAIR spectra.

2.4 CO₂ containing ices

2.4.1 Results

Pure ices of CO₂ are bombarded with H-atoms to search for the possible formation of HCOOH following the reaction route as shown in Fig. 2.1. The reactivity of CO₂ can be tested by recording a decrease in the CO₂ RAIR signal and by monitoring any reaction products. Unfortunately, the CO₂ 2300 cm⁻¹ ice band is difficult to quantify, because this band overlaps with rotation-vibration transitions of CO₂ present in the purge gas in our spectrometer. The use of ¹³C¹⁸O₂ isotopic species does not improve this situation. Therefore we have focused on the strongest HCOOH band, the C=O stretching mode, at 1710 cm⁻¹, to monitor formic acid formation. The observed difference RAIR spectrum of ¹³C¹⁸O₂ bombarded by H-atoms has been compared to that of ¹²C¹⁸O₂ in Fig. 2.2a. Both spectra show very weak features at 1730 cm⁻¹ and 1500 cm⁻¹, but none at positions typical for HCOOH. The detected bands, however, occur at exactly the same positions as previously seen for H₂CO when formed upon CO hydrogenation (e.g. Watanabe et al. 2004). Furthermore, the features do not shift when a different isotopic species is used, which is expected when the formation involves CO₂ ice. In the TPD spectra of CO₂ ices bombarded with H-atoms for 3 hrs (not shown) mass 29 and 30 amu desorb in two steps around 100 K and 140 K, and the formation of other species is not detected through TPD. These temperatures and masses are identical to what was observed by Fuchs et al. (2007) for H₂CO desorption from CO ices bombarded by H-atoms. Dur-

ing H-atom bombardment an increase in the mass 28 amu signal is observed, which is likely due to degassing of both CO and N₂ from the metal parts of our experiment. It is therefore plausible that the measured low level of H₂CO formation observed in the experiment originates from hydrogenation of background gaseous CO and is not related to the CO₂ ice.

To test whether the presence of H₂O affects the reactivity of CO₂ ice upon H-atom bombardment as has been observed for CO in CO:H₂O mixtures (Watanabe et al. 2004; Fuchs et al. 2007), mixtures of 22:78% to 48:52% CO₂:H₂O have been investigated (see Fig. 2.2b). Like in the experiments with pure CO₂, weak RAIR features of similar intensity are observed at 1730 and 1500 cm⁻¹. Again we assign these features to the C=O stretching mode and the C-H bending mode of H₂CO. Thus, as for the pure ices, a small amount of background CO accretes and forms H₂CO. Within the sensitivity of our experiment, we conclude that CO₂ does not react with H-atoms even if mixed with H₂O.

Finally, mixtures of ¹²C¹⁶O and ¹³C¹⁸O₂ are studied to determine which species is more likely to react upon H-atom bombardment: CO or CO₂. Since CO hydrogenation reactions were previously reported in the literature (Watanabe et al. 2004; Fuchs et al. 2007), the answer to this question must be CO. In Fig. 2.2c and d, the resulting difference spectra for CO₂:CO mixtures are shown for different ice thicknesses and with mixture concentrations of 45:55% CO₂:CO and 80:20% CO₂:CO, respectively. Similar to H-atom bombardment of pure CO₂ ices and CO₂:H₂O mixtures, no evidence for HCOOH formation is observed in CO₂:CO mixtures. In contrast, CO does react with H-atoms to form H₂CO and CH₃OH as is evidenced by the presence of strong H₂CO absorption features at 1730 and 1500 cm⁻¹ and CH₃OH at 1030 cm⁻¹. This is consistent with H-atom bombardment experiments for pure CO and CO:H₂O mixtures by Watanabe et al. (2004) and Fuchs et al. (2007). The complementary TPD data show the same picture of no HCOOH formation and clear H₂CO and CH₃OH formation from CO. Other products than the precursor and product species H₂CO and CH₃OH are not observed.

2.4.2 Reaction rates

No hydrogenation products of CO₂, specifically HCOOH, are observed within the experimental sensitivity. The limit on the formation reaction rate for HCOOH from CO₂ is $\leq 7.0 \times 10^{-17}$ cm² s⁻¹ based on the limit on the column density for HCOOH after 1 min of H-atom bombardment for all ice morphologies (see § 2.3.2 for the derivation and Table 2.3 for the individual values for each experiment).

In Figure 2.3 the absorbance divided by the initial absorbance at $t=0$, A/A_0 , is shown for the 45:55% and 80:20% CO₂:CO ice mixtures. The data are fitted as described in § 2.3.2 and the fits are indicated in Fig. 2.3 with dotted lines. The resulting values for α_0 and β_0 as well as the k_0 are given in Table 2.4. Since the H₂CO band strength could not be determined accurately in these experiments only α_0 and β_0 are fitted. Clearly α_0 , i.e. the fraction of CO molecules available for reaction, decreases with increasing ice thickness.

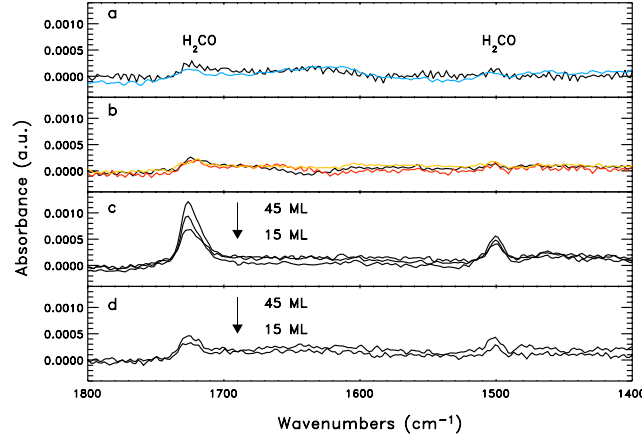


Figure 2.2. Difference spectra of the 1800–1400 cm^{-1} range after 180 minutes of H-atom bombardment. (a) 15 ML pure C^{18}O_2 ice (black line) and $^{13}\text{C}^{18}\text{O}_2$ (grey line), (b) 15 ML $\text{CO}_2:\text{H}_2\text{O}$ 39:61% (black line), 22:78% (grey line) and 48:52% (light grey), (c) 45:55% $\text{CO}_2:\text{CO}$ mixtures for 15, 30 and 45 ML ice thickness and (d) 80:20% $\text{CO}_2:\text{CO}$ mixture for 15 and 30 ML. The temperature of the ice is ~ 14.5 K. The arrows indicate how the absorbance of the H_2CO bands decreases with decreasing thickness.

Table 2.3. Upper limits on the reaction/destruction rates for HCOOH and CO_2 . The uncertainty on k_0 amounts to a factor 2.

Species	Ice matrix	T_{ice} (K)	k_0 ($\text{cm}^2 \text{s}^{-1}$)
CO_2	pure	14.5	$\leq 6.2(-17)$
CO_2	$^{13}\text{C}^{18}\text{O}_2:\text{H}_2\text{O}$ 39:61%	14.5	$\leq 6.0(-17)$
CO_2^a	$^{13}\text{C}^{18}\text{O}_2:\text{H}_2\text{O}$ 39:61%	14.5	$\leq 3.8(-17)$
CO_2	$^{13}\text{C}^{18}\text{O}_2:\text{H}_2\text{O}$ 22:78%	14.5	$\leq 6.7(-17)$
CO_2	$^{13}\text{C}^{18}\text{O}_2:\text{H}_2\text{O}$ 48:52%	14.5	$\leq 3.2(-17)$
CO_2	$^{13}\text{C}^{18}\text{O}_2:\text{H}_2\text{O}$ 39:61%	14.5	$\leq 6.0(-17)$
HCOOH	pure	12.5	$\leq 2.3(-17)$

^a Limit derived for experiment without bombardment.

2.4.3 Discussion and conclusion

Previously, CO_2+H reactions have been studied by Milligan & Jacox (1971) in UV-photolysis experiments of $\text{Ar}:\text{CO}_2:\text{H}_2\text{O}$ matrices. Only the formation of more oxygen-rich species such as CO_3 has been observed, but not HCOOH .

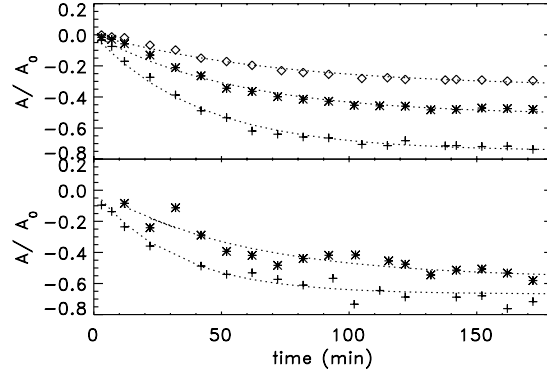


Figure 2.3. A/A_0 for the CO 2140 cm⁻¹ band in CO₂:CO mixtures at 14.5 K for the 45:55% (upper panel) and 80:20% (lower panel). The symbols refer to 15 ML +, 30 ML *, and 45 L $\diamond$. The dotted lines indicate the fits to the data.

Table 2.4. Values for α_0 , β_0 , and the reaction rate k_0 for CO in CO:CO₂ mixtures at ice temperatures of 14.5 K upon H-atom bombardment. The uncertainties for α_0 and β_0 amount to 10–20% and for k_0 are a factor 2.

Ice mixture	Ice thickness CO ₂ /total (ML)	α_0	β_0 (min ⁻¹)	k_0 (cm ² s ⁻¹)
45:55% CO ₂ :CO	8/15	0.75	0.024	2.9(-15)
45:55% CO ₂ :CO	17/30	0.51	0.018	2.2(-15)
45:55% CO ₂ :CO	25/45	0.34	0.014	1.7(-15)
80:20% CO ₂ :CO	3/15	0.67	0.032	3.8(-15)
80:20% CO ₂ :CO	6/30	0.57	0.017	2.0(-15)

Although these results cannot be compared directly with ours (see § 2.2.2), our findings are consistent with theirs that CO₂ does not react readily with H-atoms. To explain the lack of CO₂ hydrogenation reactions, Fig. 2.4 presents the relative formation energies of possible products. Reaction of CO₂ with H-atoms to either HCO+O or CO+OH is energetically highly unfavorable. This is due to the HOCO transition state being ~ 15930 K (1.4 eV) higher in energy compared to CO₂+H in the gas phase (Lakin et al. 2003). On the other hand, a hydrogenation reaction could be expected based on the higher heat of formation of CO₂+2H with respect to HCOOH of ~ 49370 K (4.3 eV). Indeed, in the chemical physics literature CO₂ is found to hydrogenate to HCOOH on ruthenium and iridium catalysts through formate complexes with the catalyst

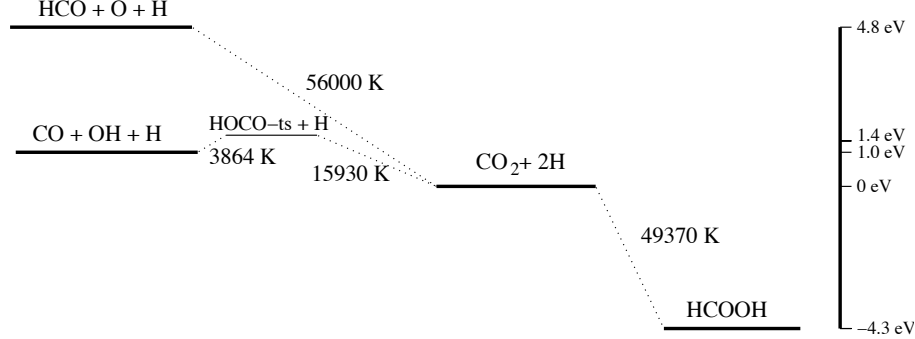


Figure 2.4. Potential energy scheme for CO₂ dissociation and hydrogenation. The relative energies are based on the heats of formation at 0 K. The scale in electronvolts is indicated on the right. The heats of formation are derived from Cox et al. (1989) for H, CO₂, CO and O, from Ruscic et al. (2002) for OH, from Gurvich et al. (1989) for HCO and HCOOH and from Lakin et al. (2003) for the HOCO transition state(ts).

(Ogo et al. 2006). The chemically bonded formate species subsequently reacts with H₃O⁺ to form HCOOH. This reaction mechanism requires acidic species as well as a catalytic surface that are not present in the current experiment. Hwang & Mebel (2004) calculated a potential energy surface for the gas phase H₂ + CO₂ reaction. The HCOOH end product is higher in energy than the initial species by ~2600 K (0.22 eV), but the CO₂ + 2H reaction is exothermic (see Fig. 2.4). For the reaction of CO₂ with H-atoms or H₂ the same transition state H₂CO₂, a complex cyclic structure, has to be overcome. This transition state lies 35000–37000 K (3.0–3.2 eV) above the starting point, CO₂ + H₂, but below CO₂ + 2H. This step can therefore not be rate-limiting for the CO₂ + 2H → HCOOH reaction. Since the reaction is clearly not observed in our experiment, the rate determining step must be the addition of the first hydrogen atom to CO₂ to form HCO₂ and the barrier to this reaction must be too high to be overcome for the ice temperatures of 12–60 K as used in our experiments.

Several recent studies have focused on reactions of CO + H leading to the formation of H₂CO and CH₃OH. Fuchs et al. (2007) find that even for the lowest ice thicknesses of 1 to 2 ML 30% of the ice is hidden from the impinging H-atoms. At higher thicknesses α_0 increases and there is a maximum layer thickness of 12 ML of CO ice that can react with H-atoms. The behavior of α_0 for our CO₂:CO mixtures is consistent with this picture, although at maximum 7±3 ML and 8±3 ML of the CO ice reacts for the 45:55% and 80:20% CO₂:CO mixtures, respectively. In other words mixing CO with CO₂ does not cause more CO to be “hidden” from the H-atom exposure.

Our reaction rates, β_0 , of e.g. 0.032 min⁻¹ in CO:CO₂ 80:20% with 15 ML total ice thickness at 14.5 K are similar to those found for pure CO ices by Fuchs et al. (2007) of ~0.030 min⁻¹ (~0.023 min⁻¹ when converted to our assumption

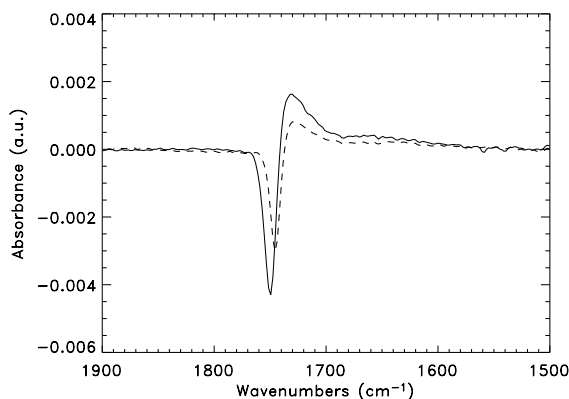


Figure 2.5. *The difference spectrum of the HCOOH $\nu_s(\text{C}=\text{O})$ stretch for HCOOH bombarded for 4 hrs with H-atoms at 12 K (solid) and at 40 K (dashed).*

for the initial number molecules) for a similar amount of CO of 11 ML at 15 K. These rates are the same within the 30–40% uncertainty. However, for CO:H₂O 17:83% mixtures Fuchs et al. (2007) find a value of $\sim 0.11 \text{ min}^{-1}$ (0.083 min^{-1}) for 12 ML at 15 K indicating that the reaction rates for CO hydrogenation are significantly higher in mixtures with H₂O ice. The similarity between the reaction rate of CO in mixtures with CO₂ and pure CO ices and the difference between those and CO:H₂O ice mixtures can be explained by CO and CO₂ only interacting through weak Van der Waals forces. The electronic structure of the CO molecule will therefore not differ significantly in mixtures with CO₂ from pure CO ices. H₂O on the other hand has a stronger dipole moment of 1.85 D compared to zero and 0.11 D for CO₂ and CO, respectively, and forms hydrogen bonds. Furthermore it is known that CO strongly interacts with and influences the band strengths of H₂O molecule (Bouwman et al. 2007). Thus, the electronic structure of the CO molecule will be perturbed in mixtures with H₂O, strongly affecting the reaction rate of CO with H-atoms. In summary the presence of CO₂ in ice mixtures with CO does not strongly affect the reactivity of CO with H-atoms.

2.5 HCOOH containing ices

2.5.1 Results

Figure 2.5 shows the difference spectrum for $\nu_s(\text{C}=\text{O})$ at $\sim 1710 \text{ cm}^{-1}$ of pure HCOOH ice bombarded with H-atoms as well as control experiments with bombardment of H₂ molecules at 12 K (for an overview of all infrared features of HCOOH see Cyriac & Pradeep 2005). The growth of an infrared feature around $\sim 1050 \text{ cm}^{-1}$ indicative for CH₂(OH)₂ formation has not been observed (for an

overview of the infrared features of $\text{CH}_2(\text{OH})_2$ see Lugez et al. 1994). A decrease on the blue side of the $\nu_{\text{S}}(\text{C}=\text{O})$ mode at 1710 cm^{-1} of HCOOH is seen at 1750 cm^{-1} as well as an increase at 1730 cm^{-1} , which means that the overall HCOOH band profile changes slightly. At 1730 cm^{-1} , the $\text{C}=\text{O}$ stretch for H_2CO is located, but other features of H_2CO , such as the 1500 cm^{-1} band, are missing. The decrease corresponds to <0.1 ML derived from our calculated RAIR band strength. These features are present in difference spectra for HCOOH ice bombarded with H-atoms at 12 and 40 K. A similar shift is seen for transmission infrared experiments with pure HCOOH ice that is heated to ~ 60 K (Bisschop et al. 2007a). At the same time the $\nu_{\text{S}}(\text{CH})$ and $\nu_{\text{S}}(\text{OH})$ vibrational modes increase due to conversion of HCOOH in dimeric form to HCOOH organized in chains. In the RAIRS spectra these bands are also seen to increase. Furthermore, the same change in RAIR profile is found for HCOOH ices of 40 K, where H-atoms cannot stick any longer onto the surface, but can only collide. Since the ice has a temperature of 40 K, the reorganization of the ice is less and consequently the signal of the difference spectrum is smaller. In conclusion, the RAIR data do suggest that some restructuring takes place in the surface but no reaction.

With TPD the masses of 48 ($\text{CH}_2(\text{OH})_2$), 46 (HCOOH), 45 (HCOO), 44 (CO_2), 32/31 (CH_3OH), 30/29 (H_2CO), and 28 amu (CO) have been monitored during warm-up. No products are detected at 48, 32, 31, or 30 amu to upper limits of <0.01 ML, indicating that HCOOH is neither hydrogenated nor dissociated. Thus, consistent with the lack of a 1500 cm^{-1} H_2CO absorption feature in the RAIRS data, no evidence for H_2CO formation is observed in the TPD experiment. The detected masses 45, 44, and 29 amu are assigned to HCOOH dissociating in the mass spectrometer, because the same relative mass ratios are seen for a TPD spectrum of pure HCOOH ice that is not bombarded by H-atoms. We conclude that within the limits of our experimental set-up the reaction of HCOOH with H-atoms is not efficient at 12 K.

2.5.2 Reaction rates

Since no unambiguous evidence for HCOOH destruction in the ice is found, it is only possible to derive an upper limit on its reaction rate, presented in Table 2.3. It is clear that the HCOOH destruction rates are below $2.3 \times 10^{-17}\text{ cm}^2\text{ s}^{-1}$ as derived from the limit on the column density after 1 min of H-atom bombardment (see § 2.3.2). As for CO_2 these reaction rates are very low.

2.5.3 Discussion and conclusion

In chemical physics literature HCOOH hydrogenation on catalytic surfaces has been shown to lead to decomposition of HCOOH rather than methanediol formation (Benitez et al. 1993). HCOOH adsorbs onto such a surface as HCOO^- and H^+ which can be further hydrogenated. The catalytic surface, however, clearly affects the end products and overcomes a reaction barrier that prohibits spontaneous decomposition. If hydrogen atom addition and dissociation occur

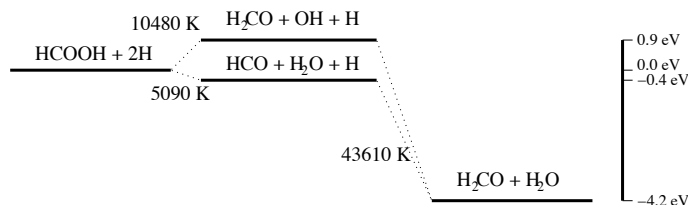


Figure 2.6. Potential energy scheme for HCOOH hydrogenation. The energies are based on the heats of formation at 0 K. The energy scale in electronvolts is indicated on the right. The heats of formation are derived from Gurvich et al. (1989) for HCO, H₂CO and HCOOH, from Ruscic et al. (2002) for OH and from Cox et al. (1989) for H and H₂O.

simultaneously, C–O bond cleavage is more energetically favorable (as shown in Fig. 2.6). However, it is clear from the results in § 2.5.1 that no H₂O and H₂CO formation occurs. Thus a high barrier for H-addition to HCOOH must exist for both mechanisms and HCOOH + H reactions in the ice are inefficient.

2.6 CH₃CHO containing ices

2.6.1 Results

The infrared spectroscopic features detected for pure CH₃CHO ice match with those detected by Bennett et al. (2005) and Moore & Hudson (1998, 2003). The strongest CH₃CHO band is the C=O stretching mode, $\nu_S(\text{C=O})$, at 1728 cm⁻¹ (5.79 μm). During H-atom bombardment the intensity decreases, but a small positive wing is observed at 1710 cm⁻¹ (see Fig. 2.7). This band is assigned to the C=O stretching mode of H₂CO. Other CH₃CHO features (e.g., the umbrella deformation mode, ν_D , at 1345 cm⁻¹) also decrease and new bands appear at 1030 and 1300 cm⁻¹ that are attributed to the C–O stretching mode of CH₃OH and the deformation mode of CH₄, respectively. No clear absorption is observed at 1050 cm⁻¹, where the strongest C₂H₅OH band, the C–O stretching mode, is expected. Since this frequency region is particularly problematic in our detector, the detection upper limit on $N(\text{C}_2\text{H}_5\text{OH})$ amounts to only 3×10^{15} molecules cm⁻², i.e. 3 ML. Another strong band of C₂H₅OH is expected at 3.5 μm . Unfortunately, this feature overlaps with a number of CH₃OH modes. Broad weak features are indeed detected in this range, but due to the complexity of both C₂H₅OH and CH₃OH absorptions and the relatively weak signal this cannot be used to determine whether C₂H₅OH is present. Additionally, it is important to note that no strong features are observed around 2140 cm⁻¹, where both CO and CH₂CO have infrared features. This is perhaps not surprising, because the formation of CO would involve not only the breaking of a C–C bond, but also hydrogen-abstraction, which is not very likely in this hydrogen-rich environment. The formation of ketene, CH₂CO, is even less likely because its formation is strongly endothermic.

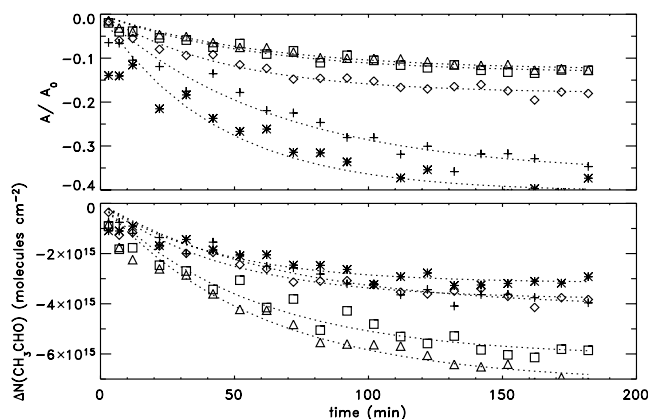


Figure 2.9. The A/A_0 ratio (upper panel) and $\Delta N(\text{CH}_3\text{CHO})$ (lower panel) for the CH_3CHO 1345 cm^{-1} band for different ice thicknesses and a constant ice temperature of 14.5 K. The symbols refer to 11.4 ML (+), 7.8 L (*), 21.2 L (◇), 45.8 ML (□) and 56.0 ML (△). The dotted lines indicate the fits to the data.

The formation of CH₄, H₂CO and CH₃OH is corroborated by the TPD spectra, where 16, 30 and 31 amu mass peaks at 45 K, 100 K and 140 K are found, respectively (see Fig. 2.8 for CH₄ and CH₃OH). The peaks for 16 amu at higher temperatures are due to O-atoms detected by the mass spectrometer when other molecules dissociate. The desorption temperatures for 16 and 31 amu are similar to those of pure CH₄ and CH₃OH ice confirms their RAIR detection. The TPD spectra and desorption temperatures of 29 amu are consistent with the desorption temperatures for H₂CO found by Watanabe et al. (2004). In addition, a TPD desorption peak is located at ~ 160 K for masses 45 and 46 amu (see Fig. 2.8). This is assigned to C₂H₅OH desorption based on a comparison with the TPD of pure non-bombarded C₂H₅OH ices. In summary, a fraction of CH₃CHO, below the infrared detection limit of the 1050 cm^{-1} band, is converted to C₂H₅OH and a larger fraction forms CH₄, H₂CO and CH₃OH. So even though the conversion of acetaldehyde to ethanol is not complete, it is important to note that a pathway in the proposed hydrogenation scheme by Tielens & Charnley (1997) is experimentally confirmed.

2.6.2 Reaction rates and production yields

The value for $N(\text{CH}_3\text{CHO})$ as derived from the $\nu_{\text{D}}(\text{umbrella})$ spectral feature at 1345 cm^{-1} is shown in Fig. 2.9 as a function of time for different ice thicknesses at 14.5 K. Also shown are the fits to the data. The $\nu_{\text{D}}(\text{umbrella})$ mode is chosen for analysis rather than the 1728 cm^{-1} band, because the latter overlaps

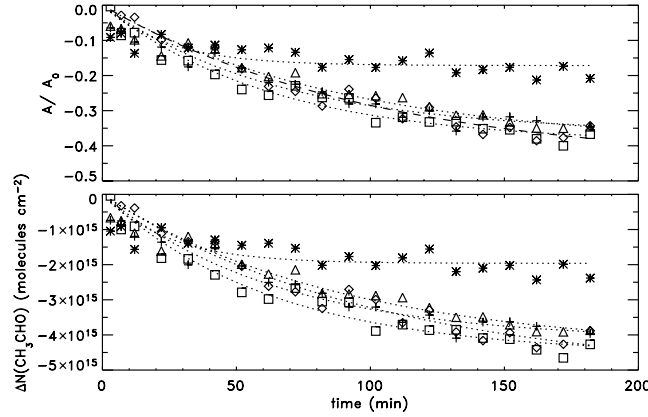


Figure 2.10. The A/A_0 ratio (upper panel) and $\Delta N(\text{CH}_3\text{CHO})$ (lower panel) for the CH_3CHO 1345 cm^{-1} band for different ice temperatures and a constant ice thickness of 11.3 ML. The symbols refer to 14.5 K (+), 12.4 K (*), 15.8 K (□), 17.4 K (◇) and 19.3 K (△). The dotted lines indicate the fits to the data.

with the $\nu_s(\text{C}=\text{O})$ of H_2CO at 1720 cm^{-1} . Clearly, the absolute amount of CH_3CHO that can react increases with ice thickness, whereas A/A_0 decreases. The temperature behavior is more complex and is shown in Fig. 2.10.

The α_0 and β_0 values derived from the fits as function of the thickness and temperature are shown in Fig. 2.11. The values for α_0 decrease with increasing thickness, but do not depend on ice temperature within the measured regime. The latter is not surprising as the CH_3CHO ice structure does not change between 15 and 75 K. The value for β_0 is independent of ice thickness, but does depend on ice temperature. It is largest for ice temperatures between 15–16 K, similar to the case of CO (Fuchs et al. 2007). This is expected as the maximum reactivity is mostly determined by the mobility of H-atoms at the surface. At low temperatures H-atoms move more slowly resulting in a lower reaction rate. At higher temperatures the diffusion rate is higher but has to compete with an increased evaporation rate.

For the $\text{C}_2\text{H}_5\text{OH}$ formation, only yields can be calculated from the TPD data because the RAIR feature at 1050 cm^{-1} overlaps with the $\nu_s(\text{CO})$ band of CH_3OH . The yields for CH_4 , CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ are given in Table 2.5. Even when considering that there is a general quantitative uncertainty of $\sim 10\%$, it is clear that the summed yield of the different products is not 100%. This is most likely due to missing H_2CO yields, because these are not reliably calibrated. Furthermore $Y(\text{CH}_4)$ is expected to be equal to $Y(\text{H}_2\text{CO} + \text{CH}_3\text{OH})$, because CH_3OH is formed from H_2CO after CH_3CHO dissociation. However, the CH_3OH yield is significantly higher than CH_4 (see § 2.6.3). The solid state $\text{C}_2\text{H}_5\text{OH}$ yields are $\leq 20\%$.

Table 2.5. Values for α_0 , β_0 , the reaction rate k_0 for CH₃CHO, and production yields, $Y(X)$ upon H-atom bombardment. The uncertainties for α_0 and β_0 amount to 10–20%, for k_0 are a factor 2 and Y 20%.

Ice temperature (K)	Ice thickness (ML)	α_0	β_0 (min ⁻¹)	k_0 (cm ² s ⁻¹)	$Y(\text{C}_2\text{H}_5\text{OH})$ (%)	$Y(\text{CH}_4)$ (%)	$Y(\text{CH}_3\text{OH})$ (%)
14.5	7.8	0.40	2.3(-2)	2.8(-15)	15	21	
14.5	11.4	0.36	1.5(-3)	1.8(-16)	10	19	
14.6	13.5	0.31	2.2(-2)	2.6(-15)	14	22	48
14.5	18.8	0.30	1.9(-2)	2.3(-15)	13	18	
14.5	21.2	0.18	2.1(-2)	2.5(-15)	17	24	
14.6	22.1	0.22	2.0(-2)	2.4(-15)	20	23	39
14.6	45.8	0.13	1.8(-2)	2.2(-15)	20	21	38
14.6	56.0	0.13	1.7(-2)	2.0(-15)	20	17	35
15.8	11.6	0.39	1.6(-3)	1.9(-16)	21	22	33
17.4	11.3	0.45	9.9(-3)	1.2(-15)	16	19	
19.3	11.2	0.39	1.1(-2)	1.3(-15)	14	13	15

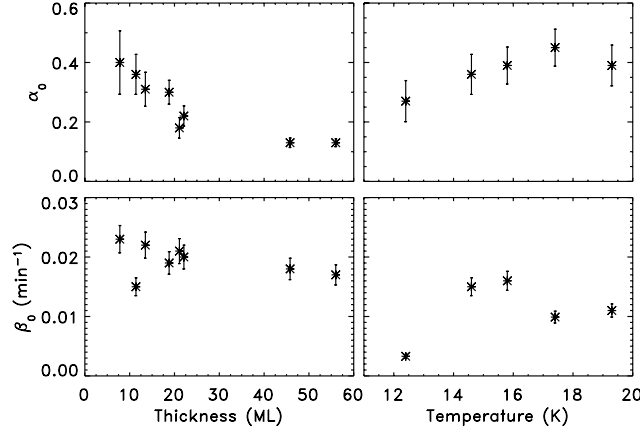


Figure 2.11. The α_0 and β_0 dependencies of the $\text{CH}_3\text{CHO}+\text{H}$ reaction on thickness and temperature. The temperature of the ices for the thickness dependence experiments is constant at 14.5 K. The ice thickness is similar for the temperature dependence experiments at 11–12 ML.

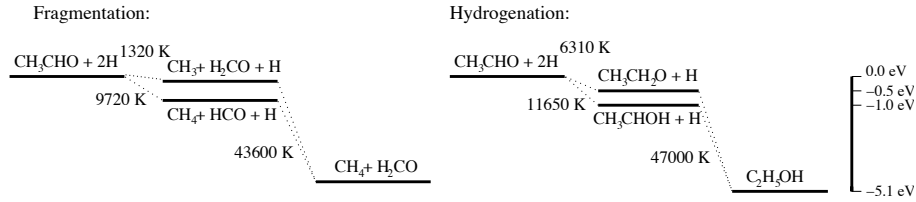


Figure 2.12. Potential energy scheme for CH_3CHO fractionation and hydrogenation. The relative energies are based on the heats of formations at 0 K. An approximate energy scale in electronvolts is given on the right. The heats of formation are derived from Wiberg et al. (1991) for CH_3CHO , Cox et al. (1989) for H, Gurvich et al. (1989) for CH_3 , H_2CO , CH_4 and HCO , Frenkel et al. (1994) for $\text{C}_2\text{H}_5\text{OH}$ and Matus et al. (2007) for the CH_3CHOH and $\text{CH}_3\text{CH}_2\text{O}$ radicals.

2.6.3 Discussion and conclusion

Previously, $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO were shown to form in interstellar ice analogues by photolysis of $\text{C}_2\text{H}_2:\text{H}_2\text{O}$ mixtures (Moore et al. 2001; Wu et al. 2002). Since in such experiments both OH and H fragments are present with excess energy, it is difficult to disentangle potential pure hydrogenation reactions and reactions involving OH radicals. Indeed, Moore & Hudson (2005) explain formation of $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO by reactions of C_2H_5 and C_2H_3 with OH, respectively. In this paper we focus on the reactions with thermal H-atoms

only.

Since H₂CO is known to react with H-atoms to CH₃OH (Watanabe et al. 2004; Hidaka et al. 2004) it is thus likely that the next more complex aldehyde, acetaldehyde (CH₃CHO), will form ethanol (C₂H₅OH). In Figure 2.12 the relative heats of formation at 0 K are shown (Wiberg et al. 1991; Cox et al. 1989; Gurvich et al. 1989; Frenkel et al. 1994; Matus et al. 2007). The exothermicity of CH₃CHOH formation is higher than that of CH₃CH₂O, but which of the species is more likely formed depends on the reaction barriers. Subsequent formation of C₂H₅OH is likely fast, because reactions of radicals with H-atoms commonly have no activation barriers. As described in § 2.6.2 only a fraction of CH₃CHO is converted to C₂H₅OH, and a larger fraction leads to CH₄, H₂CO, and CH₃OH formation. For hydrogenation of CH₃CHO a C=O bond is converted to a C–O bond instead of breaking a C–C bond. Since the C=O bond is intrinsically stronger it is likely that the entrance channel to hydrogenation is higher in energy compared to dissociation.

Thus H-atoms can break the C–C bond as well as the C=O bond to form CH₄, H₂CO and CH₃OH or C₂H₅OH in ices as prepared here. As shown in Fig. 2.12 the formation of CH₄+HCO is more exothermic than that for CH₃+H₂CO. Furthermore, the energy released in this step is higher than the binding energy of CH₄ to the surface, which is ~700 K (0.06 eV). This likely explains why the $Y(\text{CH}_4)$ is lower than $Y(\text{CH}_3\text{OH}+\text{H}_2\text{CO})$, because the formation energy is sufficient for CH₄ desorption. The energy released during the formation of H₂CO, CH₃OH and C₂H₅OH is even higher and may also cause a fraction of the molecules to desorb.

2.7 Astrophysical implications

Our experiments show that CO₂ reaction rates with H-atoms are very low, making it an implausible route for HCOOH formation. A number of other HCOOH formation routes are possible (see e.g., Milligan & Jacox 1971; Hudson & Moore 1999; Keane 2001), from either HCO+OH → HCOOH or HCO+O → HCOO+H → HCOOH. In addition, experiments suggest that under specific catalytic conditions CO₂ can react to form HCOOH (Ogo et al. 2006) but this requires catalytic surface sites, i.e., CO₂ directly attached to a silicate or metallic grain site. Such a situation is less likely in dense interstellar clouds where thick ice layers have already formed and cover any potential catalytic sites. In conclusion, under astrophysically relevant conditions solid CO₂ in bulk ice is a very stable molecule that is not likely to react with H-atoms.

Similar to CO₂, reaction rates of HCOOH with H-atoms are below the detection limit in our experiment. Formation of the so far undetected interstellar species CH₂(OH)₂ in this way thus seems unlikely. Unless other formation mechanisms are found an observational search for this species based upon solid state astrochemical arguments is not warranted. We conclude that CO₂, HCOOH and CH₂(OH)₂ do not appear to be related through successive hydrogenation in interstellar ice analogues under the conditions as used in the present study.

In contrast to CO_2 and HCOOH , CO does react with H-atoms. The reaction rates of CO in $\text{CO}:\text{CO}_2$ mixtures are very similar to those found by Fuchs et al. (2007) for pure CO ices. CO hydrogenation in interstellar ices will thus not be strongly affected by the presence of CO_2 in the ice. It is likely that the reaction rate is the same for $\text{H}+\text{CO}$ independent of the CO concentration and that of other species in apolar interstellar ices.

Reactions of CH_3CHO in interstellar ices proceed at similar rates compared to CO hydrogenation. A maximum of 20% will be converted to ethanol, $\text{C}_2\text{H}_5\text{OH}$, while another major reaction channel leads to CH_4 , H_2CO and CH_3OH . The precise abundance of CH_3CHO in interstellar ice is not yet well determined. However, abundances of 1–5% are quoted in the literature (Schutte et al. 1997, 1999; Gibb et al. 2004; Boogert et al. 2004). These values can be used to derive an upper limit on the $\text{C}_2\text{H}_5\text{OH}$ abundance that could thus be formed. As an example we compare the abundances for the high mass source W 33A, where CH_3CHO has a solid state abundance of 9.8×10^{-6} and CH_3OH of $1.4\text{--}1.7 \times 10^{-5}$ both with respect to H_2 . If we assume that all solid CH_3CHO is present in the surface layer and the $\text{C}_2\text{H}_5\text{OH}$ yield is $\sim 20\%$, an abundance of $\text{C}_2\text{H}_5\text{OH}$ of at most 2.0×10^{-6} with respect to H_2 can be formed. This leads to an upper limit on the $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ ratio of 0.14. In reality this value will be lower as part of the CH_3CHO ice may be shielded from incoming H-atoms and other destruction reactions will likely be competing with hydrogenation reactions. The limit of 0.14 is clearly higher than the observationally derived $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ abundance ratio in the gas phase of 0.025 ± 0.013 (Bisschop et al. 2007c). Formation of $\text{C}_2\text{H}_5\text{OH}$ from solid state hydrogenation of CH_3CHO is thus sufficient to explain the observed abundances of $\text{C}_2\text{H}_5\text{OH}$.

2.8 Summary and conclusions

Hydrogenation reactions of CO_2 , HCOOH and CH_3CHO interstellar ice analogues have been studied under ultra-high vacuum conditions. RAIRS and TPD have been used to analyze the results. From these experiments reaction rates and upper limits on destruction and formation rates of the above mentioned species are calculated. The main conclusions derived from this work are:

- ▷ CO_2 and HCOOH do not react with H-atoms at a detectable level. Only minor fractions of the species desorb due to the bombardment. Solid state formation of HCOOH from CO_2 and $\text{CH}_2(\text{OH})_2$ from HCOOH are likely inefficient in interstellar ices.
- ▷ Hydrogenation of CO to H_2CO and CH_3OH from CO mixed with CO_2 has similar reaction rates compared to pure CO ices. The presence of CO_2 in interstellar ices with CO therefore does not affect the formation of H_2CO and CH_3OH .
- ▷ Hydrogenation of CH_3CHO leads for $\sim 20\%$ to $\text{C}_2\text{H}_5\text{OH}$, showing for the first time that a thermal hydrogenation reaction can be responsible for the $\text{C}_2\text{H}_5\text{OH}$ abundances detected in dense interstellar clouds. Other reaction

products are H₂CO, CH₃OH (15–50%) and CH₄ (~10%). Due to the energy released a fraction of the produced species may evaporate into the gas phase upon formation.

Acknowledgements

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Chapter 3

Laboratory studies of the spectroscopy and physical behavior of CO-containing interstellar ices

Abstract

Context: High resolution observations of the $4.67\ \mu\text{m}$ stretching vibration of solid CO towards low mass star forming regions show remarkably consistent trends in the component features of the CO ice band. Key questions arising from this analysis point towards the need for a combined physical-chemical explanation of these phenomena.

Aims: To understand and interpret observations of CO ice features by comparing the trends seen in interstellar ice spectra with the physical behavior of CO in molecular ices under controlled laboratory conditions.

Methods: Binary ice mixtures and sequentially deposited layered ices of CO with CO_2 , CH_4 , HCOOH and CH_3OH , are grown in situ in a high vacuum chamber, on a CsI substrate cooled to 15 K. Fourier transform infrared transmission spectra are recorded at $0.5\ \text{cm}^{-1}$ resolution as the ices are heated, in 3–5 K steps, from 15 to 200 K. Systematic trends in the spectroscopy and desorption behavior of the CO ice are extracted from the data and are compared to existing data on binary CO- H_2O ices.

Results: The spectroscopy of CO changes very little between the pure and layered ice systems. The main $2140\ \text{cm}^{-1}$ feature can be decomposed into amorphous, crystalline and dimer domains, whose relative contributions depend on other components and temperature. The CO band is consistently broadened and shifted in mixed ice spectra, as well as in layered ices at high temperatures when mixing starts to occur. Red-shifted components at $2136\ \text{cm}^{-1}$ are found when hydrogen-bonding constituents like CH_3OH and CH_4 are present. Upon heating, trapping of CO in other ice components occurs, especially for ices initially deposited as mixtures. As an exception HCOOH traps CO more strongly when it is deposited on top. The release of the remaining CO in the ice is often related to solid state phase changes or evaporation of the other ice component.

Conclusions: We show that for CO-dominated interstellar ices characterized by a strong $2140\ \text{cm}^{-1}$ feature, layered ices are consistently a better laboratory model at low temperatures than an intimately mixed ice. For the red-shifted $2136\ \text{cm}^{-1}$ feature, other hydrogen-bonding mixed-ice environments besides CO- H_2O can explain the data. Our laboratory data can be used to predict the degree to which CO molecules may become trapped within various ice mantles upon heating, prior to desorption, thus providing a carbon-source in interstellar ice mantles for subsequent complex chemistry.

Fraser, Bisschop, Alsindi & van Dishoeck, submitted to A&A

3.1 Introduction

In the solid state, CO is a key source of carbon and is postulated to partake in chemical reactions that generate a number of more complex interstellar organic species (Brown et al. 1988). This chemistry could involve thermally induced reactions between atoms/radicals and the CO molecule at the ice surface and in the bulk of the ice, or an electron or photon mediated process in the bulk of the ice layer. On the ice surface, addition reactions involving the hydrogenation or oxidation of CO are most significant, leading to the formation of CO₂ and HCO. Subsequent surface reactions, adding H or OH, lead to the formation of H₂CO, HCOOH and CH₃OH. Substitution reactions with N-atoms (leading to HNCO formation from HCO) or S-atoms (leading to OCS formation) are also possible. If CO resides in a H₂O dominated ice environment, CO₂, HCOOH and CH₃OH can be formed via photon mediated process in the ice layer, where first the H-OH bond is photo-dissociated, then one or both dissociated fragments react with CO. Therefore, in interstellar ices CO will reside in an ice matrix in close proximity to one or many of these reaction products. Further energetic processes or surface reactions could lead to a plethora of more complex molecules, or back-reactions destroying the molecules, e.g. the formation of CH₄ from CH₃OH.

Detections of solid CO (CO ice) are inferred by the presence of a broad absorption feature at around 2139 cm⁻¹ (4.675 μm), and have been made on lines-of-sight towards dense interstellar regions, the galactic center and high and low mass Young Stellar Objects (YSOs), (e.g., Tielens et al. 1991; Chiar et al. 1994, 1995, 1998; Ehrenfreund et al. 1997; Whittet et al. 1998; Boogert et al. 2002a,b; Thi et al. 2002). By “mixing and matching” of laboratory spectra (from mixed ices at different temperatures) to these observations, it has been shown that CO resides in two distinct interstellar ice environments: the first, evinced by a broad band at 2139 cm⁻¹, is assigned to CO in pure CO or CO-rich ices: the second, evinced by a band at 2136 cm⁻¹ is thought to be related to CO in H₂O-rich ice (Tielens et al. 1991). Pontoppidan et al. (2003b) detected solid CO on lines-of-sight towards over 30 low and medium mass YSOs at much higher spectral resolution and signal-to-noise than previous studies. Rather than employ the “mix and match” approach, they used a phenomenological fit to decompose the interstellar CO ice band into only three components: at 2136.5 cm⁻¹ (the “red” component: Lorentzian, FWHM = 10.6 cm⁻¹), 2139.9 cm⁻¹ (the “middle” component: Gaussian, FWHM = 3.5 cm⁻¹), and 2143.7 cm⁻¹ (the “blue” component: Gaussian, FWHM = 3.0 cm⁻¹). In this chapter these three interstellar components of the CO ice band are referred to as CO_{ISM}-2136, CO_{ISM}-2140 and CO_{ISM}-2144, respectively. On each line-of-sight, only the intensities of these three components had to be altered to obtain overall fits to the CO ice band that are significantly better than those obtained with the “mix and match” approach.

A number of questions arise from this band analysis which demand answers from the laboratory, specifically:

- ▷ What is the origin of the constant peak positions for CO_{ISM}-2136, CO_{ISM}-2140 and CO_{ISM}-2144 in interstellar ices with similar line widths along all

lines-of-sight of observations?

- ▷ What possible physical or chemical factors can influence only the relative intensities of the fitted components of the observed CO ice band?
- ▷ If CO in H₂O environments is not the singular carrier of the CO_{ISM}-2136 component of the CO ice band, what else can it be?

This chapter focuses on laboratory experiments designed to address these questions, by studying the spectroscopy and desorption behavior of CO molecules with other known major ice species. Specifically, layers and mixtures with CO₂, CH₄, HCOOH and CH₃OH are studied. The behavior of CO on top of, underneath, or within H₂O ices and its astrophysical implications have been extensively studied by Collings et al. (2003a,b, 2005) and their data are used for comparison. Whereas previous laboratory studies have focused (almost) exclusively on mixed ice systems (Sandford & Allamandola 1988; Ehrenfreund et al. 1997; Palumbo & Strazzulla 1993, for an overview see Table 3.4), it is clear from the findings of Pontoppidan et al. (2003b) that a significant fraction of the CO frozen-out in interstellar ice mantles is spatially separated from other ice constituents, in an almost pure form. Such layered ices have been studied in the laboratory extensively for CO-H₂O (Collings et al. 2003a,b, 2004; Martin et al. 2002, for an overview see Table 3.5), often in combination with desorption studies. The CO-H₂O studies used reflection absorption infrared spectroscopy, however, which is not directly comparable to interstellar ice spectra. Published transmission spectra of layered ices are limited to the CO-CO₂ system (van Broekhuizen et al. 2006).

In this work we have made a systematic study of both mixed (CO:X), and layered, i.e., CO above X (CO/X) or below X (X/CO), ice morphologies, as well as pure ice systems to understand the spectroscopy and desorption behavior of CO in different ice environments. Moreover, our data are taken at a high spectral resolution of 0.5 cm⁻¹, required to compare with new high spectral resolution observational data of the intrinsically narrow solid CO band (FWHM 2–3 cm⁻¹). Previous laboratory data were taken at 1–2 cm⁻¹ resolution.

This chapter is organized as follows: § 3.2 presents the experimental methodology, § 3.3 discusses the results of the spectroscopy of CO in all ice morphologies, § 3.4 describes the astrophysical implications, and § 3.5 summarizes the main conclusions.

3.2 Experimental method

The apparatus used for this experiment has been described in detail elsewhere (Gerakines et al. 1995). Briefly, an IR-transparent substrate (CsI) is mounted at the base of a closed-cycle He cryostat cold-head, at the center of a high vacuum (HV) chamber capable of reaching base pressures of $\sim 3 \times 10^{-7}$ mbar. The whole system is mounted within the optical path of a Fourier Transform Infrared (FTIR) Spectrometer. Sample temperatures are controlled to better

Table 3.1. *Summary of experimental parameters used for ice growth and thermal processing.*

Ice system	Exposure time (s)				Thickness (μm)	Temperature (K)
	CO	X	CO-X	total		
<u>Pure ices</u>						
CO	120			120	0.42	deposited at 15 heated to
X		120		120	0.42	
<u>Mixed ices</u>						18, 20, 22.5,
CO:CH ₃ OH			900	900	3.15	25, 28, 30,
CO:CH ₄			120	120	0.42	35, 40, 50,
CO:CO ₂			240	240	0.84	60, 70, 80,
CO:HCOOH			240	240	0.84	90, 100, 115,
<u>Layered ices</u>						130, 145,
CO-CH ₃ OH	120	120		240	0.84	160 or until ices desorb
CO-CH ₄	120	120		240	0.84	
CO-CO ₂	120	120		240	0.84	
CO-HCOOH	120	120		240	0.84	

than ± 0.25 K using an externally controlled feedback loop, and measured from 12 to 300 K, using a calibrated Silicon diode.

3.2.1 Ice system growth

Gas bulbs of CO (Praxair 99.997%), CO₂ (Praxair 99.997%), and CH₄ (Praxair 99.997%), are prepared on a gas-handling line, separate from the main experiment, with equivalent bulb pressures of 20 mbar. Bulbs of HCOOH (J. T. Baker 99.95%) and CH₃OH (Jansen Chimica 99.9%) are produced from the vapor above a liquid sample, obtained after 20 to 25 freeze-thaw cycles, to remove dissolved air and CO₂. These samples are used for all the pure ice (control) and layered ice experiments. The observed solid state abundances of the molecules studied here differ strongly from up to ~ 30 – 40% for CO, CO₂ and CH₃OH with respect to H₂O (Gibb et al. 2004, Pontoppidan et al., in prep.) and up to a few % for HCOOH and CH₄ (Boogert et al. 2007, Öberg et al., in prep.). However, it is often found that certain ice features can be better reproduced by ice mixtures with much higher local ice abundances. For example, the CO₂ 15 μm band toward high-mass sources is best fitted by a H₂O:CH₃OH:CO₂=1:1:1 ice mixture (Ehrenfreund et al. 1998). The aim of this chapter is to classify the different ice components, so that predictions can be made for other ice species or more complex mixtures. We have therefore studied CO mixed with CO₂, CH₃OH, CH₄, HCOOH and H₂CO in equimolar ratios. Separate bulbs are similarly pre-prepared, with the same final bulb pressure as the pure gases.

The deposition line on the main chamber was configured such that two pre-prepared bulbs could be attached to a single entry port into the main chamber, but connected to separate leak valves, so their flows can be individually con-

trolled. The ices are grown by vapor deposition from the gas phase through ballistic deposition. There is a distance of 0.21 cm between the deposition tube and the substrate, so the dosing is directed along the surface normal. This leads to the formation of non-porous, amorphous ices (Kimmel et al. 2001a,b). For all these CO ice systems a sticking probability of ~ 1 can be inferred, because the main-chamber pressure does not rise during dosing.

An identical procedure is used to grow all the ice samples reported in this chapter. Prior to cooling the sample, gas flows are set such that the pressure in the chamber rose to $\sim 1.0 \times 10^{-5}$ Torr, which, at the measured pumping speed, is equivalent to a deposition rate of roughly a monolayer per second (10^{15} molecules $\text{cm}^{-2} \text{s}^{-1}$). This gas flow is stopped by an on/off valve and the chamber pressure recovered rapidly (≤ 120 s) to the base pressure. The substrate is cooled to ~ 15 K, and a background spectrum is recorded. The substrate is subsequently exposed to the gas(es) of interest, for a fixed period. The exposure times and equivalent ice thicknesses are summarized in Table 3.1. As far as possible the exposures of CO and species X are kept constant throughout this study. In certain cases, however, alternative deposition times are substituted to ensure that the CO-band is neither saturated, nor too weak to be analyzed (see Table 3.1). These differences in the absolute number of CO molecules in the ice sample are accounted for during the analysis (§ 3.2.2).

FTIR spectra are recorded isothermally at 0.5 cm^{-1} resolution, in 3 to 5 K steps, from 15 K to the temperature at which all ice is desorbed, as detailed in Table 3.1. Specific FTIR settings are used to ensure the line profile of the CO stretching vibration is fully resolved. The experiments outlined here are repeated at least twice to double check the effects of certain parameters on the spectra. No discernible differences are found between repeated experiments, confirming that the CO results are entirely reproducible.

A complete set of the raw data (absorbance vs. wavenumber), prior to any data analysis or baseline correction, are available in a database at:

<http://www.strw.leidenuniv.nl/~lab/databases/>

Note that due to a misalignment in the optics at 0.5 cm^{-1} resolution, the absolute intensities of infrared bands are not reliable. Therefore these data should not be used to derive relative intensities or determine band strengths.

3.2.2 Spectral analysis

All spectra are baseline subtracted and each of the spectra are normalized with respect to the number of CO molecules in the ice (see § 3.2.1 for the derivation of the number of molecules), so that in the final analysis all the spectra could be directly compared. Then, a control spectrum of ice species X, at a specific temperature, T_i , is scaled to fit to the ice features for X in the spectrum of interest (CO:X, CO/X or X/CO) recorded at T_i and then subtracted. The resulting spectrum only contains those elements of the profile related to the presence of CO ice. In making the subtraction of the spectrum of X it is important that both spectra are recorded at the same temperature; this accounts for changes in

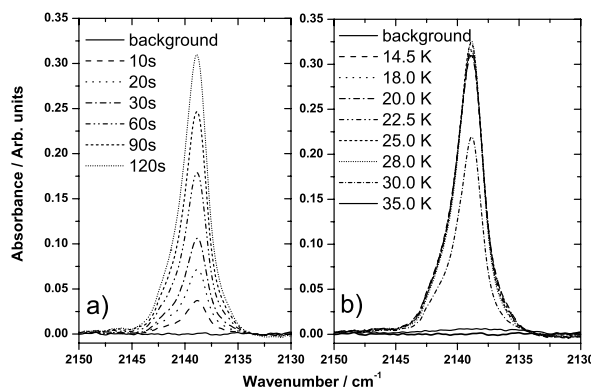


Figure 3.1. Transmission spectra of pure CO. (a) The growth of the absorption profile with exposure; (b) the line profile as a function of temperature.

the baseline slope and shift, and removes spurious libration and overtone bands, which would still be present if only the (lowest temperature) deposition spectrum is used to define the baseline. This subtraction has no discernible effect on the line profile of the CO band.

To discriminate the ice environments of CO in pure, mixed and layered ice systems, the CO stretching vibration in the 2100 to 2200 cm⁻¹ region is analyzed. A multi-component Levenberg-Marquett non-linear least squares fitting routine is used to obtain the best reproduction of the line profile, starting with the spectra of each ice system recorded after deposition at 15 K. An attempt was first made to fit the whole profile with a single Lorentzian profile, because solid-state features of pure molecular solids are expected, to a first approximation, have Lorentzian profiles (Gadzuk 1987). Such fits were always unsuccessful, so the fitting procedure was repeated, testing Gaussian and Voigt profiles before adding additional (Lorentzian) components. The positions of these components are given in Table 3.2. Despite the degeneracies one may expect, it transpired that free-fits to each spectra recorded at ≥ 18 K always give very consistent line positions within 0.5 cm⁻¹ and FWHM within the resolution-limit at which the spectra were recorded.

3.3 Results and discussion

3.3.1 General spectral features

The peak position of the CO stretch of pure CO ice found in our work is very similar to that listed in the literature (Sandford et al. 1988; Palumbo & Strazzulla 1993; Gerakines et al. 1995; Ehrenfreund et al. 1997; Chang et al. 1988; Ewing & Pimentel 1961). The absorption band is centered at around 2139 cm⁻¹ with a FWHM of ~ 2 cm⁻¹, consistent with the observational data on the “middle”

Table 3.2. FWHM and line-centers of the minimum number of fitted components required to fit each ice spectrum in this study. All ice mixtures have CO:X concentrations of 50:50% and all layered ice morphologies of CO/X or X/CO 50/50%.

Ice	Temp (K)	Peak components [FWHM] (cm^{-1})			
		CO _C	CO _A	CO _D	
Pure CO	14	2138.7-L [1.9]	2139.7-L [2.1]	2141.5-L [1.9]	
CO/CH ₃ OH	14	2138.6-L [1.4]	2139.4-L [2.2]	2141.5-L [1.5]	
	≥40	2136.3-G [9]			2150-L [3]
CH ₃ OH/CO	14	2138.9-L [1.7]	2140.0-L [2.5]	2141.5-L [1.5]	
	≥40	2136.3-G [9]			
CO:CH ₃ OH	14	2136.3-G [9]			
CO/CH ₄	14	2138.7-L [2.1]	2140.0-L [1.9]	2141.5-L [1.9]	
CH ₄ /CO	14	2138.7-L [2.1]	2140.0-L [1.9]	2141.5-L [1.9]	
CO:CH ₄	14	2138.7-L [2.3]	2140.0-L [1.9]		
CO/CO ₂	14	2138.8-L [1.8]	2139.9-L [1.9]	2141.5-L [1.9]	
	≥40				2142-G [8]
CO ₂ /CO	14	2138.7-L [1.4]	2139.6-L [1.5]	2141.1-L [1.8]	
	≥40				2142-G [8]
	14				2142-G [9]
CO:CO ₂	14				
CO/HCOOH	14	2138.6-L [1.6]	2139.7-L [2.2]		
	≥24	2138.7-L [1.6]	2139.7-L [2.3]	2140.1-G [8]	
	≥40	2138.5-G [6]			
HCOOH/CO	14	2138.6-L [1.7]	2139.8-L [2.2]		
	≥27	2138.6-L [1.7]	2139.8-L [2.2]	2140.5-G [8]	
	≥40	2137.9-G [6]			
CO:HCOOH	14	2138.9-L [1.9]	2139.8-G [8]		
	≥30	2138.5-G (6)			

L = Lorentzian, G = Gaussian.

component of Pontoppidan et al. (2003b). The narrow width clearly indicates the need to record and evaluate the line profile of the solid CO stretching vibration at a spectral resolution significantly better than the FWHM of the line itself, as done in this work. Our high-resolution data show that the 2139 cm^{-1} feature actually consists of several components. Figure 3.1a shows the effects of deposition time on the CO line shape. At very short exposures, (i.e., growing a thin ice film) the CO spectrum is clearly asymmetric, with three underlying components identifiable. The CO band intensity also increases with exposure, but the outermost features appear to saturate or become hidden under the wings of the main feature. These different components are all related to different binding sites for CO molecules within the ice film, not to contaminants. From comparison with previous literature reports of solid CO spectroscopy, these three laboratory features can be assigned to CO in libration or crystalline domains (Givan et al. 1997), lab-CO_C at 2138.7 cm^{-1} , non-libration or amorphous domains (Nary et al. 1982), lab-CO_A at 2139.7 cm^{-1} and dimer or polymer molecular cluster domains (Abe et al. 1999), lab-CO_D at 2141.5 cm^{-1} (see also Table 3.2).

Figure 3.1b shows the effects of annealing on the CO spectra. Between 10 and 25 K, pure CO ice spectra are invariant with temperature, i.e. the line profile, FWHM, intensity and position remain unchanged. This contradicts some previous reports on spectroscopy of pure, solid CO (Sandford et al. 1988; Ehrenfreund et al. 1997), which is due to the lower resolution used in these studies so that the shifts and line profile changes observed may have been artifacts of under-sampling. Our data are consistent with other higher resolution studies where no temperature effects on the pure, CO ice band are observed (Ewing & Pimentel 1961; Chang et al. 1988). Above 25 K, a very small change in intensity can be detected at the peak center because CO becomes mobile and may start to desorb. Beyond 28 K where desorption is certainly occurring, the band decreases in intensity. However unlike in the sequential deposition scan (Fig. 3.1a), the three underlying components of the CO band are never clearly visible during the heating process, possibly because the desorption proceeds so rapidly that it is difficult to detect when only a thin layer of CO remains on the substrate or because the desorption is only occurring from a single binding environment.

An overview of all the spectra from the CO-CH₃OH, CH₄, CO₂ and HCOOH ice systems is given in Fig. 3.2. Only the CO stretching region, from $2155\text{--}2125\text{ cm}^{-1}$, is shown, with the spectral intensity indicated by color (grey scale) and contours. The vertical axis shows the temperature evolution of the CO band, from 15 to 115 K where all CO has desorbed. Each matrix element can be compared directly with another, since the spectra have been normalized such that the integrated area under the 15 K spectra in each ice morphology is the same.

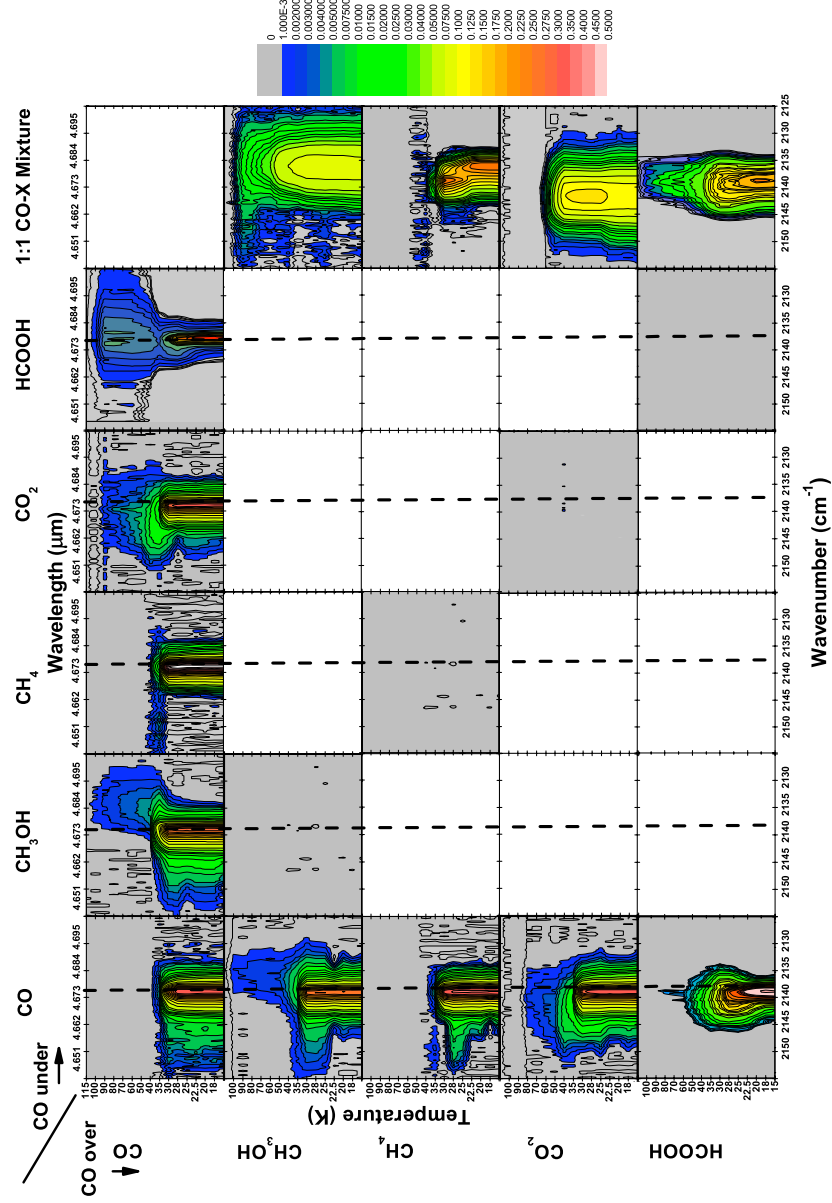


Figure 3.2. An overview matrix, summarizing all the spectra recorded in this study. In each “element”, the CO stretching vibration region, from 2155-2121 cm^{-1} , is plotted, with the spectral intensity shown in absorbance, as per the right-hand grey and contour scale, and the y-axis showing the temperature evolution of the CO ice band. Note that the scaling on the y-axis is non-linear. Ice morphologies are indicated by the external labeling. The dashed lines indicate the peak position of pure CO.

By comparing the spectra of the pure ices, on the diagonal, it can be seen that none of the ices studied, except CO, have solid state features in the 2125–2155 cm^{-1} wavelength region. At 15 K the layered ice spectra and pure CO ice spectra cannot be distinguished from each other, irrespective of layer order (see also Table 3.2). However, the spectra of the mixed ice systems bear little resemblance to the layered systems: the line profiles are not centered at the same wavelength, are broader and consequently less intense. In some mixed ices, e.g., $\text{CH}_3\text{OH}:\text{CO}$, the initial CO peak position is red-shifted, as the CO bond is weakened slightly, probably due to hydrogen bonding interactions between CO and the OH groups of HCOOH or CH_3OH , where C or O in CO act as electron donors to the proton. The broadened profile reflects the range of binding environments arising from these hydrogen bonding interactions: one CO molecule may interact with many surrounding CH_3OH molecules and vice versa. Conversely the peak position in the mixed $\text{CO}_2:\text{CO}$ mixture is blue-shifted in comparison to the pure CO ice position, indicating a slight strengthening of the CO bond, possibly due to back-donation of electrons from the CO_2 molecule. The overall profile is broadened, again reflecting the range of $\text{CO}_2\text{-CO}$ interactions within the ice (see also van Broekhuizen et al. 2006). However, in comparison to the shifts in CO vibrational frequencies seen on metal or semiconductor surfaces, all these shifts are very small (e.g., Diemant et al. 2007), and suggest that the CO bond itself is hardly perturbed by its ice environment, making it difficult to distinguish CO molecules at the ice-ice, ice-substrate and ice-vacuum interfaces from each other, or those CO molecules encapsulated by molecules from the second ice constituent.

3.3.2 Temperature evolution

The temperature evolution of the spectral features is clearly shown in Fig. 3.2 and Table 3.2. As illustrated in Fig. 3.1b, the pure CO ice band does not broaden or change in intensity as the temperature is raised. The sharp decrease around 30–35 K in the band intensity corresponds to the desorption of CO. Very similar behavior is evident in all the layered ice systems. Beyond these temperatures, CO features are still present, although the bands are significantly weaker, shifted, and broader than the original spectra, usually closely resembling the band positions of the mixed ices (see also the final column in Fig. 3.2). These features are attributed to the small fraction of the CO molecules that are trapped either because they are more tightly bound to the surface of the remaining (species X) ice layer, or have migrated into the other ice component and have become trapped due to a phase change of species X, i.e., from an amorphous to a more crystalline sample. Interestingly, in the X/CO ice systems, the majority of the CO is also able to desorb by 30–35 K, suggesting that CO molecules migrate “through” the overlying ice layer, reach the vacuum-ice interface and desorb. One possibility is that the CO molecules are able to laterally diffuse along the substrate and then desorb directly without having to get-past the overlying ice layer. Alternatively, one might assume that the two layers are not actually grown on top of each other. However, these two scenarios are ruled out

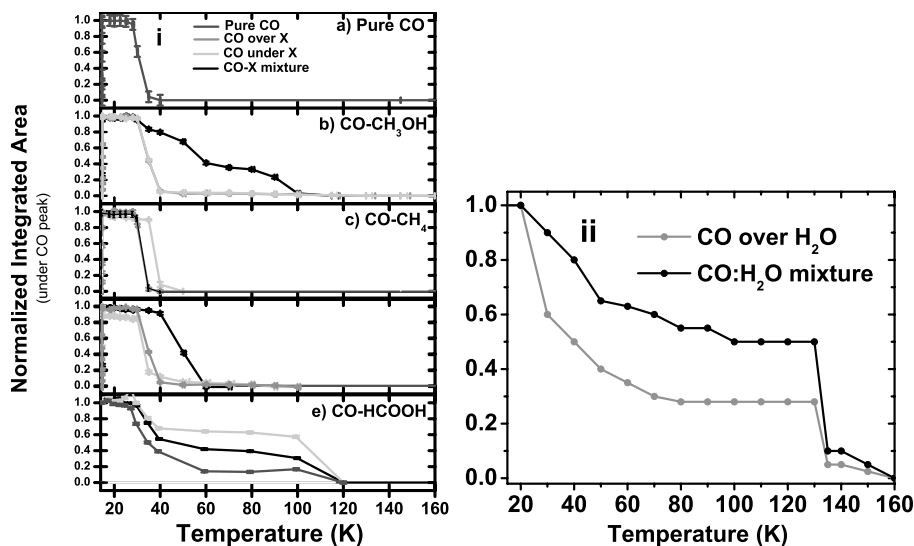


Figure 3.3. The desorption behavior of CO from the pure (dark grey trace), mixed (black trace), and layered (CO/X = grey trace, X/CO = light grey trace) ices. The integrated intensity of the CO band between 2155 and 2135 cm^{-1} is plotted against temperature in i) for ices of a) CO, b) CO-CH₃OH, c) CO-CH₄, d) CO-CO₂ and e) CO-HCOOH. Error bars indicate the uncertainty in each integrated area, and reflect the signal-to-noise level in the spectra and uncertainty in the baseline ($y=0$) used for the integration. In ii) the comparison with values for 5 L CO deposited over 100 L H₂O and 5% CO in H₂O (100 L total exposure) both deposited at 10 K are shown. These values are derived from TPD data by Collings et al. (2003b) and therefore no error bars or H₂O/CO data are shown.

by the CH₄/CO ice system (see 3rd box, top row, Fig. 3.2). In this case, the CO desorption is hindered, and no change in spectral intensity is evident until 35–40 K, 5 K higher than in the other layered ice systems. This corresponds to the temperature at which CH₄ starts to desorb, and indicates that the CO molecules are neither able to diffuse through the CH₄ overlayer, nor around it. The inability of CO to reach the ice-vacuum interface and desorb is attributed to the morphology of the CH₄ ice, which exists in a plastic disordered phase above ~ 20 K (see Table 3.3), involving rotational and possibly translational diffusion of the CH₄ molecules within the ice layer (Alsindi et al. 2003).

Figure 3.3(i) illustrates this desorption behavior more clearly. Here, the integrated area under the whole CO band profile, from 2135 to 2155 cm^{-1} , is plotted against temperature for the pure, CO/X, X/CO and CO:X ices. Comparison of Fig. 3.3(i)a, showing the desorption of pure CO, with the CO/X (in dark grey) and X/CO (in grey) traces in Fig. 3.3(i)b–e, confirms that the desorption behavior of CO molecules in all the layered ice systems (except HCOOH) are almost identical to that of pure CO. Furthermore, the CO/X and X/CO

Table 3.3. Comparison between values for the sublimation and crystallization temperatures of all the molecules used in this study, under a range of pressure conditions.

Species	$\Delta H_{\text{sub}}^{\ominus}$ ^a		T_{sub} (K) ^b		T_{crys} (K)
	(kJ mol ⁻¹)	(K)	HV (expt.) [calc.] 10 ⁻⁷ mbar	ISM (calc.) $P = 10^{-15}$ mbar	
CO	-6.9	-826	35 – 40 [35]	21	67 ^c
CH ₃ OH	-37.8	-4546	130 – 145 [140]	87	100 ^d
CO ₂	-26.3	-3163	90 – 100 [84]	64	55 ^e
CH ₄	-5.8	-698	40 – 50 [36]	17	18 ^f
HCOOH	-59.0	-7096	160 – 180 [168]	122	130 ^g

^a $\Delta H_{\text{sub}}^{\ominus}$ is give at a standard temperature of 298.15 K (Lide 2002). ^bCalculated using the Claussius-Claperon equation $\frac{1}{T_2} = \frac{1}{T_1} + \frac{R(\ln P_1 - \ln P_2)}{\Delta H_{\text{sub}}}$ including compensation for changes in ΔH_{sub} with temperature, according to Kirchhoff's laws, using C_p values from Lide (2002). ^cFrom Ewing (1962). ^dFrom Torrie & Weng (1989). ^eFrom Hanson & Jones (1981). ^fFrom Chapados & Cabana (1972). ^gFrom Bisschop et al. (2007a).

systems cannot be distinguished from each other without prior knowledge of the ice morphology, except in the cases of CH₄/CO, as explained above and illustrated in Fig 3.3(i)c, and in the HCOOH-CO ice systems. This aside, in CO plus CO₂, CH₄ and CH₃OH layered ices, over 90% of the molecules in the CO layer desorb by 35 K: the remainder are trapped in the ice matrix until the second ice constituent either undergoes a phase change (see Table 3.3), or desorbs itself, i.e., around 40 K in CH₄ (CH₄ desorbs), around 50–60 K in CO₂ (CO₂ crystallizes) and finally at 80–90 K (CO₂ desorbs), and at around 100 K in CH₃OH (CH₃OH crystallizes).

Only the behavior of the HCOOH-CO ice layers differs (see Fig. 3.3(i)e): initially at temperatures up to 30 K, no CO desorption is observed; between 30 and 60 K, 40–80% of the CO ice desorbs, dependent on whether the initial CO layer was deposited above or below the HCOOH, between 60 and 100 K the CO desorption appears to stop and between 120 and 135 K, where HCOOH undergoes its dimeric to chain-structure phase transition (see Table 3.3), all remaining CO desorbs. This behavior, particularly the complete halt to CO desorption, more closely resembles that of CO-H₂O ice layers (compare Fig. 3.3(i)e and Fig. 3.3(ii)), where the porosity and phase of the H₂O ice have a significant influence on the % of CO trapped within the ice matrix (Collings et al. 2003a,b; Fraser et al. 2004). When CO is deposited underneath the HCOOH it seems that it is much more easily trapped in the HCOOH matrix implying that HCOOH forms very porous ice structures, much like H₂O, which collapses rapidly as the ice is heated. Further experiments will be required to verify this hypothesis.

Similar to the layered ice systems, at a first glance very little temperature evolution is apparent in the mixed ices, even though the spectra are markedly different to that of the pure CO. In the CO:CH₃OH and CO:CO₂ ices, the

peak position does not shift as the ice is warmed from 15 K, although the line intensities do change. For example, in the CO:CO₂ mixture, the intensity of the CO band increases slightly beyond 30 K. This is accompanied by a slight narrowing of the band, indicating some structural reorganization within the ice matrix. Between 45 and 60 K, when pure CO₂ ice has its amorphous to α -crystalline phase change (see Table 3.3), the intensity of the CO band decreases rapidly as the CO desorbs (van Broekhuizen et al. 2006).

The CH₄:CO mixed ice exhibits a complex interaction: after deposition at 15 K, a hydrogen bonding OC-HCH₃ complex is formed, with a characteristic CO vibration at around 2136 cm⁻¹. The whole system undergoes a phase change at $\sim$ 20 K (see Table 3.3), evinced by the disappearance of the 2136 cm⁻¹ band, coincident with the appearance of a band around 2139 cm⁻¹, and an isosbestic point between the two (Alsindi et al. 2003). The change is induced by separation of the ice constituents, and corresponds to the temperature at which CH₄ forms its plastic elastic phase. Between 30 and 40 K the band decreases in intensity as CO desorbs.

The mixed HCOOH:CO ice has a broad adsorption feature, centered at around 2139 cm⁻¹, coincident with the pure CO ice band. Around 50% of the CO desorbs as the ice is warmed to 60 K. The integrated intensity of the band remains unchanged between 60 and 100 K, as in the layered HCOOH-CO ices, although the band position shifts towards 2138 cm⁻¹ (see Fig. 3.2 and Table 3.2). Beyond 100 K the CO rapidly desorbs as HCOOH undergoes its dimer to chain-structure phase transition (see Table 3.3). Again, this behavior more closely resembles that of mixed H₂O:CO ices rather than the other systems studied here.

3.3.3 Spectral decomposition

To extract further information on the ice structures, as well as their evolution with temperature, each spectrum was subjected to a component analysis and fitting (see § 3.2.2). The results of this fitting procedure are given in Table 3.2, and illustrated by Fig. 3.4, which shows fitted components arising from the pure CO, plus layered and mixed CO-CH₃OH ices, at 3 of the key temperature steps through the experiment, i.e. 15 K, where the ice was deposited, 28 K, where CO desorption commences, and 50 K where any CO molecules left on the surface must be mixed or trapped in the CH₃OH matrix.

Pure and layered ices

The laboratory component fit to the pure-CO ice spectra is illustrated in the first column of Fig. 3.4. This corresponds to the “middle” component of Pontoppidan et al. (2003a). Our data show that this band actually can be decomposed further into a minimum of 3 Lorentzian components to reproduce the line profile of the band accurately at 15 K. These bands are consistently at the same wavelengths as the three features of the CO ice spectrum identifiable by eye during differential deposition (Fig. 3.1a). As discussed above, they can be assigned to CO in

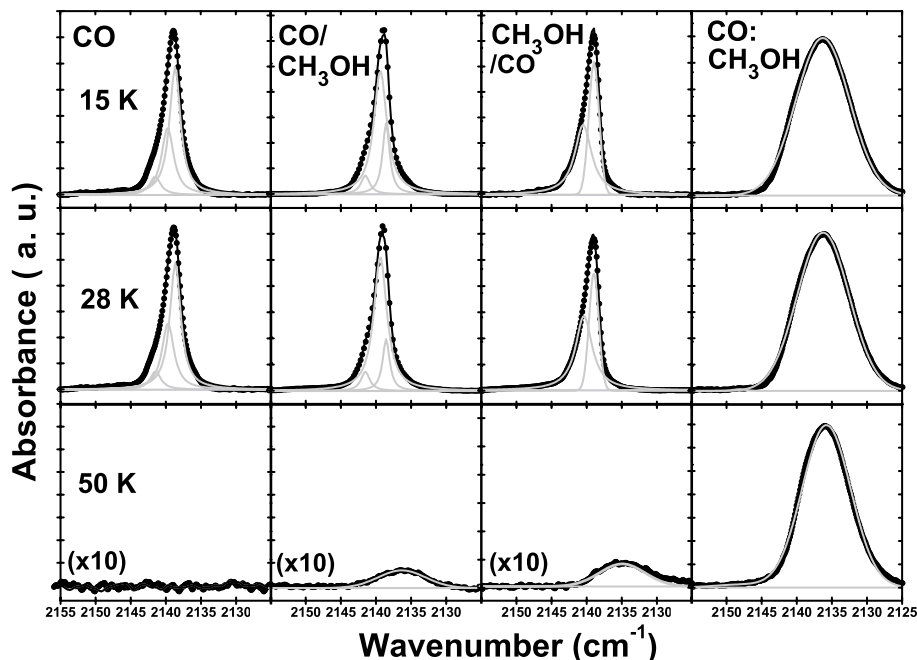


Figure 3.4. A limited set of fitted data, to illustrate the component analysis and decomposition of the laboratory spectra into their underlying features. The first column shows pure CO ice spectra, the remainder CO-CH₃OH ices, in CO/X, X/CO and CO:X morphologies respectively. Data points from the experiment are shown as black dots, the fitted components as solid grey lines, and the overall fit as a solid black line. Fits at 3 sample temperatures are given: 15 K - where the ices were deposited, 28 K - where CO starts to desorb in these experiments, 50 K - by which temperature any pure CO ice component has fully desorbed and the remaining molecules are either mixed or trapped in the ice.

crystalline, amorphous and dimer/polymer lattice environments within the ice layer (see also Table 3.2). The fitted components are shown as grey solid lines on Fig. 3.4, from which it is clear that the lab-CO_C component makes the largest contribution to the overall profile of the CO band at 15 K. At higher temperatures the same components are required to fit the overall spectra, and as Fig. 3.5 illustrates, the relative contribution of each of these components to the overall band decreases equally as the pure CO ice desorbed.

When the layered ices are heated, prior to CO desorption the relative contribution of the lab-CO_A feature generally increases with temperature, as the lab-CO_C feature decreases. This is illustrated in Fig. 3.4 for the CO/CH₃OH and CH₃OH/CO ices, that are decomposed into 3 components as described previously for pure ices (see Fig. 3.4, 2nd and 3rd columns). After deposition at 15 K, the spectral profile is dominated not by the lab-CO_C component, but the

lab-CO_A component, with only a minor fraction of the CO molecules residing in the lab-CO_D cluster domain. Clearly, depositing CO ice on top of CH₃OH, or depositing CH₃OH on top of CO influences the binding or orientation of molecules in the CO ice such that the amorphous sites dominate. When the layered CO-CH₃OH ices are heated, the contribution of the lab-CO_A component to the overall band profile increases, while the contribution of the lab-CO_C component decreases. This suggests that the CO layer is in both cases becoming increasingly disordered with temperature, which must be related to the influence of the CH₃OH layer, because such changes are not observed in the pure CO ice. At 50 K, where the CO layers have desorbed, only one component is required to fit the very weak spectral feature that remains. This Gaussian, at 2136.3 cm⁻¹, is identical to the Gaussian component required to fit the mixed ice spectra (see § 3.3.3), it is only significantly less intense and already starts to contribute to the overall profile prior to desorption in most CO/X and X/CO ices. Consequently, the small fraction of CO remaining in the layered ice samples beyond 30 K is intimately mixed with the remaining CH₃OH, CO₂ or HCOOH ice. At most, this is 5–10% of the total initial deposited fraction of CO, except in the HCOOH-CO ice system where 20–60% of the CO is trapped in the HCOOH matrix.

Mixed ices

The component evolution with temperature for the mixed ice spectra differs very little overall from the plots shown in Fig. 3.3, except in the cases of the CO:CH₄ and CO:HCOOH ices, which are the only two ice mixtures that contribute to the “middle component” of interstellar CO ices of Pontoppidan et al. (2003b). In CO:CH₄ mixtures complex formation is followed by a phase change of the whole ice system within the studied temperature range (Alsindi et al. 2003). In the CO:HCOOH ice sample, where there is a small contribution to the spectrum prior to the CO desorption temperature (30 K) of a Lorentzian feature identical to lab-CO_C, a small fraction of the CO molecules in the ice segregates from the remainder of the matrix during deposition, forming a layer of pure CO ice. By unlucky coincidence, the line position of the Gaussian component in CO:HCOOH mixed ices is identical to the position of the lab-CO_C component of pure and layered CO ices, within the resolution limits of our spectrometer. The Gaussian components required to fit the mixed ice spectra effectively reproduce any weak features remaining in the spectra of layered ices after the majority of the CO has desorbed.

In CO:CH₃OH and CO:CH₄ ice mixtures a feature at 2136 cm⁻¹ is present that corresponds to the “red” component in interstellar ices by Pontoppidan et al. (2003b). This is the same feature that is observed for CO:H₂O mixtures (Tielens et al. 1991). In the CO:CO₂ mixture the peak position occurs at 2142 cm⁻¹ at 14 K between the “middle” and “blue” components found in interstellar ices.

Summary

A summary of all the components required to fit the spectra is given in Table 3.2. For clarity, since the fitted components often change prior to and after CO desorption, the components are generally listed at 14 K and ≥ 40 K. Occasionally additional components are required at intermediate temperatures and these are also detailed. Three key points can be gleaned from these tabulated data.

First, the fitted components of the laboratory CO ice band in the pure and layered ices are identical to each other within the resolution limits. The relative contributions of each fitted component to the overall CO laboratory spectrum are best discerned from Fig. 3.5. It is seen that even after ice deposition, the relative contributions of lab-CO_C and lab-CO_A vary between the pure and layered ices, depending on the second ice component, and the deposition order. Furthermore, as the ices are heated the relative contributions of these components change, even if the overall intensity of the CO ice band remains constant. Although the dimer component lab-CO_D makes a discernible contribution to the pure CO ice band, it is either very weak or absent entirely in the CO layered ices. Excluding the CH₃OH-CO ice systems discussed previously, the major contributor to the CO/X ice band from segregated ice layers comes from CO molecules in crystalline environments (lab-CO_C), with a smaller fraction in non-libration or amorphous environments (lab-CO_A).

Second, in the mixed ices the CO band is best fitted by a single Gaussian, except in the case of CO:CH₄ and in the CO:HCOOH. The peak position is dependent on the other ice species present and at higher temperature in layered ices features remain that are similar to those observed for the ice mixtures.

Finally, most of the Gaussian components required to fit the mixed ices are red-shifted relative to the position of the pure CO ice band. Only in the case of CO:CO₂ ices is the feature blue-shifted (see also a detailed discussion of CO:CO₂ ice systems in van Broekhuizen et al. 2006). A very weak feature at 2150 cm⁻¹ is required to fit the CO/CH₃OH layered ice spectra between 30 and 50 K. Since this is coincident with the line position of CO bound to dangling OH features at H₂O ice surfaces (Collings et al. 2003a,b; Fraser et al. 2004; Al-Halabi et al. 2004), it is postulated that a similar explanation could be used in the case of CO bound at dangling OH sites on the CH₃OH ice surface.

3.4 Astrophysical implications

The aim of this study is to address the questions posed by detections of solid CO by Pontoppidan et al. (2003b) listed in § 3.1. From the spectroscopy presented in § 3.3 it appears that CO over-layers (i.e., CO/X) offer a reasonable explanation for why Pontoppidan et al. (2003b) observed that over 90% of the CO resides in pure CO layers. Irrespective of the underlying substrate, the CO spectroscopy appears identical, and varies little with temperature, until the CO itself desorbs. Figure 3.6 shows a comparison between the positions of the fitted components of the laboratory spectra, and the actual components in the phenomenological fit of Pontoppidan et al. (2003b). It is clear that the lab-CO_C, lab-CO_A and lab-CO_D

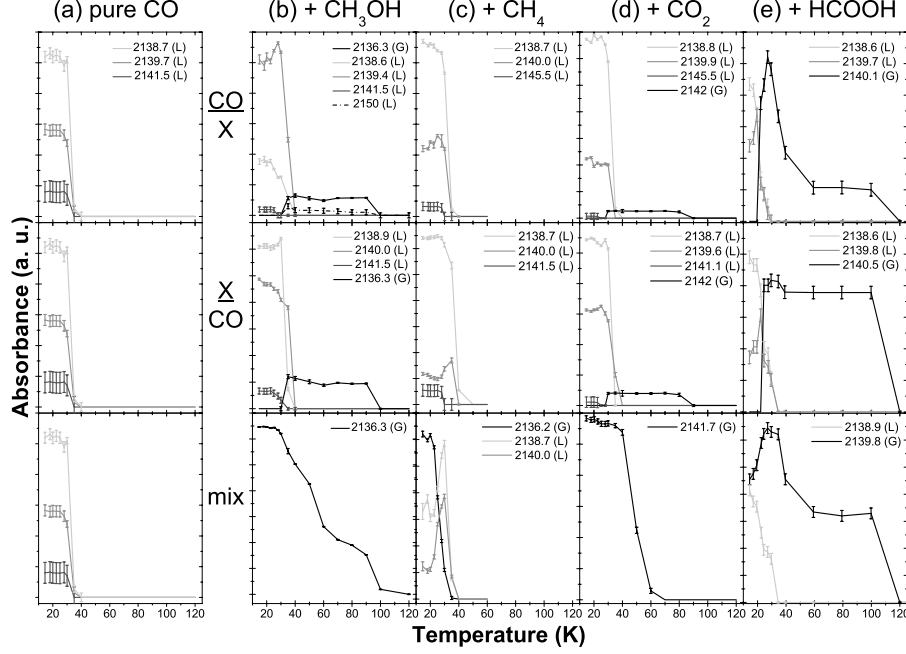


Figure 3.5. Relative contributions of each underlying fitted component of each spectrum, and their evolution with temperature. The integrated area of each fitted feature is plotted as a function of temperature. In each panel the data are normalized such that the relative contributions of each component can be compared directly in any column or row. Columns indicate different chemical constituents of the ice; rows different ice morphologies. In the left-hand-column, the pure-CO ice component evolution is reproduced 3 times, simply for ease of comparison across the row. Exact frequency fits, as per Table 3.2 are given in the legends. In every plot, the lab- CO_C component is shown in light grey, the lab- CO_A component in grey, the lab- CO_D component in dark grey, and the Gaussian component of the mixed ice in black. Additional weak components are shown as dotted lines. Error-bars shown arise from the uncertainty in the original fit to the laboratory spectrum, propagated into an uncertainty in the integrated area of each fitted component.

components all lie within the wavelength region of the $\text{CO}_{\text{ISM}}\text{-2140}$, “middle” component. Even at temperatures beyond 30 K where the CO predominantly desorbs, a number of CO ice band features are in the vicinity of this $\text{CO}_{\text{ISM}}\text{-2140}$ band. This would explain the dominance of the 2139.9 cm^{-1} band along many lines of sight towards YSOs. A combination of laboratory and observational data indicate that at least in the case of CO ices, layered rather than mixed ices are the best model analogues of interstellar ices at low temperatures. This suggests that CO is only frozen-out from the gas phase in regions of high molecular

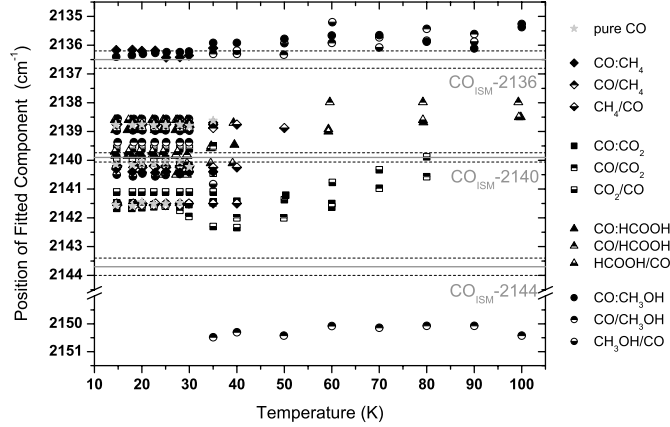


Figure 3.6. A comparison between the 3 components of the phenomenological fit to the interstellar CO ice band spectra (Pontoppidan et al. 2003b) indicated by grey labeled lines, plus their error-bars indicated with the dashed lines and the actual positions of the fitted components of the decomposed laboratory spectra (symbols). Pure CO data are shown as (*); remaining data are shown as per the legend, with filled symbols representing mixed ices, and half filled symbols representing layered ices. Symbols are plotted for each temperature at which the spectrum was recorded, against the exact frequency of the fitted Lorentzian or Gaussian peak. Error bars on fitted frequencies are omitted for clarity, but are typically $\pm 0.25 \text{ cm}^{-1}$.

density when H₂O dominated ice mantles, including CO₂ and other molecular species, have already formed, consistent with the observational ice mapping data of Pontoppidan (2006). Moving from a concept where all interstellar ices are mixed, to a concept where segregated layers exist, has significant implications for astrochemical modeling and laboratory experiments on interstellar ices (see e.g., Bergin et al. 1995; Bergin & Langer 1997).

Figure 3.6 also shows a population of laboratory CO ice band components at or around 2136 cm^{-1} , the “red” component. It has previously been shown that where CO resides in H₂O ices, a broader, red shifted component emerges in the CO spectra (e.g., Tielens et al. 1991; Chiar et al. 1994, 1995), which shifts even further to the red upon heating (e.g., Bouwman et al. 2007). Not only H₂O, but other ice constituents, e.g., CH₃OH, HCOOH and CH₄, are capable of such hydrogen bonding interactions. Potentially the origins of the CO_{ISM}-2136 component does have both a chemical and physical source from a combination of multiple ice constituents interacting with the CO (as shown here). An alternative explanation such as inferred for proto-planetary disks is scattering by large grains, but this is not thought to dominate for the general ISM or outer protostellar envelopes (Dartois 2006).

The explanation of the CO_{ISM}-2144 band is less obvious. It is clear from

the decomposition of the laboratory spectra that the majority of CO molecules in CO ices grown in the laboratory reside in the lab-CO_C crystalline domains. Although this was a condition first specified by Pontoppidan et al. (2003b) for the CO_{ISM}-2144 band to be associated with LO-TO splitting of the pure CO band (Chang et al. 1988), Palumbo et al. (2006) and Fuchs et al. (2006) have shown that this feature can arise from amorphous CO ices. Figure 3.6 shows that not one component from the fitted laboratory spectra lies in the vicinity of the interstellar CO_{ISM}-2144 band. No LO-TO splitting is expected in these laboratory spectra since the light source is unpolarized and the transmission path is aligned normal to the ice film. Boogert et al. (2002b) suggested that CO:CO₂ ices could explain the CO_{ISM}-2144 band, but this and recent work by van Broekhuizen et al. (2006) show that CO:CO₂ ices do not “match” the interstellar CO_{ISM}-2144 band well in the phenomenological fit. That is not to say that CO:CO₂ ices are not present in interstellar ice mantles, but that other bands, such as CO₂ stretching and bending modes, must be considered in combination with the profile of the interstellar CO_{ISM}-2144 component, to make a clear assignment (Pontoppidan et al., in prep.). It remains an open question whether or not the interstellar CO_{ISM}-2144 is really related to LO-TO splitting of the pure-CO ice feature.

One further spectral region is “populated” in these laboratory experiments, namely the region around 2150 cm⁻¹. This feature is only detected here in CO-CH₃OH ices (see Fig.3.2), and is only relatively strong in the CO/CH₃OH layered systems. In CO-H₂O ices laboratory spectra also have clear features at this position, assigned to CO molecules associated with the “dangling” OH-bonds at the ice surface (e.g., Fraser et al. 2004; Al-Halabi et al. 2004; Collings et al. 2003a). We therefore conclude that similar bond geometries exist at the CH₃OH ice surface, giving rise to this feature. However, such a feature has never been observed in astronomical objects, implying that CO is not present in such ice environments. Potential reasons for this have been discussed extensively elsewhere (Fraser et al. 2004).

The results presented here suggest that factors such as molecular abundance, layer thickness, and the degree to which layers have become mixed have a more significant influence on the appearance of the overall CO spectra than the specific chemical environment. In fact below 35 K in the layered systems, no change in line shape profiles or line positions are recorded as the temperature is raised. Similarly, the mixed ices, and layered ices beyond 35 K, also show very little variation with temperature, until the ices undergo a phase change or the components of the ice begin to desorb. It is therefore likely that the differences in the relative intensities of each component required to fit the observational spectra in the phenomenological fits are associated with these physical factors. From an astrochemical perspective, this means that the data presented here can be used to make an educated guess that in ices above 30 K, not dominated by HCOOH or H₂O, not more than 10% of the initial CO ice present at lower temperatures will be retained. If CO molecules need to be present to form more complex organic species or even simple molecules like CO₂ and HCO, these surface or bulk reactions must occur whilst the CO is abundant in the ice. This places

quantitative constraints on solid-state chemistry, and can be incorporated into astrochemical models.

3.5 Summary and conclusions

The spectroscopy of CO in pure, layered and mixed ice morphologies with CH₃OH, CH₄, CO₂ and HCOOH are studied under high vacuum conditions as a function of temperature. Transmission absorption infrared spectroscopy has been used to study the ices. The main conclusions on the spectroscopy and the kinetic behavior of CO ice in these ice morphologies are:

- ▷ The pure CO ice feature is decomposed into three components, related to CO in dimer, amorphous and crystalline environments within the ice. These three components all combine to produce the CO_{ISM}-2140 feature, labeled as the middle component by Pontoppidan et al. (2003b).
- ▷ In layered ices at low ice temperatures the same three features as for pure CO ices are present, although with relatively different contributions depending on the deposition order and other ice species present. When the temperature increases, CO mixes with the other ice components and a broad Gaussian feature identical to that of the corresponding ice mixture is observed.
- ▷ The spectroscopy of CO is significantly altered when mixed with other molecular solids. The CO stretch is red-shifted when the CO bond-strength is decreased by these interactions and blue-shifted when the CO-bond strength is strengthened. In hydrogen bonded matrices, this leads to a feature at or around 2136 cm⁻¹, the so-called “polar” CO, or CO_{ISM}-2136 feature. Our experiments show that not only CO:H₂O but also CO:X with X=CH₃OH or CH₄ are consistent with the peak positions in observational data.
- ▷ The CO_{ISM}-2144 feature is not well matched to any of the spectra produced here. Pontoppidan et al. (2003b) suggest it could be related to LO-TO splitting of the pure CO ice feature but the true nature of this feature remains open to discussion.
- ▷ CO ice layers desorb almost entirely in the same temperature range as pure CO ices, i.e., around 30 K under HV conditions. The remaining CO is trapped in the less volatile ice matrix that remains on the substrate, and is released as the solid restructures, undergoes a phase change or desorbs. Ices with H-bonding capabilities are more likely to trap a greater percentage of CO molecules. In mixed ice layers CO can be retained much longer than in layered systems. The CO-HCOOH ice system is an exception, because the HCOOH/CO layered system traps a larger fraction of solid CO than the CO:HCOOH mixture. These trapped CO molecules will be available in interstellar ices for chemical reactions at temperatures beyond the sublimation temperature of pure CO ice.

Overall this extensive laboratory survey of CO ice spectroscopy shows that the observational conclusion that the CO ice profile is comprised of the same three components along all lines of sight is due to the morphology of CO ice. We conclude that CO is predominantly present in an ice layer over and above other ices formed on grain surfaces at low temperatures, consistent with the idea that CO freezes out at higher visual extinction compared to other ice species. At higher temperatures, CO is predominantly retained in hydrogen bonding mixed ices.

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Appendix: Previous studies of laboratory ices

Table 3.4. Laboratory data on the CO-band profile of mixed ices containing CO as a constituent, after deposition at ≤ 30 K.

Ice mixtures Species (%)	Res. (cm^{-1})	Temp. (K)	Pos. [FWHM] (cm^{-1})
CO:H ₂ O 91:9 ^a	1	10	2138.7 [3.4] 2152 [-]
CO:H ₂ O 99:1 ^b	1	10	2138.9 [2.6] 2152 [-]
CO:H ₂ O 99:1 ^b	1	30	2138.9 [2.5] 2152 [-]
CO:H ₂ O 1:99 ^a	1	10	2136.5 [8.4] 2152 [-]
CO:H ₂ O 5:95 ^a	1	10	2136.7 [9.0] 2152 [-]
CO:H ₂ O 5:95 ^a	1	30	2136.1 [8.0] 2152 [-]
CO:H ₂ O 5:95 ^c	1	8	2139 [-] 2153 [-]
CO:H ₂ O:CH ₃ OH 4:87:9 ^a	1	10	2136.5 [9.4]
CO:H ₂ O:CH ₃ OH 8:80:12 ^d	2	10	2137 [8]
CO:H ₂ O:CH ₃ OH 6:63:31 ^a	2	10	2137 [7]
CO:CH₃OH 50:50^e	0.5	14	2136.4 [9.2]
CO:CH₃OH 50:50^d	2	10	2136 [9]
CO:CH₄ 50:50^e	0.5	14	2136.2 [3]
CO:CH ₄ 5:95 ^a	1	10	2136.5 [2.2]
CO:CO₂ 50:50^e	0.5	14	2141.7 [8.8]
CO:CO₂ 50:50^d	2	10	2141 [8]
CO:CO₂ 50:50^f	0.5	15	2142 [9]
CO:CO ₂ 5:95 ^a	1	10	2139.7 [5.8]
CO:CO ₂ 9:91 ^f	0.5	15	2140 [5.6]
CO:CO ₂ 96:4 ^b	1	10	2138.8 [2.5]
CO:CO ₂ 93:7 ^b	1	10	2139.1 [3.0]
CO:CO ₂ 86:14 ^b	1	10	2138.8 [3.8]
CO:CO ₂ 83:17 ^b	1	10	2139.2 [4.4]
CO:CO ₂ 81:19 ^b	1	10	2138.9 [6.4]
CO:CO ₂ 79:21 ^b	1	10	2138.4 [7.4]
CO:CO ₂ 67:33 ^f	0.5	15	2140 [-]
CO:CO ₂ 59:41 ^b	1	10	2139.9 [8.2]
CO:HCOOH 50:50^e	0.5	14	2138.9 [8]
CO:O ₂ 67:33 ^b	1	10	2138.9 [3.8]
CO:O ₂ 67:33 ^b	1	30	2138.8 [3.1]
CO:O ₂ 59:41 ^b	1	10	2138.6 [5.2]

Data in **bold** type refer to results from previous work that is directly comparable with that presented here. - Data not published. Data from: ^aSandford et al. (1988), ^bEhrenfreund et al. (1997), ^cCollings et al. (2003a,b), ^dPalumbo & Strazzulla (1993), ^ethis chapter (*in italics*), and ^fvan Broekhuizen et al. (2006). See also Bouwman et al. (2007) for recent systematic CO:H₂O spectroscopic studies.

Table 3.5. *Laboratory data on the CO-band profile of layered ices containing CO as a constituent, after deposition at ≤ 60 K.*

Ice layers Species (%)	Res. (cm^{-1})	Temp. (K)	Pos. [FWHM] (cm^{-1})
CO/H ₂ O 5:95 ^a	1	8	2138.6 [–] 2143.3 [–]*
		20	2139 [–] 2153 [–]
CO/H ₂ O ^b	1	56	2139 [–] 2154 [–]
<i>CO/CH₃OH 50:50^c</i>	<i>0.5</i>	<i>14</i>	<i>2138.6 [1.3]</i>
<i>CH₃OH/CO 50:50^c</i>	<i>0.5</i>	<i>14</i>	<i>2139.0 [1.7]</i>
<i>CO/CH₄ 50:50^c</i>	<i>0.5</i>	<i>14</i>	<i>2138.7 [2.1]</i>
<i>CH₄/CO 50:50^c</i>	<i>0.5</i>	<i>14</i>	<i>2138.7 [2.1]</i>
<i>CO/CO₂ 50:50^c</i>	<i>0.5</i>	<i>14</i>	<i>2138.8 [1.8]</i>
CO/CO₂ 50:50^a	0.5	15	2138.7 (1.6)
CO/CO ₂ 33:67 ^a	0.5	15	2138.7 [1.6]
<i>CO₂/CO 50:50^c</i>	<i>0.5</i>	<i>14</i>	<i>2138.7 [1.4]</i>
CO₂/CO 50:50^a	0.5	15	2138.7 [1.6]
CO ₂ /CO 67:33 ^a	0.5	15	2138.7 [1.6]
CO ₂ /CO 75:25 ^a	0.5	15	2138.7 [1.6]
CO ₂ /CO 91:9 ^a	0.5	15	2138.7 [1.6]
<i>CO/HCOOH 50:50^c</i>	<i>0.5</i>	<i>14</i>	<i>2138.7 [1.6]</i>
<i>HCOOH/CO 50:50^c</i>	<i>0.5</i>	<i>14</i>	<i>2138.6 [1.7]</i>

Data in **bold** type refer to results from this experiment, or previous work that is directly comparable with that presented here. – Data not known; *LO-TO splitting. Data from: ^aCollings et al. (2003a,b), ^bMartin et al. (2002), ^cthis chapter (*in italics*).

Chapter 4

Infrared spectroscopy of HCOOH in interstellar ice analogues

Abstract

Context: HCOOH is one of the more common species in interstellar ices with abundances of 1–5% with respect to solid H₂O. With the launch of the Spitzer Space Telescope new infrared spectra have become available of interstellar ices in different environments. So far systematic laboratory studies on HCOOH-containing interstellar ice analogues are lacking.

Aims: This study aims at characterizing the HCOOH spectral features in astrophysically relevant ice mixtures in order to interpret astronomical data.

Methods: The ices are grown under high vacuum conditions and spectra are recorded in transmission using a Fourier transform infrared spectrometer. Pure HCOOH ices deposited at 15 K and 145 K are studied, as well as binary and tertiary mixtures containing H₂O, CO, CO₂ and CH₃OH. The mixture concentrations are varied from 50:50% to ~10:90% for HCOOH:H₂O. Binary mixtures of HCOOH:X and tertiary mixtures of HCOOH:H₂O:X with X=CO, CO₂, and CH₃OH, are studied for concentrations of ~10:90% and ~7:67:26%, respectively.

Results: Pure HCOOH ice spectra show broad bands which split around 120 K due to the conversion of a dimer to a chain-structure. Broad single component bands are found for mixtures with H₂O. Additional spectral components are present in mixtures with CO, CO₂ and CH₃OH. The resulting peak position, full width at half maximum and band strength depend strongly on ice structure, temperature, matrix constituents and the HCOOH concentration. Comparison of the solid HCOOH 5.9, 7.2, and 8.1 μm features with astronomical data toward the low mass source HH 46 and high mass source W 33A shows that spectra of binary mixtures do not reproduce the observed ice features. However, our tertiary mixtures especially with CH₃OH match the astronomical data very well. Thus interstellar HCOOH is most likely present in tertiary or more complex mixtures with H₂O, CH₃OH and potentially also CO or CO₂, providing constraints on its formation.

Bisschop, Fuchs, Boogert, van Dishoeck & Linnartz, 2007, A&A, 470, 749

4.1 Introduction

Formic acid is one of the few molecules in star forming regions that is detected both in the solid state and in the gas phase (see e.g., Schutte et al. 1999; Ikeda et al. 2001). Infrared observations of ices in high mass Young Stellar Objects (YSOs) with the Infrared Space Observatory (ISO) contain absorption features that are assigned to HCOOH and that correspond to the C=O stretch, $\nu_{\text{S}}(\text{C}=\text{O})$, at 5.9 μm and the OH and CH bending modes, $\nu_{\text{B}}(\text{OH})$ and $\nu_{\text{B}}(\text{CH})$ at 7.2 μm

(Schutte et al. 1997, 1999). The $\nu_S(\text{C=O})$ band is the strongest spectral feature of HCOOH ice, but suffers from partial overlap with the OH bending mode of solid H_2O at $6\text{ }\mu\text{m}$, $\nu_B(\text{OH})$. The $\nu_B(\text{OH/CH})$ band at $7.2\text{ }\mu\text{m}$ is significantly weaker than the $\nu_S(\text{C=O})$ band, but is present in a relatively clean region and has previously been detected toward high mass star forming regions (Schutte et al. 1999). More recently, these features have also been observed toward low mass YSOs and possibly toward background stars (Boogert et al., in prep.; Knez et al. 2005). Typical abundances of HCOOH vary between individual sources from 1 to 5% with respect to solid H_2O . The aim of this chapter is to study the $\nu_S(\text{C=O})$, $\nu_B(\text{OH/CH})$ and other infrared features of HCOOH ices in different astrophysically relevant laboratory matrices and to compare the results with astronomical spectra to infer the chemical environment of HCOOH in interstellar ices.

In the gas phase HCOOH is detected in envelopes surrounding high and low mass star forming regions, as well as in shocked regions toward the galactic center (van Dishoeck et al. 1995; Ikeda et al. 2001; Bottinelli et al. 2007; Requena-Torres et al. 2006; Bisschop et al. 2007c). HCOOH is part of the surface chemistry network leading to the formation of complex organic molecules seen in hot cores (Tielens & Charnley 1997) and is therefore expected to be present in compact hot regions where it has evaporated from dust grains. In contrast, interferometric observations show that gas phase HCOOH emission can be extended beyond the hot core and is not coincident with other oxygen-bearing species such as CH_3OCHO (Liu et al. 2002; Hollis et al. 2003; Remijan & Hollis 2006). The observed gas phase HCOOH has low rotation temperatures and its abundance is a factor of 10^{-4} lower than that of solid HCOOH (Bisschop et al. 2007c). It is very likely that gaseous and solid HCOOH co-exist in the same region. A low level of non-thermal desorption due to e.g., cosmic ray spot heating is sufficient to explain the observed gas phase abundances of HCOOH.

Previously, laboratory ice spectra have been studied for pure HCOOH and mixtures of HCOOH with H_2O and/or CH_3OH by Schutte et al. (1999) and Hudson & Moore (1999). These studies only focused on specific spectral features. The data clearly showed that the morphology and composition of the ice matrix strongly influence the HCOOH infrared spectrum. Recently, experiments have been reported for the layered ice system HCOOH/ H_2O in which the interaction of HCOOH and H_2O in the interface is studied (see e.g., Cyriac & Pradeep 2005; Bahr et al. 2005; Souda 2006).

There is a clear need to understand the spectroscopy of the main ice constituents such as HCOOH, as new observational tools become available for the study of infrared features of interstellar ices, such as the Spitzer Space Telescope, the Stratospheric Observatory For Infrared Astronomy (SOFIA), and the James Webb Space Telescope (JWST). Solid HCOOH is likely mixed with species such as H_2O , CO, CO_2 and CH_3OH that are abundant in the ice and have related formation mechanisms. Infrared ice features of mixtures with these species have been studied in this chapter. Pure HCOOH is measured as well for comparison. Quantitative and qualitative analysis of the $5.9\text{ }\mu\text{m}$, $7.2\text{ }\mu\text{m}$ and other HCOOH ice features allows for a better determination of the amount of HCOOH present

in interstellar ices as well as its ice environment.

The chapter is organized as follows: § 4.2 explains the experimental method, § 4.3 the analysis techniques, § 4.4 discusses the results of experiments with pure ices, as well as mixtures with H₂O, CH₃OH, CO and CO₂, in § 4.5 the effects of ice matrix and temperature on the band strength are presented, § 4.6 discusses the physical aspects of the interactions of HCOOH in the solid state with other species, § 4.7 presents the astrophysical implications, and finally § 4.8 summarizes the main conclusions of this chapter.

4.2 Experimental procedure

The experiments are performed in a high vacuum (HV) set-up with a base pressure of $\sim 10^{-7}$ Torr, that has been previously described in detail by Gerakines et al. (1995). A CsI window mounted in close thermal contact with a closed cycle He cryostat is situated at the center of the chamber. It is used as a substrate holder and can be cooled down to 14 K. The sample temperature is controlled to better than ± 0.1 K using the cryostat cold finger, a resistive heating element and a Lakeshore 330 temperature control unit. The system temperature is monitored by two KP-type thermocouples (0.07% Au in Fe versus chromel), one mounted on the substrate face and the second close to the heater element. Ices are grown *in situ* onto the substrate, by exposing the cold surface to a steady flow of gas that is introduced into the chamber via an all metal flow control valve with a modified outlet directed at the substrate center along the surface normal. The ices are monitored by Fourier Transform Infrared (FTIR) absorption spectroscopy with 1 cm^{-1} spectral resolution covering the 4000–500 cm^{-1} range.

To test the effect of dilution of HCOOH (98% purity, J. T. Baker) by H₂O (deionized) four mixtures are prepared in a glass vacuum manifold. Both HCOOH and H₂O are further purified by subsequently freezing and thawing the samples in the vacuum manifold. The mixture ratios range from the relative abundances derived from observations of interstellar ices of 1 to 5% (see e.g., Gibb et al. 2004) to more HCOOH-rich ices with relative HCOOH:H₂O concentrations up to 50:50%. The astrophysical motivation for these higher mixture ratios is that other species such as CH₃OH are present in solid state environments with nearly equal amounts of H₂O and/or CO₂ (Ehrenfreund et al. 1998, 1999; Dartois et al. 1999). The different HCOOH:H₂O mixtures that are used here are summarized in Table 4.1. A pure H₂O sample is prepared for comparison. Furthermore, some features of the solid CO band can be explained with mixtures or layers of CO with non-hydrogen-bonding molecules or with hydrogen-bonding species other than H₂O (e.g., Tielens et al. 1991; Pontoppidan et al. 2003b; Fraser et al. 2007). Accordingly, we have also studied a set of binary mixtures of HCOOH:X and tertiary mixtures of HCOOH:H₂O:X, where X stands for CO (99.997% purity, Praxair), C¹⁸O₂ (97% purity, Icon) or CH₃OH (99.9% purity, Janssen Chimica) are prepared with concentrations of $\sim 10:90\%$ and $\sim 7:67:26\%$, respectively. These mixtures are chosen such that the matrix

Table 4.1. *Overview of ice morphologies, total ice exposure and deposition time.*

HCOOH (%)	H ₂ O (%)	X (%)	Total exposure (L)	Deposition time (min)
100	—	—	900	15
—	100	—	900	15
50	50	—	900	15
34	66	—	900	15
20	80	—	900	15
9	91	—	900	15
11	—	89(CO)	1800	30
9	—	91(C ¹⁸ O ₂)	900	15
10	—	90(CH ₃ OH)	1800	30
8	62	30(CO)	1800	30
6	67	27(C ¹⁸ O ₂)	1800	30
6	68	26(CH ₃ OH)	1800	30

species determine the structure of the ice. Uncertainties on the concentrations of the ice constituents are $\sim 10\%$ due to inaccuracies in the pressure reading. The C¹⁸O₂ isotopologue is used to distinguish solid C¹⁸O₂ from regular atmospheric gas phase CO₂.

A typical experiment starts with taking a background spectrum at 15 K. Subsequently, the ices are deposited with a flow of $\sim 1.0 \times 10^{-5}$ Torr s⁻¹. An exposure of 1.0×10^{-6} Torr s⁻¹ corresponds to 1 Langmuir (L) or equivalently 1 monolayer (ML) s⁻¹ assuming that the molecular surface density is 10^{15} molecules cm⁻² and the sticking probability is 1 at 15 K. The deposition times and total exposures are summarized in Table 4.1. After deposition, FTIR spectra are taken at 15 K, and subsequently every 15 K for binary mixtures of HCOOH with H₂O or CO₂ and every 30 K for all other mixtures up until a temperature of 165 K is reached. At each temperature, the sample stabilizes for 20 minutes before a spectrum is recorded.

One pure HCOOH experiment is performed where HCOOH is deposited at 145 K. The aim of this experiment is to determine whether the HCOOH ice structure depends on the deposition temperature and whether potential phase changes are reversible. Subsequently, the experiment is cooled down to 15 K and from then on FTIR spectra are taken every 15 K during warm-up.

4.3 Data reduction and analysis

The spectral range from 4000–500 cm⁻¹ is very rich in absorption features of complex organic species, and HCOOH is no exception. Consequently special care has to be taken in the data reduction. Depending on the mixture, different frequency ranges are used to fit third order polynomial baselines (see Table 4.2).

Table 4.2. *Frequency ranges used for baseline subtraction.*

Ice composition	Baseline range (cm^{-1})
HCOOH & HCOOH:H ₂ O	4000–3800, 1850–1800, 1050–1030, 540–500
HCOOH:CH ₃ OH & HCOOH:H ₂ O:X ^a	4000–3700, 1850–1800, 1580–1500, 950–900, 500–450
HCOOH:CO	4000–3800, 2440–2260, 2000–1800, 1550–1400, 600–500
HCOOH:CO ₂	4000–3900, 2100–1800, 1550–1430, 550–500

^aX = CO, C¹⁸O₂ or CH₃OH.

Table 4.3. *Summary of absolute band strengths for HCOOH from the literature.*

Ice matrix	$A[\nu_{\text{S}}(\text{C}=\text{O})]$ (cm molecule^{-1})	$A[\nu_{\text{S}}(\text{C}-\text{O})]$ (cm molecule^{-1})	$A[\nu_{\text{B}}(\text{OH}/\text{CH})]$ (cm molecules^{-1})
HCOOH ^a	6.7(-17)	—	2.8(-18)
HCOOH:H ₂ O 7:93% ^b	—	1.5(-17)	—
HCOOH-5(H ₂ O) ^c	8.5(-17)	5.0(-17)	1.1(-18)
HCOOH-6(H ₂ O) ^c	7.7(-17)	4.3(-17)	3.5(-18)

^aLaboratory gas phase data by Marechal (1987). ^bLaboratory solid state data by Hudson & Moore (1999). ^cTheoretical calculations by Park & Woon (2006).

An additional local baseline is subtracted in the 1800–1100 cm^{-1} frequency range. This is necessary as the HCOOH $\nu_{\text{S}}(\text{C}=\text{O})$ mode around $\sim 1700 \text{ cm}^{-1}$ ($5.9 \mu\text{m}$) overlaps with the $\nu_{\text{B}}(\text{OH})$ mode of H₂O at 1655 cm^{-1} ($6.0 \mu\text{m}$). This H₂O feature is much weaker than the HCOOH feature, even when only 10% of HCOOH is present, but it is responsible for a wing on the $\nu_{\text{S}}(\text{C}=\text{O})$ band. Finally, a correction is made on the $\nu_{\text{B}}(\text{OH}/\text{CH})$ feature around 1390 cm^{-1} ($7.2 \mu\text{m}$) as it is close to a variable background feature. Spectra that comprise only the background feature are subtracted from the sample spectra for each temperature, but due to its variability, the subtraction does not fully remove the artifact.

The absolute band strengths are difficult to calibrate in our experiment, because the number of molecules that stick to the substrate sample is not exactly known. Instead, we focus in this chapter on the relative band strengths that can be accurately measured. The relative values discussed here can be combined with previously measured values for the band strengths available from the literature (summarized in Table 4.3). The absolute band strengths for the vibrational modes depend on whether HCOOH is in the gas phase or solid state and consequently the numbers in the table do not perfectly match.

To determine the relative band strengths, the $\nu_{\text{S}}(\text{C}=\text{O})$, $\nu_{\text{B}}(\text{OH}/\text{CH})$, and $\nu_{\text{S}}(\text{C}-\text{O})$ features of HCOOH as well as the $\nu_{\text{B}}(\text{OH})$ and libration ($\nu(\text{lib})$) bands of H₂O are integrated over the frequency ranges given in Table 4.4. The integration boundaries for H₂O are identical to those used recently by Öberg et al. (2007). Since the $\nu_{\text{B}}(\text{OH})$ band at 930 cm^{-1} ($10.8 \mu\text{m}$) and the OCO bending mode ($\nu_{\text{B}}(\text{OCO})$) at 705 cm^{-1} ($14.2 \mu\text{m}$) of HCOOH overlap with the H₂O $\nu(\text{lib})$ band at 750 cm^{-1} ($13.3 \mu\text{m}$), these two features are subtracted before

Table 4.4. *Frequency ranges used for integration bounds.*

Vibrational mode	Wavenumber (cm ⁻¹)
HCOOH	
$\nu_S(\text{C=O})$	1800 – 1550
$\nu_B(\text{OH/CH})$	1450 – 1370
$\nu_S(\text{C-O})$	1300 – 1150
H ₂ O	
$\nu_S(\text{OH})$	3700 – 3000
$\nu(\text{lib})$	1000 – 500

integration.

The relative band strengths of the HCOOH and H₂O spectral features are calculated with respect to pure HCOOH and H₂O via:

$$\frac{A(\text{HCOOH} : \text{H}_2\text{O} = Y : 1)}{A_0(\text{HCOOH})} = Y \times \frac{\int_{\text{band}} I(\text{HCOOH} : \text{H}_2\text{O} = Y : 1)}{\int I_0(\text{HCOOH})}. \quad (4.1)$$

Here Y is the HCOOH ice fraction, $\int_{\text{band}} I(\text{HCOOH} : \text{H}_2\text{O} = Y : 1)$ the integrated absorbance of the band in the mixture, $A_0(\text{HCOOH})$ the band strength for pure HCOOH ice at 15 K, and $\int I_0(\text{HCOOH})$ the integrated absorbance for pure HCOOH ice at 15 K. A similar formula is used for H₂O. The resulting relative band strengths are studied as a function of temperature (see § 4.5). An extensive discussion of the uncertainties of the band strengths is given by Öberg et al. (2007). In short, the largest fraction of the uncertainties arises from inaccuracies on the mixing ratio of the ice and yields relative uncertainties that are below 10%. Additionally, baseline subtraction and deposition time inaccuracies are 1 to 2%. A conservative approach yields an overall uncertainty of ~12% in the resulting calculations for the relative band strengths. Furthermore, it is important to note that the relative uncertainty between different temperatures for a single experiment amounts to ~2% as only baseline inaccuracies contribute. Observed temperature trends are thus much more certain than concentration dependencies.

The $\nu_S(\text{C=O})$, $\nu_B(\text{OH/CH})$ and $\nu_S(\text{C-O})$ bands of HCOOH are fitted with Gaussian line profiles for the astrophysically most relevant 1800–1100 cm⁻¹ range. To fit the asymmetric profile of the $\nu_S(\text{C=O})$ stretch around 1700 cm⁻¹ two components are needed. It turned out to be difficult to disentangle the properties of the absorption bands of HCOOH in some mixtures, in particular those containing CO and CO₂. In such cases average peak positions are given. In general the uncertainties of peak positions and FWHMs are ± 1 cm⁻¹ and ± 2 cm⁻¹, except for the $\nu_B(\text{OH/CH})$ feature in the 9:91% HCOOH:H₂O mixture, where the values are ± 2 cm⁻¹ and ± 4 cm⁻¹, respectively.

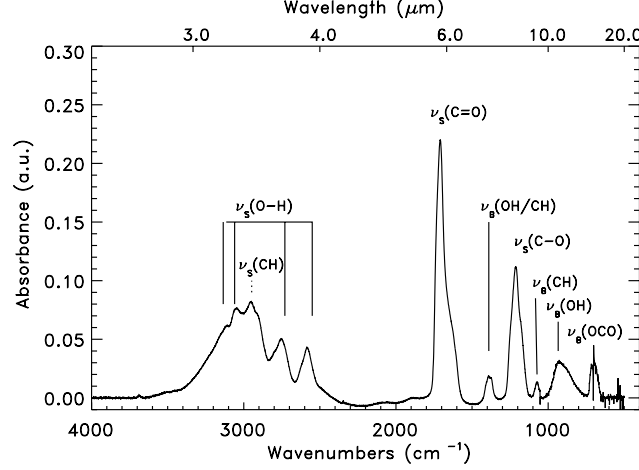


Figure 4.1. *Experimental infrared spectrum of pure HCOOH ice deposited at 15 K. The $\nu_S(\text{OH})$ band has several sub-maxima in the $\sim 3000 \text{ cm}^{-1}$ range where $\nu_S(\text{CH})$ is also located. Below 2000 cm^{-1} the following absorption features are present: the C=O stretching mode $\nu_S(\text{C=O})$, the C–O stretch $\nu_S(\text{C–O})$, the CH bending mode $\nu_B(\text{CH})$, the OH bending mode $\nu_B(\text{OH})$ and OCO bending mode $\nu_B(\text{OCO})$. Peak positions and labels are given in Table 4.5. In this study the focus is on the $\nu_S(\text{C=O})$, $\nu_B(\text{OH/CH})$, and $\nu_S(\text{C–O})$ bands.*

4.4 Results

The following section summarizes the results for the pure and mixed HCOOH ices at different temperatures. All spectra are available at:

<http://www.strw.leidenuniv.nl/~lab/databases/>.

4.4.1 Pure HCOOH ices

Clearly, the pure HCOOH ice spectrum shown in Fig. 4.1 for 15 K is complex. For completeness we summarize the spectroscopic assignments for all bands here (see Table 4.5), but in this chapter we mainly focus on the astrophysically relevant features $\nu_S(\text{C=O})$, $\nu_B(\text{OH/CH})$, as well as $\nu_S(\text{C–O})$. The measured peak positions and FWHMs in the astrophysically relevant $1800\text{--}1100 \text{ cm}^{-1}$ range are given in Table 4.7 of the online material. The features at 3115 cm^{-1} , 2754 cm^{-1} , and 2582 cm^{-1} ($3.21\text{--}3.87 \mu\text{m}$) are all due to the OH stretching mode, $\nu_S(\text{OH})$. The broad structure with different maxima of these modes are assigned to a combination of dimers and HCOOH organized in long chains (Cyriac & Pradeep 2005). The $\nu_S(\text{OH})$ bands overlap with the 2953 cm^{-1} CH stretch, $\nu_S(\text{CH})$. In observations these bands overlap with and are dominated by the $3 \mu\text{m}$ H_2O band. The astrophysically important $\nu_S(\text{C=O})$ band has its maximum around 1714 cm^{-1} and is broad and asymmetric. The C–O stretch, $\nu_S(\text{C–O})$, is located

Table 4.5. Solid state spectral features for HCOOH, H₂O, CO, CO₂, and CH₃OH at 15 K. The symbols ν_S and ν_B indicate a stretching or bending mode, respectively. The gas phase spectroscopic label is indicated as well. The astrophysically most relevant features of HCOOH are marked in bold face.

Wavenumber (cm ⁻¹)	Wavelength (μ m)	Mode	Label	Comment
HCOOH				
3115	3.21	ν_S (OH)	ν_1	has several sub-maxima
2953	3.39	ν_S (CH)	ν_2	
2754	3.63	ν_S (OH)	ν_1	has several sub-maxima
2582	3.87	ν_S (OH)	ν_1	has several sub-maxima
1714	5.83	ν_S (C=O)	ν_3	out-of-phase between adjacent chains
1650	6.06	ν_S (C=O)	ν_3	in-phase between adjacent chains
1387	7.21	ν_B (OH) & ν_B (CH)	ν_6 & ν_4	
1211	8.26	ν_S (C-O)	ν_6	
1073	9.32	ν_B (CH)	ν_8	out-of-plane
930	10.75	ν_B (OH)	ν_5	out-of-plane
705	14.18	ν_B (OCO)	ν_7	
H₂O				
3280	3.05	ν_S (OH)	ν_1, ν_3^a	
1655	5.88	ν_B (OH)	ν_2	
750	13.33	ν (lb)		
CO				
2140	4.67	ν_S (CO)	ν_1	
C¹⁸O₂				
3671	2.72	overtone	$\nu_1 + \nu_3$	
3513	2.85	overtone	$2\nu_2 + \nu_3$	
2310	4.33	ν_S (CO)	ν_3	
645	15.50	ν_B (OCO)	ν_2	
CH₃OH				
3251	3.08	ν_S (OH)	ν_1	
2951	3.39	ν_S (CH)	ν_2, ν_9	
2827	3.54	ν_S (CH)	ν_3	
1460	6.85	CH ₃ deformation and ν_B (OH)	$\nu_4, \nu_{10}, \nu_5, \nu_6^b$	
1130	8.85	CH ₃ rock	ν_7, ν_{11}	
1026	9.75	ν_S (CO)	ν_8	
694	14.41	torsion	ν_{12}	

^a ν_1 refers to the symmetric stretching mode and ν_3 to the anti-symmetric stretching mode of H₂O. ^b ν_4 and ν_{10} are anti-symmetric deformations, ν_5 is a symmetric deformation of CH₃OH and ν_6 is the OH bending mode for CH₃OH.

at 1211 cm^{-1} . Furthermore, bending modes are present of which $\nu_B(\text{CH})$ and $\nu_B(\text{OH})$ at 1073 cm^{-1} and 930 cm^{-1} (9.3 and $10.8\text{ }\mu\text{m}$), respectively, are out-of-plane.

The temperature evolution of the astrophysically relevant HCOOH features in the $1800\text{--}1100\text{ cm}^{-1}$ range is shown in Fig. 4.2a and the corresponding peak positions are given in Table 4.7 of the online material. Most features are broad and consist of multiple components at 15 K . At 135 K the $\nu_S(\text{C=O})$, $\nu_S(\text{C-O})$, and $\nu_B(\text{OH/CH})$ modes at ~ 1700 , 1250 , and 1390 cm^{-1} split into two components. The splitting of the $\nu_S(\text{C=O})$ and $\nu_S(\text{C-O})$ bands is assigned to the out-of-phase and in-phase motions of different HCOOH molecules within the same chain (Cyriac & Pradeep 2005). The out-of-phase motions are located at higher wavenumbers than the in-phase motions. The $\nu_S(\text{OH})$ and $\nu_S(\text{CH})$ in-plane bending modes overlap at 15 K , but are clearly observed as two separate peaks at higher temperatures. Our results are consistent with those of Cyriac & Pradeep (2005), who assigned the splitting to a conversion of HCOOH dimers to HCOOH organized in chains, following an experimental study by Millikan & Pitzer (1958) and calculations by Yokoyama et al. (1991).

In one experiment HCOOH is deposited at 145 K (see Fig. 4.2b). After deposition the spectrum is similar to that of HCOOH deposited at 15 K and subsequently heated to $\geq 135\text{ K}$. When the temperature is lowered to 15 K , the general features remain similar to the high temperature spectrum. Upon subsequent heating to 150 K an exact copy of the original (145 K) spectrum is obtained. Thus, the changes in ice matrix structure after heating are irreversible.

4.4.2 HCOOH:H₂O ices

Experiments with mixtures that range from $50:50\%$ to $9:91\%$ HCOOH:H₂O have been performed. In Figure 4.2c, the temperature evolution of the mixture with 20% of HCOOH is shown. Peak positions and FWHMs for the $1800\text{--}1100\text{ cm}^{-1}$ range are given in Table 4.8 of the online material. The dilution of HCOOH in H₂O clearly affects the band profiles of HCOOH. The $\nu_S(\text{C=O})$ band shifts 3 cm^{-1} to the red at 15 K and the $\nu_B(\text{OH/CH})$ feature is narrower than in pure HCOOH. Between 105 and 120 K both the peak intensity and FWHM of the $\nu_B(\text{OH/CH})$ band increase. At 150 K the H₂O features change due to a phase transition from amorphous to crystalline H₂O ice structure. At the same time the $\nu_S(\text{C=O})$, $\nu_B(\text{OH/CH})$, and $\nu_S(\text{C-O})$ modes of HCOOH split into two components. Finally, at 165 K all H₂O and most HCOOH have desorbed.

The spectra for different mixture concentrations with respect to H₂O are shown in Fig. 4.3 for 15 K (left) and 150 K (right). The $\nu_S(\text{C=O})$ band has an additional component at 15 K in HCOOH:H₂O mixtures with high HCOOH concentrations that is located at lower wavenumbers and is due to the in-phase motion between HCOOH molecules in the same chain. This implies that there is a small fraction of HCOOH ice that is in a bulk HCOOH environment. The pure HCOOH component decreases with increasing H₂O concentration. The $\nu_B(\text{OH/CH})$ and $\nu_S(\text{C-O})$ modes consist of one component and their FWHMs decrease for lower HCOOH concentrations.

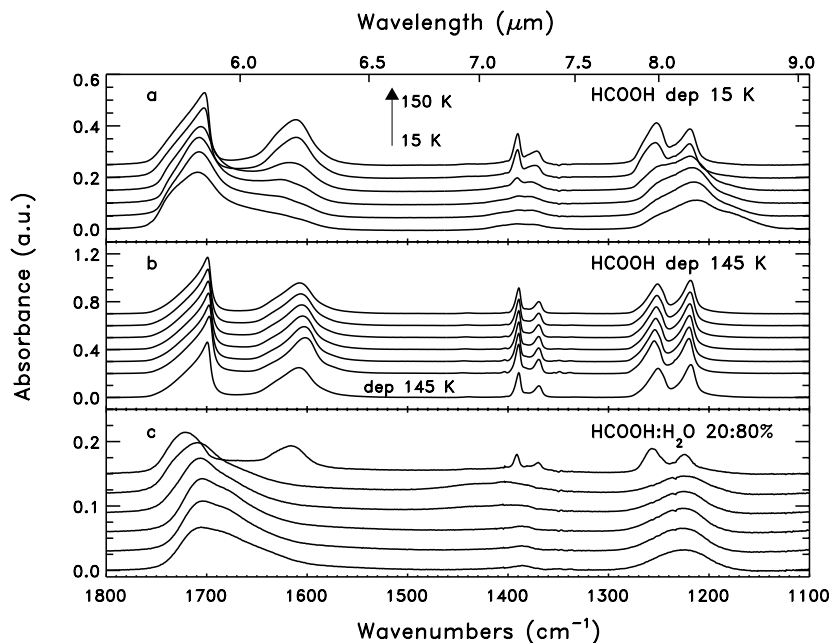


Figure 4.2. The temperature dependent spectra of a) pure HCOOH ice deposited at 15 K, b) pure HCOOH ice deposited at 145 K, subsequently cooled down to 15 K, and c) HCOOH:H₂O 20:80% mixed ice. The spectra of the ices are shown for 15, 60, 90, 105, 135, and 150 K. The $\nu_B(\text{OH})$ band of H₂O at 1655 cm⁻¹ has been removed from the spectra for the HCOOH:H₂O 20:80% mixture.

At 150 K, the $\nu_S(\text{C=O})$, $\nu_B(\text{OH/CH})$, and $\nu_S(\text{C-O})$ modes are split into two peaks for the three mixtures with the highest HCOOH concentrations. The $\nu_B(\text{OH/CH})$ mode is broader compared to pure HCOOH. At the lowest HCOOH concentration, no splitting of the $\nu_S(\text{C=O})$ spectral feature of HCOOH is observed, but only a broad band with a FWHM of 67 cm⁻¹. Furthermore, the $\nu_S(\text{C=O})$ band is shifted to 1718 cm⁻¹ and the $\nu_B(\text{OH/CH})$ feature is located at 1404 cm⁻¹.

4.4.3 HCOOH:CO, HCOOH:CO₂, and HCOOH:CH₃OH ices

Figure 4.4 shows the effects different species have on the solid state HCOOH infrared spectrum. Tables 4.9 and 4.10 of the online material summarize the profile parameters. HCOOH mixed with H₂O results in a relatively simple spectrum, but mixtures with other species, especially CO or CO₂, show multiple components. In mixtures with CO or CO₂ the $\nu_S(\text{C=O})$ band is shifted to higher wavenumbers of which the two most prominent features are located at 1717 cm⁻¹ and 1735 cm⁻¹ in both mixtures. A feature is present at 1154 cm⁻¹

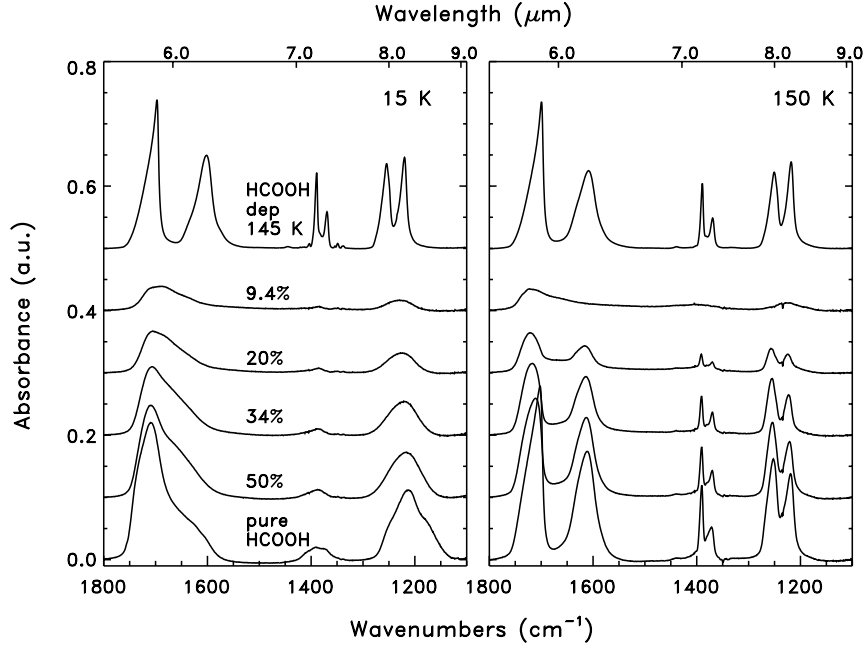


Figure 4.3. Absorption spectra for temperatures of 15 K (left) and 150 K (right) in the 1800–1100 cm^{-1} range for HCOOH deposited at 15 K, the HCOOH:H₂O mixtures and HCOOH deposited at 145 K. The $\nu_{\text{B}}(\text{OH})$ band of H₂O has been removed from the spectra.

for the $\nu_{\text{S}}(\text{C}=\text{O})$ band which is assigned to monomeric HCOOH. This band is especially strong in the HCOOH:CO₂ mixture. In CH₃OH, the absorption bands more closely resemble the overall features of mixtures with H₂O. However, the $\nu_{\text{S}}(\text{C}=\text{O})$ and $\nu_{\text{S}}(\text{C}-\text{O})$ modes are split into two components at 1721 cm^{-1} and 1691 cm^{-1} . The $\nu_{\text{B}}(\text{OH}/\text{CH})$ band cannot be compared to that in the other mixtures as it overlaps with and is dominated by the CH₃ deformation and $\nu_{\text{B}}(\text{OH})$ features of CH₃OH at 1460 cm^{-1} .

The temperature behavior of the spectral features of HCOOH ice depends strongly on the matrix species. In mixtures with H₂O, the HCOOH bands are similar for all temperatures. This is not surprising as the H₂O ice structure does not change until 135 K. HCOOH behaves differently in mixtures with CO and CO₂ at high temperatures, however. When CO has desorbed at 45 K, the $\nu_{\text{S}}(\text{C}=\text{O})$ and $\nu_{\text{S}}(\text{C}-\text{O})$ features are similar to pure HCOOH. Furthermore, its integrated intensity does not decrease after CO desorption. In the mixture of HCOOH with CO₂, the 1735 cm^{-1} and 1717 cm^{-1} bands of HCOOH only fully disappear between 75 K and 105 K at the same time that the features for pure HCOOH start to appear and after CO₂ has desorbed. Thus even when HCOOH is present as a minor component in CO or CO₂ it does not co-desorb at low temperatures. The HCOOH bands in CH₃OH have a similar lack

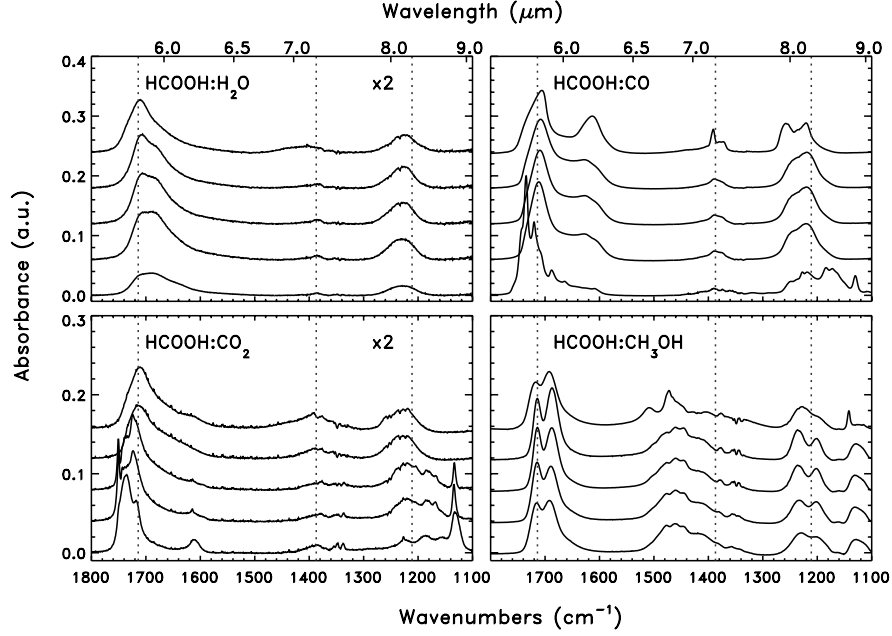


Figure 4.4. Absorption spectra in the $1800\text{--}1100\text{ cm}^{-1}$ regime for mixtures with $\sim 90\%$ H_2O , CO , CO_2 and CH_3OH at 15 (bottom curve), 45, 75, 105, and 135 K (top curve). The $\nu_{\text{B}}(\text{OH})$ has been removed for the $\text{HCOOH}:\text{H}_2\text{O}$ mixture. The peak positions of pure HCOOH at 15 K are indicated by the dotted lines. The intensities of the bands are multiplied by a factor 2 for the $\text{HCOOH}:\text{H}_2\text{O}$ and $\text{HCOOH}:\text{CO}_2$ mixtures as indicated in the first and third panel, respectively.

of temperature variation as for mixtures with H_2O . Between 105 and 135 K CH_3OH has a phase transition that is observed around 1500 cm^{-1} where both the CH_3 deformation and $\nu_{\text{B}}(\text{OH})$ modes of CH_3OH are located. The HCOOH $\nu_{\text{S}}(\text{C}=\text{O})$ and $\nu_{\text{S}}(\text{C}-\text{O})$ bands do not resemble pure HCOOH features at 135 K, which indicates that both species are still mixed.

4.4.4 Tertiary mixtures

Spectra of tertiary mixtures $\sim 7:67:26\%$ of $\text{HCOOH}:\text{H}_2\text{O}:\text{CO}$, $\text{HCOOH}:\text{H}_2\text{O}:\text{CO}_2$ and $\text{HCOOH}:\text{H}_2\text{O}:\text{CH}_3\text{OH}$ have been measured at 15 K. In Table 4.6 and Table 4.10 of the online material peak positions and FWHMs are given. The $\nu_{\text{S}}(\text{C}=\text{O})$ and $\nu_{\text{S}}(\text{C}-\text{O})$ features are similar to those in mixtures with H_2O , but are shifted by a few wavenumbers. The $\nu_{\text{B}}(\text{OH}/\text{CH})$ band is located at lower wavenumbers, especially for the $\text{HCOOH}:\text{H}_2\text{O}:\text{CH}_3\text{OH}$ mixture and have FWHMs of $\sim 14\text{--}19\text{ cm}^{-1}$.

Table 4.6. *The peak positions, FWHMs, and relative band strengths of $\nu_B(\text{OH/CH})$ at 15 K of tertiary mixtures of $\text{HCOOH:H}_2\text{O:X}$, where X stands for CO, CO_2 , and CH_3OH . The uncertainties on the peak positions and FWHMs are $\pm 1 \text{ cm}^{-1}$ and $\pm 2 \text{ cm}^{-1}$, respectively.*

Mixture	Peak position (cm^{-1})	FWHM (cm^{-1})	A/A_0
$\text{HCOOH:H}_2\text{O:CO}$	1386	19	4.2
$\text{HCOOH:H}_2\text{O:CO}_2$	1386	19	3.0
$\text{HCOOH:H}_2\text{O:CH}_3\text{OH}$	1382	13	8.3

4.4.5 Comparison to previous laboratory data

Prior to this study, only Schutte et al. (1999) and Hudson & Moore (1999) reported infrared spectra of HCOOH mixtures with H_2O and CH_3OH at 1 and 4 cm^{-1} resolution, respectively. Their experiments only focused on the $\nu_B(\text{OH/CH})$ and $\nu_S(\text{C-O})$ bands and consequently it is difficult to make a full comparison with our data which also includes other HCOOH bands. The peak positions of the $\nu_B(\text{OH/CH})$ features in pure HCOOH ice and 10:100% HCOOH: H_2O mixtures by Schutte et al. (1999) are shifted and the FWHMs are narrower compared to our data. However, the tertiary HCOOH: $\text{H}_2\text{O:CH}_3\text{OH}$ 8:66:26% mixture results agree very well within the experimental uncertainties. These discrepancies are likely due to a different baseline subtraction. In pure HCOOH and mixtures with H_2O the $\nu_B(\text{OH/CH})$ mode has a wing on the blue side, which is not subtracted in the present work. The peak position and FWHM for the $\nu_S(\text{C-O})$ feature for a 7:93% HCOOH: H_2O mixture by Hudson & Moore (1999) are the same within the uncertainties.

4.5 Band strength changes in ice mixtures

As stated before in § 4.3 absolute band strengths are difficult to measure in our experiment, whereas the relative band strengths can be accurately determined. The relative values discussed in this section can be used in combination with existing values in the literature given in Table 4.3 to derive absolute band strengths in different ice environments.

4.5.1 HCOOH

When HCOOH ice is mixed with H_2O the band strengths of HCOOH are strongly affected. In Figure 4.5 the relative band strengths of the $\nu_S(\text{C=O})$, $\nu_S(\text{C-O})$ and $\nu_B(\text{OH/CH})$ spectral features are shown with error-bars of 12% superimposed. Clearly the uncertainties are relatively large, but still it is possible to note a number of effects with concentration and temperature. As discussed in § 4.3 the error-bars in the same experiment at different temperatures are only 2%, and observed temperature trends are thus much more accurate

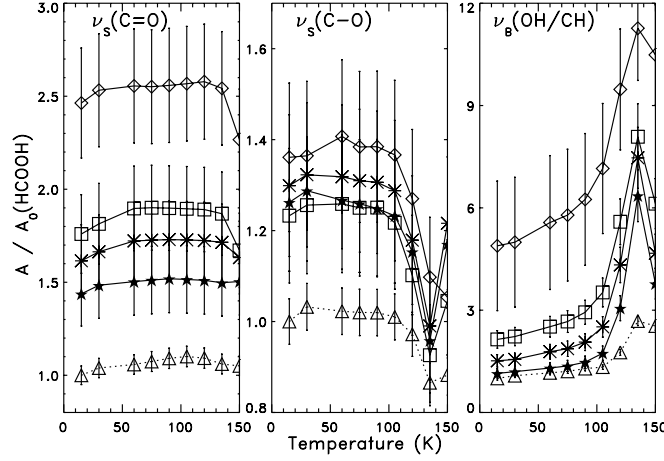


Figure 4.5. $A/A_0(\text{HCOOH})$ with respect to temperature for the HCOOH $\nu_S(\text{C}=\text{O})$, $\nu_B(\text{OH/CH})$, and $\nu_S(\text{C}-\text{O})$ bands in HCOOH:H₂O. The $\star$ symbols refer to the 50:50% mixture, $*$ to 34:66%, $\square$ to 20:80%, $\diamond$ to 9:91% HCOOH:H₂O, and $\triangle$ to pure HCOOH. Note the different scales on the vertical axes.

than concentration trends.

All mixtures with H₂O show a similar temperature trend as pure HCOOH. Even though between 135 and 150 K the $\nu_S(\text{C}=\text{O})$ band splits, its band strength is constant with temperature. In contrast, that of the $\nu_S(\text{C}-\text{O})$ feature shows a pronounced dip around 135 K, which is partly recovered at 150 K. For the most diluted mixture where chain-formation does not occur, no such dip is present. The band strength of the $\nu_B(\text{OH/CH})$ mode increases with temperature and peaks at 135 K. A striking difference between the three absorption bands is that the band strength increases by a factor 2 to 5 with decreasing HCOOH ice concentration for the $\nu_S(\text{C}=\text{O})$ and $\nu_B(\text{OH/CH})$ bands, but is the same within 30% for the $\nu_S(\text{C}-\text{O})$ feature in all mixtures.

A similar comparison for the relative band strength with respect to temperature is made for mixtures with CO, CO₂, and CH₃OH (see Fig. 4.6). The band strengths in mixtures with CO are higher compared to those in pure HCOOH, even when all CO has evaporated. However, the band strengths in CO₂ are close to or smaller than those for pure HCOOH. The $\nu_S(\text{C}=\text{O})$ and $\nu_S(\text{C}-\text{O})$ modes are largest around 75–90 K, decrease between 90–135 K and finally increase again up to 150 K. The $\nu_S(\text{C}=\text{O})$ and $\nu_S(\text{C}-\text{O})$ bands are relatively little affected in the mixtures with CH₃OH.

The relative band strengths for the $\nu_B(\text{OH/CH})$ mode in the tertiary mixtures are shown in Table 4.6 and those of the other bands in Table 4.10 of the online material. Clearly, the band strength in the tertiary mixtures with H₂O and CO, CO₂ or CH₃OH are enhanced at 15 K.

In summary, the relative band strengths of the $\nu_S(\text{C}=\text{O})$ and $\nu_S(\text{C}-\text{O})$

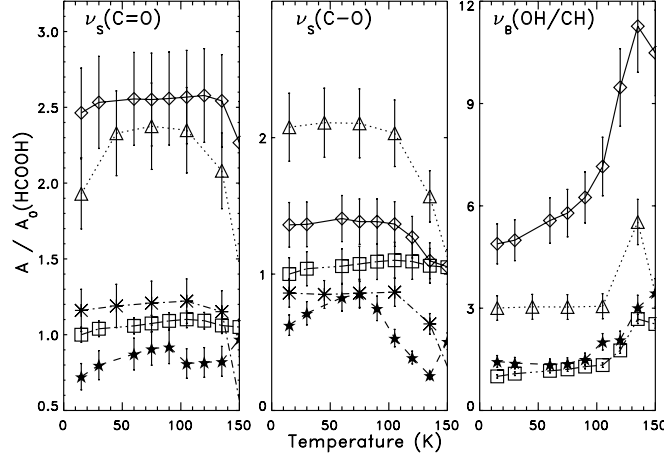


Figure 4.6. $A/A_0(\text{HCOOH})$ with respect to temperature for the HCOOH $\nu_s(\text{C}=\text{O})$, $\nu_B(\text{OH}/\text{CH})$, and $\nu_s(\text{C}-\text{O})$ bands. The $\square$ symbols refers to pure HCOOH , $\diamond$ to 9:91% $\text{HCOOH}:\text{H}_2\text{O}$, $\triangle$ to 11:89% $\text{HCOOH}:\text{CO}$, $\star$ to 9:91% $\text{HCOOH}:\text{CO}_2$, and $*$ to 10:90% $\text{HCOOH}:\text{CH}_3\text{OH}$. Note the different scales on the vertical axes.

bands can range from 0.8–3 $A_0(\text{HCOOH})$ and of the $\nu_B(\text{OH}/\text{CH})$ band from 1–12 $A_0(\text{HCOOH})$ in different ice environments.

4.5.2 H_2O

Water absorption bands are strongly affected by the presence of other ice components like CO_2 (Öberg et al. 2007). In Figure 4.7 the relative band strengths compared to pure H_2O of the $\nu_s(\text{OH})$ and the $\nu(\text{lib})$ modes in the mixtures with HCOOH are shown versus temperature. The $\nu_s(\text{OH})$ band strength is significantly smaller in all mixtures compared to that of pure H_2O , but does not depend on the mixing ratio. The $\nu(\text{lib})$ mode behaves differently. It decreases as a function of HCOOH concentration, with the smallest band strength for the highest HCOOH concentrations. As the temperature increases the relative band strength of the $\nu(\text{lib})$ band increases, until a temperature of 135 K is reached. The different behavior of $\nu_s(\text{OH})$ and the $\nu(\text{lib})$ mode are further illustrated in the right panel of Fig. 4.7. For pure H_2O the absorbance ratio $A_{\nu_s(\text{OH})}/A_{\nu(\text{lib})}$ (the 3.0/13 μm features) starts at ~ 7.5 and increases with temperature to 9.5. The mixtures have a higher ratio at 15 K, but decrease with temperature. The $A_{\nu_s(\text{OH})}/A_{\nu(\text{lib})}$ ratio furthermore increases with HCOOH concentration at 15 K. In conclusion, the ratio of the relative band strengths of the 3.0/13 μm features with a value larger than 10 implies that H_2O is present in ice with HCOOH concentrations $>20\%$, and a lower value implies that the HCOOH concentration is $<20\%$.

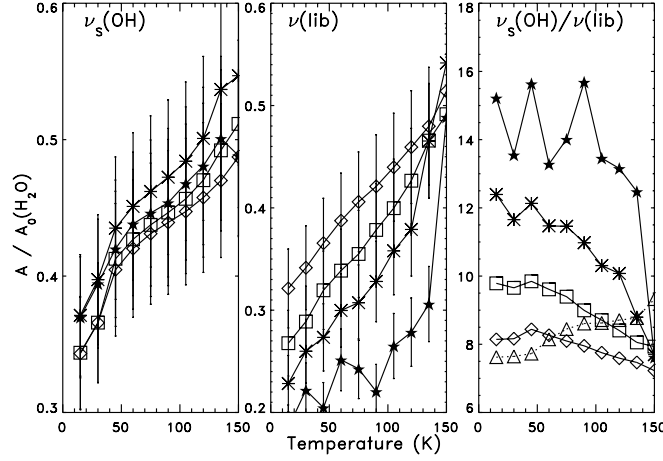


Figure 4.7. $A/A_0(\text{H}_2\text{O})$ of the H_2O $\nu_{\text{S}}(\text{OH})$, $\nu(\text{lib})$, and the band strength ratio $A_{\nu_{\text{S}}(\text{OH})}/A_{\text{lib}}$ with respect to temperature in $\text{HCOOH}:\text{H}_2\text{O}$ mixtures and pure H_2O . The dotted line with $\triangle$ in the $A_{\nu_{\text{S}}(\text{OH})}/A_{\text{lib}}$ panel indicates the trend for pure H_2O , the $\star$ for the 50:50% mixture, $*$ for 34:66%, $\square$ for 20:80%, and $\diamond$ for 9:91% $\text{HCOOH}:\text{H}_2\text{O}$. Note the different scales on the vertical axes.

4.6 Discussion

In this section, our results are discussed in the light of recent chemical physics experiments of HCOOH-containing ices. The behavior of HCOOH in different ices may lead to important clues regarding the behavior of the species under interstellar conditions. Of particular relevance for interstellar chemistry is the mobility in the ice and desorption behavior of the ice constituents with temperature.

The infrared spectrum of pure HCOOH distinguishes itself from HCOOH mixtures by the presence of dimers to a chain-like structure of HCOOH molecules at 120–135 K for HCOOH deposited on a KBr substrate at 15 K (see e.g., Cyriac & Pradeep 2005). The chain-structure at higher temperatures results in a spectrum in which the $\nu_{\text{S}}(\text{C}=\text{O})$ and $\nu_{\text{S}}(\text{C}-\text{O})$ bands are split. The transition from dimers to HCOOH-chains is irreversible as evidenced by the splitting of the $\nu_{\text{S}}(\text{C}=\text{O})$ mode at 15 K for HCOOH deposited at 145 K (see Fig. 4.2 and § 4.4.1).

In binary mixtures with H_2O , the HCOOH ice spectral features remain relatively similar throughout a large temperature regime. Only from 120 K onwards, changes are observed for our experiments (see Fig. 4.3). Initially, only the $\nu_{\text{B}}(\text{OH}/\text{CH})$ mode increases in intensity and broadens, but between 135 K and 150 K the $\nu_{\text{S}}(\text{C}=\text{O})$ band splits into the out-of-phase and in-phase modes for $>10\%$ HCOOH, similar to what is observed for pure HCOOH ice. This implies that the molecules first reorganize locally at 120 K and subsequently become

mobile throughout the ice at higher temperatures. This is corroborated by studies of layered binary HCOOH-H₂O ices (Cyriac & Pradeep 2005; Borodin et al. 2005; Bahr et al. 2005; Souda 2006). In addition to the infrared experiments by Cyriac & Pradeep (2005), Meta-stable Impact Electron Spectroscopy (MIES) and Temperature Programmed Desorption (TPD) have been used to probe the layered HCOOH/H₂O ices. No mixing is observed in any of these experiments up to 120 K. Furthermore, the splitting of the $\nu_s(\text{C=O})$ mode between 135 K and 150 K in our experiments implies that H₂O and HCOOH segregate at high temperatures. This is consistent with TPD data from Bahr et al. (2005), where HCOOH desorbs after H₂O, even in ices where H₂O has been deposited on top of HCOOH.

The interactions between HCOOH with CO, CO₂ and CH₃OH are different compared to H₂O. Very little has been published about either dimers or ice mixtures of these species. Park et al. (2002) performed experiments with HCOOH dissolved in liquid CO₂ and C₂H₆. The dimer/monomer ratio for HCOOH was higher in C₂H₆ than CO₂. This is due to the stronger electrostatic interactions of HCOOH with CO₂ compared to C₂H₆. A similar effect may be responsible for the difference between CO and CO₂ as the monomeric HCOOH feature at 1154 cm⁻¹ is stronger in the mixture with CO₂ compared to CO. When HCOOH is diluted in an ice dominated by other molecules with no or very small dipole-moments like CH₄, N₂ and O₂, a similar HCOOH ice spectrum is likely obtained. The monomer/dimer ratio will depend on the HCOOH concentration as well as the strength of the electrostatic interaction between HCOOH and the other ice species. A similar behavior is observed for H₂O ice diluted in CO₂, CO, N₂ and O₂ (e.g., Öberg et al. 2007; Bouwman et al. 2007; Awad et al., in prep.).

The CH₃OH spectrum is very little affected by HCOOH. This is probably due to a comparable strength of hydrogen bonds between HCOOH and CH₃OH. The infrared spectra of HCOOH:CH₃OH 10:90% mixtures shown in Fig. 4.4 clearly illustrate that both species do not segregate at temperatures below 135 K, even when CH₃OH has a phase transition. It is likely that HCOOH and CH₃OH only become mobile between 135 K and 150 K, as is found for mixtures of HCOOH with H₂O. Since CH₃OH has a smaller dipole-moment and fewer possibilities for making hydrogen-bonds compared to H₂O, it is also expected to segregate from, and desorb prior to, HCOOH. Other polar or hydrogen-bonding species such as NH₃ and H₂CO may interact with HCOOH and affect its infrared spectrum in the same way.

4.7 Astrophysical implications

4.7.1 HCOOH ice identification

Formic acid ice has been observed in many different astrophysical objects, such as high mass and low mass star-forming regions (e.g., Schutte et al. 1997, 1999; Boogert et al., in prep.). In this section we compare the laboratory spectra with the observed ISO spectrum toward the low mass YSO HH 46 and the

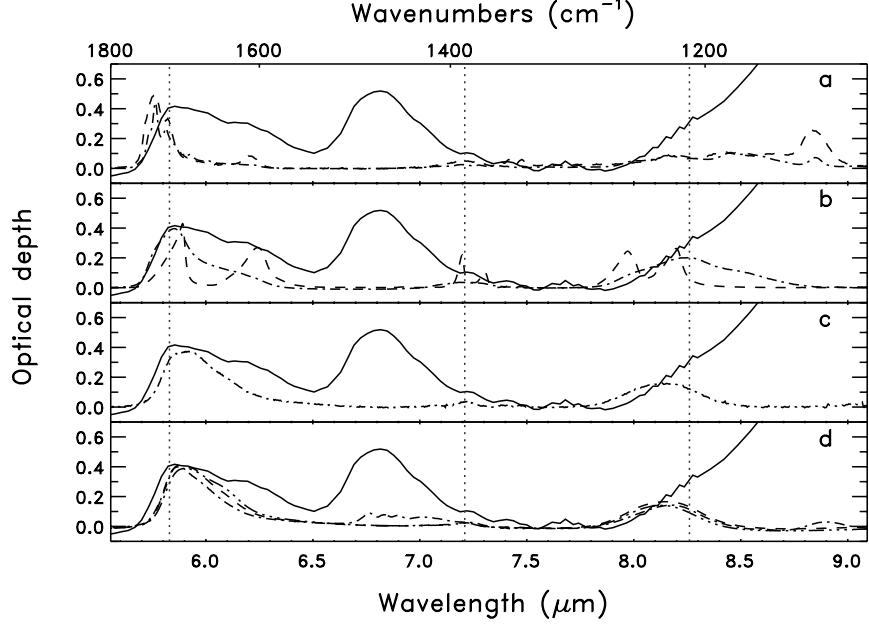


Figure 4.8. The observed ice spectrum toward HH 46 in the 5–9 μm range (Boogert et al. 2004). Also included are in a) the $\sim 10:90\%$ mixtures of HCOOH:CO (dot-dash) and HCOOH:CO₂ (dashed), in b) pure HCOOH spectra at 15 K for ice deposited at 15 K (dot-dash) and at 145 K (dashed), in c) the $\sim 10:90\%$ mixtures of HCOOH:H₂O (dash-dot) and CH₃OH (dash-dot-dot-dot) and in d) the tertiary mixtures 7:67:26% of HCOOH:H₂O:CO (dash-dot-dot-dot), HCOOH:H₂O:CO₂ (dashed), and HCOOH:H₂O:CH₃OH (dot-dash) at 15 K. The relevant peak positions of pure HCOOH ice at 15 K are indicated with dotted lines to guide the eye.

high mass YSO W 33A (Boogert et al. 2004; Gibb et al. 2000b). The 5.9 μm ($\nu_{\text{S}}(\text{C}=\text{O})$) 7.2 μm ($\nu_{\text{B}}(\text{OH}/\text{CH})$) and 8.1 μm ($\nu_{\text{S}}(\text{C}-\text{O})$) bands are used to determine the ice environment in which HCOOH is located. The 5.9 μm HCOOH feature is blended with other interstellar bands and the 8.1 μm band overlaps with the wing of a strong silicate feature. Nonetheless they can be used to exclude some astrophysical HCOOH ice environments. In Figure 4.8 the 5–9 μm range is shown toward the low mass YSO HH 46 with the experimental spectra over-plotted. In Figure 4.8a the spectra for the $\sim 10:90\%$ HCOOH:CO and HCOOH:CO₂ mixtures are shown. These mixtures can clearly be ruled out for HH 46 because the $\nu_{\text{S}}(\text{C}=\text{O})$ feature is shifted too far to the blue. Similarly, pure high temperature HCOOH (Fig. 4.8b) can be discarded as the out-of-phase $\nu_{\text{S}}(\text{C}-\text{O})$ mode at 8.1 μm band is not detected. Furthermore, for all pure ices and mixtures except the binary HCOOH:CH₃OH ice, the $\nu_{\text{S}}(\text{C}-\text{O})$ band causes a small wing on the silicate band at 8.1 μm , which is not observed due to the

much larger intensity of the silicate absorption.

The integrated absorbance and peak position is determined most accurately from the $\nu_B(\text{OH/CH})$ band, because it is the least blended feature of HCOOH. In Figure 4.9 the spectrum observed with ISO toward W 33A is shown for the $\nu_B(\text{OH/CH})$ feature. The ISO data are chosen for comparison because they have higher spectral resolution ($\lambda/\Delta\lambda \approx 800$, or 2 cm^{-1} at $7.2 \mu\text{m}$) than the Spitzer data ($\lambda/\Delta\lambda \approx 100$, or 14 cm^{-1} at $7.2 \mu\text{m}$). In Figure 4.9a the 15 K spectra of pure HCOOH and 20:80% HCOOH:H₂O are shown. Clearly, the pure HCOOH ice spectrum is too broad to fit the astronomical feature. The $\nu_B(\text{OH/CH})$ mode is also too far shifted to the blue for the HCOOH:H₂O mixture. The tertiary mixtures depicted in Fig. 4.9b match the observations better. The HCOOH spectral features in the HCOOH:H₂O:CO and HCOOH:H₂O:CO₂ mixtures are almost identical, but have a blue wing that is not observed for W 33A. However, the HCOOH:H₂O:CH₃OH 6:68:26% mixture reproduces the observed spectrum very well.

This sensitivity of peak position and FWHM of the $\nu_B(\text{OH/CH})$ band at $7.2 \mu\text{m}$ is further illustrated in Fig. 4.10, together with the observed values toward the high mass YSO W 33A. A Gaussian fit is made to the observations in the same way as to the experimental data. The black horizontal line corresponds to the fitted peak position in the observations and the black vertical line to the fitted FWHM. The dotted and dashed lines represent 2 cm^{-1} and 1 cm^{-1} error-bars for the FWHM and peak position, respectively. Clearly, the binary mixtures with H₂O as well as pure HCOOH are too broad and shifted too far to the blue side compared to the observed feature in W 33A. The tertiary mixtures provide better fits. The 6:27:67% HCOOH:CO₂:H₂O and 8:62:30% HCOOH:H₂O:CO mixtures have FWHMs that are too broad compared to the observations within their uncertainties. Furthermore, their peak positions are shifted to 1386 cm^{-1} , a few wavenumbers too high. Potentially, CO₂/CO:H₂O ratios higher than $\sim 30:70\%$ could shift the $\nu_B(\text{OH/CH})$ feature to lower wavenumbers and match the observations toward W 33A better. This is not unlikely as Öberg et al. (2007) find that they can fit the observed Spitzer spectrum toward HH 46 well if also a 33:67% CO₂:H₂O mixture is included. The $7.2 \mu\text{m}$ band for the HCOOH:CH₃OH:H₂O mixture fits the observed spectrum very well.

4.7.2 HCOOH ice formation

The presence of HCOOH in a complex mixture dominated by H₂O but also including CO, CO₂ or CH₃OH or a combination of these three species is not unlikely when potential formation mechanism are evaluated. CO or CO₂ are both potential precursors to HCOOH and CH₃OH is known to form from CO through H-atom bombardment (Watanabe et al. 2004; Fuchs et al. 2007). H-bombardment of CO or CO₂ in mixtures with H₂O (Fuchs et al. 2007; Bisschop et al. 2007b) and UV-irradiation of CO:H₂O and CO₂:H₂O mixtures (Watanabe et al. 2004; Watanabe & Kouchi 2002; Gerakines et al. 2000) do not give HCOOH as one of the main products. Since the UV experiments were performed under

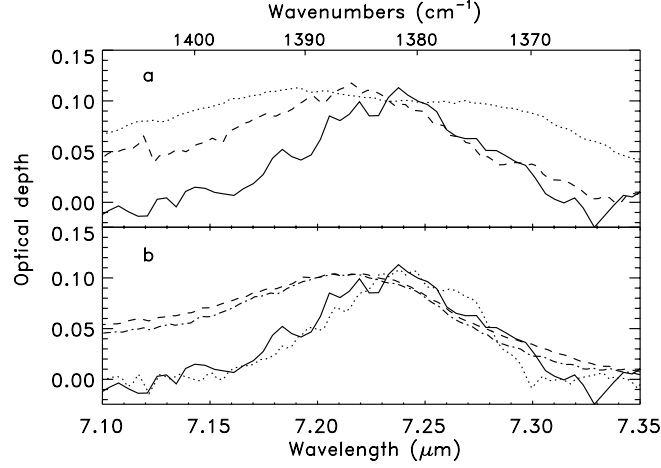
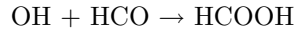
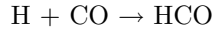
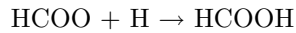
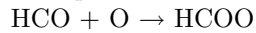


Figure 4.9. The observed ice spectrum in the 7.10–7.35 μm range toward W 33A indicated by the solid line (Gibb et al. 2000b). Also included are in a) the spectra at 15 K of pure HCOOH (dotted) and 20:80% HCOOH:H₂O (dashed) and in b) the tertiary mixtures HCOOH:H₂O:CO 8:62:30% (dashed), HCOOH:H₂O:CO₂ 6:67:27% (dash-dot) and HCOOH:H₂O:CH₃OH 6:68:26% (dotted).

HV conditions, they need to be repeated under ultra high vacuum conditions to fully exclude this route. In H₂O:CO mixtures that are bombarded by 0.8 MeV protons, to simulate cosmic rays, HCOOH is formed (Hudson & Moore 1999). Its formation is explained by:



where the H and OH result from H₂O dissociation in the experiment. In space, H-atoms from the gas phase can react with the adsorbed O to form OH. HCO is formed by H addition to CO, which will further react to H₂CO and finally to CH₃OH, unless HCO encounters an OH radical first. Garrod & Herbst (2006) use this formation mechanism for HCOOH in the solid state. However, in their model HCOOH can only form at higher temperatures because the OH and HCO radicals are not mobile at low temperatures. This would be inconsistent with the detection of HCOOH ice in cold sources such as HH 46 and background stars unless OH is produced with excess energy. This is for example found in theoretical calculations by Andersson et al. (2006) for the photo-dissociation of H₂O ice. The newly formed OH radicals are not very mobile in bulk ice, but can move more than 80 Å over the surface. Thus HCOOH formation through this reaction mechanism is expected to be strongly localized at the ice surface. Another potential formation mechanism is given by Keane (2001).



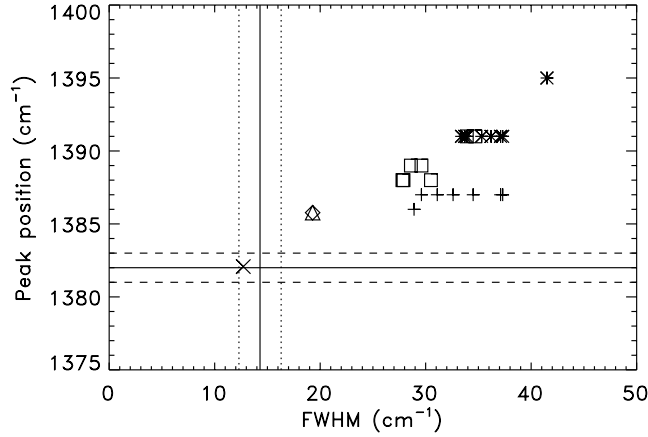


Figure 4.10. Comparison between the observed $7.2 \mu\text{m}$ band of HCOOH in $W 33A$ with laboratory spectra of HCOOH ice. The black lines indicate the peak position and FWHM of the observed feature and the dotted and dashed lines 2 cm^{-1} uncertainties on the FWHM and 1 cm^{-1} on the peak position, respectively. Mixture ratios for all temperatures have the same symbol. The + symbols refer to pure HCOOH , * to 50:50% $\text{HCOOH}:\text{H}_2\text{O}$, $\square$ to 9:91% $\text{HCOOH}:\text{H}_2\text{O}$, $\triangle$ to $\text{HCOOH}:\text{H}_2\text{O}:\text{CO}$ 8:62:30%, $\diamond$ to 6:67:27% $\text{HCOOH}:\text{H}_2\text{O}:\text{CO}_2$ and $\times$ to 6.5:26:68% $\text{HCOOH}:\text{CH}_3\text{OH}:\text{H}_2\text{O}$.

In this case successive H- and O-addition leads to HCOOH formation, and HCOOH may be produced at low ice temperatures at the same time as H_2O and CH_3OH are formed.

In summary, both reaction pathways make it likely that HCOOH is formed in an environment where H_2O and CH_3OH are located. Potentially CO , CO_2 , and H_2CO are present in the ice as well, if conversion to CH_3OH and HCOOH is incomplete. As discussed in § 4.7.1 it is probable that H_2CO will have a similar effect on the ice structure as CH_3OH and H_2O and thus also on the HCOOH infrared bands. In the future both reaction paths can be tested experimentally and thus resolve whether HCOOH is formed during ice formation, ice processing at low temperatures or potentially even both.

4.8 Summary and conclusions

The main conclusions derived from this work are:

- ▷ The peak positions, FWHM and profiles of the $\nu_{\text{S}}(\text{C}=\text{O})$, $\nu_{\text{B}}(\text{OH}/\text{CH})$ and $\nu_{\text{S}}(\text{C}-\text{O})$ bands are strongly affected by the ice matrix. At high temperatures and when HCOOH is deposited at high temperatures, the $\nu_{\text{S}}(\text{C}=\text{O})$, $\nu_{\text{B}}(\text{OH}/\text{CH})$ and $\nu_{\text{S}}(\text{C}-\text{O})$ modes split into two bands. In binary mixtures

with H₂O, the HCOOH features have very simple profiles, whereas multiple bands are found in binary ice mixtures with CO, CO₂ and CH₃OH. The peak positions of the HCOOH $\nu_S(\text{C=O})$, $\nu_B(\text{OH/CH})$, and $\nu_S(\text{C-O})$ bands are shifted up to $\sim 40 \text{ cm}^{-1}$. The spectra for tertiary mixtures resemble the spectra of binary mixtures with H₂O, but small shifts exist.

- ▷ The band strengths of the $\nu_S(\text{C=O})$, $\nu_B(\text{OH/CH})$, and $\nu_S(\text{C-O})$ features are strongly affected by the ice structure. They are enhanced in mixtures of HCOOH with H₂O and CO by factors of 2–10, but are similar to those of pure HCOOH ice for binary mixtures with CO₂ and CH₃OH. Strong temperature effects are also observed.
- ▷ Comparison of our data with the Spitzer spectrum of HH 46 and the ISO spectrum toward the high mass YSO W 33A excludes the presence of the high temperature HCOOH chain-structure, as well as binary mixtures of HCOOH with any of the other species H₂O, CO, CO₂ and CH₃OH. The $7.2 \mu\text{m}$ feature toward W 33A is very similar to that found in tertiary mixtures of $\sim 7:67:26\%$ HCOOH:H₂O:X, where X stands for CO, CO₂ or CH₃OH. Especially the HCOOH:H₂O:CH₃OH mixture reproduces the observed W 33A spectrum very well. Potentially, such tertiary or even more complex ices consisting of HCOOH, H₂O, CH₃OH, CO and CO₂ may be responsible for the observed spectrum. The presence of HCOOH in such complex ice mixtures is consistent with its possible formation mechanisms.

Acknowledgements

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Appendix A: Line parameters of HCOOH in the 1800-1000 cm^{-1} range

Table 4.7. Peak positions, FWHMs and A/A_0 for the $\text{HCOOH } \nu_{\text{S}}(\text{C=O})$, $\nu_{\text{B}}(\text{OH/CH})$, and $\nu_{\text{S}}(\text{C-O})$ bands for all temperatures for pure HCOOH . The peak positions are given in both wavenumbers and wavelengths for the ice deposited at 15 K and 145 K. The uncertainties on the peak positions and FWHMs are ± 1 and $\pm 2 \text{ cm}^{-1}$, respectively.

T (K)	$\nu_{\text{S}}(\text{C=O})$				$\nu_{\text{B}}(\text{OH/CH})$				$\nu_{\text{S}}(\text{C-O})$			
	ν_{S} ($\text{cm}^{-1}(\mu\text{m})$)	FWHM (cm^{-1})	out-of-phase ν_{S} ($\text{cm}^{-1}(\mu\text{m})$)	in-phase FWHM (cm^{-1})	A/A_0^a	ν_{S} ($\text{cm}^{-1}(\mu\text{m})$)	FWHM (cm^{-1})	A/A_0^a	ν_{S} ($\text{cm}^{-1}(\mu\text{m})$)	FWHM (cm^{-1})	A/A_0^a	
HCOOH deposited at 15 K												
15	1714(5.84)	45	1650(6.06)	69	1.0	1387(7.21)	37	1.0	1211(8.26)	64	1.0	
30	1713(5.84)	43	1651(6.06)	71	1.0	1387(7.21)	37	1.1	1213(8.24)	61	1.0	
60	1710(5.85)	41	1644(6.08)	65	1.1	1387(7.21)	35	1.2	1219(8.20)	53	1.0	
75	1710(5.85)	40	1641(6.09)	65	1.1	1387(7.21)	33	1.2	1221(8.19)	51	1.0	
90	1709(5.85)	39	1637(6.11)	64	1.1	1387(7.21)	31	1.3	1223(8.18)	50	1.0	
105	1709(5.85)	39	1634(6.12)	63	1.1	1387(7.21)	30	1.3	1224(8.17)	50	1.0	
120	1709(5.85)	41	1625(6.15)	56	1.1	1386(7.21)	29	1.8	1228(8.15)	51	1.0	
135	1703(5.87)	10	1615(6.19)	43	1.1	1391(7.19)	8	2.7	1255(7.97)	22	0.9	
	1716(5.83)	39				1375(7.27)	14		1221(8.19)	21		
150	1703(5.87)	11	1615(6.19)	40	1.1	1391(7.19)	7	2.5	1254(7.97)	22	0.9	
	1719(5.82)	34				1374(7.28)	13		1221(8.19)	17		
165	1704(5.87)	11	1617(6.18)	36	—	1391(7.19)	7	—	1253(7.98)	20	—	
	1722(5.81)	32				1373(7.28)	12		1220(8.20)	15		

^a A_0 refers to the band strength in pure HCOOH at 15 K. Continued following page.

Table 4.7. *continued.*

T (K)	$\nu_S(\text{C=O})$				$\nu_B(\text{OH/CH})$				$\nu_B(\text{C-O})$				
	out-of-phase ν_S ($\text{cm}^{-1}(\mu\text{m})$)	FWHM (cm^{-1})	ν_S ($\text{cm}^{-1}(\mu\text{m})$)	in-phase FWHM (cm^{-1})	A/A_0^a		ν_S ($\text{cm}^{-1}(\mu\text{m})$)	FWHM (cm^{-1})	A/A_0^a		ν_S ($\text{cm}^{-1}(\mu\text{m})$)	FWHM (cm^{-1})	A/A_0^a
HCOOH deposited at 145 K													
15	1699(5.89)	10	1606(6.23)	36	1.5		1390(7.19)	6	3.7		1256(7.96)	18	1.3
	1712(5.84)	32					1371(7.29)	9			1222(8.18)	15	
30	1699(5.89)	9	1606(6.23)	36	1.5		1390(7.19)	6	3.7		1256(7.96)	18	1.3
	1712(5.84)	32					1371(7.29)	9			1222(8.18)	15	
45	1699(5.89)	9	1606(6.22)	36	1.5		1390(7.19)	6	3.7		1255(7.97)	18	1.3
	1713(5.84)	32					1371(7.29)	9			1222(8.18)	15	
60	1699(5.89)	8	1607(6.22)	36	1.5		1390(7.19)	6	3.6		1255(7.97)	18	1.3
	1712(5.84)	32					1371(7.29)	9			1222(8.19)	15	
75	1699(5.88)	8	1608(6.22)	36	1.5		1390(7.19)	6	3.6		1255(7.97)	18	1.3
	1713(5.84)	32					1371(7.29)	9			1222(8.19)	15	
90	1700(5.88)	8	1608(6.22)	37	1.5		1390(7.19)	6	3.5		1254(7.97)	18	1.3
	1713(5.84)	32					1371(7.29)	10			1221(8.19)	15	
105	1700(5.88)	9	1609(6.21)	37	1.5		1390(7.19)	6	3.5		1254(7.98)	18	1.3
	1713(5.84)	32					1371(7.29)	10			1221(8.19)	15	
120	1700(5.88)	9	1610(6.21)	38	1.4		1390(7.19)	6	3.4		1253(7.98)	18	1.3
	1713(5.84)	32					1371(7.29)	10			1220(8.19)	15	
135	1700(5.88)	9	1611(6.21)	39	1.4		1390(7.20)	6	3.3		1252(7.99)	18	1.3
	1714(5.84)	32					1371(7.29)	11			1220(8.10)	15	
150	1701(5.88)	9	1612(6.20)	39	1.4		1390(7.20)	6	3.2		1252(7.99)	19	1.3
	1714(5.83)	31					1371(7.29)	11			1219(8.20)	14	
165	1701(5.88)	9	1614(6.20)	38	1.3		1390(7.20)	6	2.8		1250(8.00)	19	1.2
	1715(5.83)	31					1371(7.30)	11			1219(8.20)	14	

^a A_0 refers to the band strength in pure HCOOH at 15 K.

Table 4.8. Peak positions, FWHMs and A/A_0 for the $\text{HCOOH } \nu_S(\text{C}=\text{O})$, $\nu_B(\text{OH}/\text{CH})$, and $\nu_S(\text{C}-\text{O})$ bands for all temperatures for mixtures of HCOOH with H_2O . The uncertainties on the peak positions and FWHMs are ± 1 and $\pm 2 \text{ cm}^{-1}$, respectively.

T (K)	$\nu_S(\text{C}=\text{O})$			$\nu_B(\text{OH}/\text{CH})$			$\nu_S(\text{C}-\text{O})$		
	out-of-phase ν_S (cm^{-1})	FWHM (cm^{-1})	A/A_0^a	in-phase ν_S (cm^{-1})	FWHM (cm^{-1})	A/A_0^a	ν_S (cm^{-1})	FWHM (cm^{-1})	A/A_0^a
15	1708(5.85)	48	1.4	1658(6.03)	103	1.4	1391(7.19)	37	1.1
30	1709(5.85)	39	1.5	1675(5.97)	75	1.5	1391(7.19)	37	1.2
45	1711(5.85)	36	1.5	1665(6.01)	78	1.5	1391(7.19)	36	1.3
60	1710(5.85)	33	1.5	1672(5.98)	83	1.5	1391(7.19)	35	1.3
75	1709(5.85)	35	1.5	1668(6.00)	77	1.5	1391(7.19)	34	1.4
90	1709(5.85)	34	1.5	1670(6.00)	78	1.5	1391(7.19)	33	1.5
105	1709(5.85)	35	1.5	1669(5.99)	75	1.5	1392(7.19)	34	1.7
120	1710(5.85)	37	1.5	1671(5.98)	75	1.5	1395(7.17)	42	3.1
135	1713(5.84)	45	1.5	1670(5.99)	69	1.5	1403(7.13)	59	6.4
150	1707(5.86)	10	1.5	1616(6.19)	40	1.5	1391(7.19)	7	3.8
165	1720(5.82)	16	—	1619(6.18)	34	—	1372(7.29)	13	—
	1706(5.86)	12	—	—	—	—	1391(7.19)	6	—
	1723(5.80)	32	—	—	—	—	1373(7.29)	12	—
15	1707(5.86)	44	1.6	1652(6.05)	95	1.6	1391(7.19)	35	1.5
30	1706(5.86)	38	1.7	1688(5.92)	94	1.7	1391(7.19)	35	1.6
45	1707(5.86)	36	1.7	1667(6.00)	83	1.7	1391(7.19)	33	1.7
60	1706(5.86)	37	1.7	1668(6.00)	77	1.7	1391(7.19)	32	1.8
75	1706(5.86)	36	1.7	1669(5.99)	75	1.7	1391(7.19)	32	1.9
90	1706(5.86)	36	1.7	1670(5.99)	74	1.7	1391(7.19)	32	2.1
105	1706(5.86)	36	1.7	1671(5.98)	73	1.7	1393(7.18)	34	2.5
120	1708(5.85)	39	1.7	1674(5.98)	73	1.7	1399(7.15)	46	4.3
135	1714(5.84)	47	1.7	1670(5.99)	69	1.7	1406(7.11)	62	7.5
150	1711(5.84)	4	1.6	1617(6.18)	42	1.6	1391(7.19)	7	4.7
165	1719(5.82)	34	—	1621(6.17)	32	—	1371(7.29)	13	—
	1726(5.79)	28	—	—	—	—	1391(7.19)	5	—
							1372(7.29)	11	—
15	1707(5.86)	44	1.6	1652(6.05)	95	1.6	1391(7.19)	35	1.5
30	1706(5.86)	38	1.7	1688(5.92)	94	1.7	1391(7.19)	35	1.6
45	1707(5.86)	36	1.7	1667(6.00)	83	1.7	1391(7.19)	33	1.7
60	1706(5.86)	37	1.7	1668(6.00)	77	1.7	1391(7.19)	32	1.8
75	1706(5.86)	36	1.7	1669(5.99)	75	1.7	1391(7.19)	32	1.9
90	1706(5.86)	36	1.7	1670(5.99)	74	1.7	1391(7.19)	32	2.1
105	1706(5.86)	36	1.7	1671(5.98)	73	1.7	1393(7.18)	34	2.5
120	1708(5.85)	39	1.7	1674(5.98)	73	1.7	1399(7.15)	46	4.3
135	1714(5.84)	47	1.7	1670(5.99)	69	1.7	1406(7.11)	62	7.5
150	1711(5.84)	4	1.6	1617(6.18)	42	1.6	1391(7.19)	7	4.7
165	1719(5.82)	34	—	1621(6.17)	32	—	1371(7.29)	13	—
	1726(5.79)	28	—	—	—	—	1391(7.19)	5	—
							1372(7.29)	11	—
15	1707(5.86)	44	1.6	1652(6.05)	95	1.6	1391(7.19)	35	1.5
30	1706(5.86)	38	1.7	1688(5.92)	94	1.7	1391(7.19)	35	1.6
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60	1706(5.86)	37	1.7	1668(6.00)	77	1.7	1391(7.19)	32	1.8
75	1706(5.86)	36	1.7	1669(5.99)	75	1.7	1391(7.19)	32	1.9
90	1706(5.86)	36	1.7	1670(5.99)	74	1.7	1391(7.19)	32	2.1
105	1706(5.86)	36	1.7	1671(5.98)	73	1.7	1393(7.18)	34	2.5
120	1708(5.85)	39	1.7	1674(5.98)	73	1.7	1399(7.15)	46	4.3
135	1714(5.84)	47	1.7	1670(5.99)	69	1.7	1406(7.11)	62	7.5
150	1711(5.84)	4	1.6	1617(6.18)	42	1.6	1391(7.19)	7	4.7
165	1719(5.82)	34	—	1621(6.17)	32	—	1371(7.29)	13	—
	1726(5.79)	28	—	—	—	—	1391(7.19)	5	—
							1372(7.29)	11	—
15	1707(5.86)	44	1.6	1652(6.05)	95	1.6	1391(7.19)	35	1.5
30	1706(5.86)	38	1.7	1688(5.92)	94	1.7	1391(7.19)	35	1.6
45	1707(5.86)	36	1.7	1667(6.00)	83	1.7	1391(7.19)	33	1.7
60	1706(5.86)	37	1.7	1668(6.00)	77	1.7	1391(7.19)	32	1.8
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90	1706(5.86)	36	1.7	1670(5.99)	74	1.7	1391(7.19)	32	2.1
105	1706(5.86)	36	1.7	1671(5.98)	73	1.7	1393(7.18)	34	2.5
120	1708(5.85)	39	1.7	1674(5.98)	73	1.7	1399(7.15)	46	4.3
135	1714(5.84)	47	1.7	1670(5.99)	69	1.7	1406(7.11)	62	7.5
150	1711(5.84)	4	1.6	1617(6.18)	42	1.6	1391(7.19)	7	4.7
165	1719(5.82)	34	—	1621(6.17)	32	—	1371(7.29)	13	—
	1726(5.79)	28	—	—	—	—	1391(7.19)	5	—
							1372(7.29)	11	—
15	1707(5.86)	44	1.6	1652(6.05)	95	1.6	1391(7.19)	35	1.5
30	1706(5.86)	38	1.7	1688(5.92)	94	1.7	1391(7.19)	35	1.6
45	1707(5.86)	36	1.7	1667(6.00)	83	1.7	1391(7.19)	33	1.7
60	1706(5.86)	37	1.7	1668(6.00)	77	1.7	1391(7.19)	32	1.8
75	1706(5.86)	36	1.7	1669(5.99)	75	1.7	1391(7.19)	32	1.9
90	1706(5.86)	36	1.7	1670(5.99)	74	1.7	1391(7.19)	32	2.1
105	1706(5.86)	36	1.7	1671(5.98)	73	1.7	1393(7.18)	34	2.5
120	1708(5.85)	39	1.7	1674(5.98)	73	1.7	1399(7.15)	46	4.3
135	1714(5.84)	47	1.7	1670(5.99)	69	1.7	1406(7.11)	62	7.5
150	1711(5.84)	4	1.6	1617(6.18)	42	1.6	1391(7.19)	7	4.7
165	1719(5.82)	34	—	1621(6.17)	32	—	1371(7.29)	13	—
	1726(5.79)	28	—	—	—	—	1391(7.19)	5	—
							1372(7.29)	11	—
15	1707(5.86)	44	1.6	1652(6.05)	95	1.6	1391(7.19)	35	1.5
30	1706(5.86)	38	1.7	1688(5.92)	94	1.7	1391(7.19)	35	1.6
45	1707(5.86)	36	1.7	1667(6.00)	83	1.7	1391(7.19)	33	1.7
60	1706(5.86)	37	1.7	1668(6.00)	77	1.7	1391(7.19)	32	1.8
75	1706(5.86)	36	1.7	1669(5.99)	75	1.7	1391(7.19)	32	1.9
90	1706(5.86)	36	1.7	1670(5.99)	74	1.7	1391(7.19)	32	2.1
105	1706(5.86)	36	1.7	1671(5.98)	73	1.7	1393(7.18)	34	2.5
120	1708(5.85)	39	1.7	1674(5.98)	73	1.7	1399(7.15)	46	4.3
135	1714(5.84)	47	1.7	1670(5.99)	69	1.7	1406(7.11)	62	7.5
150	1711(5.84)	4	1.6	1617(6.18)	42	1.6	1391(7.19)	7	4.7
165	1719(5.82)	34	—	1621(6.17)	32	—	1371(7.29)	13	—
	1726(5.79)	28	—	—	—	—	1391(7.19)	5	—
							1372(7.29)	11	—
15	1707(5.86)	44	1.6	1652(6.05)	95	1.6	1391(7.19)	35	1.5
30	1706(5.86)	38	1.7	1688(5.92)	94	1.7	1391(7.19)	35	1.6
45	1707(5.86)	36	1.7	1667(6.00)	83	1.7	1391(7.19)	33	1.7
60	1706(5.86)	37	1.7	1668(6.00)	77	1.7	1391(7.19)	32	1.8
75	1706(5.86)	36	1.7	1669(5.99)	75	1.7	1391(7.19)	32	1.9
90	1706(5.86)	36	1.7	1670(5.99)	74	1.7	1391(7.19)	32	2.1
105	1706(5.86)	36	1.7	1671(5.98)	73	1.7	1393(7.18)	34	2.5
120	1708(5.85)	39	1.7	1674(5.98)	73	1.7	1399(7.15)	46	4.3
135	1714(5.84)	47	1.7	1670(5.99)	69	1.7	1406(7.11)	62	7.5
150	1711(5.84)	4	1.6	1617(6.18)	42	1.6	1391(7.19)	7	4.7
165	1719(5.82)	34	—	1621(6.17)	32	—	1371(7.29)	13	—
	1726(5.79)	28	—	—	—	—	1391(7.19)	5	—
							1372(7.29)	11	—
15	1707(5.86)	44	1.6	1652(6.05)	95	1.6	1391(7.19)	35	1.5
30	1706(5.86)	38	1.7	1688(5.92)	94	1.7	1391(7.19)	35	1.6
45	1707(5.86)	36	1.7	1667(6.00)	83	1.7	1391(7.19)	33	1.7
60	1706(5.86)	37	1.7	1668(6.00)	77	1.7	1391(7.19)	32	1.8
75	1706(5.86)	36	1.7	1669(5.99)	75	1.7	1391(7.19)	32	1.9
90	1706(5.86)	36	1.7	1670(5.99)	74	1.7	1391(7.19)	32	2.1
105	1706(5.86)	36	1.7	1671(5.98)	73	1.7	1393(7.18)	34	2.5
120	1708(5.85)	39	1.7	1674(5.98)	73	1.7	1399(7.15)	46	4.3
135	1714(5.84)	47	1.7	1670(5.99)	69	1.7	1406(7.11)	62	7.5
150	1711(5.84)	4	1.6	1617(6.18)	42	1.6	1391(7.19)	7	4.7
165	1719(5.82)	34	—	1621(6.17)	32	—	1371(7.29)	13	—
	1726(5.79)	28	—	—	—	—	1391(7.19)	5	—
							1372(7.29)	11	—
15	1707(5.86)	44	1.6	1652(6.05)	95	1.6	1391(7.19)	35	1.5

Table 4.8. *continued.*

T (K)	$\nu_S(\text{C=O})$				$\nu_B(\text{OH/CH})$			$\nu_S(\text{C-O})$			
	out-of-phase ν_S ($\text{cm}^{-1}(\mu\text{m})$)	FWHM (cm^{-1})	ν_S ($\text{cm}^{-1}(\mu\text{m})$)	in-phase FWHM (cm^{-1})	A/A_0^a	ν_S ($\text{cm}^{-1}(\mu\text{m})$)	FWHM (cm^{-1})	A/A_0^a	ν_S ($\text{cm}^{-1}(\mu\text{m})$)	FWHM (cm^{-1})	A/A_0^a
	20.80% HCOOH:H ₂ O										
15	1707(5.86)	40	1643(6.09)	81	1.8	1391(7.19)	35	2.1	1215(8.23)	44	1.2
30	1704(5.87)	43	1667(6.00)	89	1.8	1390(7.19)	33	2.2	1227(8.15)	55	1.3
45	1703(5.87)	44	1660(6.02)	77	1.9	1390(7.19)	31	2.3	1230(8.13)	47	1.3
60	1703(5.87)	40	1669(5.99)	83	1.9	1390(7.19)	31	2.5	1229(8.13)	48	1.3
75	1703(5.87)	42	1664(6.01)	76	1.9	1391(7.19)	31	2.7	1229(8.13)	47	1.3
90	1703(5.87)	39	1670(5.99)	79	1.9	1391(7.19)	32	2.9	1229(8.14)	46	1.3
105	1705(5.87)	40	1668(5.99)	75	1.9	1393(7.18)	35	3.5	1228(8.14)	46	1.2
120	1709(5.85)	39	1675(5.97)	76	1.9	1403(7.13)	51	5.6	1227(8.15)	47	1.1
135	1714(5.83)	45	1673(5.98)	72	1.9	1413(7.08)	61	8.2	1225(8.16)	49	0.9
150	—	—	1619(6.17)	51	1.7	1392(7.19)	8	6.1	1256(7.96)	19	1.0
	1717(5.82)	41	—	—	—	1372(7.29)	17	—	1223(8.17)	19	—
165	—	—	1622(6.16)	31	—	1392(7.18)	4	—	1255(7.97)	15	—
	1730(5.78)	27	—	—	—	1375(7.27)	11	—	1226(8.16)	11	—
	9.4:91% HCOOH:H ₂ O										
15	1708(5.86)	38	1636(6.11)	70	2.5	1391(7.19)	35	4.9	1214(8.24)	42	1.4
30	1706(5.86)	40	1680(5.95)	128	2.5	1388(7.21)	31	4.9	1233(8.11)	59	1.4
45	1698(5.89)	45	1662(6.02)	94	2.6	1389(7.20)	29	5.2	1231(8.12)	42	1.4
60	1699(5.89)	55	1649(6.06)	90	2.6	1388(7.20)	28	5.6	1231(8.12)	46	1.4
75	1698(5.89)	49	1655(6.04)	100	2.6	1388(7.20)	28	5.8	1231(8.12)	45	1.4
90	1700(5.88)	52	1641(6.10)	88	2.6	1389(7.20)	30	6.2	1230(8.13)	44	1.4
105	1701(5.88)	50	1645(6.08)	89	2.6	1391(7.19)	34	7.2	1230(8.13)	44	1.4
120	1706(5.86)	47	1664(6.01)	94	2.6	1402(7.13)	52	9.5	1228(8.14)	45	1.3
135	1713(5.84)	46	1658(6.03)	76	2.5	1415(7.06)	59	11.3	1226(8.15)	47	1.1
150	1718(5.82)	43	1674(5.97)	93	2.3	1404(7.12)	67	10.5	1223(8.18)	51	1.1

^a A_0 refers to the band strength in pure HCOOH at 15 K.

Table 4.9. Peak positions, FWHMs and A/A_0 for the $\text{HCOOH } \nu_{\text{S}}(\text{C}=\text{O})$ and $\nu_{\text{S}}(\text{C}-\text{O})$ bands for all temperatures for $\sim 10\text{:}90\%$ $\text{HCOOH}:\text{CH}_3\text{OH}$. The uncertainties on the peak positions and FWHMs are ± 1 and $\pm 2 \text{ cm}^{-1}$, respectively.

T (K)	$\nu_S(\text{C=O})$			$\nu_S(\text{C-O})$		
	out-of-phase ν ($\text{cm}^{-1}(\mu\text{m})$)	FWHM ν (cm^{-1})	in-phase FWHM A/A_0^a ($\text{cm}^{-1}(\mu\text{m})$)	out-of-phase ν ($\text{cm}^{-1}(\mu\text{m})$)	FWHM ν (cm^{-1})	in-phase FWHM A/A_0^a (cm^{-1})
15	1721(5.81)	15	1691(5.91)	1231(8.12)	29	1198(8.35)
45	1717(5.82)	18	1690(5.92)	1235(8.10)	24	1203(8.31)
75	1716(5.83)	11	1689(5.92)	1234(8.10)	24	1201(8.33)
105	1716(5.83)	13	1686(5.93)	1234(8.10)	21	1202(8.32)
135	1725(5.80)	13	1696(5.90)	1230(8.13)	27	1201(8.33)

^a A_0 refers to the band strength in pure HCOOH at 15 K.

Table 4.10. Peak positions and band strengths for the $\nu_S(\text{C=O})$ and $\nu_S(\text{C-O})$ bands for the binary $\sim 10:90\%$ HCOOH:CO and HCOOH:CO₂ mixtures and tertiary $\sim 7:67:26\%$ HCOOH:H₂O:CO, HCOOH:H₂O:CO₂ and HCOOH:H₂O:CH₃OH mixtures at 15 K. The uncertainties on the peak positions are $\pm 1 \text{ cm}^{-1}$.

Mode	ν (cm^{-1})	A/A_0^a
11:89% HCOOH:CO		
$\nu_S(\text{C=O})$	1743, 1735, 1721, 1702	1.9
$\nu_B(\text{OH/CH})$	1390	3.0
$\nu_S(\text{C-O})$	1250, 1235, 1227, 1218, 1185, 1172, 1130	2.1
9:91% HCOOH:C ¹⁸ O ₂		
$\nu_S(\text{C=O})$	1744, 1734, 1717, 1612	0.7
$\nu_B(\text{OH/CH})$	1387	1.4
$\nu_S(\text{C-O})$	1227, 1187, 1157, 1132	0.6
8:62:30% HCOOH:H ₂ O:CO		
$\nu_S(\text{C=O})$	1705, 1685	4.7
$\nu_S(\text{C-O})$	1227	2.4
6:67:27% HCOOH:H ₂ O:C ¹⁸ O ₂		
$\nu_S(\text{C=O})$	1695	4.2
$\nu_S(\text{C-O})$	1229	1.5
6:68:26% HCOOH:H ₂ O:CH ₃ OH		
$\nu_S(\text{C=O})$	1703	3.7
$\nu_S(\text{C-O})$	1223	1.5

^a A_0 refers to the band strength in pure HCOOH at 15 K.

Chapter 5

Desorption rates and sticking coefficients for CO and N₂ interstellar ices

Abstract

We present Temperature Programmed Desorption (TPD) experiments of CO and N₂ ices in pure, layered and mixed morphologies at various ice “thicknesses” and abundance ratios as well as simultaneously taken Reflection Absorption Infrared Spectra (RAIRS) of CO. A kinetic model has been developed to constrain the binding energies of CO and N₂ in both pure and mixed environments and to derive the kinetics for desorption, mixing and segregation. For mixed ices N₂ desorption occurs in a single step whereas for layered ices it proceeds in two steps, one corresponding to N₂ desorption from a pure N₂ ice environment and one corresponding to desorption from a mixed ice environment. The latter is dominant for astrophysically relevant ice “thicknesses”. The ratio of the binding energies, R_{BE} , for pure N₂ and CO is found to be 0.936 ± 0.03 , and to be close to 1 for mixed ice fractions. The model is applied to astrophysically relevant conditions for cold pre-stellar cores and for protostars which start to heat their surroundings. The importance of treating CO desorption with zeroth rather than first order kinetics is shown. The experiments also provide lower limits of 0.87 ± 0.05 for the sticking probabilities of CO-CO, N₂-CO and N₂-N₂ ices at 14 K. The combined results from the desorption experiments, the kinetic model, and the sticking probability data lead to the conclusion that these solid-state processes of CO and N₂ are very similar under astrophysically relevant conditions. This conclusion affects the explanations for the observed anti-correlations of gaseous CO and N₂H⁺ in pre-stellar and protostellar cores.

Bisschop, Fraser, Öberg, van Dishoeck & Schlemmer, 2006, A&A, 449, 1297

5.1 Introduction

CO and N₂ are two of the most abundant species in molecular clouds and therefore control the abundances of many other molecules. CO is the second most abundant molecule after H₂, both in the gas phase and in the solid state. Gaseous CO abundances up to 2.7×10^{-4} with respect to H₂ are found in warm regions (Lacy et al. 1994), indicating that CO contains most of the carbon not locked up in refractory material. In cold clouds, CO ice absorption features are seen superposed on the spectra of background sources or embedded protostars (e.g., Chiar et al. 1994; Pontoppidan et al. 2003b). The solid CO abundance varies strongly from source to source, but can be as high as 10^{-4} with respect to H₂ in the coldest cores (Pontoppidan et al. 2005). Such high abundances are consistent with indirect determinations of the amount of CO frozen out in

the densest parts of pre-stellar cores based on submillimeter line and continuum data, which suggest that more than 90% of the CO is removed from the gas (e.g., Caselli et al. 1999; Tafalla et al. 2004; Jørgensen et al. 2005c).

The amount of N₂ present in the gas and solid state is more uncertain, since N₂ cannot be detected directly as it lacks a permanent dipole moment. The abundance of gas phase N₂ is usually inferred from the presence of the daughter species N₂H⁺. Early work by Womack et al. (1992) inferred gas phase N₂ abundances of $2\text{--}6 \times 10^{-6}$ with respect to H₂ in star-forming regions, indicating that N₂ contains at most 10% of the nitrogen abundance. Up to an order of magnitude higher abundances were found by van Dishoeck et al. (1992), suggesting that at least in some sources the transformation to molecular form is complete. More recent determinations of the N₂ abundance have focused on dark cores for which the physical structure is well determined from complementary data. For example, Bergin et al. (1995) and Bergin et al. (2002) find typical gas-phase N₂ abundances of $1\text{--}2 \times 10^{-5}$. Indirect indications for N₂ freeze-out onto grains can be obtained from analysis of the millimeter N₂H⁺ data, which suggest a decline in the gas-phase abundance by at least a factor of two in the centers of dense cores (Bergin et al. 2002; Belloche & André 2004). Constraints on the amount of solid N₂ that might be present come from analysis of the solid CO band profile (Elsila et al. 1997). The most stringent limits indicate that the N₂:CO ratio must be less than 1:1, derived for sources for which both ¹²CO and ¹³CO ices have been detected (Boogert et al. 2002a; Pontoppidan et al. 2003b). This limit only holds for mixed ices of CO and N₂, not when N₂ ice has formed a separate layer.

The chemistries of CO, N₂ and their daughter products are intimately linked, even though the two molecules belong to different elemental families. This is due to the fact that CO is one of the main destroyers of N₂H⁺ in the gas phase. When CO is frozen out onto the grains, N₂H⁺ is enhanced, as confirmed observationally by the anti-correlation of the abundances of N₂H⁺ with CO and HCO⁺ in pre- and protostellar regions (Bergin et al. 2001; Tafalla et al. 2002; Di Francesco et al. 2004; Pagani et al. 2005; Jørgensen 2004). This anti-correlation is often quantitatively explained by a factor of 0.65 difference in the binding energies for CO and N₂, allowing N₂ to stay in the gas phase while CO is frozen out. These models do not contain an active grain-surface chemistry, but only include freeze-out and desorption. The relative freeze-out behavior of CO and N₂ also affects the abundance of H₃⁺ and its level of deuterium fractionation (Roberts et al. 2002). Indeed, observations of H₂D⁺ in cold cores and in protoplanetary disks often invoke large (relative) depletions of CO and N₂ (Ceccarelli & Dominik 2005).

The above discussion clearly indicates the need for a good understanding of the processes by which CO and N₂ freeze-out and desorb from the grains under astrophysically relevant conditions. To describe desorption, accurate values for the binding energies and the kinetics of the process are needed. For freeze-out, the sticking probability is the main uncertainty entering the equations. In an earlier paper (Öberg et al. 2005, hereafter paper I), we presented a limited set of experiments using our new ultra-high vacuum (UHV) set-up to show that the

ratio of the binding energies R_{BE} for CO and N₂ in mixed and layered ices is at least 0.923 ± 0.003 and in many circumstances close to unity. This result can be understood chemically by the fact that the two molecules are iso-electronic. Indeed, the sublimation enthalpies calculated from the IUPAC accredited data for pure ices were found to be 756 ± 5 K and 826 ± 5 K for pure N₂ and CO ices respectively, giving a ratio of 0.915 (Lide 2002). This experimental ratio is much larger than the value $R_{\text{BE}} = 0.65$ adopted in chemical models to explain the observational data (Bergin & Langer 1997; Ceccarelli & Dominik 2005). In an alternative approach, Flower et al. (2005) used the results from paper I and instead varied the sticking probabilities of CO and N₂, which were assumed to be 1 below 15 K in all previous models. They could only reproduce the observed anti-correlation of N₂H⁺ and HCO⁺ if the sticking probability for N₂ was lowered to 0.1 compared with 1 for all other molecules.

In this chapter, we present new experiments on N₂-CO ices, both in pure, layered and mixed ice morphologies with varying ice “thicknesses” and relative abundances. In addition to TPD, RAIRS is used to probe the mixing, segregation and desorption processes in the ices. The aim of these experiments is to understand the N₂-CO ice system to an extent that the experimental desorption kinetics can be modeled and reproduced, and to subsequently use these model parameters to predict the behavior of CO and N₂ under astrophysically relevant conditions. The key parameters to be derived for the N₂-CO ice are: i) the CO-CO, N₂-CO, and N₂-N₂ binding energies, ii) the desorption kinetics (i.e., the desorption rates), iii) the diffusion kinetics (i.e., the mixing and segregation rates), and iv) lower limits to the sticking probabilities.

This chapter is organized as follows: §5.2 focuses on the experimental procedure and choice of ice layers and mixtures, § 5.3 presents the experimental results on desorption, § 5.4 a kinetic model of the experimental data, and § 5.5 experiments on the sticking probabilities. § 5.6 discusses how the kinetic model can be applied to astrophysically relevant situations and predicts the desorption behavior of CO and N₂ for astrophysically relevant heating rates. In § 5.7 all important conclusions are summarized.

5.2 Experimental procedure

The experimental apparatus used for this work, CRYOPAD (Cryogenic Photoproduct Analysis Device) (van Broekhuizen 2005), is very similar to the SURFRESIDE (SURFace REaction SIMulation DEvice) Leiden surface astrochemistry instrument described in detail elsewhere (Fraser & van Dishoeck 2004). Briefly, all experiments were performed in an ultra-high vacuum (UHV) chamber, capable of reaching base pressures of better than 1×10^{-10} Torr. At the center of the chamber is a gold-coated copper substrate, mounted in close thermal contact with a closed cycle He cryostat, which cools the whole substrate to 14 K. The cryostat and substrate assembly is mounted on a rotation stage which can be rotated through 360 deg. The sample temperature is controlled to better than ± 0.1 K using the cryostat cold finger, a resistive heating ele-

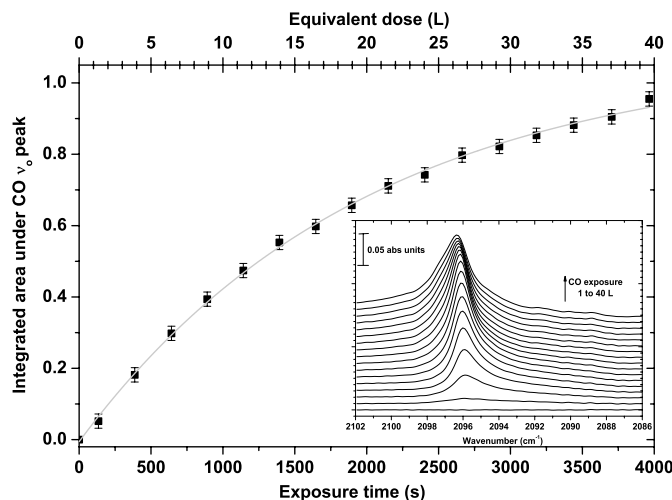


Figure 5.1. Integrated intensity of the ^{13}CO RAIR spectra with deposition time. Individual RAIR spectra are shown in the inset for ice exposures of 1 to 40 L in steps of 3 L (Langmuir).

ment and a Lakeshore 340 temperature control unit. The system temperature is monitored with two KP-type (0.07% Au in Fe versus chromel) thermocouples, one mounted on the substrate face, the second by the heater element. Ices are grown *in situ* onto the substrate, by exposing the cold surface to a steady flow of gas, introduced into the chamber via an all metal flow control valve, with a modified outlet directed at the substrate center, along the surface normal. TPD is induced by heating the substrate (and ice sample) at a steady rate of 0.0017 K s^{-1} , using a linear heating ramp controlled by a positive feedback loop from the Lakeshore instrument. The ice film is monitored using FT-RAIRS (Fourier Transform RAIRS), which is an analysis technique providing information on the orientation and constituents of the ice film. The RAIR spectra cannot be directly compared to observational data, however, since they differ from transmission spectra. During flow setting, deposition and desorption, gases liberated from the surface are monitored using a quadrupole mass spectrometer (Pfeiffer Prisma).

To enable CO and N₂ to be discriminated from each other (and the background signal) with mass spectrometry, isotopes of both molecules were used, i.e. ^{13}CO (Icon Isotopes 99.998% $m/e = 29$), and $^{15}\text{N}_2$ (Cambridge Isotopes Inc. 98% $m/e = 30$). This isotopic substitution is simply an experimental asset and does not affect the results presented in § 5.3: ^{12}CO and $^{14}\text{N}_2$ will behave identically. In the pure and layered ice morphologies, the gases were used as supplied; to form the mixed ices a 1:1 gas mixture of $^{13}\text{CO}:$ $^{15}\text{N}_2$ was pre-prepared and mounted on the UHV chamber gas-dosing system. The dosing rate for ice-film growth was set prior to cooling the sample, by sequentially backfilling the cham-

ber with the gas(es) of interest, to a pressure of around 1×10^{-8} Torr, equivalent to an ion reading on the mass spectrometer of 7.5×10^{-10} A for both $^{15}\text{N}_2$ and ^{13}CO . The flow was then stopped, and the background pressure within the chamber allowed to recover to $\sim 1 \times 10^{-10}$ Torr, before the sample was cooled to 14 K. A background RAIRS spectrum was recorded prior to ice growth. The ice films were then grown by reopening the pre-set flow valve for exposure times equivalent to the gas dose required per sample gas (see Table 5.1), according to the morphology of the ice to be grown, assuming 1 L (Langmuir) is $\sim 1 \times 10^{-6}$ Torr s $^{-1}$, which roughly corresponds to ~ 1 monolayer per unit area (cm ^{2}) of material on the substrate. In the remainder of this chapter, the ices are discussed in terms of the gas exposure (in L) to which the substrate was subjected during ice-growth; for quick conversion to astronomically relevant surface concentrations, it can be assumed that a direct relationship exists between the “exposure” value quoted, and surface coverage or “thickness” of the resulting ice, which will be approximately n monolayers of material, assuming an exposure of n L and a surface concentration of 10^{15} molecules cm $^{-2}$.

During film growth, the CO-gas uptake on the cold surface was monitored directly with RAIRS (see Fig. 5.1) and indirectly by detecting residual CO and N $_2$ gas with the mass spectrometer. Since N $_2$ has no permanent dipole, it is infrared inactive and can only be monitored with the mass spectrometer. CO ice growth was initially seen to be non-linear (Fig. 5.1), most probably due to the preferential formation of isolated “islands” of CO on the substrate (as is for example also seen by Nekrylova et al. 1993) rather than an even, flat “thin-film” of CO ice, where the substrate surface is fully saturated. Around 40 L, CO ice growth becomes linear, indicating that the structure of the ice that is forming no longer changes during deposition and the ice is present as a “thin-film”. This is a key reason for using an ice thickness of 40 L CO for experiments in which the relative abundance of N $_2$ is varied. The ice was then heated in a TPD experiment (for a detailed discussion of TPD experiments see e.g., Menzel 1982), and 1 cm $^{-1}$ resolution RAIR spectra were recorded as the temperature reached $\sim 15, 20, 22, 24, 25, 26, 27, 28, 29, 30, 35$ and 40 K.

The ice samples studied are summarized in Table 5.1. Throughout this chapter, the notation X/Y indicates a layered ice morphology with X on top of Y, whereas X:Y denotes a fully mixed ice system. The 1/1 and 1:1 notation denotes identical amounts of both species, whereas the x/40 L notation refers to experiments in which the “thickness” of the overlying N $_2$ layers is varied, but that of the CO layer is kept constant at 40 L. The “thicknesses” have been chosen to be of astrophysical relevance: if all condensible carbon were frozen out as CO it would form an ice layer equivalent to ~ 40 monolayers on an interstellar grain (Pontoppidan et al. 2003b). This is a fortuitous coincidence with the point at which, experimentally, thin-film CO ice growth dominates in our apparatus. A layered ice morphology is indicated by analysis of the interstellar solid CO profiles, which reveal a component of pure CO ice which contains 60–90% of the total solid CO abundance and which is clearly separated from the H $_2$ O ice (Tielens et al. 1991; Chiar et al. 1994; Pontoppidan et al. 2003b). Chemical models show that nitrogen is transformed into N $_2$ at later times and at higher

Table 5.1. *Overview of ice morphologies and ice exposure used in the experiments.*

	¹³ CO (L)	¹⁵ N ₂ (L)	Total (L)
Pure ¹³ CO	20	—	20
	40	—	40 ^a
	80	—	80
Pure ¹⁵ N ₂	—	20	20
	—	40	40 ^a
	—	80	80
¹³ CO: ¹⁵ N ₂	10	10	20
	20	20	40
	40	40	80 ^a
	80	80	160
¹³ CO/ ¹⁵ N ₂	10	10	20
	40	40	80 ^a
	80	80	160
¹⁵ N ₂ / ¹³ CO	10	10	20
	20	20	40
	40	40	80 ^a
	80	80	160
	5	40	45
	10	40	50
	20	40	60
	30	40	70
	50	40	90

^adata previously reported in paper I.

extinction when compared with the conversion of carbon from atomic form into CO (d’Hendecourt et al. 1985; Hasegawa et al. 1992). Thus, either CO starts freezing out before N₂ is formed so that N₂ forms a “pure” overlayer, or both molecules are present in the gas phase and freeze out together. This makes N₂/CO and N₂:CO the most astrophysically relevant ice morphologies to study; CO/N₂ ices were however also included in this study, to complete our understanding of the behavior of the ice systems. In terms of relative abundances, observational evidence (§ 5.1) suggests that the N₂ abundance is always less than or equal to that of CO. Models including gas-grain chemistry predict N₂ ice abundances that are typically a factor 5–20 lower than those of CO ice (Hasegawa & Herbst 1993; Shalabiea & Greenberg 1994; Bergin et al. 1995; Aikawa et al. 2005). Together, these arguments led to the choice of ice morphologies and exposures summarized in Table 5.1.

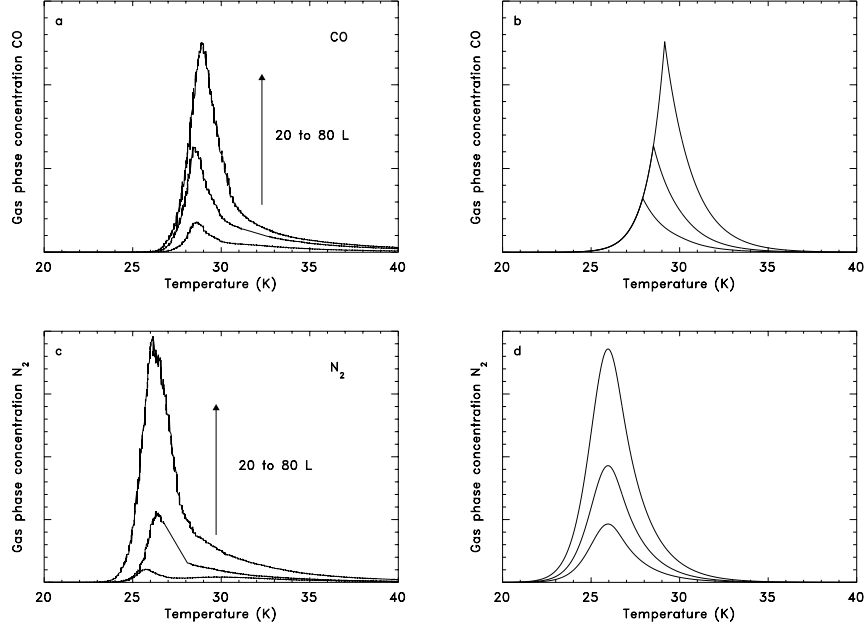


Figure 5.2. TPD spectra for pure ices with exposures of 20, 40, 80 L. (a) CO experiments, (b) CO model, (c) N_2 experiments, and (d) N_2 model.

5.3 Experimental results

5.3.1 Pure CO and N_2 ices

In Figure 5.2a and c, the TPD spectra for three different ice exposures, i.e. 20, 40, and 80 L, for pure CO and N_2 ices are shown. The CO TPD curves indicate that the onset for desorption is at around 26 K in the laboratory. The leading edges of the TPD curves for the 40 and 80 L exposures overlap, suggesting that the desorption process occurs at a rate that is independent of the ice thickness. Consequently the peak of the CO TPD curve shifts to higher temperatures for increasing ice thicknesses, peaking at 28 K for an exposure of 40 L. This indicates the presence of multilayer films, since the number of molecules that desorb depends only upon the number of molecules in the surface, which is identical at ice exposures of 40 and 80 L. Thus the desorption rate is constant until there are no molecules left on the surface and desorption stops. This type of kinetics is called zeroth order kinetics. The order of the kinetics is defined as the power of the number of molecules in the surface with which the rate of desorption scales (for details see § 5.4.1). Since the differences in the CO TPD spectra are smaller for all ice morphologies, this is the only time they are discussed (Fig. 5.2a). The TPD signal for the 20 L experiment has a lower intensity than expected from scaling the 40 L data. This is due to island growth

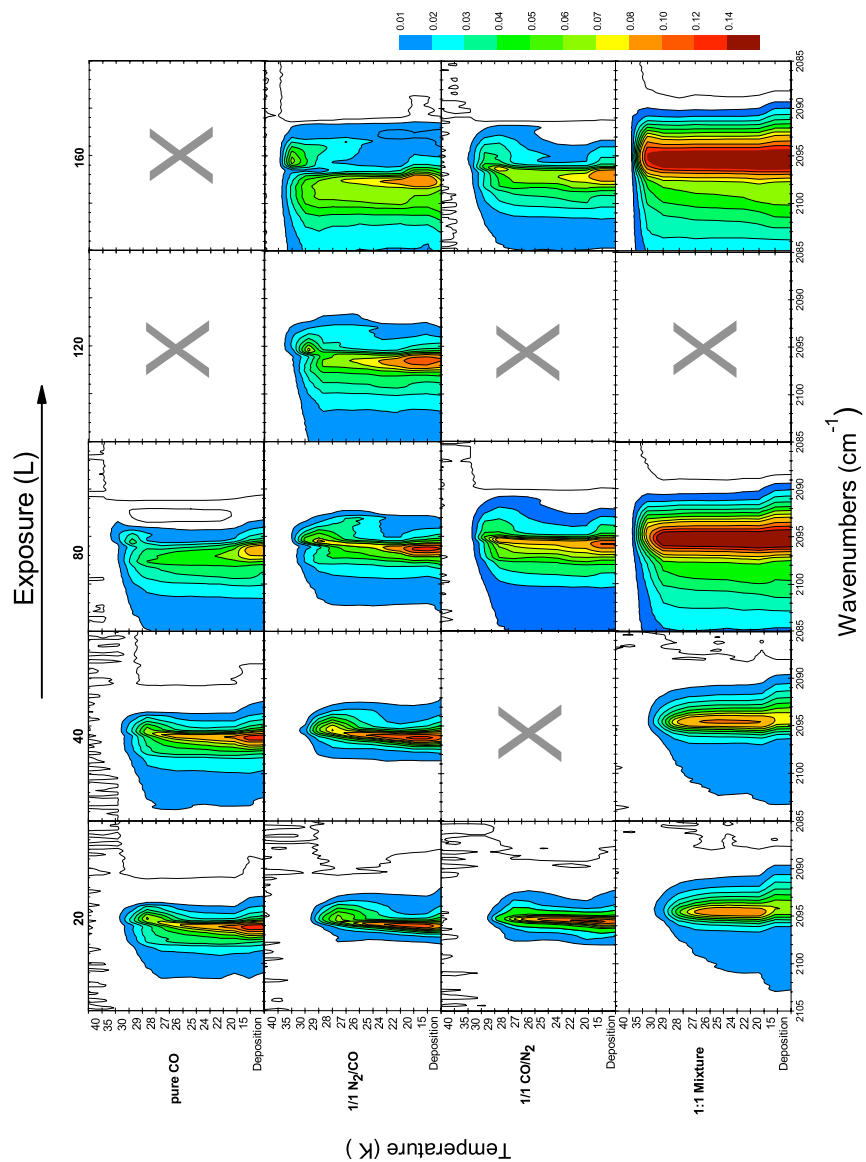


Figure 5.3. 2-D RAIR spectra of ¹³CO plotted as frequency vs. temperature (on a non-linear temperature scale), in pure CO, mixed and layered CO:N₂ ices, with exposures indicated at the top of the matrix and ice morphologies on the left hand side. X= data not available.

at low exposures (see Fig. 5.1 and § 5.2).

The onset of N_2 desorption shifts from 25 K for 20 and 40 L exposures, to 24 K for 80 L (see Fig. 5.2c). The peak position of N_2 remains the same for the 40 and 80 L experiments. This indicates that in contrast to CO, the desorption rate of N_2 increases with increasing ice thickness. This kind of kinetics is called first order kinetics. Note that, in general, desorption kinetics do not have to have an exact integer value. For example Bolina et al. (2005) find that multilayer desorption of CH_3OH on highly oriented pyrolytic graphite (HOPG) has a desorption order of 0.35. In most cases, however, the desorption kinetics will approach either zeroth, first or even second order.

RAIRS data for pure ^{13}CO 20, 40 and 80 L exposures are shown in the first row of Fig. 5.3. The peak position is around 2096 cm^{-1} with a full width half maximum of 2 cm^{-1} . When the temperature increases above $\sim 20\text{ K}$, a reduction in intensity and narrowing is observed on the blue side of the CO band. This change is probably due to restructuring of the ice. It is likely that the initial ballistic deposition results in an “open” amorphous ice structure; at around 20 K the CO molecules become torsionally mobile about their lattice points, resulting in an “on the spot” rotation about each molecule’s center of mass, and the formation of a more closely packed structure. Finally, around 26 K when pure CO ice starts desorbing, more dramatic changes occur in the CO band. The origin of these changes is thought to be due to crystallization and is described in more detail in a future publication. The intensity decreases due to desorption, and a small peak grows on the blue side of the main feature.

5.3.2 Layered ices

The N_2 TPD spectra for the 1/1 N_2/CO experiments and $x/40\text{ L}$ N_2/CO are shown in Fig. 5.4a and c, respectively. Additionally, the 1/1 experiments of CO/N_2 are shown in Fig. 5.5. In all cases at least one peak is observed in the TPD spectra, but from the majority of the data it is evident that the TPD spectra are actually composed of two peaks, one at around 26 K (labeled peak I) and one at around 28 K (labeled peak II). In all the spectra, peak I coincides with the position of the TPD desorption peak in pure N_2 , so it is attributed to N_2 desorbing from a pure N_2 layer; peak II coincides with the position of the pure CO TPD desorption peak and is therefore assigned to co-desorption of N_2 with CO, hypothesizing this occurs from a mixed phase of N_2 -CO ice. The formation of this mixture would require bulk diffusion of N_2 and/or CO between the two separate layers. This mobility is found to commence at significantly higher temperatures than those expected for the hopping process on surfaces (Tielens & Allamandola 1987). The energy-barrier to hopping is typically assumed to be $0.3\times$ the binding energy, corresponding to around $\sim 285\text{ K}$ for CO and N_2 and implying that CO and N_2 are mobile around 10 K. Our much higher temperature for mobility is probably due to a much larger barrier to bulk diffusion than for surface diffusion. For comparison, experiments by Collings et al. (2003a) suggest CO molecules become mobile at around 12–15 K on both CO and H_2O -ice surfaces, suggesting the barrier to surface diffusion is only slightly higher than

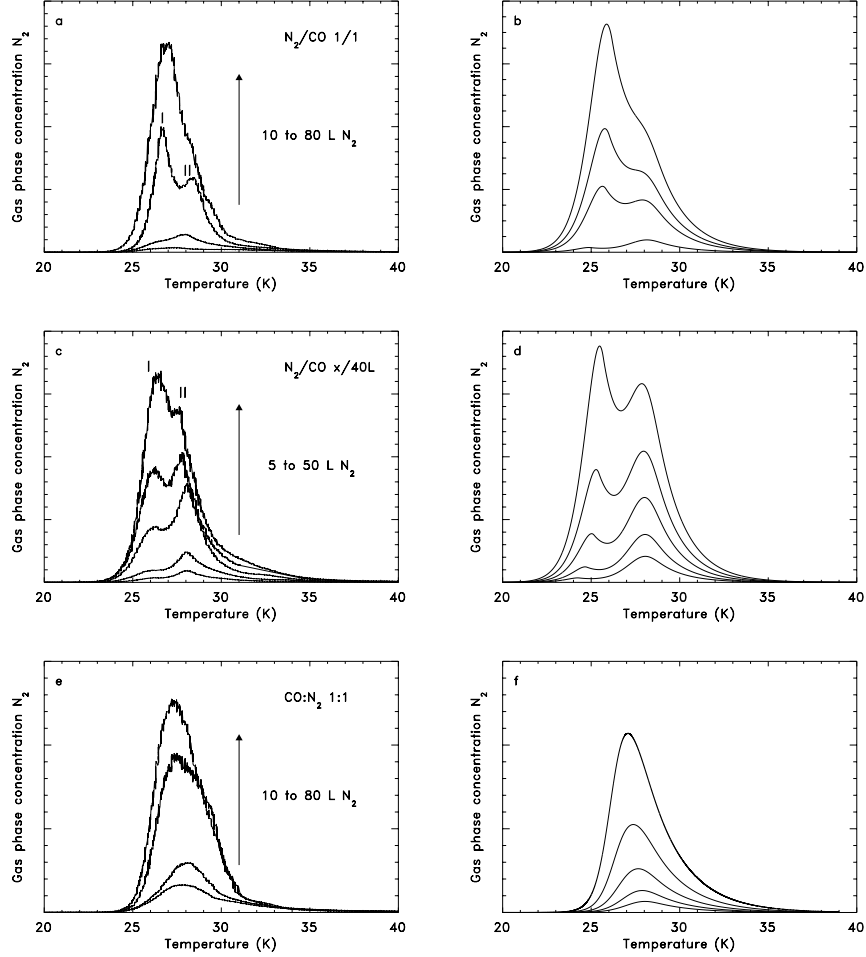


Figure 5.4. *N₂ TPD spectra: (a) (10-20-40-80 L)N₂/(10-20-40-80 L)CO, 1/1 layer, (c) (5-10-20-30-50 L)N₂/(40 L)CO, differential layer, e) (10-20-40-80 L)N₂:(10-20-40-80 L)CO, mixed ice 1:1. The equivalent model spectra are shown in b, d, and f, respectively. The two experimental TPD peaks are labeled I and II, corresponding to desorption of N₂ from pure and mixed ice phases respectively.*

the theoretical approximation used in astrochemical models. Furthermore it is clear that the mixing process occurs during ice annealing, and not immediately on deposition, first because there is significant N₂ desorption from a pure ice phase and second because the desorption profiles of the layered and mixed ice systems differ significantly (see § 5.3.3).

Important information about the N₂-CO ice system can be derived from the

relative intensities of peak I and II. In the 1/1 and x/40 L N₂/CO experiments, a turnover is observed between the peak intensities (see Fig. 5.4a and c), with peak II being more intense than peak I for low “thickness”, and visa versa at high “thickness”. This turn-over occurs between the 40/40 L and 60/60 L exposures for the 1/1 experiments, and between the 30/40 L and 50/40 L in the x/40 L experiments, i.e. both sets of experiments consistently have the turn-over point around 40/40 L.

The CO RAIR spectra of the layered ices (second and third rows of Fig. 5.3) have a ¹³CO feature that is almost identical to that for pure ¹³CO, although the red-wing is less pronounced. As for pure CO, the intensity of the blue-wing decreases around 20 K, where the ice restructures, and a new peak grows around 26 K, where CO starts to desorb. Since the changes in the layered ice spectra at 20 K are commensurate with similar changes in the pure CO ice spectra, this is unlikely to be an indicator of the mixing process. Additionally, a blue wing appears around 24–25 K, concurrently to the onset of N₂ desorption in the TPD spectra (see Fig. 5.4). This feature is probably due to mixing of both molecules, as will be discussed in § 5.4.3. The appearance of a blue wing around 24 K rather than 20 K reaffirms that the mixing process relies on bulk rather than surface diffusion.

Finally, the TPD spectra of 1/1 CO/N₂ ice layers at exposures of 20, 80 and 160 L are shown in Fig. 5.5. These experiments were used primarily to test whether the ices were indeed grown as separate layers on top of each other. The turn-over point where peak I becomes more intense than peak II occurs at slightly higher exposures compared with N₂/CO ice layers, i.e., between 40/40 L and 80/80 L. It is therefore clear that N₂ desorption is retarded by the CO overlayer, desorbing only after it has mixed with, and (a fraction of which has) subsequently segregated from, the CO ice. As the spectra do not resemble those of the pure N₂ ice, these experiments provide positive evidence that the layer growth is sequential and coincident on the substrate. However, this ice structure is not thought to be astrophysically relevant, so it is not discussed further in this article.

5.3.3 Mixed ices

The N₂ TPD spectra for mixed ices (Fig. 5.4e) differ from those of pure or layered ices in that only one peak is observed, skewed to the low, and not high temperature side of the desorption range. As the “thickness” of the mixed ice increases, the TPD peak maximum shifts from 28 to 26 K. This behavior indicates that at low exposures, N₂ desorbs predominantly from a mixed-ice environment, whereas as the exposure increases, a more significant fraction of the N₂ is able to desorb from a pure N₂ layer. Furthermore, the TPD peaks are broadened with respect to those observed for pure and layered ice morphologies (see § 5.3.1 and 5.3.2). This broadening is likely to be due to the merging of peaks I and II, and the potential for a wider range of binding environments to exist in the intimately mixed ice morphology. Desorption occurring from a pure N₂ ice environment suggests that segregation must also occur within mixed N₂-

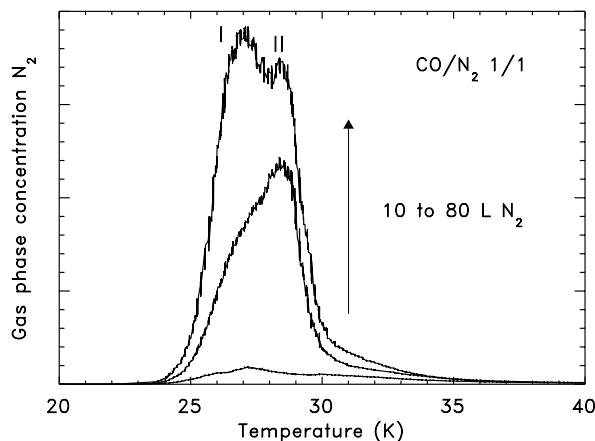


Figure 5.5. *N₂ TPD spectra of (10-40-80 L)CO/(10-40-80 L)N₂, 1/1 layer. The two experimental TPD peaks are labeled I and II, corresponding to desorption of N₂ from pure and mixed ice phases respectively.*

CO ice systems, including the mixed phases that are formed in the layered ice systems. However the fact that some desorption from the mixed phase is always observed indicates that the segregation happens at a lower rate than the mixing process, potentially because the energy barrier to segregation is greater than that for mixing. This would suggest that over certain temperature ranges the mixed ice phase is thermodynamically more stable than the segregated layers.

The RAIR spectra of the mixed ices (final row Fig. 5.3) differ from those of the pure and layered ices, being broader (4 cm⁻¹) and shifted to 2094 cm⁻¹, reflecting, as with the TPD data, that the structure of the mixed ices is unique. Again, the CO band changes shape at around 20 K, possibly due to a similar restructuring as observed for the pure and layered ices, discussed in § 5.3.1 and 5.3.2, but no further changes are observed as the temperature increases until the ice starts desorbing. This implies that all or most of the CO remains in a mixed ice phase until it starts to desorb; even if the concentration of this phase changes slightly as the N₂ segregates and desorbs, it is not evident in the RAIR spectra.

5.4 Empirical model of N₂-CO desorption

A model was built to gain a clearer qualitative and quantitative understanding of the thermal annealing processes including diffusion, mixing and desorption of the ices. The aims of this model are twofold; to reproduce the experimental data and then apply the same kinetic parameters to astrophysically relevant ice morphologies, temperatures and heating rates.

5.4.1 Constructing the model

The kinetic processes for desorption, mixing and segregation in this system have a reaction barrier (i.e. they are thermodynamically limited) and can therefore be described by the following equation:

$$r_{\text{des}} = \frac{dN}{dt} = \nu_i [N_s]^i e^{-E/T}, \quad (5.1)$$

where r_{des} is the desorption rate (molecules cm⁻² s⁻¹), N is the number of molecules evaporating from the substrate (assuming throughout the remainder of these calculations that the substrate has unit surface area (cm²)), t is time in s, ν_i the pre-exponential factor (molecules^{1- i} cm^{2($i-1$)} s⁻¹), i is the reaction order, $[N_s]$ is the number of molecules partaking in a particular reaction per unit surface area (molecules cm⁻²), E is the reaction barrier in K, which for the desorption processes can be read as the binding energy, and T is temperature in K. The physical meaning of the pre-exponential factor ν_i depends upon the reaction order i . For a first order reaction it refers to the lattice vibrational frequency which is typically in the range 10¹¹–10¹³ s⁻¹; for zeroth order desorption it consists of the product of the lattice vibrational frequency with the surface density of order 10¹⁵ molecules cm⁻². Depending on the type of reaction, the reaction order i can vary, taking positive, negative and any non-integer real value. Both E and ν_i depend in principle upon “thickness”. However, this dependence is not thought to be large since no major changes are observed between the FTIR spectra at different coverages indicating that the intermolecular environments are very similar.

In order to calculate the temperature-dependent rate measured in the TPD experiments, the following conversion needs to be made:

$$\frac{dN}{dt} = \frac{dN}{dT} \frac{dT}{dt}, \quad (5.2)$$

where dN/dT is the temperature-dependent rate (molecules cm⁻² K⁻¹), and dT/dt the TPD heating rate (K s⁻¹). At each time step, a fraction of the molecules that have evaporated into the gas phase will be removed by the pump; subtracting this rate from the desorption into the gas phase will reproduce the experimental conditions. The pump-rate is given by:

$$r_{\text{pump}} = \frac{dN}{dt} = -\nu_{\text{pump}} N(g), \quad (5.3)$$

in which ν_{pump} is the pump constant in s⁻¹ and $N(g)$ the number of molecules entering the gas phase having desorbed from a unit surface area. To ensure the equations balance, $N(g)$ is given in molecules cm⁻², implying that the molecules actually occupy a unit volume. Combining equations (5.1), (5.2), and (5.3), the experimental results can be simulated in a simple way. The reactions are summarized in Table 5.2.

5.4.2 Constraining the model

First, the reactions h and i given in Table 5.2 plus the pump constants ν_{pump} for CO and N₂ were constrained, by fitting a first-order exponential to the pump-down curves of both CO and N₂ at 14 K, accounting for the pumping effects of the turbo-pump and the cryostat in the experiment. Note that the ν_{pump} values shown in Table 5.2 are experimentally determined and consequently fixed for further iterations of the kinetic model.

Next, the parameters associated with reactions a and b , desorption from pure ice environments, were constrained. Since the binding energies for pure CO ice desorption found by Collings et al. (2003a) and paper I are identical within experimental error, the CO binding energy was initially set to the same value reported in paper I; ν was fixed at the value reported by Collings et al. (2003a). For N₂, the desorption kinetics appear to be first order (see § 5.3.1) and therefore the pre-exponential factor ν was initially estimated to be somewhere between 10^{11} – 10^{13} s⁻¹, then varied in order to obtain the best fit to the experimental data. The N₂ binding energy was initially set to the value reported in Paper I, but also allowed to vary in iterations of the model. The final values of these parameters are given in Table 5.2 and the corresponding TPD models are presented next to the experimental data in Fig. 5.2b and d.

Desorption from the mixed ice fraction was assumed to be first order. This is thought to be a good assumption since the rate of desorption depends on the number of molecules on the surface and this will change after each molecule desorbs. Initially, the binding energy for desorption from the mixed ice layer was taken to be the same as that of pure CO desorption, because peak II appears to occur at the same temperature as the desorption of pure CO. However, when running the model this value had to be increased to reproduce the experimental effect.

From the TPD spectra described in § 5.3 no direct measurement of the mixing rates was possible. Mixing can, however, be inferred from the presence of peak II in the layered ice experiments. Assuming a simple, single step process, reactions e and f in Table 5.2 describe the mixing, assuming both molecules contribute equally to the process. Good physical arguments can be made for modeling this process as zeroth, first or second order kinetics, and all three processes were investigated (see Appendix A for a more detailed discussion). The outcome is that experimental data are best reproduced if the mixing process is zeroth order. Since mixing occurs only at the interface between the CO and N₂ ice layers this description makes physical sense. A CO or N₂ molecule at the interface has a certain chance of overcoming the “mixing barrier” and diffusing into the opposite layer, but the molecules remaining at the interface will still see the same number of molecules, regardless of whether there are 20 or 80 L of ice above or below it.

The final reaction to constrain is the segregation reaction g . The relative number of molecules desorbing from pure N₂ environments in mixed ice morphologies increases with exposure, as was discussed in § 5.3.3. Segregation is modeled as one reaction, in a second order process depending on the initial

Table 5.2. Rate equations for desorption, mixing, and segregation of CO and N₂ in the N₂-CO ice systems.

	Reaction	Rate equation	ν (molecules ⁽¹⁻ⁱ⁾ cm ²⁽ⁱ⁻¹⁾ s ⁻¹)	E (K)	i
a	CO(s) → CO(g)	$\nu_0 e^{-E/T}$	$7.0 \times 10^{26 \pm 1, a}$	855 ± 25	0
b	N ₂ (s) → N ₂ (g)	$\nu_1 [\text{N(s)}]^i e^{-E/T}$	$1.0 \times 10^{11 \pm 1}$	800 ± 25	1
c	CO(mix) → CO(g)	$\nu_1 [\text{CO(mix)}]^i e^{-E/T}$	$7.0 \times 10^{11 \pm 1}$	930 ± 25	1
d	N ₂ (mix) → N ₂ (g)	$\nu_1 [\text{N}_2(\text{mix})]^i e^{-E/T}$	$1.0 \times 10^{12 \pm 1}$	930 ± 25	1
e	CO(s) → CO(mix)	$\nu_0 e^{-E/T}$	$5.0 \times 10^{26 \pm 1}$	775 ± 25	0
f	N ₂ (s) → N ₂ (mix)	$\nu_0 e^{-E/T}$	$5.0 \times 10^{26 \pm 1}$	775 ± 25	0
g	CO(mix) + N ₂ (mix) → CO(s) + N ₂ (s)	$\nu_2 [\text{CO(mix)}][\text{N}_2(\text{mix})] e^{-E/T}$	$1.0 \times 10^{-4 \pm 1}$	930 ± 25	2
h	CO(g) → CO(pump)	$\nu_{\text{pump}} [\text{CO(g)}]$	$1.0 \times 10^{-3, a}$	–	1
i	N ₂ (g) → N ₂ (pump)	$\nu_{\text{pump}} [\text{N}_2(\text{pump})]$	$8.2 \times 10^{-4, a}$	–	1

^aParameters are fixed according to experimental constraints see § 5.4.2.

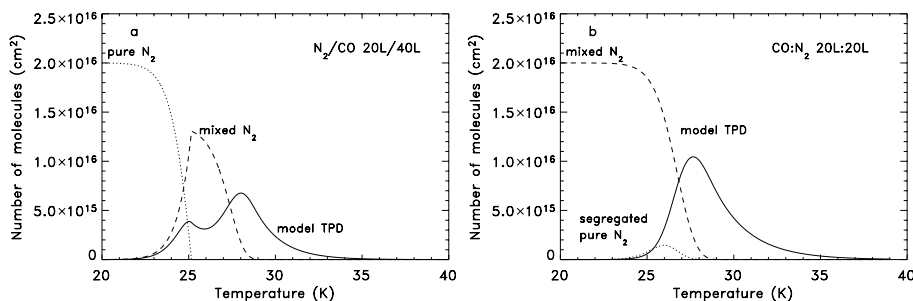


Figure 5.6. Model results for the ice and gas phase concentrations as functions of temperature. The number of molecules in pure N₂ ice (dotted line), in mixed ice (dashed line), and in the gas phase (solid line) are shown for 20/40 L N₂/CO (a) and the 20:20 L CO:N₂ (b).

number of molecules in the mixed ice phase for both species. In reproducing all the mixed ice experiments these values were, of course, equal. In the layered ices, however, it is unlikely that the relative abundances of CO and N₂ in the mixed ice phases are equal. Consequently, equation *g* suggests that segregation is fastest from a equimolar ice, decreasing as the relative abundances of either species deviate from 1:1. Finally, from the TPD spectra of the layered ices it was clear that the mixing was more efficient than the segregation process, so, as discussed in § 5.3.2, the *E* of reaction *g* was always assumed to be greater than *E* of reactions *e* and *f*.

5.4.3 Results

In Table 5.2, all the model equations and best fit parameters “by eye” are given after running a large number of models. The error-bars arise from (i) the range of values over which simultaneous fits of ν and *E* gave degenerate solutions to the model, (ii) the uncertainty in the number of molecules present on the surface, and (iii) the experimental uncertainties in the temperature. It is important to realize that the degeneracy in the simultaneous fits of ν and *E* means that the combination of these values is more accurate than the individual values. Thus, in astrochemical models both parameters need to be used in combination to accurately reproduce the behavior of CO and N₂.

A comparison between Fig. 5.2a and c with Fig. 5.2b and d clearly shows that the model described here very reasonably reproduces the data of the pure CO and N₂ ice system. The leading edges for the CO TPD spectra of the experiment do not quite overlap as perfectly as the model does, probably because CO desorption is close to, but not quite, zeroth order. As was discussed by Collings et al. (2003a) the error resulting from this deviation from zeroth order is significantly smaller than all other errors made in astrochemical models. The best-fitted parameters for *E* are 855 K and 800 K for CO and N₂ respectively.

The desorption peaks I and II observed in the TPD spectra for the layered ices are also well reproduced by the model. The appearance of peak II depends on equations c and d which describe desorption of CO and N₂ from the mixed ice phase. From Table 5.2 it is seen that ν and E are within the model error-bars identical in each reaction, confirming that N₂ and CO co-desorb from this mixed ice phase. Since E from the mixed ice is greater than E from the pure ice, it seems CO and N₂ are both more strongly bound in the mixed ice. The results give a R_{BE} of 0.936 ± 0.03 for the pure N₂ and CO ices and 1.0 for the mixed ices, within experimental error of paper I. Note that even for layered ices of “thicknesses” less than 40 L, most N₂ desorbs from a mixed ice environment.

Mixing kinetics were confirmed to be zeroth order. The best-fit E value equals 775 K, which is rather close to E found for desorption of pure N₂ and indicates that significant mixing only occurs close to desorption of N₂, corresponding to the change in RAIR spectra found around 24 K in § 5.3.2. This behavior is also illustrated in Fig. 5.6a for the 20/40 L N₂/CO experiment, where the growth of the mixed ice phase is commensurate with the loss of the pure ice phase and the desorption of the pure N₂ layer. For higher ice thicknesses of N₂, the competition between mixing and desorption is in favor of desorption from the pure ice layer, leading to the turn-over in peak intensity from peak I and II.

Segregation starts close to the desorption temperature of CO, which is illustrated by Fig. 5.6b for the 20:20 L CO:N₂ experiment. This occurs at a higher temperature than the onset of mixing, due to a barrier difference; E equals 930 K for segregation and 775 K for mixing. This difference makes segregation a relatively unimportant process for layered ices. As for mixed ices, however, the segregation rate increases with ice thickness, leading to a larger segregated fraction for higher initial ice thickness, which shifts the TPD peak to lower temperatures.

5.5 Sticking probability

The data presented so far are key to our understanding of CO and N₂ desorption rates in interstellar environments. However, because the binding energies of CO and N₂ in the solid phase are essentially so similar, this parameter cannot be the main factor which accounts for the anti-correlation of N₂H⁺ with CO and HCO⁺ in pre-stellar cores. The freeze-out rate, or a difference in the sticking probability of each molecule to the grain, may also be relevant.

Without a molecular beam facility, it is very difficult to quantify sticking probabilities directly. Nevertheless, during these experiments, the gas load reaching the mass spectrometer was monitored during the flow setting for a time period equivalent to the dosing period (when the substrate was warm) and the entire dosing period (when the substrate was cold). By combining the measurements over a range of deposition times and experiments, it is possible to extract a value for the uptake coefficient. From the uptake coefficient only a lower limit to the sticking probability can be derived since the mass spectrometer signal at low temperatures also includes an unknown fraction of molecules

Table 5.3. *Lower limits to the sticking probabilities at 14 K.*

System	Sticking probability
CO → CO	$\geq 0.9 \pm 0.05$
N ₂ → N ₂	$\geq 0.85 \pm 0.05$
N ₂ → CO	$\geq 0.87 \pm 0.05$

that miss the substrate (for a more detailed explanation of the derivation of the uptake coefficient see Fuchs et al. 2006). The uptake coefficient at surface temperatures of 14 K is given by

$$S(\theta) = \frac{\int N_x^w dt - \int N_x^c dt}{\int N_x^w dt}, \quad (5.4)$$

where θ is the “thickness” in L, and $\int N$ is the integrated area under the mass spectrometer signal for species x during the dosing period, warm (w) or cold (c), respectively, which is directly proportional to the fraction of molecules that do not stick, i.e. either they never reach the substrate, scatter from the surface without sticking, or are trapped and desorb on a very short time scale (<1 s).

However, since the sticking probability is dependent of ice “thickness” and ice morphology, the growth of islands or non-linear thin films during deposition, such as is observed in these experiments (see Fig. 5.1), results in the sticking probability changing as a function of ice “thickness”, tending exponentially (in this case) towards a constant (lower value) at flat, multilayer ice thicknesses (Kolanski 2001). To determine this “constant” S -value for CO sticking to CO, N₂ sticking to N₂, and N₂ sticking to CO, the S -values were plotted as a function of exposure (in L), and fitted to an exponential decay curve, for every experiment where the final ice morphology was identical. The asymptotic values of S are given in Table 5.3. The errors on the uptake coefficients, i.e., the lower limits of the sticking probabilities, arise from a combination of the reproducibility of the experiments plus the error bar on the fitted exponential decay curve.

It is clear that at 14 K these values are identical within experimental error, averaging 0.87 ± 0.05 . The values given in Table 5.3 represent the lower limits to the sticking probabilities at surface temperatures of 14 K; at higher ice thicknesses these values will not change, and at lower ice thicknesses they tend exponentially towards 1. In our experiments, the non-unity sticking probability may arise because the gases are dosed effusively into the chamber at 300 K, even though the substrate itself is at 14 K.

Based on comparison with other systems it is expected that for a single molecule incident upon any of these surfaces, the sticking probability will tend towards 1, particularly as its incident energy is reduced from 300 to 100 or even 10 K, and the surface temperature of the ice is reduced to 10 K. The data clearly show that the relative differences between the S -values of CO-CO, N₂-N₂ and N₂-CO are negligible relative to other uncertainties in astrochemical models, and are certainly not as large as one order of magnitude, as adopted by Flower et al. (2005).

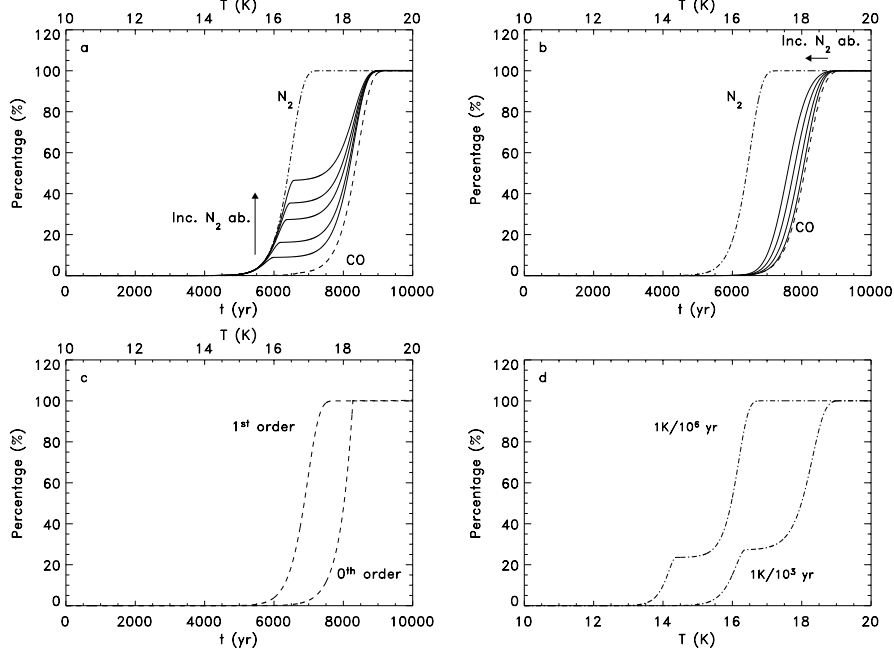


Figure 5.7. Astrophysical simulations for heating rates of $1 \text{ K}/10^3 \text{ yr}$ with ice thicknesses ranging from 10 to 80 L for both species. (a) (10-20-40-80 L) N_2 /(10-20-40-80 L) CO , 1/1 layer, (b) (10-20-40-80 L) N_2 :(10-20-40-80 L) CO , 1:1 mixed ice; (c) zeroth and first-order desorption for 40 L pure CO , and (d) a simulation for N_2/CO 20/40 L for heating rates of $1 \text{ K}/10^3 \text{ yr}$ and $1 \text{ K}/10^6 \text{ yr}$. N_2 desorption from the mixed or layered ices is shown in full, pure N_2 in dash-dot, and CO in dashed lines.

5.6 Astrophysical implications

The model described in § 5.4 can be refined to simulate the behavior of N_2 - CO ices in astrophysical environments, simply by replacing the heating rate used in the experiment with an appropriate heating rate for the astrophysical conditions and removing the pumping reactions.

Figure 5.7a shows output of the astrophysical model for 1/1 layered N_2/CO ices (solid lines), at heating rates of $1 \text{ K}/1000 \text{ yr}$. This heating rate was chosen because it matches the time scale over which a newly-formed protostar increases the temperature in its surrounding envelope from $<10 \text{ K}$ to 20 K (Lee et al. 2004). In addition, the desorption profiles of pure N_2 and CO in layered ice are shown on the same plot. Under these conditions, pure N_2 desorbs between 15 and 17 K, $\sim 2 \text{ K}$ or 2000 yr earlier than CO , which desorbs between 17 and 19 K. However, if N_2 were to freeze-out on top of an existing CO ice layer, the desorption of N_2 takes place in two steps. Only for unrealistically thick ices of more than 80–120 monolayers does 50% of N_2 desorb as pure N_2 . For

lower ice thicknesses, N₂ desorption from the mixed environment dominates, and the majority of the frozen-out N₂ desorbs with CO. Fig. 5.7b shows a very similar plot, but for 1:1 mixed ices, where the desorption occurs in a single step. As the total ice thickness increases, i.e., more CO and N₂ are equally frozen out, the desorption profile shifts towards the pure N₂ case, but generally the profile resembles that of pure CO much more closely than that of pure N₂. It is important to note that the thermodynamics, i.e., R_{BE} of the CO and N₂ ice systems have not been altered in any of these models; the differences arise entirely from the kinetics of the desorption processes. This illustrates that it is important to know the initial morphology of the ice as well the abundance of N₂ with respect to CO to make accurate predictions for the interstellar desorption behavior of N₂ compared to CO.

Many astrochemical models use first order desorption kinetics for pure CO instead of zeroth order kinetics (e.g., Ceccarelli & Dominik 2005). To get an impression of the magnitude of the error made by using incorrect desorption kinetics, a simulation for pure CO desorption from an ice of 40 L was made for both cases using identical binding energies (see Fig. 5.7c). Clearly, desorption for first order kinetics occurs ~ 1 K or 1000 yr earlier, corresponding to an error of 12.5% on the desorption time scale. Although this seems a small overall error, it is 50% of the time difference between desorption of pure N₂ and CO, so this incorrect treatment could have a comparatively large effect on the relative desorption behavior of layered ices of N₂ and CO. It is also important to notice that CO desorption in pure CO ice is completed ~ 0.5 K earlier than desorption of CO from a mixed or layered ice environment. This is due to the lower surface concentration of CO in a mixed ice environment as was found in the experiments.

In Fig. 5.7d, the difference between heating rates of 1 K/10³ yr and 1 K/10⁶ yr is shown for an ice with 20/40 L N₂/CO. The relevance of the faster rate was defined previously; the slower rate would be appropriate for a cold pre-stellar core at near constant temperature. It is clear that the qualitative picture remains the same; N₂ desorbs in two steps, but desorption is complete by 16.5 K for 1 K/10⁶ yr versus at 18.5 K for 1 K/1000 yr, a difference of 2 K for a difference in heating rate of 10³. One further issue is that at the lower heating rates a slightly greater fraction of the N₂ desorbs from a mixed ice environment, which implies that the mixing rate becomes faster relative to the desorption rate. An infinitely slow heating rate of 1 K/10¹⁰ yr shows the same trend.

The overall conclusion from our experiments is that there are some subtle differences in the N₂ and CO desorption behavior, but that they are unlikely to fully explain the observed anti-correlations between N₂H⁺ and CO in pre-stellar dense cores. Also, any difference in sticking probabilities for CO and N₂ is very small, so that other scenarios must be explored to explain the observations.

So far, H₂O ice has been neglected in our studies. The CO–H₂O system has been extensively studied by Collings et al. (2003a), who found a binding energy of CO to H₂O of 1180 K. Kimmel et al. (2001b) derive a binding energy of ≥ 950 K for N₂ on H₂O. The combination of these two results in a R_{BE} on H₂O of ≥ 0.81 . Furthermore, Manca et al. (2004) and Manca & Martin (2003) report a ratio for the condensation enthalpies on H₂O of 0.83. Concluding, R_{BE}

on H₂O for CO and N₂ is very close to that found for the binary N₂-CO system. The desorption behavior will thus also be quite similar for CO and N₂ in mixed or layered ices with H₂O as is observed in the TPD experiments by Collings et al. (2004), where both species desorb in multiple steps. The addition of H₂O to the N₂-CO ice system therefore could not significantly alter the conclusions of this chapter. A significant difference in binding energies between CO and N₂ could only occur if most of the CO were residing in a H₂O-dominated environment with N₂ in a pure, separate layer on top. This would be in contradiction with the observations which show that a large fraction of the CO is in a pure CO ice layer (Pontoppidan et al. 2003b).

Modifications to the gas-phase chemistry are an alternative possibility to explain the observations. For example, Rawlings et al. (2002) show that a higher initial H/H₂ ratio can affect the relative N₂H⁺ and HCO⁺ abundances in cores where the chemistry has not yet reached equilibrium. Even in models including freeze-out, there are regimes of densities and temperatures where the N₂H⁺ abundance initially rises as CO and N₂ freeze out. Dissociative recombination with electrons then becomes the dominant N₂H⁺ destruction mechanism (Jørgensen et al. 2004a), leading mostly to NH rather than N₂ (Geppert et al. 2004). Eventually, this results in N₂H⁺ depletion at high densities and later times.

5.7 Concluding remarks

New experimental data have been presented for the desorption and sticking of N₂-CO ice systems. Furthermore a kinetic model has been constructed that allows for accurate simulations of the TPD experiments as well as predictions for the behavior of CO and N₂ ices under astrophysical conditions. The key results are:

- ▷ The ratio for the binding energies for N₂ and CO in pure ices is 0.936 ± 0.03 . For mixed ices, the ratio for the binding energies is 1.0 (see § 5.4.3).
- ▷ Desorption of N₂ from layered ices occurs in two steps, due to mixing of N₂ with CO. This indicates that for astrophysically relevant ice abundances, desorption from the mixed layer dominates, with less than 50% of N₂ able to desorb prior to CO.
- ▷ In mixed ices, segregation causes the peak temperature for N₂ desorption to shift to lower temperatures for higher ice thicknesses, even though most of the ice desorbs from a mixed ice environment. Since the onset of segregation is concurrent with desorption, a single broad desorption step is observed for N₂. For astrophysically relevant ice thicknesses, N₂ desorption occurs close to the CO desorption temperature.
- ▷ The desorption kinetics for CO ice are zeroth order instead of the commonly adopted first order process, resulting in an error in the desorption time scale of 12.5%, with a shift to lower temperatures for the first order

process. Since this corresponds to 50% of the difference between N₂ and CO desorption, it results in a comparatively large effect on the relative desorption behavior of layered ices of N₂ and CO.

- ▷ The lower limits on the sticking probabilities for N₂ and CO are found to be the same within experimental error, 0.87 ± 0.05 at 14 K (see § 5.5). In reality the sticking probabilities will be even closer to 1.0 for lower temperatures.

The main conclusion from this work is that the solid-state processes of CO and N₂ are very similar under astrophysically relevant conditions.

Acknowledgements

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Appendix A: Comparison between zeroth, first and second order mixing

Since there is no direct measurement of the mixing rate in our experiment, the correct description of mixing kinetics is derived from comparison of models for zeroth, first and second order mixing kinetics with the TPD data. All three mechanisms are physically relevant. Zeroth order can be viewed as a process in which a molecule at the interface between CO and N₂ has a certain chance of moving into the overlying layer; the chance for this to occur is completely independent of whether there are 20 or 80 L on top of this molecule and thus the mixing process is “thickness” independent. First order mixing would be possible in case mixing of one species with another is independent of the total number of molecules of the other species, i.e. there is no saturation possible. Second-order reactions are possible if the rate of mixing would depend upon both the total number of CO and N₂ molecules, since the presence of both molecules is required for mixing. Models for all scenarios were tested in order to determine which most accurately describes the experiments.

The three different scenarios are shown for 1/1 N₂/CO experiments in Fig. 5.8 with the best fitting parameters in Table 5.4. Zeroth order mixing gives rise to a turn-over in the spectrum for the peak intensities with peak II initially being more intense than peak I. This behavior is also observed for the experimental data (see Fig. 5.4a). The turn-over is due to most N₂ molecules mixing unhindered. When the pure ice layer is depleted due to desorption and mixing, mixing stops and the remainder of the molecules desorb from the mixed ice environment. Thus mixing occurs up to higher temperatures with increasing initial ice “thickness”. Desorption and mixing are therefore competing processes. This behavior is not correctly reproduced by the models for first and second-order

Table 5.4. Rate equations for the zeroth, first and second order mixing processes.

	Reaction	Rate equation	ν (molecules ⁽¹⁻ⁱ⁾ cm ²⁽ⁱ⁻¹⁾ s ⁻¹)	E (K)	i
A	CO(s)+N ₂ (s)→CO(mix)+N ₂ (mix)	$\nu_0 e^{-E/T}$	$5.0 \times 10^{26 \pm 1}$	775 ± 25	0
B	CO(s)+N ₂ (s)→CO(mix)+N ₂ (mix)	$\nu_1 [\text{CO(s)}]/[\text{N}_2(\text{s})] e^{-E/T}$	$1.0 \times 10^{12 \pm 1}$	885 ± 25	1
C	CO(s)+N ₂ (s)→CO(mix)+N ₂ (mix)	$\nu_2 [\text{CO(s)}][\text{N}_2(\text{s})] e^{-E/T}$	$5.0 \times 10^{-5 \pm 1}$	865 ± 25	2

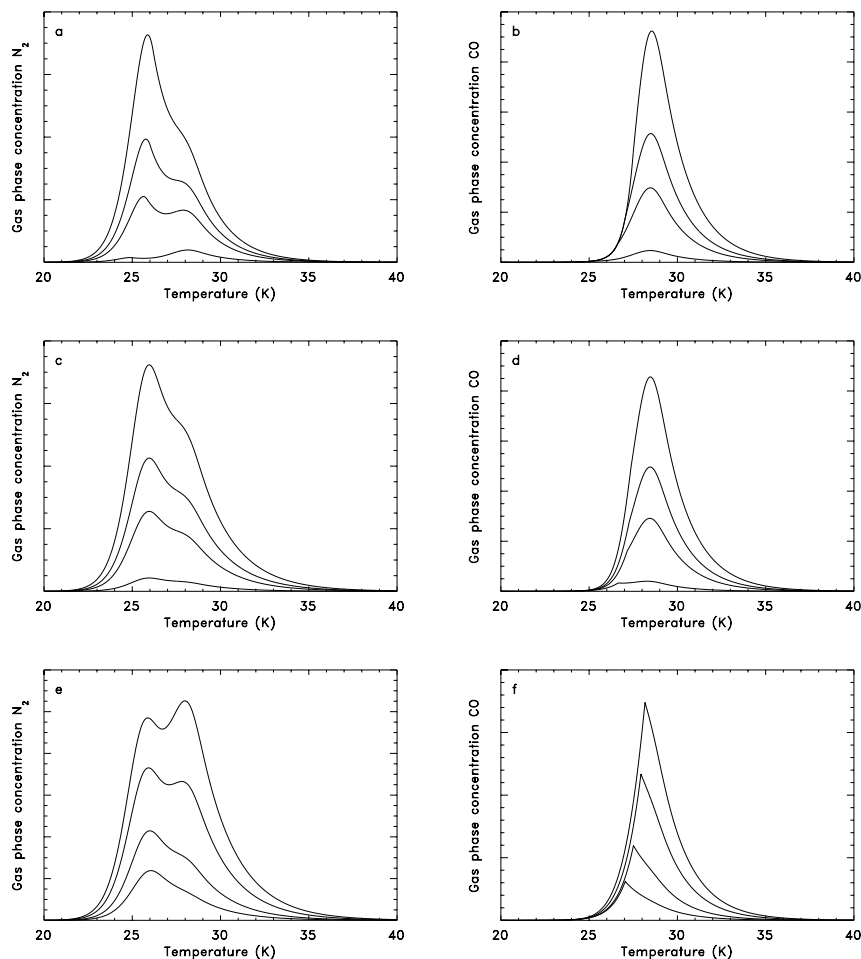


Figure 5.8. Comparison between model output for the 1/1 ices using alternative rates for mixing where (a)+(b) have zeroth order mixing kinetics, (c)+(d) first order, and (e)+(f) second order. N₂ TPD simulations are shown in (a), (c), and (e); CO TPD simulations are shown in (b), (d), and (f). The N₂ model results should be compared with experimental data in Fig. 5.4a, the CO model results with data in Fig. 5.9

mixing (see Fig. 5.8c and e). As the initial number of molecules in the layers increases, the number of molecules in the mixed fraction of the ice also increases for first order mixing kinetics (see reaction B in Table 5.4). However, this increase is proportional to the number of molecules in the pure layer, resulting in a constant ratio between peak I and II. Second order mixing behaves differently from both zeroth and first-order mixing in that the turn-over is now

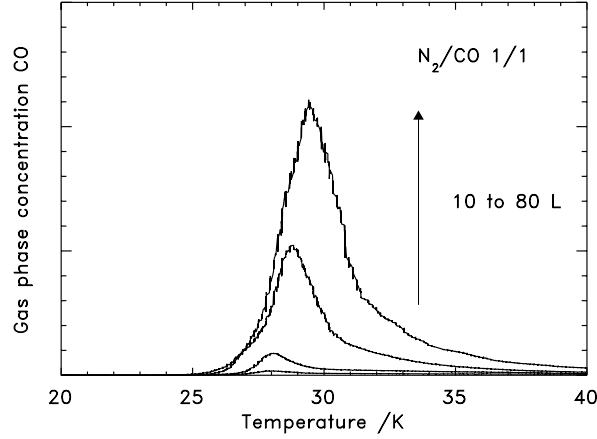


Figure 5.9. *CO TPD spectra for 1/1 (10-20-40-80 L)N₂/(10-20-40-80 L)CO.*

reversed. This is due to the rate of mixing being proportional to the number of molecules for both species. Thus at low ice “thicknesses” the rate is low and both molecules remain mostly pure, whereas for high ice “thicknesses” the rate of mixing is very high and all molecules end up in a mixed environment. A comparison between Fig. 5.8a, b, and c with Fig. 5.4 shows clearly that the scenario for zeroth order mixing reproduces the experimental data best.

The zeroth order mixing mechanism is exemplified by comparison between the CO TPD data output from the model with the experimental data for N₂/CO 1/1 (Fig. 5.9). Second order mixing (Fig. 5.8f) produces a CO desorption spectrum that looks zeroth order. For first order mixing, a two-peak structure is observed for lower “thickness” ices and desorption is dominated by first order kinetics for higher ice “thicknesses”, which is not observed in the experimental data. Zeroth order mixing kinetics are, however, able to predict the increasing overlap for the leading edges plus the slight broadening of the TPD profile with respect to the pure CO TPD spectra in Fig. 5.2a with increasing ice thickness observed in the experimental data fairly well.

Part II

Submillimeter observations

Chapter 6

Testing grain-surface chemistry in massive hot-core regions

Abstract

Aim: To establish the chemical origin of a set of complex organic molecules thought to be produced by grain surface chemistry in high mass young stellar objects (YSOs).

Methods: A partial submillimeter line-survey was performed toward 7 high-mass YSOs aimed at detecting H_2CO , CH_3OH , CH_2CO , CH_3CHO , $\text{C}_2\text{H}_5\text{OH}$, HCOOH , HNCO and NH_2CHO . In addition, lines of CH_3CN , $\text{C}_2\text{H}_5\text{CN}$, CH_3CCH , HCOOCH_3 , and CH_3OCH_3 were observed. Rotation temperatures and beam-averaged column densities are determined. To correct for beam dilution and determine abundances for hot gas, the radius and H_2 column densities of gas at temperatures >100 K are computed using $850\ \mu\text{m}$ dust continuum data and source luminosity.

Results: Based on their rotation diagrams, molecules can be classified as either cold (<100 K) or hot (>100 K). This implies that complex organics are present in at least two distinct regions. Furthermore, the abundances of the hot oxygen-bearing species are correlated, as are those of HNCO and NH_2CHO . This is suggestive of chemical relationships within, but not between, those two groups of molecules.

Conclusions: The most likely explanation for the observed correlations of the various hot molecules is that they are “first generation” species that originate from solid-state chemistry. This includes H_2CO , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, HCOOCH_3 , CH_3OCH_3 , HNCO , NH_2CHO , and possibly CH_3CN , and $\text{C}_2\text{H}_5\text{CN}$. The correlations between sources implies very similar conditions during their formation or very similar doses of energetic processing. Cold species such as CH_2CO , CH_3CHO , and HCOOH , some of which are seen as ices along the same lines of sight, are probably formed in the solid state as well, but appear to be destroyed at higher temperatures. A low level of non-thermal desorption by cosmic rays can explain their low rotation temperatures and relatively low abundances in the gas phase compared to the solid state. The CH_3CCH abundances can be fully explained by low temperature gas phase chemistry. No cold N-containing molecules are found.

Bisschop, Jørgensen, van Dishoeck & de Wachter, 2007, A&A, 465, 913

6.1 Introduction

A characteristic stage of high-mass star formation is the hot core phase where high abundances of complex molecules are found in the gas-phase and in the ice mantles around the dust grains in the cold extended envelope (e.g., Millar 1996; Ikeda et al. 2001; Boogert & Ehrenfreund 2004). The existence of both ices and gas-phase molecules around the same high-mass protostars suggests that

the envelopes have temperatures that range from >200 K in the inner region to as low as 10 K in the cold outer part (e.g., van der Tak et al. 2000b; Gibb et al. 2000b; Ikeda et al. 2001). Together the submillimeter and infrared data indicate that there is a rich chemistry which involves interactions between gas and grain-surface species. The precise origin of complex molecules is still heavily debated: are they “first generation” species formed on the grains during the cold collapse phase (e.g., Tielens & Charnley 1997), or “second generation” species produced by high-temperature gas phase reactions following ice evaporation (e.g., Millar et al. 1991; Charnley et al. 1992; Charnley 1995)? The aim of this work is to test the formation schemes of key complex organic molecules by presenting submillimeter observations of a sample of high-mass cores using the same instrument and frequency settings.

High column densities of the organic molecules CH_3OH , CH_4 , HCOOH , OCN^- and potentially H_2CO have been detected in ice mantles in the cold outer envelopes of high-mass young stellar objects (YSOs) (Gibb et al. 2004). Abundances for some ice species such as CH_3OH and OCN^- are large, up to 30% with respect to H_2O ice or 3×10^{-5} with respect to H_2 (Brooke et al. 1999; Dartois et al. 1999; Pontoppidan et al. 2003b; van Broekhuizen et al. 2005). Information on minor species such as CH_4 , HCOOH , H_2CO and CH_3CHO is more limited, but they appear to have constant abundances at the level of a few % with respect to H_2O ice (Schutte et al. 1999; Keane et al. 2001; Gibb et al. 2004). More complex species with abundances lower than 0.1% cannot be detected by infrared observations because of their small optical depth. Moreover, features of the same functional groups such as CH and OH groups overlap, so that they can only be assigned to a class of molecules rather than to a specific species. Deep submillimeter surveys in the gas phase are more sensitive to detect these minor species.

The abundances of the detected ice species are so large that they cannot be produced by pure gas-phase processes but must be formed on the grains. A proposed scheme for the formation of various “first generation” molecules on grains (based on Tielens & Charnley 1997) is shown in Fig. 6.1. Through successive addition of H, C, O, and N to CO, many complex organic species are formed. The outcome depends on the relative gas-phase abundances of the atoms, their mobility on the grains, and the CO abundance. If the formation routes depicted in Fig. 6.1 are indeed valid and proceed under similar initial conditions, this would imply that the molecules in this scheme are related and that they will have correlated abundance ratios upon evaporation. For different initial conditions, the relative abundances will vary from source to source; the $\text{H}_2\text{CO}/\text{CH}_3\text{OH}$ ratio depends for example on ice temperature, and the $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ ratio on the atomic carbon abundance. In contrast, gas phase formation of second generation species is expected to cause time-dependent abundance variations where “first” and “second generation” as well as non-related “first generation” species are uncorrelated. A combination of rotation temperatures and relative abundances between species can determine which species are part of the same chemical group. To test the basic grain surface chemistry scheme, our survey has targeted emission lines of all species depicted in Fig. 6.1. Only CO_2 , the unsta-

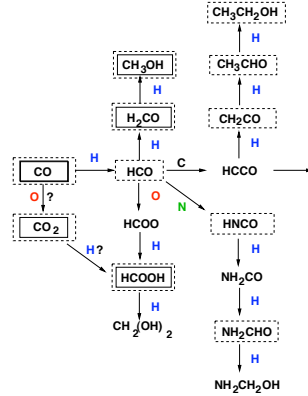


Figure 6.1. Grain-surface chemistry routes involving hydrogenation of CO. Solid rectangular boxes contain molecules which have been detected in interstellar ices, whereas dashed boxes indicate molecules that have been detected in the gas phase (based on Tielens & Charnley 1997).

ble species HCOO, HCCO, and NH_2CO , as well as $\text{CH}_2(\text{OH})_2$ and $\text{NH}_2\text{CH}_2\text{OH}$ for which no laboratory frequencies are available, are lacking.

Many line surveys have been performed to study the molecular composition of high mass star forming regions (e.g., Blake et al. 1987; Sutton et al. 1995; Helmich & van Dishoeck 1997; Schilke et al. 1997; Nummelin et al. 2000; Gibb et al. 2000a; Schilke et al. 2001). However, they often cover a single atmospheric window, each at a different telescope. These data thus probe a variety of excitation conditions with different beam-sizes, which complicates the comparison of column densities and abundances between different sources. Our observing strategy employs deep, partial line surveys in multiple atmospheric windows rather than complete, unbiased line surveys. Partial line surveys exist, but are usually targeted at a few specific molecules such as CH_3OH (van der Tak et al. 2000a) and HNCO (Zinchenko et al. 2000). The advantage of our survey is that it efficiently covers lines with a large range of excitation temperatures and that the settings and telescopes are the same for all sources. The lines of the molecules targeted in this work are sufficiently strong so that no complete line survey is needed for their identification. Compared with previous studies such as those by Ikeda et al. (2001) and Zinchenko et al. (2000) our observations cover higher frequencies, which implies smaller beams and, for some species, lines from higher energy levels.

This chapter is organized as follows: § 6.2 presents the selection of sources plus frequencies, and the observational techniques, § 6.3 presents the data reduction techniques, § 6.4 the results on the derived rotation temperatures plus column densities and compares those to other high mass YSOs. In § 6.5 the correlations of the abundances between different molecular species are determined. § 6.6 discusses the origin of the constant abundance ratios and compares these to

Table 6.1. *Positions, luminosities, distances and typical line width of selected sources.*

Sources	$\alpha(2000)$ (hh:mm:ss)	$\delta(2000)$ ($^{\circ}$ ' ")	L^a ($10^5 L_{\odot}$)	d^b (kpc)	Δv (km s $^{-1}$)
AFGL 2591	20:29:24.6	+40:11:19	0.2	1.0	3
G24.78	18:36:12.6	−07:12:11	7.9	7.7	6
G75.78	20:21:44.1	+37:26:40	1.9	4.1	4
NGC 6334 IRS1	17:20:53.0	−35:47:02	1.1	1.7	5
NGC 7538 IRS1	23:13:45.4	+61:28:12	1.3	2.8	4
W 3(H ₂ O)	02:27:04.6	+61:52:26	0.2	2.0	6
W 33A	18:14:38.9	−17:52:04	1.0	4.0	5

^aFrom van der Tak et al. (2000b), except for G24.78 and G75.78 where the luminosities are from Zhang (2005) and Churchwell et al. (1990), respectively.

^bFrom van der Tak et al. (2000b), except for G24.78 and G75.78 which are based on Forster & Caswell (1989) and Churchwell et al. (1990), respectively.

astrochemical models, and finally in § 6.7 the main conclusions are summarized.

6.2 Observations

6.2.1 Source sample

The basis for this survey is formed by a sample of 7 high-mass young stellar objects summarized in Table 6.1. The sources are known to have hot gas in their inner envelope where ices have evaporated and they either show complex organic molecules due to hot core chemistry or are on the verge of reaching that stage (e.g., Boonman et al. 2001). Most of the sources were selected from the sample of high mass YSOs studied in detail by van der Tak et al. (2000b) based on the following criteria: (i) narrow line widths ($\lesssim 6$ km s $^{-1}$) to minimize line confusion; (ii) detection of CH₃OH lines, where the strongest lines in the 7_K–6_K 338 GHz band should have main-beam temperatures of ≥ 1 K; (iii) distances < 5 kpc and (iv) visible from the James Clerk Maxwell Telescope (JCMT)¹. Preference was also given to sources for which infrared absorption line data of ices are available. The source list additionally includes G75.78 and G24.78. G75.78 has been previously observed by Hatchell et al. (1998) and obeys all previously mentioned selection criteria. G24.78 has a distance > 5 kpc, but was selected based on the large line intensities of CH₃CN detected by Beltrán et al. (2005). Trial JCMT observations of the 7_K–6_K 338 GHz CH₃OH band

¹ The James Clerk Maxwell Telescope is operated by the Joint Astronomy Centre, on behalf of the Particle Physics and Astronomy Research Council of the United Kingdom, the Netherlands Organization for Scientific Research and the National Research Council of Canada. Project IDs are m04bn12, m05an05, and m05bn11.

confirmed that the strongest lines are >1 K and G24.78 was therefore added to the sample.

6.2.2 Observed frequency settings

The observed frequencies are shown in Table 6.2 and were selected based on whether they contained at least one strong line for a target molecule as well as lines of other interesting species. Strong lines of target molecules were chosen because of their high main-beam temperatures and minimum line confusion in line surveys of Orion A by Sutton et al. (1985) and Orion KL by Schilke et al. (1997) at 230 GHz and 345 GHz respectively. The aim was to cover at least two transitions for each molecule to determine rotation temperatures: one with $E_u > 100$ K, and one with $E_u < 100$ K. Table 6.2 shows the additional lines present in the rest frequency side band. The molecular species detected in the image band differed, because it varied per source. Finally, for H_2CO , CH_3OH , and HNCO lines of the isotopic species were observed to determine the optical depth of the main isotopologues.

An additional number of settings have been observed for CH_2CO , CH_3CHO , and HCOOH with the Institut de Radioastronomie Millimétrique² (IRAM) 30 m telescope for AFGL 2591, G75.78, NGC 7538 IRS1, and W 3(H_2O). The settings were chosen because of their high line strengths and low excitation temperatures. Combined with the JCMT settings, they allow for the determination of any cold component of these molecules.

6.2.3 JCMT observations

The frequencies given in the first part of Table 6.2 were observed for the 7 sources with the JCMT on Mauna Kea, Hawaii from August 2004 to January 2006. The beam size (θ_{beam}) is $20\text{--}21''$ for observations in the 230 GHz band and $14''$ in the 345 GHz band. The spectra were scaled from the observed antenna temperature scale, T_A^* , to main beam temperatures, T_{MB} , using main beam efficiencies η_{MB} of 0.69 and 0.63 at 230 GHz and 345 GHz, respectively. The front-ends consisted of the facility receivers A3 and B3; the back-end was the Digital Autocorrelation Spectrometer (DAS), covering 500 MHz instantaneous bandwidth with a spectral resolution of 312.5 and 625 kHz respectively. Pointing was checked every 2 hrs or whenever a new source was observed and was always within $3''$. To subtract atmospheric and instrumental backgrounds beam switching with a chop throw of $180''$ was used. We aimed for a $T_{\text{rms}} \sim 20$ mK on the T_A^* scale when binned to a ~ 1 km s $^{-1}$ channel, which was obtained with integration times of ~ 1 hr at 230 GHz and 2 hrs at 345 GHz dependent on weather. For NGC 6334 IRS1 the confusion limit was reached after 30 minutes of integration, however, at which point the observation was terminated. The

² The IRAM 30 m telescope is operated by the Institut de Radioastronomie Millimétrique on behalf of the Centre National de la Recherche Scientifique of France, the Max Planck Gesellschaft of Germany, and Instituto Geográfico Nacional of Spain.

Table 6.2. *List of observed frequency settings and molecular lines covered at the JCMT.*

Molecule	Freq. (GHz)	E_u (K)	$\mu^2 S$ (D ²)	Transition	Additional molecules
JCMT					
HCO	346.725	41.61	7.341	4 _{0,4,5,4} –3 _{0,3,4,3}	C ₂ H ₅ CN/C ₂ H ₅ OH/H ₂ C ¹⁸ O/HCOOCH ₃
	348.778	172.36	5.313	4 _{2,3,4,4} –3 _{2,2,3,3}	HCOOCH ₃ /CH ₃ ¹³ CN/C ₂ H ₅ OH
H ₂ CO	218.222	20.96	16.299	3 _{0,3} –2 _{0,2}	CH ₃ OH/C ₂ H ₅ CN/HCOOCH ₃
	364.275	158.42	52.165	5 _{3,3} –4 _{3,2}	C ₂ H ₅ OH
CH ₃ OH	338.344	69.36	5.343	7 _{3,4,0} –6 _{3,4,0}	HCOOCH ₃
CH ₂ CO	240.187	88.01	71.489	12 _{1,12} –11 _{1,11}	CH ₃ OH/H ₂ C ¹⁸ O/C ₂ H ₅ CN/CH ₃ CN/HCOOCH ₃
	220.178	76.48	65.434	11 _{1,11} –10 _{1,10}	CH ₃ ¹³ CN/ ¹³ CH ₃ OH/HCOOCH ₃
	222.298	182.26	61.083	11 _{3,9} –10 _{3,8}	CH ₃ OCH ₃ /CH ₃ CCH/HCOOCH ₃
CH ₃ CHO	226.590	71.30	77.779	12 _{0,12} –11 _{0,11}	HCOOCH ₃
C ₂ H ₅ OH	230.991	85.53	48.953	16 _{5,11} –16 _{4,12}	CH ₃ OH/C ₂ H ₅ CN
	347.916	250.88	66.314	20 _{4,17,0} –19 _{4,16,0}	C ₂ H ₅ CN/HCOOCH ₃ /H ₂ C ¹⁸ O
	339.979	57.89	17.724	9 _{4,6} –8 _{3,5}	C ₂ H ₅ CN
HNCO	219.798	58.02	28.112	10 _{0,10} –9 _{0,9}	H ₂ ¹³ CO/C ₂ H ₅ CN
	352.898	187.25	43.387	16 _{1,15} –15 _{1,14}	C ₂ H ₅ CN/C ₂ H ₅ OH/HCOOCH ₃
HN ¹³ CO	240.881	112.53	30.431	11 _{1,11} –10 _{1,10}	CH ₃ OCH ₃ /CH ₃ OH/HNCO
NH ₂ CHO	339.904	245.79	539.342	16 _{6,11} –15 _{6,10}	same setting as C ₂ H ₅ OH
	340.491	165.59	605.520	16 _{3,14} –15 _{3,13}	same setting as CH ₂ CO
	345.183	151.59	664.219	17 _{0,17} –16 _{0,16}	HCOOCH ₃ /C ₂ H ₅ OH/ ¹³ CH ₃ OH
HCOOH	225.238	88.02	17.734	10 _{3,8} –9 _{3,7}	H ₂ CO/HCOOCH ₃ /CH ₃ OCH ₃ / ¹³ CH ₃ OH
	338.144	180.53	27.155	15 _{4,12} –14 _{4,11}	CH ₃ OH/C ₂ H ₅ OH
	346.719	143.92	28.726	15 _{2,13} –14 _{2,12}	same setting as HCO
	356.137	158.67	30.665	16 _{2,15} –15 _{2,14}	NH ₂ CHO/HCOOCH ₃ /C ₂ H ₅ CN/H ₂ ¹³ CO/CH ₃ OH

Table 6.3. *List of observed frequency settings and molecular lines covered at IRAM.*

Molecule	Freq. (GHz)	E_u (K)	$\mu^2 S$ (D ²)	Transition
IRAM				
CH ₂ CO	81.586	22.86	22.4974	4 _{1,3} – 3 _{1,2}
	140.127	39.97	41.1295	7 _{1,7} – 6 _{1,6}
	244.712	89.42	71.4841	12 _{1,11} – 11 _{1,10}
	262.619	140.63	25.3788	13 _{2,12} – 12 _{2,11}
CH ₃ CHO	98.901	16.51	31.2087	5 _{1,4} – 4 _{1,3}
	112.249	21.14	37.9261	6 _{1,6} – 5 _{1,5}
	149.507	34.59	51.1868	8 _{1,8} – 7 _{1,7}
	168.093	42.66	57.7848	9 _{1,9} – 8 _{1,8}
HCOOH	223.916	71.93	18.7011	10 _{2,9} – 9 _{2,8}
	247.514	150.71	17.0080	11 _{5,6/7} – 10 _{5,5/6}
	257.975	83.91	23.2080	12 _{1,12} – 11 _{1,11}
	262.103	82.77	23.2998	12 _{0,12} – 11 _{0,11}

absolute calibration is accurate to better than 15% from comparison to spectral line standards.

The JCMT B3 345 GHz receiver was operated in single side band mode to minimize line confusion. The A3 230 GHz receiver does not have the option of image sideband suppression. For line-rich sources like Orion (Sutton et al. 1985), it is difficult to assign a line to the correct sideband. For our sources the 230 GHz spectra are not confusion limited except for NGC 6334 IRS1 (see Fig. 6.3). For NGC 6334 IRS1, pairs of spectra with 10 MHz offsets were taken. This shifts lines in the image sideband by 20 MHz with respect to those observed in the rest sideband making a unique identification possible.

6.2.4 IRAM observations

The frequencies given in the second part of Table 6.2 have been observed with the IRAM 30 m telescope. The beam size (θ_{beam} in arcsec) is 29'' at 86 GHz, 17'' at 140 GHz, and 10.5'' at 235 GHz. The front-ends were the B100, C150, B230, and C270 facility receivers. The VESPA auto-correlator was used as the back-end, with a bandwidth of 120 MHz, and a channel spacing of 80 kHz. Pointing was checked every 1.5 hrs and was always within 2–3''. Atmospheric and instrumental backgrounds were subtracted through “wobbler” switching where the telescope alternately observes positions +220'' and -220'' away from the source. Integration times differed per source and depended on the atmospheric conditions, but were generally 30 minutes for AFGL 2591 and G75.78, and 1 hr for NGC 7538 IRS1 and W 3(H₂O). All observations were converted

to the main-beam temperature scale using $F_{\text{eff}}/B_{\text{eff}}$ of 0.78 at 86 GHz to 0.46 at 260 GHz. Conveniently, all observations were performed in single-sideband mode.

6.3 Data analysis

6.3.1 Rotation diagrams

Line assignments were made by comparing the observed frequencies corrected for source velocity with the JPL³, CDMS⁴ and NIST⁵ catalogs. Possible assignments had to be within ~ 1 MHz, unless the uncertainty of the frequencies in the catalogs was larger. For NH_2CHO , for example, lines were only assigned if multiple transitions were detected in the same spectrum.

Integrated intensities for the identified lines are given in Tables 6.12–6.28. These were used to derive rotation temperatures and column densities through the rotation diagram method (Goldsmith & Langer 1999) when three or more lines were detected over a sufficiently large energy range. The integrated main-beam temperatures are then related to the column density in the upper energy level by:

$$\frac{N_u}{g_u} = \frac{3k \int T_{\text{MB}} dV}{8\pi^3 \nu \mu^2 S} \quad (6.1)$$

where N_u is the column density of the upper level, g_u is the degeneracy in the upper level, k is Boltzmann's constant, ν is the transition frequency, μ is the dipole moment, and S is the line strength. The total *beam-averaged* column density N_T in cm^{-2} can then be computed from:

$$\frac{N_u}{g_u} = \frac{N_T}{Q(T_{\text{rot}})} e^{-E_u/T_{\text{rot}}} \quad (6.2)$$

where $Q(T_{\text{rot}})$ is the rotational partition function, and E_u is the upper level energy in K.

The calculated rotation temperatures and column densities can be used to make predictions for the intensities of other lines for a specific species. This was used as an independent check on line-assignments. If lines predicted to have high intensities in the observed frequency ranges are not seen, a detection is considered questionable. In the analysis, a correction has been made for the different beam-sizes at different frequencies. The assumption has been made that the maximum source size is equal to the smallest observed beam-size of the JCMT for all sources, i.e. $14''$. The calculations have also been performed assuming that the emission is extended with respect to the largest JCMT beam-size of $21''$. In this case, the rotation temperatures are higher and have larger errors by a factor of 2. In reality, as will be discussed in § 6.3.2, the hot core gas will be even more severely beam-diluted. Finally, the calibration uncertainties

³ <http://spec.jpl.nasa.gov/ftp/pub/catalog/catform.html>

⁴ <http://www.ph1.uni-koeln.de/vorhersagen/>

⁵ <http://physics.nist.gov/PhysRefData/Micro/Html/contents.html>

are taken into account in the rotation diagram analysis and are shown as error-bars on the rotation diagram plots.

When only very few lines were detected or only a small range in E_u was covered, no rotation temperatures or column densities could be derived. If the detection of the species was considered real, the column density was estimated assuming the rotation temperature to be the average for the same molecule in other sources. If no lines were detected, a 3σ upper limit was determined. For lines from isotopologues, rotation temperatures equal to the main species were used to estimate the column densities.

A number of assumptions are implicitly made in the rotation diagram method. In short, they are that the excitation can be characterized by a single temperature T_{rot} and that the lines are optically thin. Even though the first assumption will almost certainly be incorrect, the rotation diagram method does give the average excitation temperature of the region from which most of the molecular emission arises. If the lines are sub-thermally excited because the density is below the critical density (n_{cr}), the rotation temperature is a lower limit to the kinetic temperature. This could also be partly responsible for the scatter in the rotation diagrams. Since for most molecules studied here no collisional rate coefficients are known, a more sophisticated statistical equilibrium analysis is not possible. The critical density, n_{cr} , for the $\text{CH}_3\text{OH } 7_{6,\text{K}}-6_{6,\text{K}}$ transitions is $\sim 10^6 \text{ cm}^{-3}$ while for the $\text{H}_2\text{CO } 3_{0,3}-2_{0,2}$ transition it is $\sim 5 \times 10^6 \text{ cm}^{-3}$. Since n_{cr} is proportional to μ^2 and ν^3 , transitions with high values for either will be most affected. Most species in this study have dipole moments μ close to the CH_3OH value of 1.7 Debye. H_2CO , CH_3CHO , HNCO , NH_2CHO , and CH_3CN have dipole moments 2–3 times larger and for these species sub-thermal effects should thus be more important. Optical depth can significantly influence the results as well. Column densities derived from optically thick lines will be severely under- and rotation temperatures overestimated. Lines of isotopic species can be used to determine the optical depth. Alternatively, it is possible to predict which lines are optically thick based on the rotation diagram results and exclude those from the fit. In this chapter both approaches have been used. A final uncertainty is infrared pumping. It is a well-studied phenomenon for HNCO (Churchwell et al. 1986). Its importance for other species is unknown, although all molecules have dipole-allowed mid-infrared transitions. However, no vibrationally excited lines have been detected in this survey except for CH_3OH . With these limitations the rotation diagram method gives a useful indication of the temperature region where the abundance of a molecule peaks.

6.3.2 Beam dilution correction and hydrogen column density in hot gas

If the emission from the complex organic species comes from a warm region where the temperature is higher than the ice evaporation temperature of 100 K, it becomes important to properly take the amount of beam dilution into account, especially for inter-comparison of the sources. The region where the temperature is above 100 K is expected to be small ($\sim 1''$) compared to the size of the single-

dish beam, and is related to the luminosity L . Also, the beam-dilution depends on the distance as d^2 . To correct for the amount of beam dilution we established a set of models for the dust envelopes of our sources based on SCUBA 850 μm data⁶. For simplification we fix the inner radii of the envelopes to 500 AU, the outer radii to 100,000 AU (~ 0.5 pc) and adopt a power-law density profile, $n \propto r^{-1.5}$, typical of a free-falling core. r_o is chosen to be so large that gas extending beyond this radius will not significantly contribute. We assume that the total luminosity quoted in Table 6.1 is provided by a single 30,000 K blackbody at the center of the envelope and fit the observed 850 μm fluxes of each source by adjusting the mass of the envelope using the DUSTY dust radiative transfer code (Ivezić et al. 1999) as described in Jørgensen et al. (2002). The results of these models provide a temperature profile for each source from which the radius where the temperature increases above 100 K ($R_{T=100 \text{ K}}$), and the beam-dilution can be estimated (see Table 6.4). Figure 6.2 compares the inferred source sizes of the warm gas in arcsec with luminosity of the sources with all distances set to 1 kpc. These correlate very strongly with luminosity as expected, i.e. the correlation coefficient is 0.95. Our results are consistent with the independently derived relation from dust modeling of a large range of sources, $R_{T=100 \text{ K}} \approx 2.3 \times 10^{14} (\sqrt{L/L_\odot}) \text{ cm}$ (Doty private communication). In fact, the luminosity itself can be used to estimate the linear size of the region where the temperature is higher than 100 K. We therefore adopt these radii for the beam dilution correction for molecules that unambiguously probe warm ≥ 100 K gas estimated from the rotation diagrams. The derived beam dilution (η_{bf}),

$$\eta_{\text{bf}} = \frac{(R_{T=100 \text{ K}}/d)^2}{(\theta_{\text{beam}}/2)^2 + (R_{T=100 \text{ K}}/d)^2} \quad (6.3)$$

is then used to calculate *source-averaged* column densities ($N_{T \geq 100 \text{ K}}$) of hot molecules (X) in § 6.4.4:

$$N_{T \geq 100 \text{ K}}(X) = \frac{N_{\text{T}}(X)}{\eta_{\text{bf}}}. \quad (6.4)$$

The radiative transfer models used to calibrate the $R_{T=100 \text{ K}} - L$ relation can also be used to calculate the hydrogen mass in the inner warm regions and thereby provide an H_2 column density to determine molecular abundances for $T \geq 100$ K. With the derived density and temperature profiles listed in Table 6.4, the number of H_2 molecules, $Mol(\text{H}_2)$, within $R_{T=100 \text{ K}}$, can be calculated from:

$$Mol(\text{H}_2) = \int_{r_i}^{R_{T=100 \text{ K}}} 4\pi r^2 n_i \left(\frac{r}{r_i}\right)^{-\alpha} dr = \frac{4\pi n_i r_i^\alpha}{3-\alpha} (R_{T=100 \text{ K}}^{3-\alpha} - r_i^{3-\alpha}), \quad (6.5)$$

where n_i is the density of H_2 molecules at the inner radius, and α the power of the density profiles. The column density of H_2 in gas with $T \geq 100$ K,

⁶ The SCUBA 850 μm data were retrieved through the JCMT archive as a Guest User at the Canadian Astronomy Data Center, which is operated by the Dominion Astrophysical Observatory for the National Research Council of Canada's Herzberg Institute of Astrophysics

$N_{T \geq 100 \text{ K}}(\text{H}_2)$ in cm^{-2} is then simply $Mol(\text{H}_2)$ divided by $\pi R_{T=100 \text{ K}}^2$

$$N_{T \geq 100 \text{ K}}(\text{H}_2) = \frac{4n_i r_i^\alpha}{(3 - \alpha) R_{T=100 \text{ K}}^2} (R_{T=100 \text{ K}}^{3-\alpha} - r_i^{3-\alpha}). \quad (6.6)$$

Since both $N_{T \geq 100 \text{ K}}(\text{H}_2)$ and $N_{T \geq 100 \text{ K}}(\text{X})$ refer to column densities for the same temperature region, they can be used directly to calculate abundances for a species X in the hot gas through:

$$[\text{X}] = \frac{N_{T \geq 100 \text{ K}}(\text{X})}{N_{T \geq 100 \text{ K}}(\text{H}_2)}. \quad (6.7)$$

It is clear from Table 6.4 that the derived values of $N_{T \geq 100 \text{ K}}(\text{H}_2)$ and $R_{T=100 \text{ K}}$ are rather similar for most sources with the exception of AFGL 2591 and G24.78. AFGL 2591 has a significantly smaller and G24.78 a much larger radius and H_2 column density. These are related to their low and very high luminosities. The beam-dilution for G24.78 is thus very similar to that for the other sources in our sample. This makes a good comparison between G24.78 and the other sources possible.

Some of our sources have previously been modeled in more detail (e.g., van der Tak et al. 2000b; Mueller et al. 2002; Hatchell & van der Tak 2003); these models show some differences, e.g., in the slope of the density distribution from source to source and even for the same source depending on method. As an example, van der Tak et al. (2000b) found that $R_{T=100 \text{ K}}$ is 5.3×10^3 AU for NGC 6334 IRS1 and 2.8×10^3 AU for W 3(H_2O) with a density slope $\alpha=2$. Both values are within 10–15% of our model result. Together with the good agreement with the models by Doty (private communication) this implies that the model-dependent uncertainty has a rather small effect on $R_{T=100 \text{ K}}$ and the column densities. We therefore consider our adopted approach to provide the internally most consistent set of estimates - even though we caution that a full self-consistent set of models (explaining, e.g., both single-dish and interferometric continuum data) is required to estimate abundances to better than a factor 2–3.

Finally, interferometric observations have shown that even on scales as small as a few thousand AU, there may be strong chemical differentiation, e.g., oxygen-bearing molecules peaking at a different position than nitrogen-bearing species (Liu 2005; Blake et al. 1996, 1987; Wyrowski et al. 1999; Sutton et al. 1995; Watt & Mundy 1999; Mookerjee et al. 2007). From single-dish observations of a single source, it is not possible to determine whether the emission of various species arises from different regions. A comparison of the abundances of the species studied in this chapter for a number of sources does, however, show whether the emission likely comes from the same or a different region (§ 6.5).

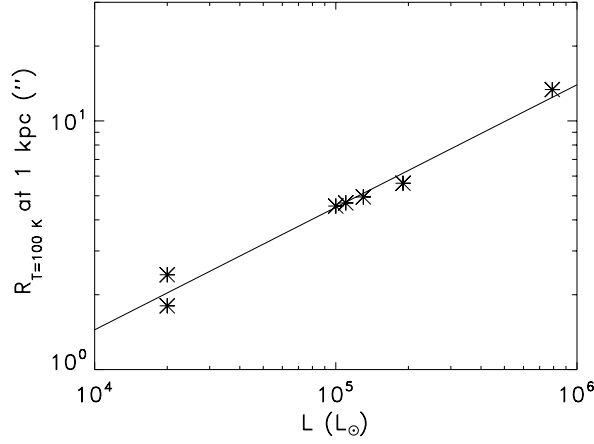


Figure 6.2. Comparison of luminosity with source size where $T = 100$ K. $R_{T=100 \text{ K}}$ is given in arcsec assuming all sources to have a distance of 1 kpc. The solid line represent the best fit to the data.

Table 6.4. Parameters of temperature and density profiles, and beam-filling factors derived from 850 μm SCUBA data and source luminosities.

Sources	n_i^a (cm^{-3})	$R_{T=100 \text{ K}}$ (AU)	τ^b	$N_{T \geq 100 \text{ K}}(\text{H}_2)$ (cm^{-2})	η_{bf}^c
AFGL 2591	8.5(6)	1.8(3)	0.4	7.6(22)	6.2(-2)
G24.78	1.0(8)	1.3(4)	4.8	4.0(23)	5.8(-2)
G75.78	2.1(7)	5.6(3)	1.0	1.2(23)	3.7(-2)
NGC 6334 IRS1	3.8(7)	4.7(3)	1.8	2.4(23)	1.3(-1)
NGC 7538 IRS1	3.4(7)	4.9(3)	1.6	2.1(23)	6.0(-2)
W 3(H ₂ O)	6.2(7)	2.4(3)	2.9	1.8(23)	2.9(-2)
W 33A	4.1(7)	4.5(3)	1.9	2.6(23)	2.6(-2)

^aDensity at inner radius of 500 AU. ^bThe optical depth τ is given for the dust at 100 μm . ^c η_{bf} is the beam-filling factor.

6.4 Results

6.4.1 General comparison between sources

Figure 6.3 shows the spectra at 240.25 and 353.05 GHz toward all sources and Tables 6.12–6.28 contain all measured line intensities for the molecules discussed in this chapter. There is a clear difference in the “richness” of the sources in molecular lines. The intensities and thus also column densities of “line-poorer” sources are lower for most organic species for sources such as AFGL 2591, G75.78, NGC 7538 IRS1, and W 33A. Some lines, such as the HCOOCH_3

$31_{4,27}-30_{4,26}$ at 352.922 GHz, are weak relative to the HNC $16_{1,15}-15_{1,14}$ at 352.898 GHz for the “line-poorer” sources, but strong for the “line-richer” sources, i.e., G24.78, NGC 6334 IRS1, NGC 7538 IRS1, and W 3(H₂O). There therefore seems to be an intrinsic chemical difference between the “line-rich” and “line-poor” sources.

The two settings shown in Fig. 6.3 were aimed at detecting the CH₂CO $12_{1,12}-11_{1,11}$ transition at 240.187 GHz and the C₂H₅OH $21_{1,20,2}-20_{2,19,2}$ line at 352.858 GHz. Both transitions were detected in most sources, indicating that the selected settings are suitable for obtaining detections or otherwise limits. Many lines of other target molecules have been detected in these settings as well.

6.4.2 Optical depth determinations

Some species such as CH₃OH, H₂CO, and CH₃CN have previously been found to be optically thick in their main lines in this type of source (see e.g., Helmich & van Dishoeck 1997). Lines for selected isotopic species were used to determine whether the lines of the main species are optically thick and to derive column densities for the main isotopologues (see Tables 6.12, 6.13, 6.14, 6.20, and 6.22). For H₂CO and HNC, the same transition could be used for different isotopologues. For CH₃CN, the optical depth was determined by comparing the column density derived from the rotation diagram analysis for the main species and that derived from the detected transition for the isotopologues. The ratios for the beam-averaged column densities are given in Table 6.5, and the corrected source-averaged column densities in Table 6.6. In the remainder of the chapter a ¹²C/¹³C ratio value of 53 and a ¹⁶O/¹⁸O ratio value of 327 determined for the 4 kpc molecular ring has been used (Wilson & Rood 1994). Note that this value is uncertain, however, and known to depend on the distance to the galactic center. However, for simplicity we have assumed the same ratio for all sources.

The rotation diagram results by van der Tak et al. (2000a) were not corrected for optical depth, because no isotopologues were observed. In our data, however, lines for H₂¹³CO and H₂C¹⁸O are observed. The optical depth of H₂CO has been determined from the $3_{1,2}-2_{1,1}$ transition. The observed H₂CO/H₂¹³CO ratio ranges from 6.5 for NGC 6334 IRS1 to 37 for AFGL 2591 and NGC 7538 IRS1, lower than the expected ratio, which implies that the main isotopologue is optically thick in many of its transitions. The results for W 3(H₂O) are consistent with the optical depth found by Helmich & van Dishoeck (1997). The optical depth of H₂¹³CO was estimated based on the $5_{2,3}-4_{2,2}$ transition observed for both H₂¹³CO and H₂C¹⁸O. The H₂¹³CO/H₂C¹⁸O ratio is lower than the expected value of 5–8 for most sources, but it is unclear whether this difference is significant. We assume therefore for simplicity that H₂¹³CO is optically thin for all sources.

No direct comparison of the same transition is possible for CH₃OH with ¹³CH₃OH. Many detected lines have strengths that are lower by more than an order of magnitude compared to the strongest transitions. It is therefore possible to determine the column density of the main isotopic species by excluding lines

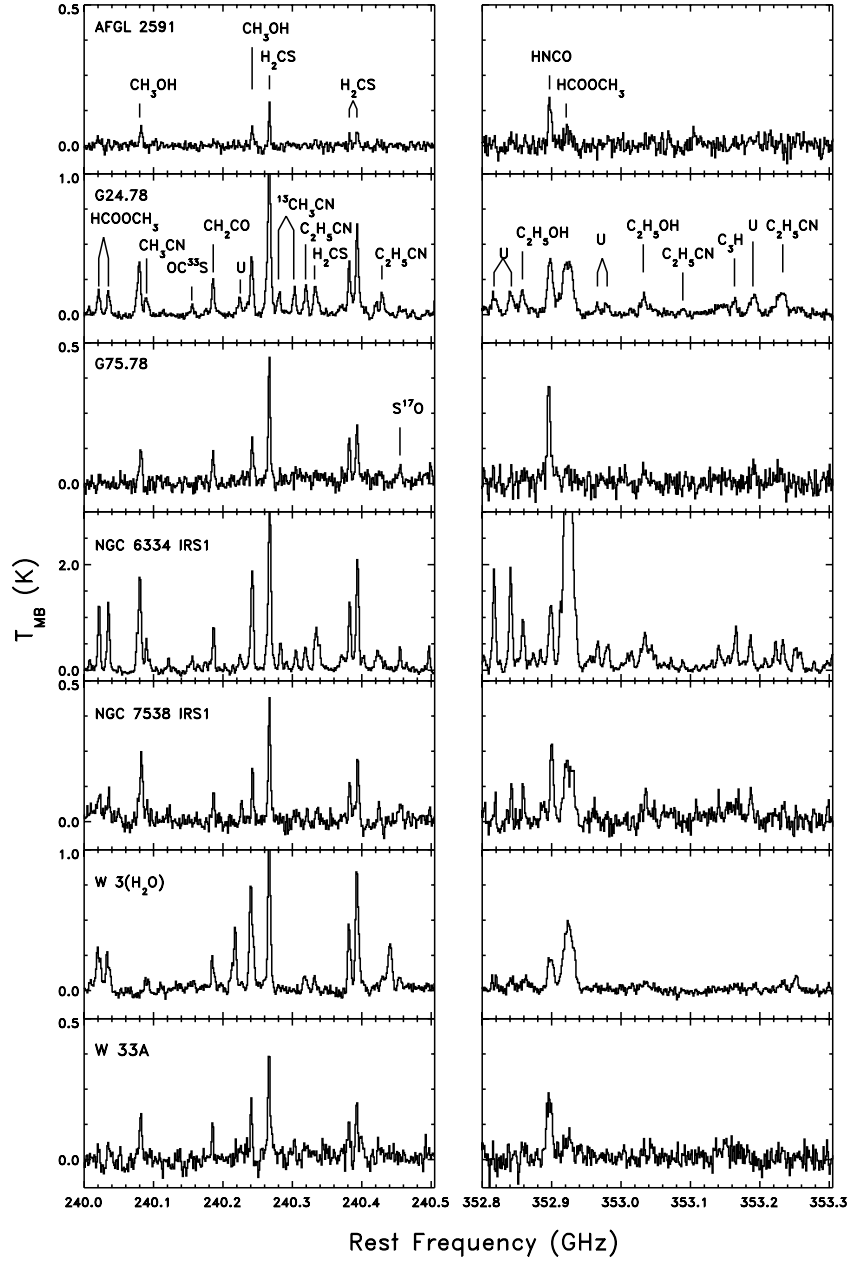


Figure 6.3. Spectra centered at 240.25 and 353.05 GHz for all sources. Note that the T_{MB} scales are different for individual sources.

Table 6.5. *Line intensity ratios for $H_2CO/H_2^{13}CO$, $H_2^{13}CO/H_2C^{18}O$, $HNCO/HN^{13}CO$, and $CH_3CN/CH_3^{13}CN$ before correction for optical depth.*

Species	Sources							
	AFGL 2591	G24.78	G75.78	NGC 6334	IRS1	NGC 7538	IRS1	W 3(H ₂ O)
$H_2CO/H_2^{13}CO^a$	37	9.3	22	6.5		37		31
$H_2^{13}CO/H_2C^{18}O^b$	<2.4	2.8	>1.7	2.4		<1.6		>3.0
$HNCO/HN^{13}CO^c$	>2.4	>11	>6.5	>8.6		>2.0		>3.6
$CH_3CN/CH_3^{13}CN^d$	–	5.8	>5.9	25		7		>9.5
								14
								>3.5
								>7.3
								7.6

^aDerived from the $3_{1,2}-2_{1,1}$ transition. ^bDerived from the $5_{2,3}-4_{2,2}$ transition. ^cDerived from the $10_{0,10}-9_{0,9}$ transition. ^dDerived from the overall column density determined from all detected transitions.

Table 6.6. *Column densities N for hot core molecules (source-averaged) and cold molecules (beam-averaged)^a (cm^{-2}).*

Species	Sources						
	AFGL 2591	G24.78	G75.78	NGC 6334 IRS1	NGC 7538 IRS1	W 3(H ₂ O)	W 33A
Hot molecules							
H ₂ CO ^b	1.3(16)	6.4(16)	2.2(16)	1.3(17)	2.5(16)	1.8(17)	5.4(16)
H ₂ ¹³ CO	2.4(14)	1.2(15)	4.0(14)	2.5(15)	4.8(14)	3.3(15)	1.0(15)
H ₂ C ¹⁸ O	7.4(13)	4.3(14)	<2.5(14)	1.1(15)	1.3(14)	<1.7(15)	<3.0(14)
CH ₃ OH ^c	4.7(16)	2.8(17)	1.1(17)	9.7(17)	1.2(17)	1.0(18)	2.0(17)
¹³ CH ₃ OH	<1.8(15)	2.9(16)	4.3(15)	8.5(16)	6.7(15)	3.2(16)	6.5(15)
C ₂ H ₅ OH	<1.0(15)	7.1(15)	<2.4(15)	1.9(16)	5.7(15)	8.4(15)	4.7(15)
HNCO	8.3(14)	5.0(15)	3.8(15)	4.3(15)	2.3(15)	4.9(15)	6.6(15)
HN ¹³ CO	<4.7(14)	<9.3(14)	<1.2(15)	<3.8(14)	<1.2(14)	<2.7(15)	<1.2(15)
NH ₂ CHO	<1.3(15)	7.2(14)	2.0(14)	7.4(14)	5.7(14)	1.3(15)	2.1(15)
CH ₃ CN	<3.5(15)	5.9(16) ^d	1.8(15)	2.9(16) ^d	<8.2(15)	7.0(15)	2.7(16)
CH ₃ ¹³ CN	<5.3(14)	1.1(15)	<3.0(14)	5.6(14)	<1.2(15)	<7.2(14)	<5.0(14)
C ₂ H ₅ CN	<7.5(14)	4.0(15)	<1.2(15)	5.1(15)	<9.2(14)	4.5(15)	<2.1(15)
HCOOCH ₃	<2.4(16)	3.1(16)	7.1(15)	1.2(17)	1.4(16)	5.2(16)	2.5(16)
CH ₃ OCH ₃	<7.7(15)	1.2(17)	2.3(16)	5.8(17)	<1.6(16)	1.5(17)	2.7(16)
Cold molecules							
CH ₂ CO	1.6(13)	2.1(14)	6.4(13)	7.2(14)	9.7(13)	1.1(14)	6.3(13)
CH ₃ CHO	3.1(12)	<1.5(13)	<2.1(13)	<1.2(14)	2.8(13)	3.5(13)	<3.0(13)
HCOOH	3.4(13)	2.1(14)	7.9(13)	4.9(14)	9.8(13)	1.5(14)	1.3(14)
CH ₃ CCH	7.9(14)	2.3(15)	8.6(14)	5.2(15)	8.4(14)	1.5(15)	1.3(15)

^aThe column densities for the hot core molecules are corrected for beam-dilution using the values of η_{bf} listed in Table 6.2. The cold molecules are given as a beam-averaged column density for a beam of $14''$. ^bFrom H₂¹³CO multiplied by 53. ^cFrom rotation diagram excluding optically thick lines. ^dFrom CH₃¹³CN multiplied by 53.

predicted to be optically thick for the *source-averaged* column density from the rotation diagram. This also circumvents the additional error introduced by the uncertain isotopic ratios. As seen in Fig. 6.10, this excludes mainly lines lying below the fit to the optically thin lines and results in a much better determined rotation temperature.

The limits on the HNC/HN¹³CO ratios are smaller than ~ 53 , and HNC could thus be optically thick for all sources. Note that the optical depth determination of HNC is potentially complicated by the close spacing of the lines of the main species and its isotopologue of only ~ 5 MHz. However, since most of our sources have line widths of only $3\text{--}4\text{ km s}^{-1}$, the upper limits for HN¹³CO are significant. Since HN¹³CO has not been detected for any of our sources and most sources studied by Zinchenko et al. (2000), HNC is assumed to be optically thin throughout the remainder of this chapter.

Since it was not one of the target molecules, CH₃CN was not observed for all sources. Its lines and those of CH₃¹³CN were coincidentally present in the image sidebands for some of the sources. For G24.78, NGC 6334 IRS1, and W 33A, both the main species and its isotopologue have been detected and CH₃CN is found to be optically thick in the 12–11 and 13–12 transitions with ratios ranging from 5.8 for G24.78 to 24 for NGC 6334 IRS1. For G24.78, this result confirms the findings by Beltrán et al. (2005).

Since HCOOCH₃ and CH₃OCH₃ have relatively high column densities, predictions were made for which lines were optically thick. All lines detected for both molecules were found to be optically thin, if we assume that the emission does not come from a radius smaller than $R_{T=100\text{ K}}$.

6.4.3 Rotation temperatures

In the following subsection we discuss each molecule individually and compare it with literature; the main results are summarized at the end of this subsection. The rotation temperatures were derived from single temperature fits to rotation diagrams (see § 6.3.1). Calibration uncertainties of 15% are shown as error bars on the rotation diagrams. All rotation diagrams are shown in Appendix A, and resulting rotation temperatures in Table 6.7.

H₂CO: For H₂CO, the data are taken from van der Tak et al. (2000b) except for G24.78 and G75.78 (see Fig. 6.9). The rotation temperatures for all sources except NGC 6334 IRS1 and W 3(H₂O) are ~ 80 K. NGC 6334 IRS1 and W 3(H₂O) have temperatures of about 100 K higher. However, as the optical depths are similar for most sources, this temperature difference between the sources is real.

CH₃OH: For CH₃OH no clear temperature trend is seen, but the temperature is generally higher than 100 K. This implies that the emission is coming from warm gas. The CH₃OH rotation diagram for some sources like W 33A appears to consist of two temperature components as seen previously by van der Tak et al. (2000a) (Fig. 6.10). However, deducing the presence of two components from a rotation diagram is non-trivial as this behavior could also result from sub-thermal excitation and optical depth effects. Indeed, excluding lines of high

optical depth leads to the disappearance of the two-component structure for most sources other than W 33A. The fits in Fig. 6.10 are especially sensitive to lines with high excitation temperatures and are therefore thought to probe the hot component of the CH_3OH gas.

CH_2CO : CH_2CO has temperatures that are very low, generally only around 40 K. Slightly higher temperatures are found for NGC 6334 IRS1 and W 3(H_2O). These temperatures suggest that this molecule is not present in hot regions, but rather in the cold envelope. The IRAM and JCMT detections for NGC 7538 IRS1 and W 3(H_2O) are consistent. MacDonald et al. (1996) find very high values of 273 K for G34.3 based on three lines with $E_u > 100$ K. However the integrated intensity for the CH_2CO $17_{1,16}$ – $16_{1,15}$ line at 346.6 GHz with $E_u > 150$ K in this survey, also detected by MacDonald et al. (1996), is consistent with the low rotation temperature found in our survey.

CH_3CHO : Due to unfavorable weather conditions, IRAM observations of CH_3CHO have only been performed for AFGL 2591, G75.78, NGC 7538 IRS1, and W 3(H_2O). Almost all targeted lines were detected toward the sources NGC 7538 IRS1 and W 3(H_2O). Both sources have rotation temperatures < 20 K, consistent with the results found by Ikeda et al. (2001, 2002). Although its relatively high dipole moment of 2.69 D implies that sub-thermal excitation can play a role, it is unlikely that the temperature is above 100 K, especially since molecules with similarly high dipole moments such as HNCO and CH_3CN have much higher rotation temperatures.

$\text{C}_2\text{H}_5\text{OH}$: $\text{C}_2\text{H}_5\text{OH}$ consistently has temperatures of more than 100 K. This is somewhat higher than was found by Ikeda et al. (2001), which could be due to the detection of more high excitation lines in this study. For the lower energy transitions, a steeper slope is observed, which indicates a lower temperature.

HCOOH : HCOOH has relatively low temperatures ranging from ~ 40 K for G24.78, and W 33A to ~ 70 K for NGC 6334 IRS1 and NGC 7538 IRS1. For NGC 7538 IRS1 and W 3(H_2O), it was possible to combine results from both IRAM and the JCMT. For NGC 7538 IRS1, low rotation temperatures are confirmed, whereas for W 3(H_2O) a scatter of more than one order of magnitude is present. As the W 3(OH) region is close to W 3(H_2O) it is possible that emission from this region is picked up in one of the settings. Alternatively, HCOOH could be present in both hot and cold gas with only the cold component present for NGC 7538 IRS1. Due to the larger beam size of the JCMT, the 230 GHz observations are more sensitive to extended emission, whereas the IRAM 270 GHz observations probe a more compact region. Since most sources have low rotation temperatures, we conclude that it is mostly located in a cold environment. Low rotation temperatures have previously been inferred for HCOOH in other high mass star forming regions (Ikeda et al. 2001).

HNCO : The rotation temperature of HNCO varies between the different sources. This is not unexpected since the HNCO excitation is known to be dominated by radiation and not collisions (Churchwell et al. 1986). It is therefore not likely to provide much information about the actual kinetic temperature of the species. However it does need to be close to an infrared source to be excited, and thus must be present in hot gas. Finally, it is important to note

Table 6.7. *Derived rotation temperatures^a in K from rotation diagram analysis (see Appendix A).*

Species	Sources									
	AFGL 2591	G24.78	G75.78	NGC 6334	IRS1	NGC 7538	IRS1	W 3(H ₂ O)	W 33A	
H ₂ CO	89 ^b	83±9	69±6	193 ^b		87 ^b		181 ^b	88 ^b	
CH ₃ OH	147±11	211±13	113±7	178±10		156±10		139±8	259±16	
C ₂ H ₅ OH	[139]	104±7	[139]	166±15		164±17		129±16	122±16	
HNCO	64±8	96±11	108±13	105±12		278±88		147±24	85±8	
NH ₂ CHO	[119]	170±20	78±22	166±29		164±28		71±7	40±13	
CH ₃ CN	[218]	261±20	189±25	170±13		[218]		196±14	278±44	
C ₂ H ₅ CN	[96]	99±5	[96]	92±3		[96]		94±16	[96]	
HCOOCH ₃	[119]	121±6	87±13	144±7		134±8		109±7	112±15	
CH ₃ OCH ₃	[130]	134±12	[130]	241±35		[130]		94±5	43±7	
CH ₂ CO	[47]	39±6	40±6	67±20		37±4		54±8	45±7	
CH ₃ CHO	[20]	[20]	[38]	[38]		18±5		16±3	[38]	
HCOOH	[55]	42±7	[55]	75±15		73±12		189±108	38±6	
CH ₃ CCH	45±12	59±6	59±14	63±12		58±10		82±15	40±6	

^aThe bracket notation indicates assumed rotation temperature, when no temperature could be derived from a rotation diagram.^bH₂CO data from van der Tak et al. (2000b).

that excluding the line with $E_u > 300$ K (see Fig. 6.15) strongly reduces the inferred rotation temperature for NGC 6334 IRS1 from 180 K to 106 K.

NH₂CHO: NH₂CHO has a variety of rotation temperatures. The scatter in the derived rotation temperatures appear to be relatively large, with especially NGC 7538 IRS1 being an outlier (Fig. 6.16). There is also some indication that there may be two temperature components - most clearly seen for the sources where many lines with $E_u > 200$ K are detected. Since NH₂CHO has lines very close to the detection limit, this component may also be present for the other sources, but simply below the detection limit.

CH₃CN: Rotation temperatures of CH₃CN range from 170–280 K. It is thus always present in hot gas (see Fig. 6.17). The particularly high temperatures for G24.78 and W 33A are upper limits due to high optical depths. Pankonin et al. (2001) find lower rotation temperatures of 89 K for G24.78 which confirm this picture. For NGC 6334 IRS1 only three lines with $E_u \geq 500$ K have been detected, making the resulting rotation temperature uncertain. However, it seems clear that the rotation temperature for CH₃CN is high, and the species must be present in hot gas.

C₂H₅CN: The other cyanide, C₂H₅CN, only has enough detected lines for three of the sources to allow a determination of the rotation temperature (see Fig. 6.18). For all three sources temperatures of ~ 90 K are found. Fewer lines have been detected for W 3(H₂O), but the fact that the results for this source are rather similar gives additional credibility to the derived temperatures.

CH₃CCH: CH₃CCH generally has rotation temperatures below ~ 80 K - except for G24.78, NGC 6334 IRS1, and W 3(H₂O). The higher temperatures for these three sources are, however, questionable. Removing the point with $E_u > 300$ K gives significantly lower temperatures for G24.78 and NGC 6334 IRS1 (see Fig. 6.19). The W 3(H₂O) generally has a higher uncertainty and scatter on the data, which may in fact cause the higher temperature found for this source.

HCOOCH₃: HCOOCH₃ is detected in almost all of the sources, but with a relatively large scatter on the data. The temperature generally seems to be between 100–150 K, with somewhat lower values when less lines have been detected. For G75.78 the results are inconclusive as the upper limits on high energy transitions are not significant. Somewhat lower temperatures were found by Ikeda et al. (2001), which could be due to a difference in the number of detected lines.

CH₃OCH₃: CH₃OCH₃ also appears to have a relatively large spread in rotation temperatures (see Fig. 6.21). For W 33A, only lines with $E_u < 100$ K were detected, which result in low rotation temperatures. The upper limits on lines with $E_u > 150$ K are not significant, however, and do not exclude temperatures above 100 K. Rotation temperatures above 100 K are commonly seen for CH₃OCH₃ (Ikeda et al. 2001).

In summary, the temperatures for most molecules are rather consistent between all sources. The molecules can clearly be divided into “hot” ($T > 100$ K) and “cold” ($T < 100$ K) where H₂CO, CH₃OH, C₂H₅OH, HNCO, NH₂CHO, CH₃CN, C₂H₅CN, HCOOCH₃, and CH₃OCH₃ belong to the first and CH₂CO, CH₃CHO, HCOOH and CH₃CCH to the second category.

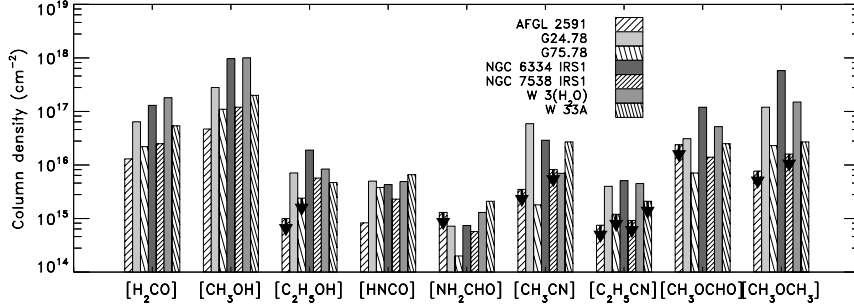


Figure 6.4. Histogram of molecular column densities of hot molecules corrected for beam dilution for all sources for a source size defined by $T > 100$ K.

6.4.4 Column densities

Table 6.6 and Figure 6.4 present the *source-averaged* column densities, i.e., corrected for beam dilution (§ 6.3.2), for the hot molecules per source. Absolute column densities are compared to determine the variability between different sources. Since we have assumed the beam dilution to be the same for all molecules, the trends for the *beam-averaged* column densities are similar. Molecules with rotation temperatures below 100 K are present in a different, cold region, presumably the envelope surrounding the hot region, and beam-averaged column densities are therefore given for those. Thus, the column densities for the hot and cold molecules in Fig. 6.4 and 6.5 cannot be compared directly.

Clearly, most molecules have column densities that vary by about an order of magnitude in the hot gas between the different sources. The column density variations do not scale with the luminosity and thus total mass in the hot region. CH_3OH , H_2CO , but also HCOOCH_3 , and CH_3OCH_3 - if detected - have column densities that are orders of magnitude higher than those of $\text{C}_2\text{H}_5\text{OH}$, HNCO , and NH_2CHO . As will be discussed in § 6.5 abundances show a similar trend. The advantage of comparing column densities is that they come directly from the observations and no assumption on the H_2 column in the hot gas enters the analysis.

Most hot molecules have source-averaged column densities that are highest for the line-rich sources NGC 6334 IRS1, G24.78, and W 3(H_2O). For the oxygen-bearing molecules $\text{C}_2\text{H}_5\text{OH}$, CH_3OCH_3 , HCOOCH_3 , G24.78 has a higher column density than W 3(H_2O). W 3(H_2O) has a higher column density of CH_3OH and H_2CO , however. Thus H_2CO and CH_3OH have variable column densities compared to the other oxygen-bearing molecules. Nonetheless the column density trends between the oxygen-bearing species are similar.

The HNCO and NH_2CHO column densities peak for W 33A and G24.78, and have very similar column density trends with respect to each other. W 33A has

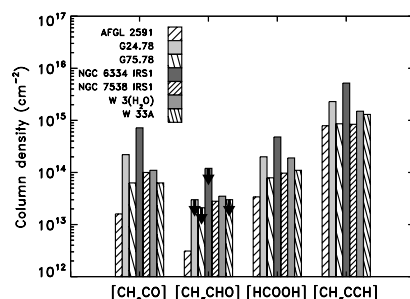


Figure 6.5. Histogram of molecular beam-averaged column densities of the cold molecules for all sources.

the highest and G75.78 the lowest column densities. NGC 7538 IRS1 has a relatively high column density for these species compared with the oxygen-bearing species. The column densities of the nitrogen-bearing species do, therefore, behave different from the oxygen-bearing species.

CH_3CN has a relatively high column density for G24.78 and W 33A, but the uncertainties make it more difficult to compare its column density trends with other molecules (see § 6.4.3). The general CH_3CN column density trends appear more similar to those of HNCO and NH_2CHO than to the O-bearing species. However, if we consider only the two sources for which both the main species and its isotopologue $\text{CH}_3^{13}\text{CN}$ were detected with $E_u < 500$ K, the relative column densities appear more similar to those of the oxygen-bearing species.

Figure 6.5 shows the *beam-averaged* column densities for the cold molecules, CH_2CO , HCOOH , and CH_3CCH . Clearly all three have very similar trends. NGC 6334 IRS1 has the highest column density and AFGL 2591 the lowest. For CH_3CHO , the number of sources with detections is limited and it was thus not possible to compare its column density trends with the other species.

In summary, the molecular abundances vary about an order of magnitude between the sources. Furthermore, all oxygen-bearing species have similar abundance trends, but the abundances of HNCO and NH_2CHO behave differently.

6.5 Column density and abundance correlations

Molecular column densities and abundances can be compared between sources in different ways, two of which will be presented here. Abundances can be estimated relative to column densities of (i) H_2 calculated on the basis of CO , (ii) H_2 derived from dust continuum observations (see § 6.3.2) or (iii) one of the observed molecules, typically CH_3OH . The disadvantage of method (i) is that CO gas is likely extended over much larger scales than the hot molecules due to its lower desorption temperature. Observations of high excitation lines of CO isotopologues which probe only hot gas, will make this method possible in the

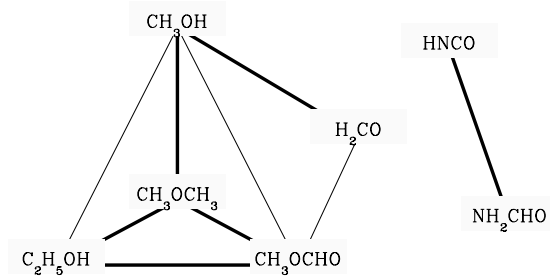


Figure 6.6. Empirical correlations between the different molecules based on the Pearson correlation coefficients. All solid lines indicate correlations coefficients > 0.8 and the thick lines > 0.9 . When two species correlate, it does not mean that they are directly chemically related. Two species can also correlate if they are both formed from the same mother species.

future. In this chapter, we use (ii) and (iii), and adopt (i) only for the cold molecules.

Abundances with respect to H_2 column densities from modeling of dust continuum observations (§ 6.3.2) and to CH_3OH column densities (§ 6.5.2) have the advantage that they allow comparisons to “only material at high temperatures” or “species probing the regions solely of interest”. Both approaches also have disadvantages, however. Since H_2 is not directly observed, one has to rely on other tracers, in our case dust. Extrapolations of density and temperature profiles are made to scales smaller than actually probed by the observations. CH_3OH is directly observed, but this method implicitly assumes that the abundance of CH_3OH is constant from source to source. If this is not the case incorrect correlations of abundances with respect to CH_3OH can be found, as we will return to in § 6.5.2.

6.5.1 Abundances in $T \geq 100$ K gas

Table 6.8 lists the molecular abundances within the gas with $T \geq 100$ K for each source in our sample calculated through Eq. (6.7). The abundances have the same trends between the different sources as the column densities. Most molecules have abundances that vary one order of magnitude from source to source, as was also seen for CH_3OH by van der Tak et al. (2000a). The standard deviation on the average abundances is larger than our estimated uncertainty of a factor 2–3 (§ 6.3). Thus the observed variations are real. Furthermore, the overall abundances are relatively high compared to values in the literature. This is because we have determined the abundances with respect to the H_2 column density within $R_{T=100\text{ K}}$, whereas in e.g., Ikeda et al. (2001) they are determined based on CO transitions, which trace gas that is cooler and extended with respect to the hot core.

Table 6.8. *Molecular abundances ($N(X)/N(H_2)$).*

	AFGL 2591	G24.78	G75.78	NGC 6334 IRS1	NGC 7538 IRS1	W 3(H ₂ O)	W 33A	Average	σ^a
Hot molecules ^b									
H ₂ CO	1.7(-7)	1.6(-7)	1.8(-7)	5.4(-7)	1.2(-7)	1.0(-6)	2.1(-7)	3.4(-7)	3.2
CH ₃ OH	7.0(-7)	6.5(-7)	9.2(-7)	4.0(-6)	5.7(-7)	5.4(-6)	7.3(-7)	1.9(-6)	2.0
C ₂ H ₅ OH	<1.4(-8)	1.9(-8)	2.0(-8)	7.5(-8)	2.5(-8)	4.4(-8)	1.8(-8)	3.6(-8)	2.3
HNCO	7.0(-9)	1.3(-8)	3.2(-9)	1.8(-8)	1.1(-8)	2.7(-8)	2.5(-8)	1.6(-8)	0.91
NH ₂ CHO	<1.7(-8)	1.8(-9)	1.7(-9)	3.1(-9)	2.6(-9)	5.6(-9)	8.5(-9)	3.9(-9)	2.7
CH ₃ CN	<4.6(-8)	1.5(-7)	1.5(-8)	1.2(-7)	<3.9(-8)	3.9(-8)	1.0(-7)	8.5(-8)	5.6
C ₂ H ₅ CN	<9.9(-9)	1.0(-8)	<1.0(-8)	2.1(-8)	<4.4(-9)	2.5(-8)	<8.1(-9)	1.7(-8)	0.77
HCOOCH ₃	<3.2(-7)	7.3(-8)	5.9(-8)	4.6(-7)	6.7(-8)	2.9(-7)	9.6(-8)	1.7(-7)	1.6
CH ₃ OCH ₃	<1.0(-7)	3.0(-7)	1.9(-7)	2.4(-6)	<7.6(-8)	8.3(-7)	1.0(-7)	7.7(-7)	9.6
Cold molecules ^c									
CH ₂ CO	3.1(-11)	8.8(-10)	8.5(-11)	2.8(-10)	4.1(-10)	1.3(-10)	4.1(-10)	3.2(-10)	2.9
CH ₃ CHO	6.1(-12)	<6.3(-11)	<2.8(-11)	<4.7(-11)	1.2(-10)	4.1(-11)	<1.9(-10)	5.6(-11)	5.8
HCOOH	6.7(-11)	8.8(-10)	1.0(-10)	1.9(-10)	4.2(-10)	1.8(-10)	8.4(-10)	3.8(-10)	3.4
CH ₃ CCH	1.5(-9)	9.6(-9)	1.1(-9)	2.1(-9)	3.6(-9)	1.8(-9)	8.4(-9)	4.0(-9)	3.5

^a σ refers to the same order of magnitude as the average. ^bThe abundances are derived with respect to the column density of H₂ within $R_T=100$ K in § 6.3.2 and Table 6.4. ^cThe abundances are derived using the CO column densities from van der Tak et al. (2000b), except G24.78 and G75.78 for which the data comes from Cesaroni et al. (2003) and Hatchell et al. (1998) respectively.

Table 6.9. *Abundance correlations with respect to H_2 for the abundances within $R_{T=100}$ K for hot core molecules.*

	H_2CO	CH_3OH	C_2H_5OH	$HNCO$	NH_2CHO	CH_3CN	$HCOOCH_3$	CH_3OCH_3	$HCOOH$
H_2CO	1.00	0.98	0.76	0.46	0.53	-0.07	0.88	0.75	0.76
CH_3OH	0.98	1.00	0.86	0.38	0.39	-0.07	0.92	0.86	0.70
C_2H_5OH	0.76	0.86	1.00	0.02	0.22	0.12	0.92	0.95	0.30
$HNCO$	0.46	0.38	0.02	1.00	0.38	0.81	0.16	-0.27	0.98
NH_2CHO	0.53	0.39	0.22	0.38	1.00	0.17	0.42	-0.02	0.65
CH_3CN	-0.07	-0.07	0.12	-0.81	0.17	1.00	0.29	0.20	-0.51
$HCOOCH_3$	0.88	0.92	0.92	0.16	0.42	0.29	1.00	0.90	0.49
CH_3OCH_3	0.75	0.86	0.95	-0.27	-0.02	0.20	0.90	1.00	0.09
$HCOOH^a$	0.76	0.70	0.30	0.98	0.65	-0.51	0.49	0.09	1.00

^a Assuming that the $HCOOH$ emission comes from within $R_{T=100}$ K.

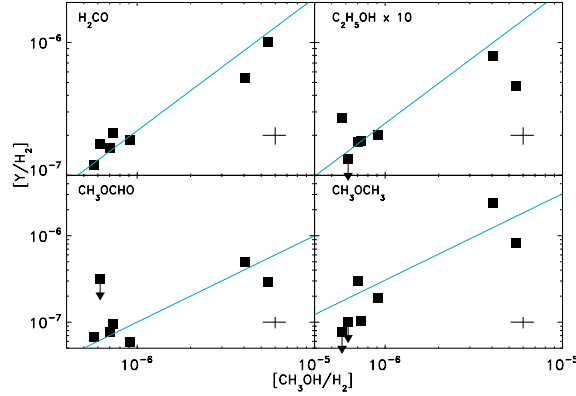


Figure 6.7. Comparison of molecular abundances with respect to H_2 within $R_{T=100\text{ K}}$ for the oxygen-bearing molecules. The gray lines indicate the linear fit to the data. An error-bar representing the calibration uncertainties is depicted in the lower right corner.

The abundances of the species detected in our sources with $T \geq 100\text{ K}$ were compared by estimating the Pearson correlation coefficients between $\log(X/H_2)$ vs $\log(Y/H_2)$ (see Table 6.9). C_2H_5CN is not compared with the other species due to the low number of sources with detections. Although the number of sources for the other molecules are limited and correlations therefore only suggestive, a number of interesting trends are seen. These result from groups of molecules with very similar abundance trends.

First, the abundances of the nitrogen-bearing species do not correlate with those of oxygen-bearing species. Strong correlations are, however, found between the oxygen-bearing species H_2CO , CH_3OH , C_2H_5OH , $HCOOCH_3$, and CH_3OCH_3 . Figure 6.7 shows the abundances of all hot oxygen-bearing species with respect to H_2 compared to CH_3OH/H_2 . The nitrogen-bearing species $HNCO$ and NH_2CHO also appear to be well correlated, which follows from the column density trends (§ 6.4 and shown in Fig. 6.8). The NH_2CHO abundance for G75.78 is uncertain, as only few lines were detected. The correlation coefficient is 0.38 with this source included and 0.92 without.

If the $HCOOH$ emission is assumed to arise in hot instead of cold gas, its abundance correlates with very few molecular species. Its strongest correlation is with $HNCO$ with a coefficient of 0.98. This result is surprising and due to the low rotation temperatures for $HCOOH$ questionable.

The abundances of the hot molecules presented in Table 6.8 and Fig. 6.7 assume the same beam dilution factor corresponding to $R_{T=100\text{ K}}$. As Table 6.7 shows, the rotation diagram temperatures of several species are significantly higher than 100 K. The $T = 200\text{ K}$ radius is typically a factor of ~ 3 smaller than that for 100 K so that the beam dilution and abundances can be a factor

Table 6.10. *Average abundance ratio for our sources and other well-known high mass YSOs with respect to CH_3OH for the oxygen-bearing species and with respect to HNCO for NH_2CHO . σ is the standard deviation between the sources in our sample.*

Molecule	Abundance ratio(σ) with respect to CH_3OH	Orion Compact Ridge ^a	G34.3 ^b	Sgr B2(N) ^c	G327.3 ^d	GC clouds ^e
H_2CO	0.22 $\pm$ 0.05	0.10	0.009	>0.0025	–	$\sim$ 0.01
$\text{C}_2\text{H}_5\text{OH}$	0.025 $\pm$ 0.013	0.004	0.19	0.005	0.05	$\sim$ 0.04
HCOOCH_3	0.10 $\pm$ 0.03	0.08	0.86	0.005	0.96	$\sim$ 0.04
CH_3OCH_3	0.31 $\pm$ 0.20	0.05	–	0.015	7	$\sim$ 0.04
with respect to HNCO						
NH_2CHO	0.36 $\pm$ 0.08	–	–	0.23	0.07	–

^aSutton et al. (1995), ^bMacDonald et al. (1996), ^cNummelin et al. (2000), ^dGibb et al. (2000a), ^eRequena-Torres et al. (2006).

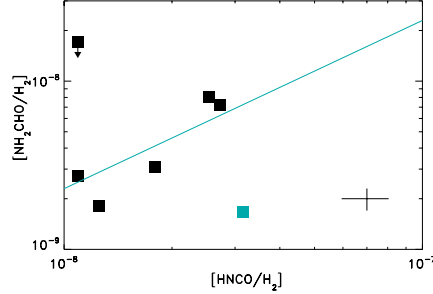


Figure 6.8. Comparison of molecular abundances with respect to H_2 for $HNCO$ with NH_2CHO within $R_{T=100K}$. The source indicated in gray is G75.78 and the limit is AFGL 2591. An error-bar representing the calibration uncertainties is depicted in the lower right corner.

~ 9 larger. If all emission of hot molecules would arise from a smaller region, the correlations would remain the same. If some species are present in 100 K gas and others in 200 K gas, the correlations would disappear, however. The differences in rotation temperatures in Table 6.7 are assumed to arise largely from other effects such as optical depth, sub-thermal excitation, or the detection of very high or low lying energy levels affecting the overall fit. Future interferometric observations of multiple high mass sources could determine whether the assumption of a single source size for all molecules is correct.

For the molecules that have abundances that do correlate, the abundance ratios were calculated with respect to either CH_3OH/H_2 or $HNCO/H_2$ and are shown in Table 6.10. Figure 6.6 shows the empirical relations for molecules with Pearson coefficients of 0.8 and higher. Per set of species the ratios vary no more than a factor of three, the previously found uncertainty in the abundances. H_2CO , $HCOOCH_3$, and CH_3OCH_3 have 5–10 times lower abundances than CH_3OH . NH_2CHO is a factor 3 times lower than $HNCO$. Possibly, coefficients between 0.8–0.9 are present between species that are not directly chemically related, but that are both strongly correlated with a third species.

6.5.2 Abundances with respect to CH_3OH

The Pearson correlation coefficients of $\log(X/CH_3OH)$ vs. $\log(Y/CH_3OH)$ differ significantly from the correlations in § 6.5.1. First, strong correlations are not present between the same species. This is due to the variability of the CH_3OH abundance between the different sources, and to the dependence of the correlations on three (X , Y , and CH_3OH) rather than two (X and Y) species. The abundances of two species with respect to CH_3OH will correlate when their abundances with respect to H_2 correlate but also when the abundance of one of the species correlates with that of CH_3OH . This makes it difficult to use correlations of abundance ratios with respect to CH_3OH to chemically link

molecules. Instead it is better to compare $X/\text{CH}_3\text{OH}$ with the CH_3OH column density or abundance, i.e. $N(\text{CH}_3\text{OH})$ or $\text{CH}_3\text{OH}/\text{H}_2$ as has been done by e.g., Requena-Torres et al. (2006).

6.5.3 Comparison with other well known sources

The abundance ratios with respect to CH_3OH are compared in Table 6.10 to other well-studied high mass star forming regions, specifically the Orion Compact Ridge (Sutton et al. 1995), G34.3 (MacDonald et al. 1996), Sgr B2(N) (Nummelin et al. 2000), and G327.3 (Gibb et al. 2000a). The ratios for the Orion Compact Ridge all agree within the error bars for H_2CO and HCOOCH_3 . CH_3OCH_3 has a relatively low abundance with respect to CH_3OH . Only three lines have been detected for this species in the Compact Ridge and it has a rather low excitation temperature of 75 K implying that it is perhaps present in a colder region.

In contrast, the relative abundances for G34.3 deviate more from those in our work. The $\text{H}_2\text{CO}/\text{CH}_3\text{OH}$ ratio by MacDonald et al. (1996) is probably a lower limit as only one line was detected for G34.3 and the column density of H_2^{13}CO was calculated to be higher than the main H_2CO isotopologue based on their respective line intensities. Both $\text{C}_2\text{H}_5\text{OH}$ and HCOOCH_3 have relatively high abundances with respect to CH_3OH . This could potentially be due to high optical depth in the lines of CH_3OH . MacDonald et al. (1996) assumed the emission to be optically thin, and thus underestimate the CH_3OH column density. The relative abundances of $\text{C}_2\text{H}_5\text{OH}$ and HCOOCH_3 are similar between G34.3 and the sources studied in this chapter.

The abundance ratios with respect to CH_3OH for Sgr B2(N) from Nummelin et al. (2000) appear to be significantly lower than for the sources in our sample. This is due to the CH_3OH emission being decomposed into a core and a halo component for Sgr B2(N), whereas that of the other molecules is not. For this source it is more relevant to compare the relative ratios between the different molecules. The $\text{C}_2\text{H}_5\text{OH}$ abundance is high compared to HCOOCH_3 and CH_3OCH_3 . However, the $\text{HCOOCH}_3/\text{CH}_3\text{OCH}_3$ and the $\text{NH}_2\text{CHO}/\text{HNCO}$ ratios of 0.33 are similar to those for our sources.

G327.3 in the study of Gibb et al. (2000a) has a $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ abundance ratio a factor of 2 higher compared to the average for our sample. Small deviations could be caused by their relatively low rotation temperature for $\text{C}_2\text{H}_5\text{OH}$ of 66 K. HCOOCH_3 and CH_3OCH_3 have relatively high abundances with respect to CH_3OH , but $\text{HCOOCH}_3/\text{CH}_3\text{OCH}_3$ is within a factor two of the ratio derived for our sample. Again $\text{NH}_2\text{CHO}/\text{HNCO}$ is the same within error to our sample.

Molecular abundance ratios can also be compared to those found in shocked gas in the galactic center by Requena-Torres et al. (2006). Their sources have relatively constant ratios of complex molecules with respect to CH_3OH of 0.04. The $\text{H}_2\text{CO}/\text{CH}_3\text{OH}$ and $\text{CH}_3\text{OCH}_3/\text{CH}_3\text{OH}$ ratios are significantly higher for our hot cores. Small differences may be due to the fact that Requena-Torres et al. (2006) observed rotational transitions with $E_u < 40\text{--}50$ K, whereas lines

with excitation energies that range from 20–900 K have been observed in this study.

In summary, the overall emerging picture is that of relatively constant abundance ratios between various molecules comparable to the sources for our sample. Distinct differences for individual species can often be ascribed to specific observation or analysis problems.

6.5.4 Comparison with ice abundances

It is interesting to relate the gas-phase abundances derived above to the ice abundances from mid-infrared observations. Of the sources in our sample, AFGL 2591, NGC 7538 IRS1 and W 33A were also observed at mid-infrared wavelengths with ISO (Gibb et al. 2004). Table 6.11 lists the abundances of the ice species from that paper assuming an H_2O abundance of 10^{-4} with respect to H_2 . W 33A is particularly rich in organics in the solid state whereas the other two sources mainly have upper limits. The solid state abundances of CH_3OH are at least an order of magnitude higher than the comparable source-averaged gas phase abundances. The H_2CO abundance of $\sim 2 \times 10^{-6}$, although more uncertain, is also larger by an order of magnitude (Keane et al. 2001). For W 33A, however, the solid $\text{H}_2\text{CO}/\text{CH}_3\text{OH}$ abundance ratio is consistent with the gas phase abundance ratio.

Where detected toward high mass YSOs, solid HCOOH and CH_3CHO have abundances of 10^{-6} – 10^{-5} and $\sim 10^{-5}$ respectively (Schutte et al. 1999; Keane et al. 2001; Gibb et al. 2000b, 2004). Similar abundances for solid HCOOH are found toward background stars by Knez et al. (2005). These absolute solid state abundances are four to five orders of magnitude higher than the gas phase abundances for the same sources.

The XCN band is detected in many objects and usually assigned to OCN^- (Grim & Greenberg 1987; Demyk et al. 1998; Pendleton et al. 1999; Gibb et al. 2000b; van Broekhuizen et al. 2005). OCN^- is thought to convert to and evaporate off grains as HNCO (§ 6.6.1). Abundances of solid OCN^- vary and range from 1×10^{-7} – 4×10^{-6} (van Broekhuizen et al. 2005; Thi et al. 2006). Gas phase abundances of HNCO are factors of 100–1000 times lower.

Many of the species are expected to have abundances in the ice below the detection limit. Boudin et al. (1998) determined upper limits for the column densities of a number of more complex organic molecules, including C_2H_6 and $\text{C}_2\text{H}_5\text{OH}$ toward NGC 7538 IRS9. The upper limit on the $\text{C}_2\text{H}_5\text{OH}$ abundance is 1.2×10^{-6} with $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH} < 0.28$. This is consistent with the $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ abundance ratio of 0.009 in the gas phase for our sample of sources.

In summary, the absolute ice abundances of observed “first generation” species, CH_3OH and OCN^- , are 10 – 10^2 times higher compared to the gas phase values, and as much as a factor of 10^4 – 10^5 for HCOOH and CH_3CHO .

Table 6.11. *Solid state abundances with respect to H_2 , assuming H_2O ice to have an abundance of 10^{-4} .*

Species	W 33A ^a 10^{-5}	NGC 7538 10^{-5}	IRSI ^b 10^{-5}	AFGL 2591 ^b 10^{-5}	HH 46 ^c (low mass) 10^{-5}	CK 2 ^c (field star) 10^{-5}	gas phase ^d
H_2CO	0.65	–	–	–	–	–	3.2(-7)
CH_3OH	1.4 – 1.7	<0.4	–	1.4	1.2	<0.11	2.0(-6)
$HCOOH$	0.37 – 0.71	2.2	–	<1.7	<1.5	0.11	3.8(-10)
CH_3CHO	0.98	1.2	–	<0.66	–	–	5.6(-11)
OCN^-	0.63	<0.05	–	–	<0.12	–	1.6(-8) ^e

^aGibb et al. 2000b; Dartois et al. 1999; Schutte et al. 1999; Whittet et al. 2001; Demyk et al. 1998, ^bGibb et al. (2004), ^cKnez et al. (2005) and references therein, ^dthis chapter. ^eAssuming that OCN^- evaporates as $HNCO$.

6.6 Discussion and comparison to astrochemical models

6.6.1 General model considerations

Pure gas phase chemistry models such as presented in e.g., Lee et al. (1996), are unable to explain the high abundances of many complex organics, especially of highly saturated molecules in hot gas phase environments. CH_3OH , for example, is estimated to have abundances of $\sim 10^{-12}$ through pure gas phase chemistry, whereas abundances of 10^{-6} are found. For CH_3CN abundances of $\sim 10^{-10}$ are modeled (Lee et al. 1996) whereas abundances of $\sim 10^{-7}$ are detected. Furthermore, they are not able to explain the presence of complex organics in ices by simple freeze-out of gas phase species (see Herbst 2005, for a review). For highly saturated molecules, solid state chemistry provides a likely alternative. Here one can distinguish basic grain surface chemistry and chemistry induced by energetic processing (UV irradiation, energetic particle bombardment and/or thermal heating) which can proceed also inside the ice.

Surface chemistry models have been developed by several groups (e.g., Hasegawa & Herbst 1993; Charnley 2001; Keane 2001) (see Fig. 6.1). The results are generally very sensitive to the atomic C, O, and N abundances in the gas. Moreover, the dust temperature (T_{dust}) plays a crucial role in the mobility of the atoms and radicals as well as the availability of CO as a reaction partner on the grain, which evaporates at $T_{\text{dust}} > 20$ K (Tielens & Hagen 1982; Caselli et al. 1993). However, if CO is located in an ice environment that is dominated by H_2O it will be available for reactions in the ice up to much higher temperatures (Sandford & Allamandola 1993; Collings et al. 2003a).

If grain surface chemistry is the explanation for our observed correlations, the constant abundance ratios for different sources must imply very similar conditions during ice formation, at least of the ice layer that contains the “hot” molecules. This is also confirmed by the similarity between the composition of ices observed toward background stars compared to those toward low and high mass star forming regions (Knez et al. 2005). Perhaps the simplest explanation is that the bulk of the ice forms at similarly low temperature conditions in which the bulk of the oxygen and nitrogen are in atomic form and C/CO is at a fairly constant ratio, around 0.01 as computed for dense clouds (Gredel et al. 1989). When these “first generation” species evaporate together and have similar destruction rates, a constant abundance ratio would result even in regions where the temperatures of the gas and UV-flux are very different.

In contrast, “second generation” species are expected to peak at different times dependent on their formation and destruction processes. While this argument has been used to explain the anti-coincidences between the nitrogen and oxygen-bearing species (Caselli et al. 1993; Rodgers & Charnley 2003), it is inconsistent with our observed correlations of supposedly “second generation” species HCOOCH_3 and CH_3OCH_3 with other “first generation” oxygen-bearing molecules. Indeed, in models by Garrod & Herbst (2006) where HCOOCH_3 is formed in the solid state, many of the oxygen-bearing species have similar gas phase abundance variations throughout the chemical evolution and have con-

stant abundance ratios. Solid state formation is therefore more likely for the supposedly “second generation” oxygen-bearing species. However, the abundances of oxygen-bearing and nitrogen-bearing species do not correlate. This can be due to a different time-dependence of formation and destruction or a variable N/C abundance ratio.

Laboratory experiments show that beyond a certain minimum dose of irradiation the reaction products often do reach a constant plateau (Gerakines et al. 1996; Moore & Hudson 2000; van Broekhuizen et al. 2004; Hagen et al. 1979). Oxygen-bearing species, such as H_2CO , and nitrogen-bearing species, e.g., OCN^- and NH_2CHO , can be formed this way (Grim et al. 1989). However, there is not enough information in the literature on the formation of the more complex molecules observed here to make a quantitative test of this scheme. It is plausible, though, that an equilibrium between formation and destruction is reached in interstellar ices and could be responsible for the constant abundance ratios between the oxygen-bearing species or $\text{HNCO}/\text{NH}_2\text{CHO}$.

Recent work by Garrod & Herbst (2006) combines both grain surface chemistry and UV-induced chemistry with thermal evolution of the ices during the protostellar phase. In particular, radicals created in the ices by ultraviolet radiation become mobile at the higher dust temperatures during the warm-up phase and lead to the formation of many complex organic species. This suggests that the ice composition changes with temperature. Potentially only the ices on grains that are close to the evaporation temperature have similar relative abundances to those observed in the gas phase. Since the detected ice features are observed in a column, they will contain both cold and warmer ices, which complicates the comparison of the ice abundances with the gas phase, even within one source.

Species such as HCOOH and CH_3CHO are detected with much lower column densities in the gas phase than in the ice (see Section 6.5.4) and have low rotation temperatures. Possibly, these species are formed in the solid state at low temperatures and destroyed due to reactions at high temperatures. Since their desorption temperatures are typically ~ 100 K (Viti et al. 2004), thermal desorption cannot account for their low temperatures. However, non-thermal mechanisms induced by, for example, cosmic rays (Léger et al. 1985), can explain the low gas phase abundances if they cause a small fraction (10^{-4}) of the ice to evaporate (see § 6.6.2). Alternatively, cold gas phase ion-molecule reactions are able to reproduce the abundances of e.g., CH_3CHO and CH_2CO (Lee et al. 1996, see also § 6.6.2).

Ices are expected to be layered because different molecules such as H_2O , CO , and N_2 form or condense at different densities. Since nitrogen is transformed into N_2 deepest in the cloud it is expected to freeze-out last. To form species such as HNCO or NH_2CHO a more reactive form of nitrogen, i.e. N-atoms are needed. N-atoms could potentially be present in a non-hydrogen bonding layer dominated by CO or a layer dominated by H_2O . If they were present in the non-hydrogen bonding layer a small fraction of non-thermal desorption would result in cold gas phase N-bearing species. The lack of these cold N-bearing molecules and high rotation temperatures of HNCO and NH_2CHO suggests that they

desorb at higher temperatures and must thus be present in a different, more tightly bound ice layer.

In summary, pure gas-phase reactions cannot reproduce the abundances of most species depicted in Fig. 6.1, and second generation gas phase chemistry is inconsistent with the observed correlations for the oxygen-bearing species. Constant abundance ratios after ice evaporation can be explained either by similar initial conditions for ice formation or an equilibrium between formation and destruction due to energetic processes. The low abundances of cold gas phase species could be due to gas phase ion-molecule reactions or non-thermal desorption of a small fraction of the ices e.g., by cosmic rays.

6.6.2 Individual molecules

This subsection elaborates on the general conclusions stated in § 6.6.1 for individual molecules, grouped according to the different branches of Fig. 6.1.

H₂CO and CH₃OH: CH₃OH and H₂CO are molecules commonly expected to originate from grain-surface chemistry. They are formed through successive hydrogenation of CO on grains, a scheme that has been tested experimentally by Hiraoka et al. (2002), Watanabe et al. (2004) and Fuchs et al. (2007). Both H₂CO and CH₃OH have been detected in these experiments with different abundance ratios dependent on the exact conditions. H₂CO can also be formed by UV-irradiation of CH₃OH containing ices (Allamandola et al. 1988; Bernstein et al. 1995). However, the high ice abundances of CH₃OH (e.g., Gibb et al. 2004) and the constant abundance ratio between H₂CO/CH₃OH in this chapter are inconsistent with this CH₃OH destruction mechanism. Our data imply that hydrogenation reactions are more feasible formation mechanisms.

Furthermore as discussed in § 6.5.4, the solid state abundance of CH₃OH appears to be at least an order of magnitude higher than the comparable source-averaged gas phase abundances. This could be due to a number of effects: i) CH₃OH is partly destroyed upon evaporation, ii) intrinsic CH₃OH ice variations from source to source (Brooke et al. 1999; Dartois et al. 1999; Pontoppidan et al. 2004), iii) an underestimate of the beam-filling factor of the CH₃OH emitting gas. Possibly, all three factors contribute to the relatively low gas phase abundance.

CH₂CO, CH₃CHO, and C₂H₅OH: In Figure 6.1 CH₂CO, CH₃CHO, and C₂H₅OH are thought to be interrelated through successive hydrogenation as well as to H₂CO and CH₃OH by successive H- and C-atom addition. All three species are expected to evaporate from the ice together with H₂O (Viti et al. 2004) and have similar rotation temperatures. This is not the case, however. Indeed, interferometric observations of CH₃CHO in high mass star forming regions show that CH₃CHO emission is extended with respect to hot cores species such as HCOOCH₃ and CH₃OCH₃ (Liu 2005). This suggest that CH₂CO, CH₃CHO, and C₂H₅OH gas are not present in the same region. Possibly, H-atom addition to CH₂CO and CH₃CHO on grains is very efficient and completely converts them to C₂H₅OH at high temperatures, so that only C₂H₅OH evaporates from the ice and is detected in the warm inner regions. Non-thermal desorption of

a small fraction due to e.g., cosmic ray spot heating of CH_2CO and CH_3CHO ice in cold regions could explain the low gas phase abundances and rotation temperatures, as well as the high ice abundances of CH_3CHO . Alternatively, $\text{C}_2\text{H}_5\text{OH}$ could be formed through another surface reaction related to CH_3OH and H_2CO formation, explaining its constant abundance ratio.

For CH_2CO and CH_3CHO there are also potential gas phase formation mechanisms. Millar & Nejad (1985) argue that CH_2CO could result from radiative associative reactions between CH_3^+ and CO . Assuming that CH_3CO^+ dissociative recombination results in CH_2CO for 50% of the cases, this would allow for CH_2CO abundances of $\sim 10^{-10}$, comparable to our observed abundances and also to those by Turner et al. (1999). Gas phase models by Lee et al. (1996) predict fractional abundances of 5×10^{-12} for CH_3CHO and its isomers. This is lower than the abundances of Ikeda et al. (2001) and Charnley (2004) but close to the abundances for some of our sources. Herbst & Leung (1989) proposed that H_3O^+ and C_2H_2 react to form CH_3CHO after dissociative recombination, which results in higher abundances of up to $\sim 10^{-10}$ in dark clouds. Many of these conclusions depend on high branching ratios toward these products in dissociative recombination. If three body break-up prevails as found for some species, pure gas phase production becomes untenable (Geppert et al. 2005).

HCOOH: High abundances of HCOOH in the ice, low gas phase rotation temperatures, and orders of magnitude lower abundances in the gas phase compared to the solid state can be due to two reasons: i) HCOOH is quickly destroyed in the gas phase upon evaporation, and ii) HCOOH is abundant in low temperature ice, but destroyed at higher temperatures due to reactions in the ice. Gas phase destruction is a possibility, but it is unclear why the destruction rate of HCOOH would be orders of magnitude larger compared to other species. Even if this would be the case, most high mass star-forming regions are expected to have an evaporation front that moves outward through the envelope as the luminosity increases. HCOOH should thus continuously freshly evaporate from icy grains. The second possibility of HCOOH destruction in the ice at high temperatures is much more likely and can be tested in the laboratory. The lower gas phase abundance can then be explained by a small fraction of the ice ($\sim 10^{-4}$) that evaporates due to non-thermal desorption mechanisms. The low rotation temperatures of $\sim 40\text{--}70$ K for most sources in our sample are also consistent with this picture. Finally, it can explain the high HCOOH abundances in shocked regions by e.g. Requena-Torres et al. (2006), where the ice is warmed up and evaporated over much shorter timescales.

The precise formation of HCOOH through surface chemistry still remains a puzzle, however. In Figure 6.1 the formation mechanisms in the solid state is either through CO or CO_2 . Laboratory experiments indicate that it only evaporates at very high temperatures (~ 100 K) similar to H_2O (Collings et al. 2004). This is even the case for HCOOH diluted in CO or CO_2 ices (Bischof et al. 2007a). Keane (2001) predicts the formation of HCOOH through successive atom addition to CO and finds that the HCOOH ice concentration is proportional to the O/O_2 ratio. Alternatively, Allen & Robinson (1977) proposed the reaction $\text{HCO} + \text{OH}$ in the solid state leading to HCOOH. New

models by Garrod & Herbst (2006) have HCOOH gas phase abundances that are much higher than found for our sources with most of the HCOOH actually formed in the gas. If this occurs at intermediate temperatures, a fraction of the HCOOH may freeze out on grains. Further laboratory experiments are needed to elucidate the exact formation mechanism for HCOOH.

HNCO and NH₂CHO: HNCO formation has been explained by surface chemistry formation and gas phase reactions (Turner et al. 1999; Keane 2001). Both Turner et al. (1999) and Keane (2001) argue that NH₂CHO is formed on grain-surfaces due to its high level of hydrogen saturation. The strong correlation between the two species in § 6.5.1 suggests they are related. Alternatively, both OCN⁻ and NH₂CHO can form in ices due to energetic processes such as UV-irradiation (van Broekhuizen et al. 2004; Muñoz Caro & Schutte 2003; Allamandola et al. 1999). Van Broekhuizen et al. (2004) conclude that thermal formation of OCN⁻ can, however, also not be ruled out. Concluding, solid state processes appear to be the most likely formation mechanism for both species, whether they involve energetic processing or not.

HCOOCH₃ and CH₃OCH₃: HCOOCH₃ and CH₃OCH₃ were previously thought to form from protonated methanol in the gas phase (Millar et al. 1991). Horn et al. (2004) recently found the barrier for the gas phase formation of HCOOCH₃ to be higher than previously anticipated. Moreover, the gas phase routes assume that H₂COOCH₃⁺ and (CH₃)₂OH⁺ recombine to HCOOCH₃ and CH₃OCH₃ respectively. Measurements by Geppert et al. (2004, 2005) have shown that dissociative recombination of CH₃OH₂⁺ mostly results in a three-body break-up instead of its deprotonated counterpart. If this would also be the case for species such as HCOOCH₃ and CH₃OCH₃, they are more likely to be at least partially formed on grain surfaces. The constant abundance ratios between both species and CH₃OH also confirm this scenario. Indeed Garrod & Herbst (2006) explain surface formation of HCOOCH₃ and CH₃OCH₃ through reactions of CH₃O and HCO radicals, first proposed by Allen & Robinson (1977).

CH₃CN, C₂H₅CN, and CH₃CCH: CH₃CN can be formed from the fast association reaction CH₃⁺ + HCN and the radiative association reaction of CH₃ + CN (Charnley et al. 1992). The abundances in the gas phase for Orion are, however, $\sim 10^{-10}$ (Charnley et al. 1992) compared to 10^{-8} in our sources. The relatively high abundances plus the high degree of hydrogenation for C₂H₅CN and CH₃CN imply that they are possibly formed on grain-surfaces. CH₃CCH usually has very low rotation temperatures, and its formation is explained in dark and translucent clouds through gas phase ion-molecule or neutral-neutral reactions.

In summary, most species, such as H₂CO, CH₃OH, C₂H₅OH, HCOOCH₃, and CH₃OCH₃ probably result from “first generation” chemistry in ices, likely dominated by surface chemistry. This is possibly also true for CH₃CN and C₂H₅CN. CH₂CO, CH₃CHO, HCOOH and CH₃CCH have all been detected in the gas with low rotation temperatures and, for some species, abundances that are orders of magnitude lower than those in ices. Non-thermal desorption of a small fraction of the ice ($\sim 10^{-4}$) is sufficient to explain the abundances in the

cold gas phase. For CH_2CO , CH_3CHO , and HCOOH formation plus destruction in the ice at higher temperature are plausible, but gas phase chemistry cannot be excluded. Models of gas phase reactions are able to accurately reproduce the observed CH_3CCH abundances.

6.7 Summary and conclusions

We have performed a survey of selected frequency settings for 7 high mass YSOs. The survey was targeted at detecting species thought to be produced by the grain surface chemistry depicted in Fig. 6.1. Other species such as CH_3CN , $\text{C}_2\text{H}_5\text{CN}$, CH_3CCH , HCOOCH_3 and CH_3OCH_3 have also been detected. To compare abundances between sources, the source luminosity and $850\ \mu\text{m}$ dust emission was used to constrain the radius within which $T \geq 100\ \text{K}$ and the column density out to this radius, $N_{T \geq 100\ \text{K}}$. The main conclusion derived in this work are:

- ▷ Most detected molecules have similar rotation temperatures for all sources. The following molecules can be classified as cold ($T < 100\ \text{K}$): CH_2CO , CH_3CHO , HCOOH , and CH_3CCH ; and the following as hot ($T \geq 100\ \text{K}$): H_2CO , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, HNCO , NH_2CHO , CH_3CN , $\text{C}_2\text{H}_5\text{CN}$, HCOOCH_3 , and CH_3OCH_3 .
- ▷ Groups of molecules have their highest column densities for the same sources. This is the case for the oxygen-bearing species H_2CO , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, HCOOCH_3 and CH_3OCH_3 . HNCO and NH_2CHO have their highest column in other sources than the oxygen-bearing species, but both are highest for the same sources. Due to optical depth effects and a limited number of detections it is difficult to establish the trends for CH_3CN and $\text{C}_2\text{H}_5\text{CN}$.
- ▷ Absolute abundances in the hot regions vary by an order of magnitude. Relative abundances of the oxygen-bearing species and the two nitrogen-bearing species are, however, very constant. The absolute abundances are much higher than can be produced by gas phase chemistry. The constant abundance ratios plus the similar rotation temperatures imply that the oxygen-bearing species, H_2CO , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, HCOOCH_3 and CH_3OCH_3 , as well as the two nitrogen-bearing species, HNCO and NH_2CHO , share a common solid state formation scheme. This can be the result of very similar conditions during ice formation or a balance between formation and destruction in the ice. The oxygen-bearing species and the two nitrogen-bearing species are not related, however. The abundances of two cyanides, CH_3CN and $\text{C}_2\text{H}_5\text{CN}$, are likely due to “first generation” ice chemistry as well.
- ▷ CH_2CO , CH_3CHO , CH_3CCH and HCOOH have very low rotation temperatures. The formation of CH_2CO , CH_3CHO , and HCOOH can be explained by solid state or gas phase reactions. For HCOOH and CH_3CHO

gas phase abundances are a factor of 10^4 lower than those observed in the solid state. Solid state formation for these species is thus more likely. A low fraction of non-thermal desorption could be responsible for the low gas phase abundances. Models of ion-molecule reactions in the cold gas phase can, however, also reproduce the abundances of CH_2CO and CH_3CHO . CH_3CCH on the other hand is probably created by cold gas phase chemistry, as its abundance is similar to that found in dark clouds. Interestingly, no cold N-bearing molecules are found.

The abundance correlations and branching ratios determined in this chapter are key to understanding chemical relationships between these complex organic molecules and addressing their origins. Future spatially resolved observations with interferometers such as ALMA will make it possible to confirm molecular relations and address the chemical variations within each source. Additional laboratory experiments can explore the pathways to the formation of the most abundant species given these observational constraints of constant abundance ratios. Taken together such studies will be important to fully understand the chemistry of complex organic molecules in star forming regions.

Acknowledgements

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Appendix A: Rotation diagrams per molecule for all sources

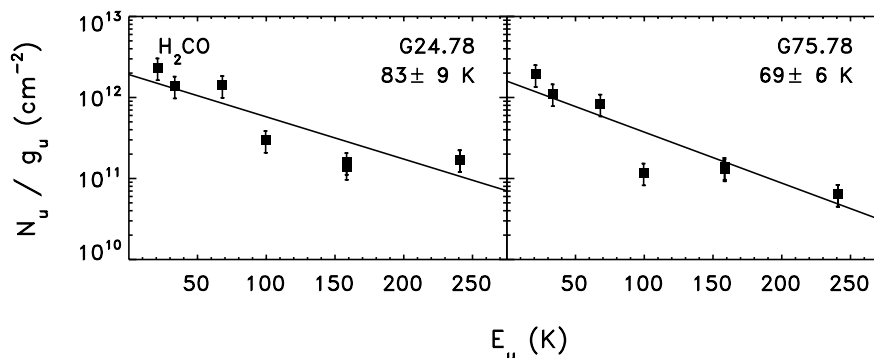


Figure 6.9. Rotation diagrams for H_2CO for G24.78, and G75.78.

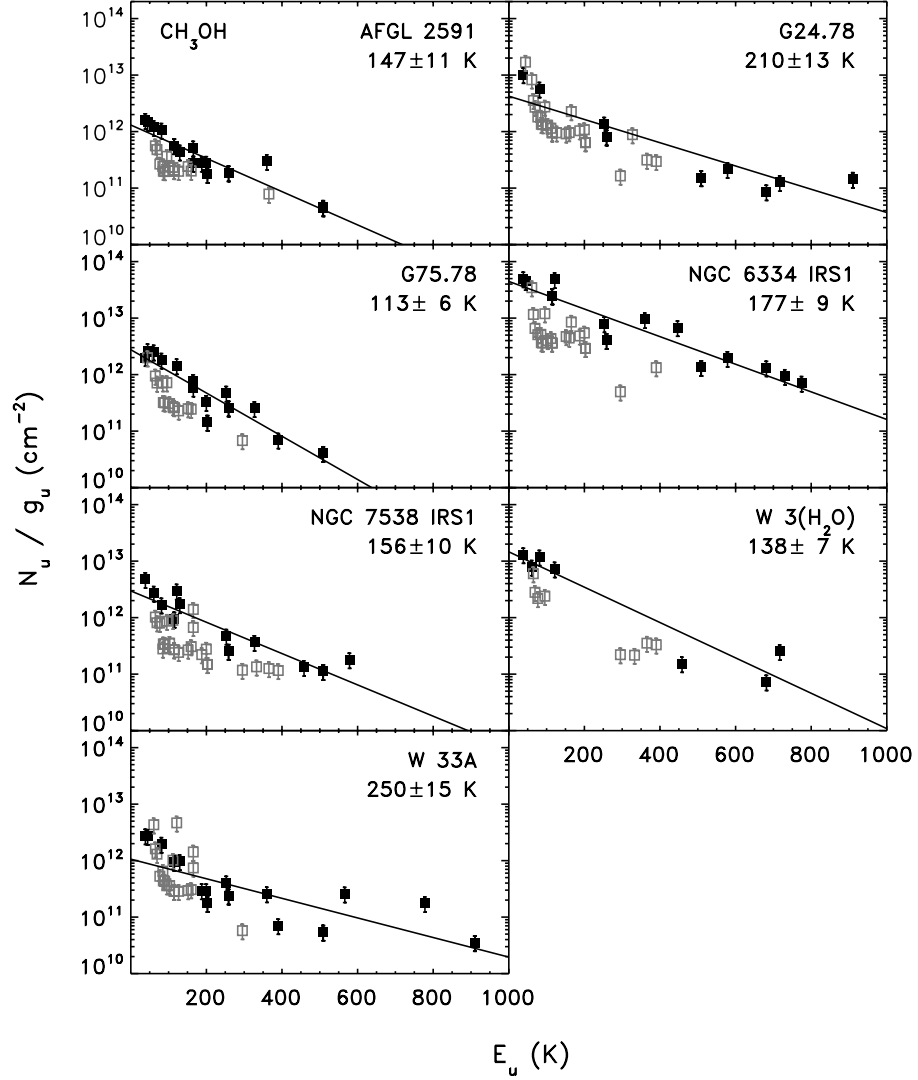


Figure 6.10. Rotation diagrams for CH_3OH for respectively AFGL2591, G24.78, G75.78, NGC 6334IRS1, NGC 7538IRS1, W3(H_2O), and W33A. The filled black squares are optically thin lines, the open gray squares optically thick lines, based on the estimated column densities. The rotation temperatures are fits to the optically thin lines only.

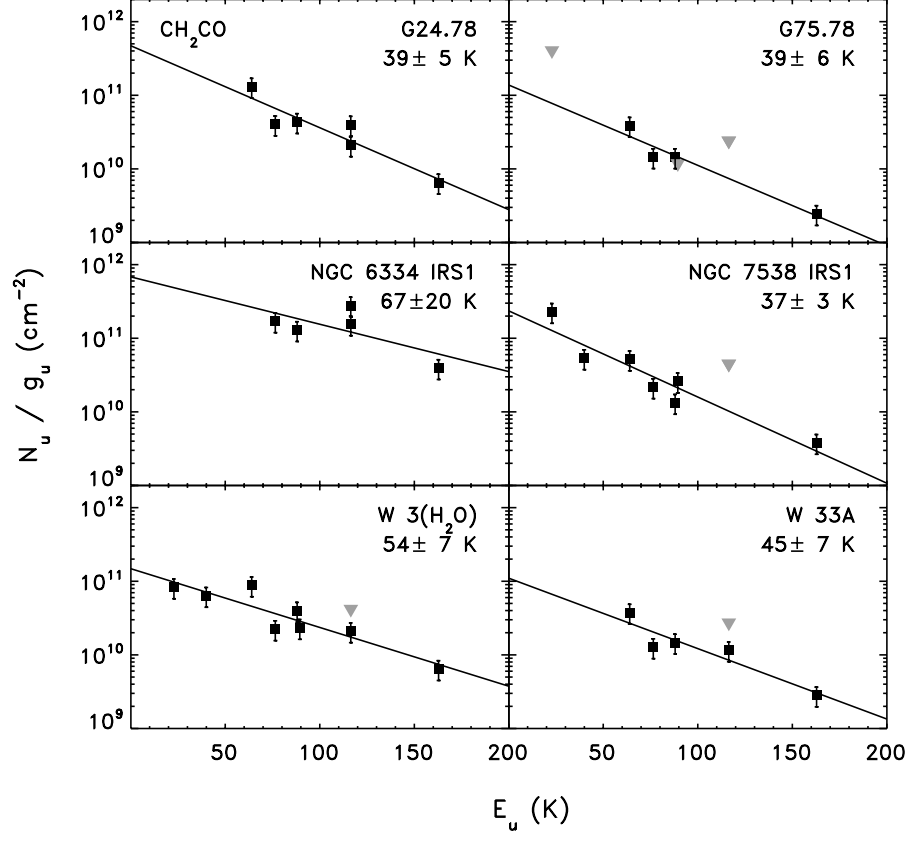


Figure 6.11. Rotation diagrams for CH_2CO for respectively G24.78, G75.78, NGC 6334IRS1, NGC 7538, W3(H_2O), and W33A. The gray triangles indicate upper limits.

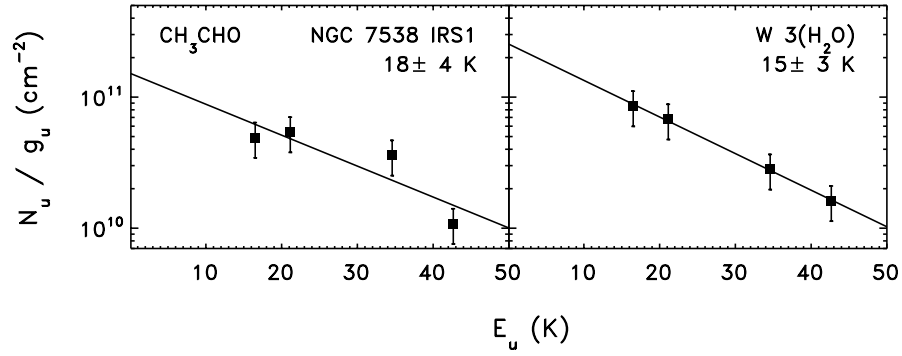


Figure 6.12. Rotation diagrams for CH_3CHO for respectively NGC 7538 IRS1, W3(H_2O), and W33A.

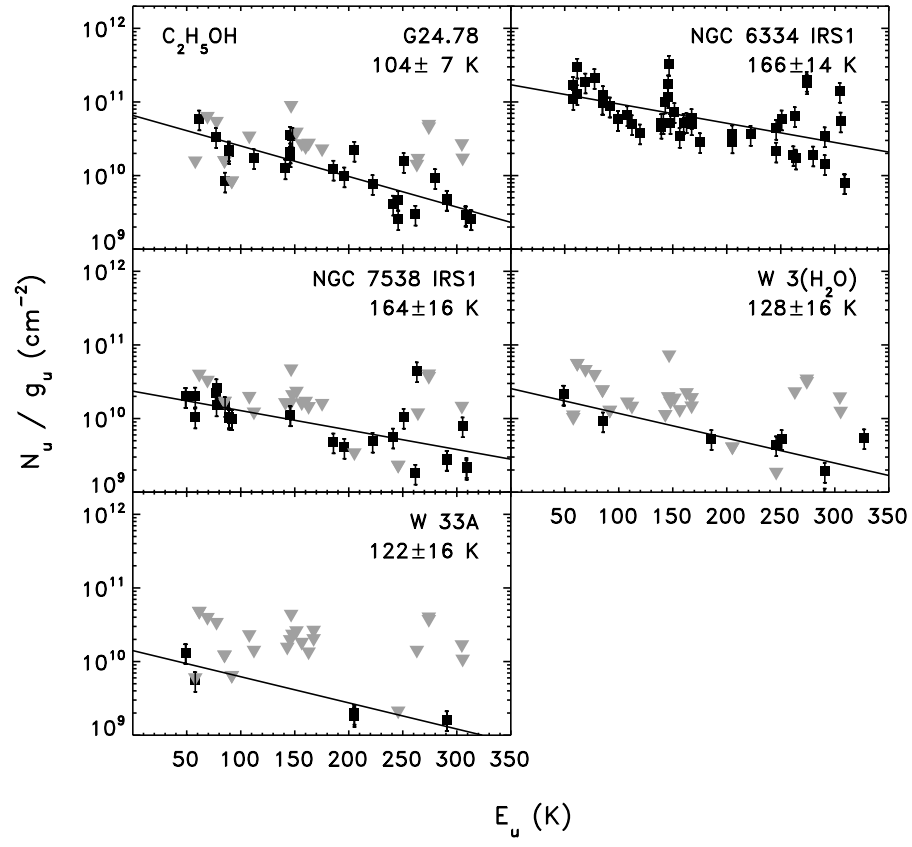


Figure 6.13. Rotation diagrams for C_2H_5OH for respectively G24, NGC 6334IRS1, NGC 7538IRS1, W3(H_2O), and W33A. The gray triangles indicate upper limits.

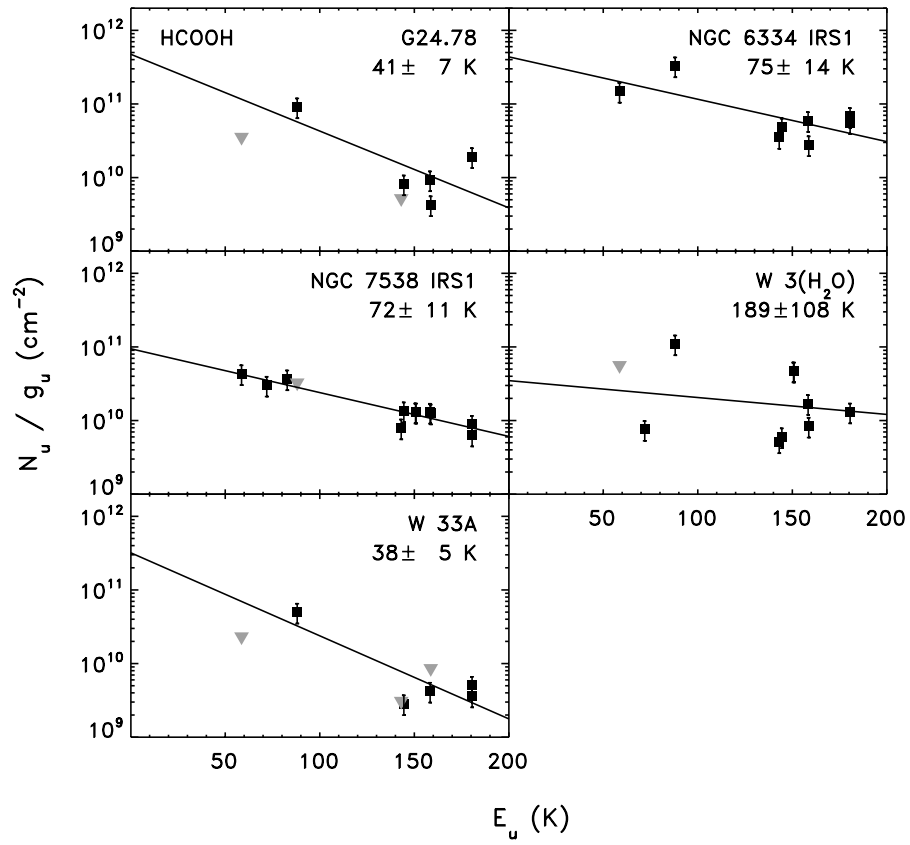


Figure 6.14. Rotation diagrams for HCOOH for respectively $G24.78$, $NGC\ 6334\text{IRS1}$, $NGC\ 7538\text{IRS1}$, $W3(\text{H}_2\text{O})$, and $W33A$. The gray triangles indicate upper limits.

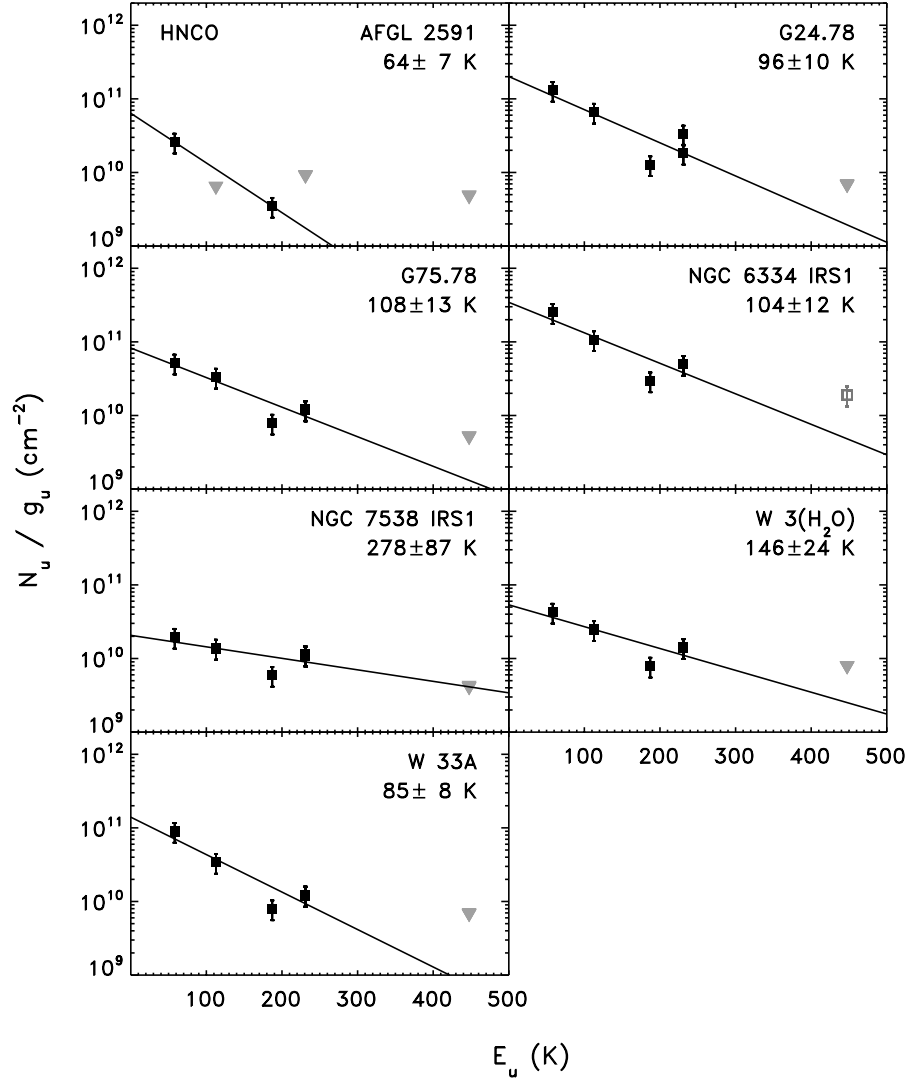


Figure 6.15. Rotation diagrams for HNC for respectively $G24.78$, $G75.78$, $\text{NGC } 6334\text{IRS1}$, $\text{NGC } 7538\text{IRS1}$, $\text{W3}(\text{H}_2\text{O})$, and W33A . The filled black squares are the points included and the gray squares excluded from the fit. The gray triangles indicate upper limits.

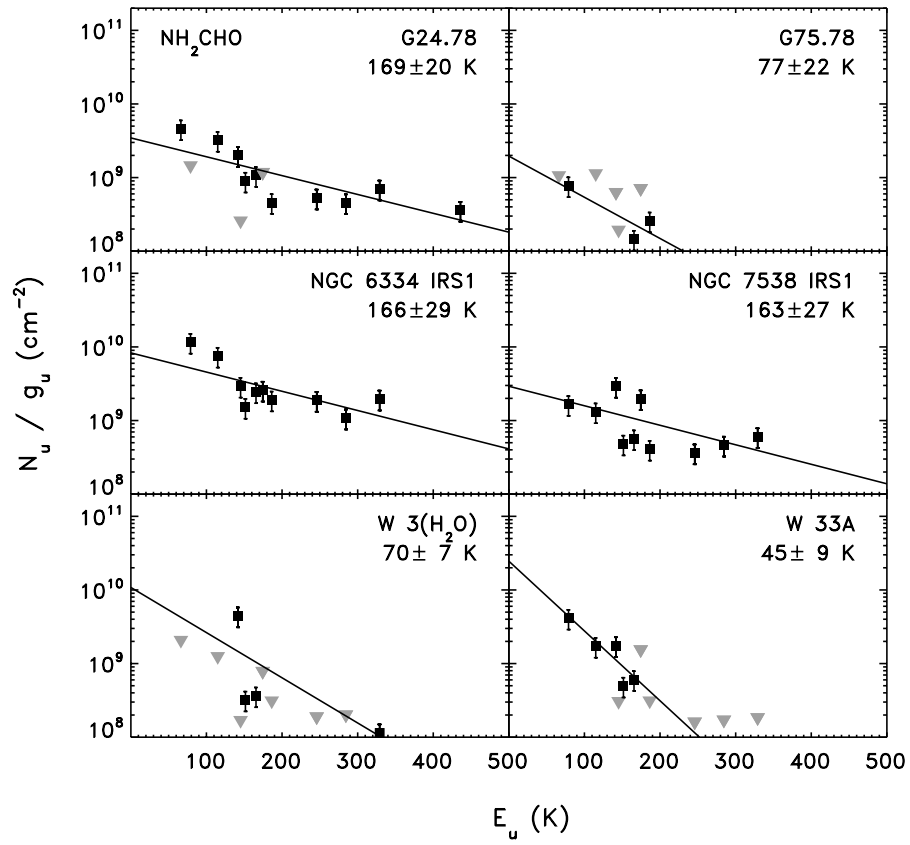


Figure 6.16. Rotation diagrams for NH_2CHO for respectively $G24.78$, $G75.78$, $NGC\ 6334\text{IRS1}$, $NGC\ 7538\text{IRS1}$, $W3(\text{H}_2\text{O})$, and $W33A$. The gray triangles indicate upper limits.

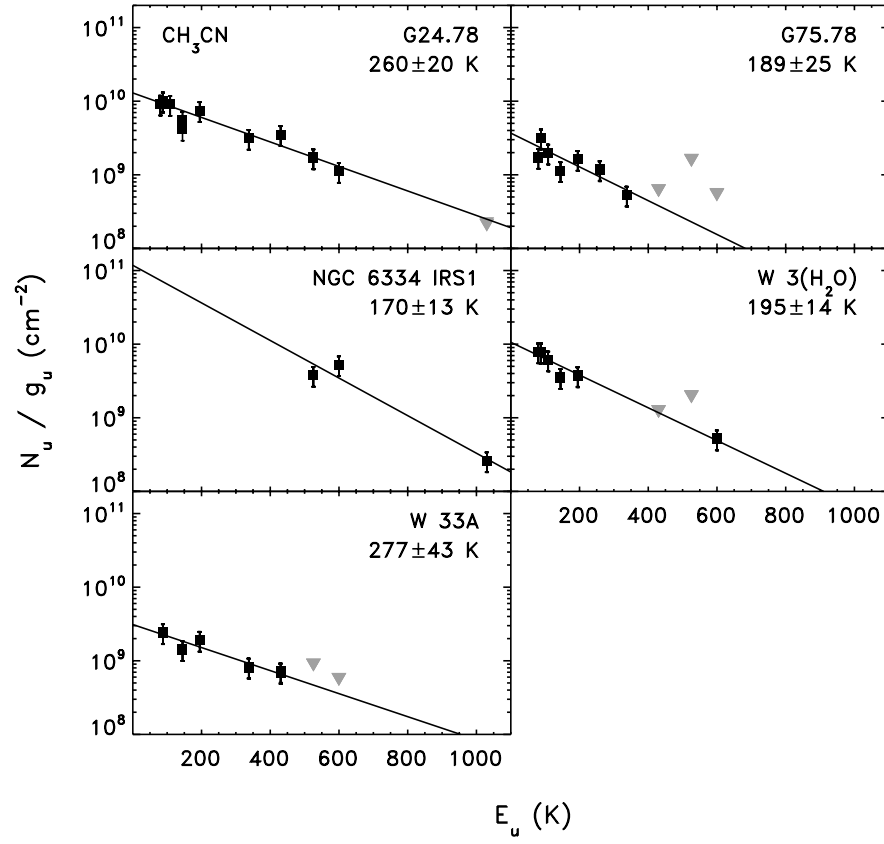


Figure 6.17. Rotation diagrams for CH_3CN for respectively $G24.78$, $G75.78$, $NGC\ 6334\text{IRS1}$, $W3(\text{H}_2\text{O})$, and $W33A$. The gray triangles indicate upper limits.

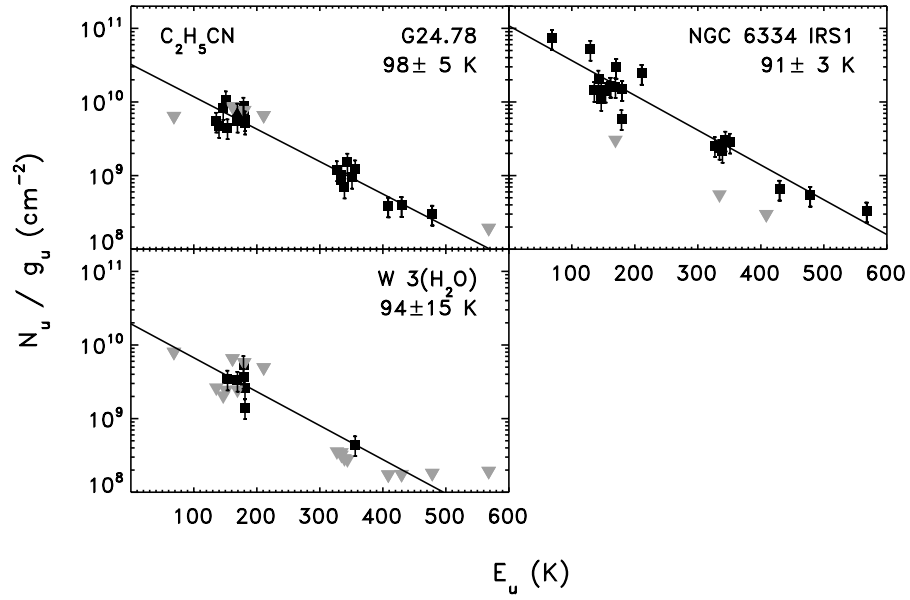


Figure 6.18. Rotation diagrams for $\text{C}_2\text{H}_5\text{CN}$ for respectively G24.78, and NGC 6334IRS1. The gray triangles indicate upper limits.

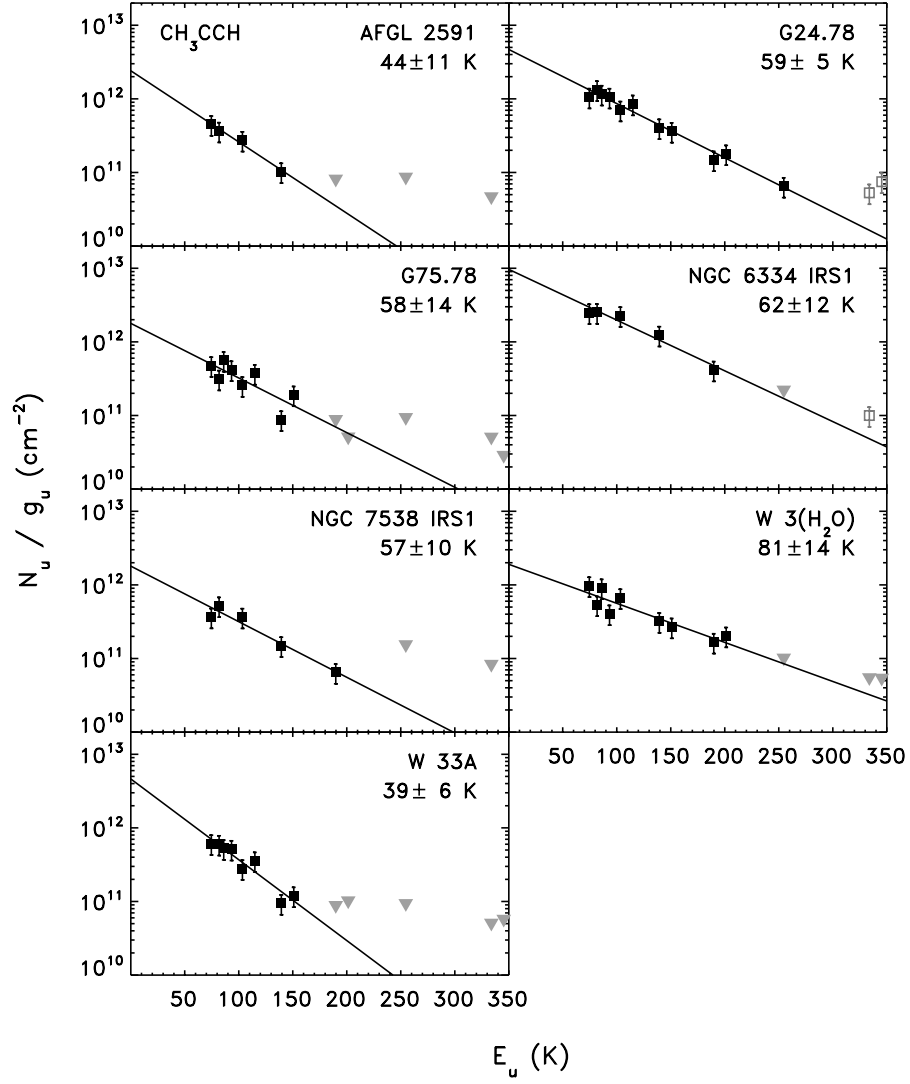


Figure 6.19. Rotation diagrams for CH_3CCH for respectively AFGL2591, G24.78, G75.78, NGC 6334IRS1, NGC 7538IRS1, W3(H_2O), and W33A. The filled black squares are the points included, the gray squares excluded from the fit and the gray triangles indicate upper limits.

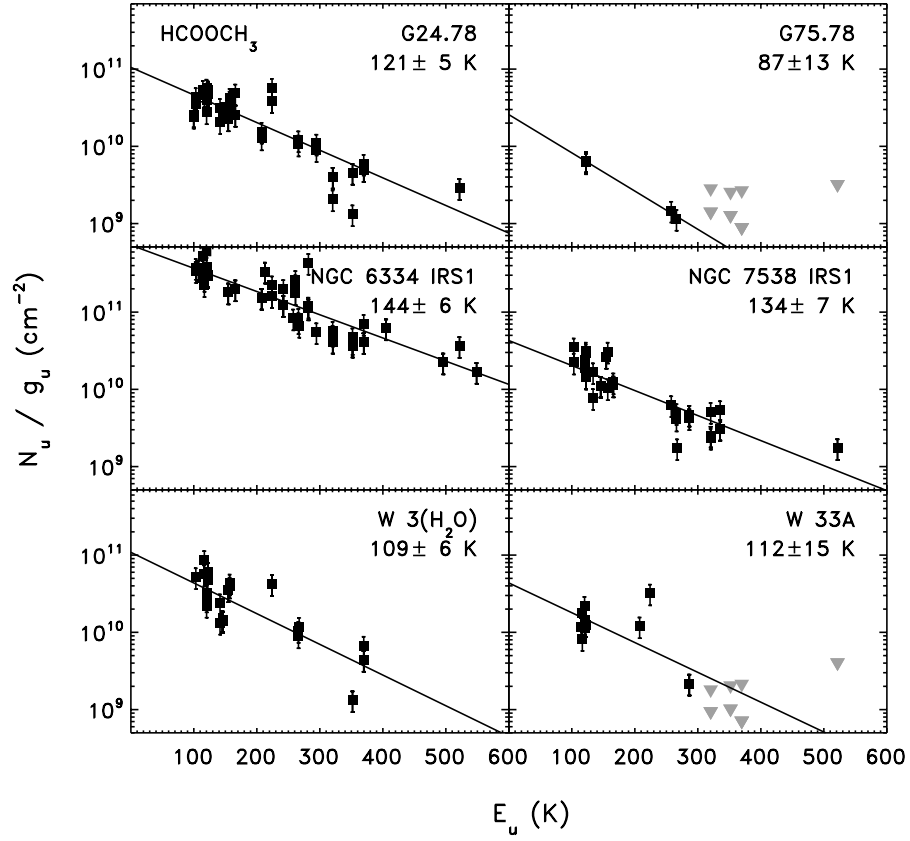


Figure 6.20. Rotation diagrams for HCOOCH_3 for respectively G24.78, G75.78, NGC 6334IRS1, NGC 7538IRS1, W3(H_2O), and W33A. The filled black squares are the points included and the gray triangles indicate upper limits.

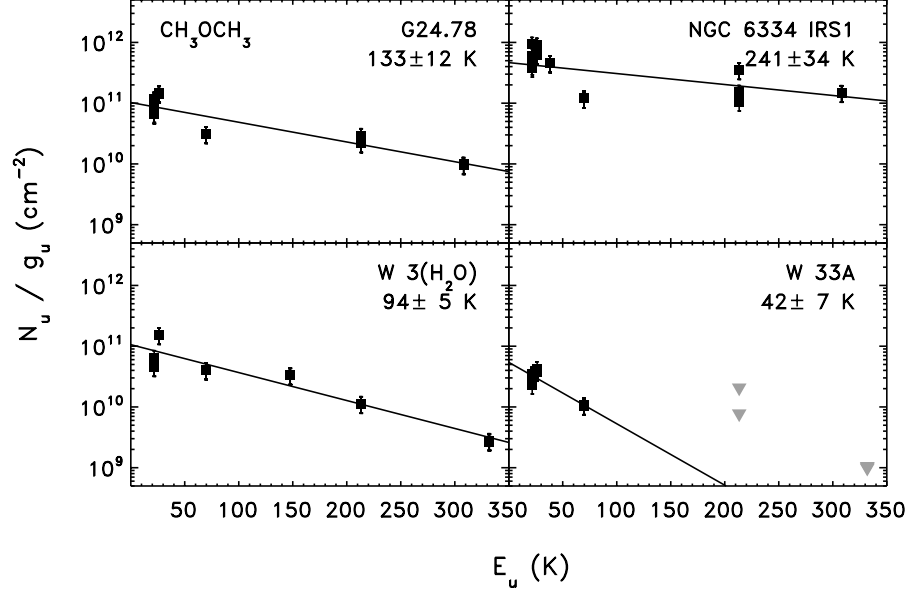


Figure 6.21. Rotation diagrams for CH_3OCH_3 for respectively *G24.78*, *NGC 6334 IRS1*, *W3(H₂O)*, and *W33A*. The filled black squares are the points included and the gray triangles indicate upper limits.

Appendix B: Detected lines per species for all sources

Table 6.12. *Observed line fluxes $\int T_{\text{MB}} dv$ ($K \text{ km s}^{-1}$) for H_2CO and its isotopic species.*

Frequency [GHz]	Transition	Sources							
		AFGL 2591	G24.78	G75.78	NGC 6334	IRS1	NGC 7538	IRS1	W 3(H ₂ O)
H ₂ CO									
218.222	3 _{0,3} –2 _{0,2}	–	17	14	–	–	–	–	–
218.476	3 _{2,2} –2 _{2,1}	–	5.6	3.3	–	–	–	–	–
225.698	3 _{1,2} –2 _{1,1}	15	27	22	57	31	–	34	22
363.946	5 _{2,4} –4 _{2,3}	–	15	5.9	–	–	–	–	–
364.103	5 _{4,K} –4 _{4,L}	–	7.3	2.7	–	–	–	–	–
364.275	5 _{3,3} –4 _{3,2}	–	16	7.5	–	–	–	–	–
364.289	5 _{3,2} –4 _{3,1}	–	18	7.9	–	–	–	–	–
H ₂ ¹³ CO									
219.909	3 _{1,2} –2 _{1,1}	0.41	2.9	1.0	8.8	0.84	–	1.1	1.6
356.176	5 _{2,3} –4 _{2,2}	<0.36	2.4	0.55	6.3	<0.41	–	0.96	0.92
H ₂ C ¹⁸ O									
348.032	5 _{2,3} –4 _{2,2}	0.15	0.85	<0.32	2.6	0.26	–	<0.32	<0.26

– means frequency not observed. K stands for 1/2. L stands for 0/1.

Table 6.13. *Observed line fluxes $\int T_{\text{MB}} dV$ ($K \text{ km s}^{-1}$) for CH_3OH in the 230 GHz window.*

Frequency [GHz]	Transition	Sources								
		AFGL 2591	G24.78	G75.78	NGC 6334	IRS1	NGC 7538	IRS1	W3(H ₂ O)	W33A
218.440	4 _{3,1,0} –3 _{2,1,0}	–	12.5	3.0	–	–	–	–	–	–
219.994	23 _{14,9,0} –22 _{14,8,0}	<0.36	<0.49	<0.26	2.0	–	<0.32	–	<0.47	<0.41
220.079	8 _{4,4,0} –7 _{4,3,0}	0.55	4.1	1.1	18	–	1.3	–	3.6	0.54
227.815	16 _{9,8,0,1} –15 _{9,7,0,1}	–	2.1	0.60	–	–	0.87	–	1.8	–
229.939	19 _{12,7,0,2} –20 _{12,8,0,2}	<0.31	0.56	<0.32	5.1	–	0.47	–	<0.38	<0.25
230.027	3 _{1,3,0} –4 _{2,3,0}	0.53	3.4	0.68	17	–	1.6	–	4.3	0.92
230.293	22 ₂₂₀₀ –21 ₃₁₉₀	<0.31	0.38	<0.32	5.1 ^a	–	<0.41	–	0.68	<0.25
230.369	22 _{13,9,0} –21 _{13,8,0}	<0.31	0.26	<0.32	4.0	–	0.67	–	0.22	<0.25
231.281	10 _{6,4,0,2} –9 _{6,3,0,2}	0.34	7.6 ^b	0.93	13	–	0.82	–	4.5	1.7
232.417	10 _{6,4,0,1} –9 _{6,3,0,1}	0.64	2.8	0.72	10	–	<0.38	–	–	0.94
232.784	18 _{11,8,0,1} –17 _{11,7,0,1}	–	–	–	17	–	–	–	–	–
232.927	14 _{6,8,1} –14 _{7,7,1}	–	–	–	1.7	–	–	–	–	–
232.946	10 _{4,7,0} –11 _{5,7,0}	–	–	–	16	–	–	–	–	–
233.097	13 _{6,7,1} –13 _{7,6,1}	–	–	–	0.83	–	–	–	–	–
234.683	4 _{3,1,0,2} –5 _{3,2,0,2}	0.62	4.3	1.3	18	–	1.4	–	4.1	2.2
234.698	5 _{1,5,0} –6 _{2,5,0,5}	<0.24	<0.36	0.31	10	–	0.64	–	1.6	1.0
240.242	5 _{4,1,0} –6 _{4,2,0,5}	0.50	3.7	0.85	12	–	0.79	–	5.6	0.92
240.741	26 _{3,23,0} –26 _{2,24,0}	<0.25	0.66	<0.3	4.8	–	0.47	–	0.33	<0.20
240.960	5 _{3,2,1,1} –4 _{3,2,1,1} ^c	0.54	3.0 ^d	0.61	17	–	1.1	–	3.4	0.94
241.043	22 _{6,16,0} –23 _{5,18,0}	<0.25	<0.40	<0.3	2.6	–	0.45	–	<0.54	<0.26
241.057	9 _{3,6,0} –10 _{0,10,0}	<0.25	<0.40	<0.3	3.3	–	<0.35	–	<0.54	<0.26
248.282	17 _{10,7,0,2} –17 _{10,8,0,1}	–	–	–	–	–	<0.35	–	3.0	–
248.885	16 _{10,7,0,2} –16 _{9,7,0,1}	0.60	2.4	0.87	–	–	0.96	–	2.7	<0.20

– means frequency not observed. ^aBlend with HCOOCH₃. ^bBlend with CH₃CN. ^cBlend with 5_{2,3,2}–4_{2,3,2}. ^dBlend with HCOOCH₃.

Table 6.14. *Observed line fluxes $\int T_{\text{MB}} dV$ ($K \text{ km s}^{-1}$) for CH_3OH in the 345 GHz window.*

Frequency [GHz]	Transition	Sources								
		AFGL 2591	G24.78	G75.78	NGC 6334	IRS1	NGC 7538	IRS1	W3(H ₂ O)	W33A
CH ₃ OH continued										
337.969	7 _{4,3,1,2} –6 _{4,3,1,2}	0.48	3.2	0.76	14	1.3	3.6	0.77		
338.125	7 _{4,4,0} –6 _{3,3,0}	2.9	20	4.7	56	5.9	24	5.8		
338.345	7 _{3,4,0} –6 _{3,4,0}	3.9	35	7.7	71	8.1	30	11		
338.409	7 _{4,4,0,1} –6 _{3,3,0,1}	3.9	39	7.9	59	–	66	11		
338.431	7 _{1,7,0} –6 _{0,6,0}	–	4.0	0.84	–	–	–	–		
338.442	7 _{7,1,0,K} –6 _{6,0,0,K}	–	4.7	1.4	–	–	–	–		
338.456	7 _{1,6,0} –6 _{1,6,0}	–	5.6	1.5	–	–	–	–		
338.475	7 _{6,1,0} –6 _{6,1,0}	–	5.9	1.8	–	–	–	–		
338.486	7 _{6,1,0,K} –6 _{6,1,0,K}	–	6.9	1.6	–	–	–	–		
338.504	7 _{2,6,0} –6 _{1,5,0}	–	6.8	1.9	–	–	–	–		
338.513	7 _{5,3,0,2} –6 _{4,2,0,2}	–	14	3.3	–	–	–	–		
338.530	7 _{6,2,0} –6 _{5,1,0}	–	7.2	1.8	–	–	–	–		
338.542	7 _{5,2,0,1/2} –6 _{5,2,0,1}	–	17	4.7	–	–	–	–		
338.560	7 _{2,5,0} –6 _{2,5,0}	–	8.6	2.1	–	–	–	–		
338.583	7 _{5,2,0} –6 _{5,2,0}	–	10	2.5	–	–	–	–		
338.615	7 _{4,3,0} –6 _{4,3,0}	–	20	8.0	–	–	–	–		
338.640	7 _{5,3,0,1} –6 _{4,2,0,1}	–	13	3.1	–	–	–	–		
338.722	7 _{3/5,5/3,0} –6 _{2/4,4/2,0}	–	27	6.5	–	–	–	–		
340.141	2 _{2,0,0,1} –3 _{2,1,0,1}	0.89	5.6	1.6	27	3.2	4.1	1.7		
340.394	16 _{11,5,0,K} –17 _{11,6,0,K}	0.65	2.2	0.58	19	1.6	1.1	0.78		
355.964	16 _{10,7,1} –16 _{9,7,1}	<0.29	<0.47	<0.53	5.6	<0.41	<0.43	<0.68		
356.007	15 _{8,7,0,2} –15 _{8,8,0,1}	2.4	9.5	3.9	29	6.8	13	3.4		

— means frequency not observed. ^aBlend with $7_{6,2,0,1/2}-6_{5,1,0,1/2}$. K stands for 1 or 2.

Table 6.15. *Observed line fluxes $\int T_{\text{MB}} dV$ ($K \text{ km s}^{-1}$) for $^{13}\text{CH}_3\text{OH}$.*

Frequency	Transition	Sources								
[GHz]		AFGL 2591	G24.78	G75.78	NGC 6334	IRS1	NGC 7538	IRS1	W3(H ₂ O)	W33A
220.363	17 _{3,15,0} –18 _{0,18,0}	<0.19	0.15	<0.36	1.3	–	<0.30	<0.46	<0.19	–
223.332	6 _{4,3,1,2} –7 _{5,3,1,2}	<0.25	–	–	1.3	–	<0.36	–	–	–
225.571	14 _{7,8,0} –13 _{6,8,0}	<0.32	0.64	<0.24	0.84	–	<0.32	0.50	<0.23	<0.23
239.169	19 _{2,17,0} –19 _{0,19,0}	–	<0.49	0.19	–	–	–	<0.38	<0.29	<0.29
241.036	22 _{0,22,0} –21 _{3,18,0}	<0.25	<0.40	<0.30	0.83	–	<0.35	<0.36	<0.42	<0.42
345.084	2 _{2,0,1} –3 _{2,1,0,1}	<0.23	0.26	<0.30	4.1	–	<0.33	<0.29	<0.19	<0.19
348.101	11 _{6,6,0} –10 _{6,5,0}	<0.18	2.0	0.27	10.0	–	0.61	<0.44	0.19	0.19

Table 6.16. *Observed line fluxes $\int T_{\text{MB}} dV$ ($K \text{ km s}^{-1}$) for CH_2CO .*

Frequency [GHz]	Transition	Sources						
		AFGL 2591	G24.78	G75.78	NGC 6334 IRS1	NGC 7538 IRS1	W3(H ₂ O)	W33A
81.586	4 _{1,3} –3 _{1,2}	0.32	–	<0.75	–	0.45	0.16	–
140.127	7 _{1,7} –6 _{1,6}	–	–	–	–	0.72	0.85	–
244.712	12 _{1,11} –11 _{1,10}	<0.39	–	<0.78	–	1.8	1.6	–
262.619	13 _{2,12} –12 _{2,11}	<0.33	–	<0.47	–	<1.7	1.5	–
220.178	11 _{1,11} –10 _{1,10}	<0.19	1.2	0.41	5.0	0.63	0.65	0.37
222.199 ^a	11 _{0,11} –10 _{0,10}	<0.31	1.3	0.38	5.9	0.51	0.87	0.37
222.229	11 _{2,10} –10 _{2,9}	<0.31	0.38	<0.22	2.7	<0.41	0.20	0.11
222.315	11 _{2,9} –10 _{2,8}	<0.31	0.20	<0.22	1.5	<0.41	<0.35	<0.25
240.187	12 _{1,12} –11 _{1,11}	<0.24	1.5	0.50	4.5	0.46	1.4	0.51
346.600	17 _{1,16} –16 _{1,15}	<0.26	1.4	0.52	8.4	0.81	1.4	0.60

– means frequency not observed. ^aBlend of lines 11₀₁₁–10₀₁₀, 11₃₉–10₃₈, and 11₃₈–10₃₇.

Table 6.17. *Observed line fluxes $\int T_{\text{MB}} dV$ ($K \text{ km s}^{-1}$) for CH_3CHO .*

Frequency [GHz]	Transition	Sources								
		AFGL 2591	G24.78	G75.78	NGC 6334	IRS1	NGC 7538	IRS1	W3(H ₂ O)	W33A
98.901	5 _{1,4} –4 _{1,3}	0.29	–	<0.14	–	–	0.22	–	0.38	–
112.249	6 _{1,6} –5 _{1,5}	–	–	–	–	–	0.40	–	0.50	–
149.507	8 _{1,8} –7 _{1,7}	<0.15	–	<0.36	–	–	0.69	–	0.54	–
168.093	9 _{1,9} –8 _{1,8}	<0.21	–	<0.30	–	–	0.30	–	0.48	–

– means frequency not observed.

Table 6.18. *Observed line fluxes $\int T_{\text{MB}} dV$ ($K \text{ km s}^{-1}$) for C_2H_5OH .*

Frequency [GHz]	Transition	Sources						
		AFGL 2591	G24.78	G75.78	NGC 6334 IRS1	NGC 7538 IRS1	W3(H ₂ O)	W33A
220.155	2 ₄₃ ,22,2–2 ₄₂ ,23,2	<0.24	<0.38	<0.36	1.1	0.78	<0.39	<0.24
222.138	19 ₇ ,K,0–18 ₇ ,L,1	<0.39	<0.43	<0.32	1.6	<0.32	<0.27	<0.32
225.279	13 ₅ ,9,1–12 ₅ ,8,1	<0.41	<0.43	<0.24	0.57	<0.26	<0.21	<0.29
225.283	13 ₅ ,8,1–12 ₅ ,7,1	<0.41	<0.43	<0.24	0.9	<0.26	<0.21	<0.29
225.457	13 ₃ ,11,1–12 ₃ ,10,1	<0.41	0.43	<0.24	0.66	<0.26	<0.21	<0.29
225.546	13 ₄ ,10,1–12 ₄ ,9,1	<0.41	<0.43	<0.24	0.56	<0.26	<0.21	<0.29
225.560	13 ₃ ,11,0–12 ₃ ,10,0	<0.41	<0.43	<0.24	1.9	<0.26	<0.21	<0.29
225.660	13 ₄ ,10,0–12 ₄ ,9,0	<0.41	<0.43	<0.24	0.85	<0.26	<0.21	<0.29
226.581	26 ₂ ,24,2–26 ₁ ,25,2	<0.30	<0.48	<0.21	2.6	<0.26	<0.35	<0.30
230.954	16 ₅ ,11,2–16 ₄ ,12,2	<0.32	0.59	<0.21	2.9	<0.29	<0.32	<0.42
230.991	14 ₀ ,14,2–13 ₁ ,13,2	<0.32	0.19	<0.21	2.8	0.34	0.21	<0.42
232.035	18 ₅ ,14,2–18 ₄ ,15,2	<0.30	<0.43	<0.26	0.56	<0.30	–	<0.41
232.319	23 ₅ ,19,2–23 ₄ ,20,2	<0.30	<0.43	<0.26	0.45	<0.30	–	<0.41
232.405	17 ₅ ,13,2–17 ₄ ,14,2	<0.30	<0.43	<0.26	0.95	<0.30	–	<0.41
232.491	14 ₀ ,14,0–13 ₀ ,13,0	<0.30	0.24	<0.26	0.99	<0.30	–	<0.41
232.809	16 ₅ ,12,2–16 ₄ ,13,2	–	–	<0.30	2.0	–	–	–
232.929	14 ₅ ,9,2–14 ₄ ,10,2	–	–	<0.30	0.54	–	–	–
233.571	13 ₅ ,8,2–13 ₄ ,9,2	<0.41	<0.43	<0.24	0.87	<0.25	<0.21	<0.29
234.524	25 ₅ ,21,2–25 ₄ ,22,2	<0.30	<0.48	<0.21	1.6	0.23	<0.35	<0.30
234.666	10 ₅ ,5,2–10 ₄ ,6,2	<0.30	<0.48	<0.21	<0.62	0.24	<0.35	<0.30
234.715	10 ₅ ,6,2–10 ₄ ,7,2	<0.30	<0.48	<0.21	2.0	0.14	<0.35	<0.30
234.853	9 ₅ ,4,2–9 ₄ ,5,2	<0.30	<0.48	<0.21	1.5	<0.25	<0.35	<0.30
234.984	8 ₅ ,3,2–8 ₄ ,4,2	<0.30	<0.48	<0.21	0.84	<0.25	<0.35	<0.30
234.992	8 ₅ ,4,2–8 ₄ ,5,2	<0.30	0.38	<0.21	1.9	<0.25	<0.35	<0.30
240.110	27 ₂ ,25,2–27 ₁ ,26,2	<0.30	<0.36	<0.26	<0.72	<0.30	0.16	<0.41
240.782	15 ₂ ,13,0–14 ₁ ,13,1	<0.32	<0.53	<0.30	1.1	<0.28	<0.45	<0.26
240.839	14 ₁ ,13,0–13 ₁ ,13,1	<0.32	<0.53	<0.30	2.0	<0.28	<0.45	<0.26

– means frequency not observed. K stands for 12/13. L stands for 11/12. *Continued following page.*

Table 6.18. *continued.*

Frequency [GHz]	Transition	Sources								
		AFGL 2591	G24.78	G75.78	NGC 6334	IRS1	NGC 7538	IRS1	W3(H ₂ O)	W33A
338.099	18 _{7,11,2} –18 _{6,12,2}	<0.30	1.7	<0.20	2.8		<0.25		<0.30	0.14
338.110	18 _{7,12,2} –18 _{6,13,2}	<0.30	<0.29	<0.20	2.2		<0.25		<0.30	0.15
338.163	10 _{2,8,1} –9 _{1,8,0}	<0.30	0.37	<0.20	1.1		<0.25		<0.30	<0.29
339.511	9 _{7,3/2,2} –9 _{6,4/3,2}	<0.30	0.64	<0.21	1.3		<0.28		<0.39	<0.21
339.544	8 _{7,2/1,2} –8 _{6,3/2,2}	<0.30	<0.26	<0.21	2.8		0.32		<0.39	<0.21
339.566	7 _{7,0/1,2} –7 _{6,1/2,2}	<0.30	<0.26	<0.21	1.6		<0.28		<0.39	<0.21
339.979	9 _{4,6,2} –8 _{3,5,2}	<0.30	1.2	<0.21	6.1		0.73		<0.39	<0.21
340.189	6 _{5,1/2,2} –5 _{4,2/1,2}	<0.36	3.4	0.68	15		1.6		1.7	1.1
340.420	9 _{4,5,2} –8 _{3,6,2}	<0.36	<0.55	<0.26	4.0		0.38		<0.36	0.78
345.173	7 _{7,0/1,0} –6 _{6,0/1,1}	<0.29	<0.43	<0.30	2.4		<0.26		<0.21	<0.24
345.295	21 _{1,21,1} –20 _{1,20,1}	<0.29	0.55	<0.30	2.5		<0.26		<0.21	<0.24
345.408	21 _{0,21,1} –20 _{0,20,1}	<0.29	0.30	<0.30	5.1		<0.26		0.51	<0.24
346.620	20 _{8,12/13,0} –19 _{8,11/12,0}	<0.26	0.10	<0.36	1.3		0.34		<0.32	<0.23
346.817	20 _{7,13/14,0} –19 _{7,12/13,0}	<0.26	0.82	<0.36	3.9		0.48		0.22	0.28
346.929	20 _{6,15,1} –19 _{6,14,1}	<0.26	0.71	<0.36	1.4		<0.19		<0.32	<0.23
346.963	21 _{0,21,2} –20 _{1,20,2}	<0.26	2.0	<0.36	4.4 ^a		0.80		0.89	<0.23
347.887	20 _{5,15,0} –19 _{5,14,0}	<0.23	0.38	<0.32	2.4		0.23		<0.32	<0.26
347.916	20 _{4,17,0} –19 _{4,16,0}	<0.23	2.1	<0.32	8.1		1.4		0.74	<0.26
347.975	22 _{2,20,2} –21 _{3,19,2}	<0.23	0.57	<0.32	2.7		0.36		<0.32	<0.26
348.720	4 _{4,0/1,1} –3 _{3,0/1,0}	<0.36	0.65	<0.27	<0.36		<0.26		<0.36	<0.26
348.847	10 _{6,5/4,0} –9 _{5,5/4,1}	<0.36	0.97	<0.27	<0.36		<0.26		<0.36	<0.26
352.858	21 _{1,20,2} –20 _{2,19,2}	<0.32	1.2	<0.51	4.9		0.49		<0.29	<0.42
353.035	12 _{3,9,2} –11 _{2,10,2}	<0.32	0.97	<0.51	5.2		0.64		0.58	<0.42
363.968	21 _{7,15/14,1} –20 _{7,14/13,1}	–	0.50	<0.38	–		–		–	–
364.233	21 _{7,15/14,0} –20 _{7,14/13,0}	–	0.57	<0.38	–		–		–	–

^aBlend with C₂H₅CN.

Table 6.19. *Observed line fluxes $\int T_{\text{MB}} dV$ ($K \text{ km s}^{-1}$) for HCOOH .*

Frequency [GHz]	Transition	Sources							
		AFGL 2591	G24.78	G75.78	NGC 6334	IRS1	NGC 7538	IRS1	W3(H ₂ O)
223.916	10 _{2,9} –9 _{1,8}	<0.21	–	<0.17	–	–	0.76	–	0.19
247.514	11 _{5,6/7} –10 _{5,5/6}	–	–	–	–	–	0.66	–	2.4
257.975	12 _{1,12} –11 _{1,11}	<0.38	–	<1.9	–	–	<0.89	–	<0.95
262.103	12 _{0,12} –11 _{0,11}	–	–	–	–	–	<0.36	–	<1.3
220.038	10 _{0,10} –9 _{0,9}	<0.19	<0.29	<0.29	1.3	–	0.37	<0.46	<0.19
225.513	10 _{3,7} –9 _{3,6}	<0.32	0.73	<0.19	2.6	–	<0.25	0.88	0.40
338.144	15 _{4,12} –14 _{4,11}	0.23 ^a	2.1 ^a	<0.16	3.7	–	0.49 ^a	1.2 ^a	0.28
338.202	15 _{3,13} –14 _{3,12}	<0.24	0.53	0.26	3.4	–	0.74	0.97	0.24
338.249	15 _{4,11} –14 _{4,10}	<0.24	1.1	<0.16	3.1	–	0.35	0.72	0.20
345.031	16 _{0,16} –15 _{0,15}	<0.23	<0.32	<0.20	2.3	–	0.51	0.33	<0.19
346.719	15 _{2,13} –14 _{2,12}	0.21	0.49	0.19	2.9	–	0.81	0.36	0.17
356.137	16 _{2,15} –15 _{2,14}	0.65	0.28	0.34	1.8	–	0.83	0.55	<0.54

– means frequency not observed. ^aBlend with C₂H₅CN.

Table 6.20. *Observed line fluxes $\int T_{\text{MB}} dV$ ($K \text{ km s}^{-1}$) for HNC.*

Frequency [GHz]	Transition	Sources										
		AFGL 2591	G24.78	HNCO			NGC 6334	IRS1	NGC 7538	IRS1	W3(H ₂ O)	W33A
219.656	10 _{3,7/8} –9 _{3,6/7}	<0.29	<0.41	<0.31	1.2		<0.25		<0.47		<0.41	
219.734	10 _{2,9} –9 _{2,8}	<0.29	0.59	0.77	3.2		0.72		0.90		0.78	
219.737	10 _{2,8} –9 _{2,7}	<0.29	1.1	<i>a</i>	<i>a</i>		<i>a</i>		<i>a</i>		<i>a</i>	
219.798	10 _{0,10} –9 _{0,9}	0.88	4.4	1.7	8.4		0.65		1.4		3.0	
240.876	11 _{1,11} –10 _{1,10}	<0.25	2.7	1.3	4.3		0.55		0.99		1.4	
352.898	16 _{1,15} –15 _{1,14}	0.89	3.3	2.0	7.7		1.5		2.0		2.1	
HN ¹³ CO												
219.803	10 _{2,9} –9 _{2,8}	<0.36	<0.41	<0.26	<0.98		<0.32		<0.39		<0.41	
240.881	11 _{1,11} –10 _{1,10}	<0.25	<0.46	<0.36	<0.41		<0.28		<0.54		<0.26	

– means frequency not observed. ^aBlend with HNC line at 219734 MHz.

Table 6.21. *Observed line fluxes $\int T_{\text{MB}} dV$ ($K \text{ km s}^{-1}$) for NH_2CHO .*

Frequency [GHz]	Transition	Sources						
		AFGL 2591	G24.78	G75.78	NGC 6334 IRS1	NGC 7538 IRS1	W3(H ₂ O)	W33A
227.606	11 _{0,11} –10 _{0,10}	–	0.90	<0.20	–	0.32	<0.39	–
232.274	11 _{2,10} –10 _{2,9}	<0.5	<0.27	0.15	2.2	0.56	–	<0.60
233.529	11 _{6,5/6} –10 _{6,4/5}	<0.15	<0.32	<0.19	0.73	0.56	<0.21	<0.42
233.595	11 _{5,6/7} –10 _{5,5/6}	<0.15	0.64	<0.19	^b	0.93	1.4	0.56
233.736	11 _{4,8} –10 _{4,7}	<0.15	0.56	<0.19	1.3	0.23	<0.21	0.30
339.716	16 _{8,8/9} –15 _{8,7/8}	<0.3	1.3	<0.17	3.8	1.2	0.22	<0.34
339.780	16 _{7,9/10} –15 _{7,8/9}	<0.3	0.93	<0.17	2.2	0.95	<0.39	<0.34
339.904	16 _{6,10/11} –15 _{6,9/10}	<0.3	1.2	<0.17	4.1	0.81	<0.39	<0.34
340.491	16 _{3,14} –15 _{3,13}	<0.36	1.3	0.18	3.0	0.70	0.45	0.75
340.536	16 _{4,13} –15 _{4,12}	<0.36	0.55	0.31	2.3	0.49	<0.36	<0.36
345.183	17 _{0,17} –16 _{0,16}	<0.29	1.2	<0.24	2.1	0.66	0.44	0.34
345.327	16 _{1,15} –15 _{1,14}	<0.29	<0.32	<0.24	3.8	2.2	<0.21	<0.38

– means frequency not observed. ^aBlend with C₂H₅OH. ^bBlend with C₂H₅OH at 225-404 MHz in other sideband.

Table 6.22. Observed line fluxes $\int T_{\text{MB}} dV$ ($K \text{ km s}^{-1}$) for CH_3CN .

Frequency [GHz]	Transition	Sources							
		AFGL 2591	G24.78	G75.78	NGC 6334	IRS1	NGC 7538	IRS1	W3(H ₂ O)
CH ₃ CN									
220.476	12 _{8,0,K} –11 _{8,0,L}	<0.24	0.45	<0.43	1.0		<0.54	<0.53	<0.24
238.913	13 _{7,0,K} –12 _{7,0,L}	–	1.4	<0.25	–		–	<0.50	0.38
238.972	13 _{6,0,K} –12 _{6,0,K}	–	2.8	0.47	–		–	1.8	0.73
239.064	13 _{4,0,K} –12 _{4,0,L}	–	3.8	0.83	–		–	1.9	0.97
239.097	13 _{3,0,K} –12 _{3,0,L}	–	5.9	1.2	–		–	3.8	1.5
239.120	13 _{2,0,K} –12 _{2,0,L}	–	5.0	1.1	–		–	3.4	1.5
239.133	13 _{1,0,K} –12 _{0/1,0,L}	–	5.7	1.8	–		–	8.1	1.4
239.138	13 _{0,0,K} –12 _{0,0,L}	–	5.2	0.98	–		–	<0.50	0.69
240.090	13 _{1,2,K} –12 _{1,2,L}	<0.3	0.94	<0.31	3.0		<i>a</i>	0.29	<0.32
348.645	19 _{11,0,K} –18 _{11,0,L}	<0.36	<0.36	<0.43	0.64		<0.59	<0.58	<0.24
CH ₃ ¹³ CN									
220.485	12 _{6,0,K} –11 _{6,0,L}	<0.24	0.30	<0.43	0.35		<0.54	<0.53	<0.24
238.905	13 _{5,0,K} –12 _{5,0,L}	–	0.17	<0.25	–		–	<0.50	<0.34
238.946	13 _{4,0,K} –12 _{4,0,L}	–	0.57	<0.25	–		–	<0.50	<0.34
238.978	13 _{3,0,K} –12 _{3,0,L}	–	1.06	<0.25	–		–	<0.50	0.38
239.001	13 _{2,0,K} –12 _{2,0,L}	–	0.73	<0.25	–		–	<0.50	<0.34
348.853	19 _{8,0,K} –18 _{8,0,L}	<0.36	0.36	<0.43	<0.36		<0.59	<0.58	<0.24

— means frequency not observed. K refers to main transition of the upper level i.e. 12, 13, or 19 +1, +0, or -1. L refers to the main transition of the lower level i.e. 11, 12, or 18 +1, +0, or -1. ^aBlend with CH_3OH .

Table 6.23. *Observed line fluxes $\int T_{\text{MB}} dV$ ($K \text{ km s}^{-1}$) for C_2H_5CN .*

Frequency [GHz]	Transition	Sources								
		AFGL 2591	G24.78	G75.78	NGC 6334	IRS1	NGC 7538	IRS1	W3(H ₂ O)	W33A
218.390	2 _{4,21} –2 _{3,20}	–	0.71	<0.41	–	–	–	–	<0.39	<0.41
219.506	2 _{4,22} –2 _{3,21}	<0.36	0.85	<0.26	2.2	–	<0.32	<0.39	–	–
222.918	2 _{5,1,24} –2 _{4,1,23}	<0.32	–	–	3.4	–	<0.36	–	–	–
223.385	2 _{6,1,26} –2 _{5,1,25}	<0.32	–	–	1.9	–	<0.36	–	–	–
227.781	2 _{5,3,22} –2 _{4,3,21}	–	1.8	<0.26	–	–	<0.32	<0.39	–	–
228.483	2 _{5,2,23} –2 _{4,2,22}	<0.24	1.4	<0.36	2.4	–	<0.30	<0.33	<0.24	<0.24
231.310	2 _{6,1,25} –2 _{5,1,24}	<0.32	0.79	<0.21	2.5	–	<0.36	0.61	<0.42	<0.42
233.443	2 _{6,5,22} –2 _{5,5,21}	<0.15	1.2	<0.24	1.0	–	<0.41	0.94	<0.29	<0.29
233.498	2 _{6,5,21} –2 _{5,5,20}	<0.15	1.5	<0.24	1.9 ^a	–	<0.41	0.63	<0.29	<0.29
240.319	2 _{8,1,28} –2 _{7,1,27}	<0.30	1.4	<0.26	3.2	–	<0.38	0.66	<0.41	<0.41
240.429	2 _{8,0,28} –2 _{7,0,27}	<0.30	1.1	<0.26	<0.58	–	<0.38	<0.47	<0.41	<0.41
248.781	2 _{9,1,29} –2 _{8,1,28}	<0.32	1.1	<0.30	–	–	<0.35	0.60	<0.26	<0.26
248.869	2 _{9,0,29} –2 _{8,0,28}	<0.32	1.2	<0.30	–	–	<0.35	1.1	<0.26	<0.26

– means frequency not observed. ^aBlend with NH₂CHO. *Continued following page.*

Table 6.23. *continued.*

Frequency [GHz]	Transition	Sources								
		AFGL 2591	G24.78	G75.78	NGC 6334	IRS1	NGC 7538	IRS1	W3(H ₂ O)	W33A
339.895	39 _{2,38} –38 _{2,37}	<0.30	1.2	<0.21	2.8		<0.36		<0.39	<0.21
339.968	38 _{2,36} –37 _{2,35}	<0.30	1.4	<0.21	2.9		<0.36		<0.39	<0.21
340.149	39 _{1,38} –38 _{1,37}	<0.36	1.0	<0.26	<0.62		<0.41		<0.36	<0.23
340.433	38 _{12,26/27} –37 _{12,25/26}	<0.36	0.63	<0.26	1.1		<0.41		<0.36	<0.23
340.483	38 _{10,28/29} –37 _{10,27/28}	<0.36	0.83	<0.26	1.4		<0.41		<0.36	<0.23
340.551	38 _{15,23/24} –37 _{15,22/23}	<0.36	<0.35	<0.26	0.63		<0.41		<0.36	<0.23
340.576	38 _{9,29/30} –37 _{9,28/29}	<0.36	0.85	<0.26	<0.62		<0.41		<0.36	<0.23
346.712	25 _{8,17/18} –25 _{7,18/19}	<0.26	<0.47	<0.36	1.9		<0.24		<0.32	<0.23
346.864	22 _{8,14/15} –22 _{7,15/16}	<0.26	<0.47	<0.36	0.96		<0.24		<0.32	<0.23
346.874	38 _{4,34} –37 _{4,33}	<0.26	0.82	<0.36	2.4		<0.24		<0.32	<0.23
346.898	21 _{8,13/14} –21 _{7,14/15}	<0.26	0.49	<0.36	1.8		<0.24		<0.32	<0.23
346.925	20 _{8,12/13} –20 _{7,13/14}	<0.26	<0.47	<0.36	0.93		<0.24		<0.32	<0.23
348.261	39 _{2,37} –38 _{2,36}	<0.23	1.8	<0.21	3.6		<0.27		<0.32	<0.26
348.345	40 _{1,39} –39 _{1,38}	<0.23	1.2	<0.21	3.5		<0.27		<0.32	<0.26
353.089	23 _{3,20} –22 _{2,21}	<0.32	0.27	<0.51	0.58		<0.30		<0.29	<0.42
353.235	11 _{6,5/6} –10 _{5,6/5}	<0.32	<0.23	<0.51	2.9		<0.30		<0.29	<0.42

Table 6.24. *Observed line fluxes $\int T_{\text{MB}} dV$ ($K \text{ km s}^{-1}$) for CH_3CCH .*

Frequency [GHz]	Transition	Sources							
		AFGL 2591	G24.78	G75.78	NGC 6334 IRS1	NGC 7538 IRS1	W3(H ₂ O)	W33A	
222.014	13 ₆ –12 ₆	<0.23	<0.27	<0.25	0.51	<0.41	<0.27	<0.25	
222.061	13 ₅ –12 ₅	<0.23	0.18	<0.25	<0.59		<0.27	<0.25	
222.099	13 ₄ –12 ₄	<0.23	0.44	<0.25	1.2	0.19	0.49	<0.25	
222.129	13 ₃ –12 ₃	0.63	2.5	0.54	7.6	0.92	2.0	0.58	
222.150	13 ₂ –12 ₂	0.87	2.2	0.81	7.2	1.2	2.1	0.89	
222.163	13 ₁ –12 ₁	1.2	4.3	1.0	8.1	1.7	1.7	1.9	
222.167	13 ₀ –12 ₀	1.5	3.4	1.5	8.1	1.2	3.2	2.0	
239.088	14 ₆ –13 ₆	–	0.46	<0.17	–	–	<0.32	<0.34	
239.138 ^a	14 ₅ –13 ₅	–	0.69	0.98	–	–	<0.32	<0.34	
239.179	14 ₄ –13 ₄	–	0.62	<0.17	–	–	0.70	<0.34	
239.211	14 ₃ –13 ₃	–	2.6	1.4	–	–	1.9	0.86	
239.234	14 ₂ –13 ₂	–	3.2	1.4	–	–	8.0 ^b	1.3	
239.248	14 ₁ –13 ₁	–	4.0	1.6	–	–	1.5	1.9	
239.252	14 ₀ –13 ₀	–	4.4	2.1	–	–	3.4	2.0	

– means frequency not observed. ^aBlend with CH₃CN. ^bBlend with OCS at 231062 MHz in the main sideband.

Table 6.25. Observed line fluxes $\int T_{\text{MB}} dV$ (K km s^{-1}) for HCOOCH_3 for the 230 GHz band.

Frequency [GHz]	Transition	Sources									
		AFGL 2591	G24.78	G75.78	NGC 6334 IRS1	NGC 7538 IRS1	W3(H ₂ O)	W33A			
211.537	17 _{6,11} –16 _{6,10} E	<0.36	–	–	8.6	–	–	<0.14			
211.575	17 _{6,11} –16 _{6,10} A	<0.36	–	–	6.3	–	–	0.19			
211.771	17 _{5,13} –16 _{5,12} E	<0.36	–	–	6.2	–	–	<0.14			
211.785	17 _{5,13} –16 _{5,12} A	<0.36	–	–	6.2	–	–	<0.14			
218.281	17 _{1,16} –16 _{1,15} E	–	0.48	<0.41	–	–	–	–			
218.297	17 _{3,14} –16 _{3,13} A	–	0.46	<0.41	–	–	–	–			
220.167	17 _{2,15} –16 _{4,12} E	<0.24	0.82	<0.36	7.1	0.42	0.98	<0.24			
220.190	17 _{4,13} –16 _{4,12} A	<0.24	0.67	<0.36	6.4	0.66	<0.33	<0.24			
221.979	18 _{9,9/10} –17 _{9,8/9} A	<0.39	0.71	<0.32	5.7	0.84	1.1	<0.32			
223.125	18 _{7,11} –17 _{7,10} E	<0.32	–	–	7.2	0.30	–	–			
223.135	18 _{7,12} –17 _{7,11}	<0.32	–	–	8.9	<0.43	–	–			
223.163	18 _{7,11} –17 _{7,10} A	<0.32	–	–	<1.3	0.14	–	–			
225.609	19 _{3,16} –18 _{3,15} E	<0.41	<0.27	<0.24	4.9	<0.32	1.2	0.39			
225.619	19 _{3,17} –18 _{3,16} A	<0.41	1.0	<0.24	5.7	<0.32	1.9	0.18			
226.713	20 _{2,18} –19 _{2,18} E	<0.30	0.65	<0.21	9.1	0.56	0.60	<0.30			
226.719	20 _{2,19} –19 _{2,18} A	<0.30	1.3	<0.21	14	0.66	0.73	0.52			
226.773	20 _{3,18} –19 _{3,17} E	<0.30	<0.30	<0.21	<1.4	0.44	<0.35	<0.30			
226.779	20 _{1,19} –19 _{1,18} A	<0.30	<0.30	<0.21	<1.4	0.53	<0.35	<0.30			
227.561	21 _{1,21} –20 _{1,20} E ^a	–	5.3	0.73	–	1.4	6.1	0.34			
233.247	19 _{16,3/4} –18 _{16,2/3} A	<0.41	<0.27	<0.24	1.5	<0.32	<0.21	<0.29			
233.256	19 _{16,3} –18 _{16,2} E	<0.41	<0.27	<0.24	3.0	<0.32	<0.21	<0.29			

– means frequency not observed. ^aBlend with 21_{2,20}–20_{2,19} E, 21_{1,21}–20_{1,20} A, and 21_{0,21}–20_{0,20} A. Continued following page.

Table 6.26. *continued.*

Frequency [GHz]	Transition	Sources							
		AFGL 2591	G24.78	G75.78	NGC 6334	IRS1	NGC 7538	IRS1	W3(H ₂ O)
233.269	19 _{16,4} –18 _{16,3} E	<0.41	<0.27	<0.24	1.3		<0.32		<0.21
233.310	19 _{15,4/5} –18 _{15,3/4} A	<0.41	<0.27	<0.24	3.1		<0.32		<0.21
233.316	19 _{15,4} –18 _{15,3} E	<0.41	<0.27	<0.24	2.0		<0.32		<0.21
233.331	19 _{15,5} –18 _{15,4} E	<0.41	<0.27	<0.24	2.3		<0.32		<0.21
233.395	19 _{14,5/6} –18 _{14,4/5} A ^b	<0.41	<0.27	<0.24	4.0		<0.32		<0.21
233.414	19 _{14,6} –18 _{14,5} E	<0.41	<0.27	<0.24	2.1		<0.32		<0.21
233.505	19 _{13,6} –18 _{13,5} E ^c	<0.41	1.4	<0.24	6.1		<0.32		1.6
233.525	19 _{13,7} –18 _{13,6} E	<0.41	0.72	<0.24	2.8		<0.32		<0.21
233.649	19 _{12,7} –18 _{12,6} E	<0.41	0.22	<0.24	<0.74		<0.32		<0.21
233.655	19 _{12,7/8} –18 _{12,6/7} A	<0.41	1.5 ^d	<0.24	4.4		<0.32		<0.21
233.671	19 _{12,8} –18 _{12,7} E	<0.41	0.18	<0.24	2.3		<0.32		0.17
233.754	18 _{2,16} –17 _{2,15} E	<0.41	1.1	<0.24	7.5		<0.32		<0.21
234.502	19 _{9,10/11} –18 _{9,9/10} A	<0.30	0.94	<0.21	7.3		0.41		<0.35
240.021	19 _{1,18} –18 _{1,17} E	<0.30	1.1	<0.26	6.8		0.72		<0.42
240.035	19 _{3,16} –18 _{3,15} A	<0.30	1.1	<0.26	7.0		0.68		1.1
248.617	20 _{7,14} –19 _{7,13} A	<0.32	0.69	<0.30	–		<0.35		0.91
248.634	20 _{7,14} –19 _{7,13} E	<0.32	0.94	<0.30	–		<0.35		0.96
248.744	20 _{7,13} –19 _{7,12} E	<0.32	<0.33	<0.30	–		0.69		<0.45
248.750	23 _{2,22} –22 _{1,22} E ^e	<0.32	3.8	<0.30	–		1.3		2.0
248.787	20 _{7,13} –19 _{7,12} A	<0.32	<0.33	<0.30	–		0.24		<0.45
249.031	20 _{5,16} –19 _{5,15} E	<0.32	0.51	<0.30	–		<0.35		0.33
249.047	20 _{5,16} –19 _{5,15} A	<0.32	0.77	<0.30	–		<0.35		0.59

^b Blend with line at 233397 19_{14,5}–18_{14,4} E. ^c Blend with 19_{13,6}–18_{13,5} A, and 19_{13,7}–18_{13,6} A. ^d Blend with C₂H₅CN. ^e Blend with 23_{1,23}–22_{1,22} E, 23_{2,22}–22_{2,21} E, 23_{1,23}–22_{2,21} E.

Table 6.27. Observed line fluxes $\int T_{\text{MB}} dV$ ($K \text{ km s}^{-1}$) for HCOOCH_3 in the 345 GHz band.

Frequency [GHz]	Transition	Sources								
		AFGL 2591	G24.78	G75.78	NGC 6334	IRSI	NGC 7538	IRSI	W3(H ₂ O)	W33A
338.356	27 _{8,19} –26 _{8,18} E	<0.30	<0.30	<0.20	8.8		0.23		1.6	<0.29
338.397	27 _{7,21} –26 _{7,20} E	<0.30	<0.30	0.13	11		0.85		<0.30	<0.29
340.221	31 _{13,19} –31 _{12,19} E ^a	<0.36	<0.35	<0.26	2.7		<0.41		<0.36	<0.23
345.069	28 _{14,14} –27 _{14,13} E ^b	<0.29	1.7	<0.30	14		<0.33		1.5	<0.24
345.090	28 _{14,15} –27 _{14,14} E	<0.29	0.69	<0.30	8.2		<0.33		0.78	<0.24
345.281	18 _{13,5/6} –18 _{12,6/7} A	<0.29	<0.27	<0.30	3.5		<0.33		<0.21	<0.24
345.462	28 _{13,15} –27 _{13,14} E	<0.29	<0.27	<0.30	4.8		<0.33		<0.21	<0.24
345.467	28 _{13,15/16} –27 _{13,14/15} A	<0.29	1.1	<0.30	8.9		<0.33		0.32	<0.24
345.486	28 _{13,16} –27 _{13,15} E	<0.29	0.16	<0.30	5.7		<0.33		<0.21	<0.24
345.975	28 _{12,16} –27 _{12,15} E	–	–	–	–		0.68		<0.29	–
345.985	28 _{12,16/17} –27 _{12,15/16} A	–	–	–	–		0.78		2.0	–
346.001	28 _{12,17} –27 _{12,16} E	–	–	–	–		0.39		0.64	–
346.660	28 _{11,17} –27 _{11,16} E	<0.26	<0.47	<0.36	7.5		0.67		<0.32	<0.23
346.675	28 _{11,17/18} –27 _{11,16/17} A	<0.26	1.1	<0.36	11		0.67		<0.32	<0.23
346.687	28 _{11,18} –27 _{11,17} E	<0.26	0.27	<0.36	6.7		0.31		<0.32	<0.23
348.050	28 _{4,24} –27 _{4,23} E	<0.23	1.8	0.11	12		0.73		1.5	<0.26
348.066	28 _{6,23} –27 _{6,22} A	<0.23	1.6	<0.32	11		0.60		1.3	<0.26
348.909	28 _{9,20} –27 _{9,19} E	<0.23	1.2	<0.32	<0.43		<0.33		<0.36	<0.30
348.915	28 _{9,20} –27 _{9,19} A	<0.23	1.5	<0.32	7.7		<0.33		<0.36	<0.30
356.215	29 _{21,8/9} –28 _{21,7/8} A	<0.36	<0.47	<0.53	2.6		<0.41		<0.36	<0.68
356.297	29 _{20,9/10} –28 _{20,8/9} A	<0.36	0.49	<0.53	6.3		0.30		<0.36	<0.68
356.404	29 _{19,10/11} –28 _{19,9/10} A	<0.36	<0.47	<0.53	4.2		<0.41		<0.36	<0.68

– means frequency not observed. ^aBlend with 31_{13,18}–31_{12,19} A, and 31_{13,19}–31_{12,20} A. ^bBlend with 28_{14,14}–27_{14,13} A, and 28_{14,15}–27_{14,14} A.

Table 6.28. Observed line fluxes $\int T_{mb} dV$ ($K \text{ km s}^{-1}$) for CH_3OCH_3 .

Frequency [GHz]	Transition	Sources							
		AFGL 2591	G24.78	G75.78	NGC 6334	IRS1	NGC 7538	IRS1	W3(H ₂ O)
222.029	$21_{2,20,2/3} - 21_{1,21,2/3}$	<0.39	0.26	<0.32	3.1	<0.41		0.42	<0.25
222.035	$21_{2,20,0/1} - 21_{1,21,0/1}$	<0.39	0.72	<0.32	2.5	<0.41		0.37	<0.25
222.239	$4_{3,2,2} - 3_{2,1,2}$	<0.39	0.16	<0.32	1.6	<0.41		<0.27	<0.25
222.248	$4_{3,2,1/3} - 3_{2,1,1/3}$	<0.39	0.86	<0.32	5.3	<0.41		0.37	0.37
222.255	$4_{3,2,0} - 3_{2,1,0}$	<0.39	0.53	<0.32	4.7	<0.41		0.50	0.18
222.259	$4_{3,1,1/2} - 3_{2,1,1/2}$	<0.39	0.60	<0.32	2.6	<0.41		0.48	0.18
222.326	$25_{3,23,K} - 24_{4,20,0}$	<0.39	0.15	<0.32	2.3	<0.41		<0.27	<0.25
225.599	$12_{1,12,K} - 11_{0,11,K}$	<0.41	3.1	0.73	11.8	0.83		4.0	1.0
226.347	$14_{1,13,K} - 13_{2,12,K}$	—	1.5	<0.41	—	—		—	—
227.648	$26_{5,21,K} - 26_{4,22,K}$	—	0.40	<0.26	—	<0.32		<0.39	—
227.658	$24_{3,22,0/1} - 24_{2,23,0/1}$	—	0.81	<0.26	—	<0.32		<0.39	—
230.140	$17_{2,15,K} - 16_{3,14,K}$	<0.39	1.7	<0.32	3.3	<0.41		1.4	<0.25
233.633	$25_{5,20,K} - 25_{4,21,K}$	<0.15	1.1	<0.24	2.6	<0.32		0.46	<0.23
240.978	$5_{3,3,2} - 4_{2,2,2}$	<0.32	^a	<0.30	2.6	<0.35		<0.45	<0.26
240.985	$5_{3,3,1} - 4_{2,2,1}$	<0.32	3.4 ^a	<0.30	8.3	0.41		2.8	0.56
240.990	$5_{3,3,0} - 4_{2,2,0}$	<0.32	^a	<0.30	3.3	<0.35		<0.45	0.19

— means frequency not observed. K is either 0,1,2, or 3. ^a $5_{3,3,1} - 4_{2,2,1}$ transition is blended with $5_{3,3,2} - 4_{2,2,2}$ and $5_{3,3,0} - 4_{2,2,0}$.

Chapter 7

An interferometric study of IRAS 16293-2422: small scale organic chemistry

Abstract

Aims: To investigate the chemical relations between complex organics based on their spatial distributions and excitation conditions in the proto-binary source IRAS 16293-2422 “A” and “B”.

Methods: Interferometric observations with the SubMillimeter Array have been performed for emission lines of HNCO, CH₃CN, CH₂CO, CH₃CHO and C₂H₅OH. Rotation temperatures are determined from rotation diagrams when a sufficient number of lines are detected.

Results: Compact emission is detected for all species studied here. For HNCO and CH₃CN it mostly arises from source “A”, CH₂CO and C₂H₅OH have comparable strength for both sources and CH₃CHO arises exclusively from source “B”. The (u, v) -visibility data show that HNCO has extended emission as well. The compact emission of HNCO, CH₃CN and CH₃CHO has rotation temperatures >200 K. The rotation temperatures for HNCO and CH₃CN are the same within the uncertainties in sources A and B. The CH₃CN and HNCO abundances with respect to CH₃OH are similar to that in high-mass Young Stellar Objects (YSOs) except in Sgr B2(N). For CH₂CO and C₂H₅OH no rotation temperatures can be determined because only one line is detected for each species. The abundances for CH₂CO with respect to CH₃OH are very similar between the two IRAS 16293-2422 sources as well as to those of high-mass sources, whereas the limit on that for CH₃CHO toward source A is one order of magnitude lower than for the detection toward source B. Due to line blending the abundances of C₂H₅OH with respect to CH₃OH are difficult to determine, but the estimate for source B is similar to that found for a large sample of high-mass sources.

Conclusions: The excitation of CH₃CN and HNCO suggests that their emission arises from the same region for both sources. Higher abundances toward A relative to CH₃OH may be due to higher initial NH₃ or OCN[−] ice abundances in source A compared to B. The different spatial behavior for CH₂CO, CH₃CHO and C₂H₅OH suggests that successive hydrogenation reactions on grain-surfaces are not sufficient to explain the observed gas phase abundances. Selective destruction of CH₃CHO may result in the anti-coincidence of these species in source A. These results illustrate the limitations of single dish data to test chemical scenarios.

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7.1 Introduction

The envelopes of low-mass protostars contain many organic molecules (Blake et al. 1994; van Dishoeck et al. 1995). These objects are deeply embedded, and therefore well-suited for studies at submillimeter wavelengths. The recent detection of even more complex organics¹ in these objects (Cazaux et al. 2003; Bottinelli et al. 2004b,a, 2007; Jørgensen et al. 2005b,a; Sakai et al. 2006, 2007) suggests that the chemistry is similar to that of hot molecular cores in high-mass star forming regions. This leads to the conclusion that these are low-mass versions of “hot cores”, chemically very rich regions in high-mass star forming regions that are thought to have their origin in grain-mantle evaporation and the subsequent rapid gas phase reactions. The low-mass counterpart is called *hot corino*. The presence of warm material has long been suggested from modeling of the SEDs of these sources (e.g., Adams et al. 1987; Jørgensen et al. 2002; Shirley et al. 2002) and has now been firmly established by direct imaging (see e.g. Chandler et al. 2005; Bottinelli et al. 2004b; Jørgensen et al. 2005c). However, in some sources the emission peaks offset from the continuum source (e.g. Chandler et al. 2005). This is in disagreement with the *hot corino* hypothesis in which complex molecules evaporate through passive heating and is more in favor of other explanations such as the presence of disks or outflows that create shocks in the envelope. The aim of this work is to map the emission of complex organics to determine their most likely formation mechanism.

One method to study chemical links between species is through single-dish surveys in a large number of sources and search for *abundance* correlations (Bischoff et al. 2007c). The alternative method is to look for *spatial* correlations by interferometric observations of a single source through which it is possible to distinguish compact and extended emission as well as the exact location of the compact emission. The combination of high spectral and spatial resolution can also be used to distinguish between shock chemistry and passively heated *hot corinos*. The species that are studied here are the nitrogen-bearing species: HNC and CH₃CN and the oxygen-bearing species: CH₂CO, CH₃CHO, and C₂H₅OH. The reason these species are picked is that HNC is thought to be produced through grain-surface chemistry whereas CH₃CN is produced through gas phase reactions after evaporation (Charnley et al. 1992). The molecules CH₂CO, CH₃CHO and C₂H₅OH are proposed to be linked by successive hydrogenation (Tielens & Charnley 1997).

The source studied in this chapter, IRAS 16293-2422, is one of the best-studied low-mass star forming regions, because it is the chemically richest deeply embedded low-mass protostar known to date. It consists of at least two different sources named A and B separated by 5'' (Mundy et al. 1992). From single dish observations and modeling van Dishoeck et al. (1995) and Ceccarelli et al. (1999, 2000) concluded emission from several organic molecules arises from a compact region. The data for some species, assuming a spherical circum-binary envelope, are significantly better fitted if a “jump” in the abundance is assumed for e.g.,

¹ In this chapter molecules are considered large and complex if they contain more than four atoms.

H_2CO and CH_3CN , at 80–90 K due to grain-mantle evaporation (Ceccarelli et al. 2000; Schöier et al. 2002). Through interferometric observations it is possible to distinguish between the emission from the cold extended envelope and more compact emission as well as the peak location: is the emission coming from source A or B? Previous observations have shown that some complex species are much more abundant toward one source than the other, such as CH_3OCHO which is more prominent toward the A source (Bottinelli et al. 2004b; Huang et al. 2005; Kuan et al. 2004; Remijan & Hollis 2006).

The nitrogen-bearing species HNCO and CH_3CN have previously been detected toward IRAS 16293-2422 through single dish observations (van Dishoeck et al. 1995; Cazaux et al. 2003). In general they show high rotation temperatures implying that they are present in hot gas, as is the oxygen-bearing molecule $\text{C}_2\text{H}_5\text{OH}$ (Cazaux et al. 2003; Bisschop et al. 2007c; Requena-Torres et al. 2006). In contrast, previous observational studies of CH_2CO and CH_3CHO in high-mass sources have shown that they are often detected in colder regions with low rotation temperatures (Ikeda et al. 2002; Bisschop et al. 2007c). Recent experiments by Bisschop et al. (2007b) have shown that it is possible to explain the gas phase abundances of $\text{C}_2\text{H}_5\text{OH}$ if a solid state formation route through CH_3CHO hydrogenation is assumed. The observed absence of CH_3CHO in hot gas combined with its detection in cold ices (Keane 2001; Gibb et al. 2004), however, implies that it must be destroyed at higher ice temperatures, before evaporation commences or in the gas phase directly after evaporation. A comparison of the excitation properties as well as interferometric observations in which the spatial distribution of the species can be determined are good tools to further elucidate the chemical relations between these species.

This chapter is structured as follows: § 7.2 presents the SubMillimeter Array (SMA) observing strategy as well as maps and spectra; § 7.3 explains the analysis of the interferometric observations in the (u, v) plane and the fitting of rotation diagrams; § 7.4 presents the results of the rotation diagram and flux analysis; § 7.5 discusses the relative abundances of the different species with respect to each other as well as the implications for the chemistry; § 7.6 summarizes the main conclusions.

7.2 Observations

7.2.1 Observing strategy

The line rich low-mass protostar, IRAS 16293-2422, is surveyed using the Sub-Millimeter Array² (SMA) in a large number of frequency settings from 2004 to 2005. In this paper we focus on just the emission from a few lines for HNCO , CH_3CN , $\text{C}_2\text{H}_5\text{OH}$, CH_2CO and CH_3CHO (see Tables 7.1 and 7.2). Other papers presenting data from this survey are Takakuwa et al. (2007) and Yeh et al. (2007).

² The SubMillimeter Array is a joint project between the Smithsonian Astrophysical Observatory and the Academia Sinica Institute of Astronomy and Astrophysics and is funded by the Smithsonian Institution and Academia Sinica.

The data shown here were all covered in one spectral setup at 219.4–221.3 GHz (LSB) and 229.4–231.3 GHz (USB) on the 18th of February 2005 with 6 antennas in the compact configuration of the array, resulting in 15 baselines from 10–70 m. This frequency setup was chosen to complement a large SMA survey of Class 0 sources (Jørgensen et al. 2007) and includes, e.g., the strong CO isotopic species and a large number of lines from organic molecules (see Tables 7.1 and 7.2). The data were taken as part of dual receiver observations simultaneously with high frequency 690 GHz data (T. Bourke et al., in prep.). The weather was optimal for the 690 GHz observations with $\tau_{225\text{ GHz}}$ better than 0.03. The excellent weather conditions and the dual receiver option naturally provides a possibility for very high quality observations at the lower frequencies. At the time of observations 6 antennae were in the array. The phase center for the observations, $(\alpha, \delta)_{\text{J2000}} = (16:32:22.9, -24:28:35.5)$, is located about $1''$ to the north from the “A” component of the IRAS 16293-2422 binary. The synthesized beam was $5.5'' \times 3.2''$. The SMA correlator was set up with uniform coverage of the 2 GHz bandwidth with 128 channels for each of the 24 chunks, corresponding to a spectral resolution of 1.1 km s^{-1} . The RMS was $60\text{ mJy beam}^{-1}\text{ channel}^{-1}$ for the 220 GHz data.

The initial data reduction was performed using the MIR package (Qi 2006). The complex gains were calibrated by frequent observations of the quasar J1743-038 (3.0 Jy) offset by 27 degrees from IRAS 16293-2422. Flux and band-pass calibration was performed by observations of Uranus. Continuum subtracted line maps and further analysis was subsequently made using the Miriad package.

7.2.2 Maps and spectra

Figure 7.1 displays the maps and spectra of the species studied in this chapter toward the A and B components of IRAS 16293-2422. The line identifications are based on comparison with the JPL³, CMDS⁴ and NIST⁵ catalogs. The assignments are assumed to be secure when no other species emits close to the observed frequency. Note that for CH_3CHO the frequencies from the NIST catalog have been used, because the data in the JPL catalog are based on extrapolations of the line positions from lower frequencies. These are shifted by a few MHz from the actual measured line positions in the laboratory by Kleiner et al. (1996).

From Figure 7.1 it is clear that significant physical differences exist between the regions where the emission from these two sources arises. As previously noted by Bottinelli et al. (2004b) and Kuan et al. (2004) the spectra toward A show broad lines with a FWHM of 8 km s^{-1} , whereas the lines toward B are much narrower, typically less than 2 km s^{-1} wide (~ 2 channels). The high excitation lines of the complex organics peak at $V_{\text{LSR}} = 1.5\text{--}2.5\text{ km s}^{-1}$ toward both sources. This is in contrast to the systemic velocities of the larger scale envelope, e.g., traced by HCN, at $3\text{--}4.5\text{ km s}^{-1}$ (Takakuwa et al. 2007). The

³ <http://spec.jpl.nasa.gov/ftp/pub/catalog/catform.html>

⁴ <http://www.ph1.uni-koeln.de/vorhersagen/>

⁵ <http://physics.nist.gov/cgi-bin/micro/table5/start.pl>

Table 7.1. *Line parameters and fluxes from detected HNC and CH₃CN transitions for the A and B components.*

Molecule	Freq. (GHz)	Transition	E_u (K)	$\mu^2 S$ (D ²)	$F\Delta V$ (Jy km s ⁻¹)	
					A	B
HNC	219.657	10 _{3,7/8} -9 _{3,6/7}	447	139.2	4.9	0.54
	219.733	10 _{2,9} -9 _{2,8}	231	73.8	10.5 ^a	0.37
	219.737	10 _{2,8} -9 _{2,7}	231	73.8	10.5 ^a	0.30
	219.798	10 _{0,10} -9 _{0,9}	58	77.0	10.9	1.37
	220.584	10 _{1,9} -9 _{1,8}	102	76.2	9.6	1.19
CH ₃ CN	220.476	12 ₈ -11 ₈	526	608.6	2.4	0.45
	220.539	12 ₇ -11 ₇	419	722.8	3.1	0.44
	220.594	12 ₆ -11 ₆	326	1643.3	- ^b	1.56
	220.641	12 ₅ -11 ₅	247	905.3	- ^c	1.81
	220.679	12 ₄ -11 ₄	183	973.9	11.4	1.76
	220.709	12 ₃ -11 ₃	133	2054.4	14.8	2.21
	220.730	12 ₂ -11 ₂	97	1065.1	14.3	2.07
	220.742	12 ₁ -11 ₁	76	1088.0	- ^c	2.23
	220.747	12 ₀ -11 ₀	69	1095.6	- ^c	2.47
CH ₃ ¹³ CN	220.600	12 ₃ -11 ₃	133	2066.3	- ^d	0.88
	220.621	12 ₂ -11 ₂	97	1071.4	- ^d	0.69
	220.633	12 ₁ -11 ₁	76	1094.4	- ^d	0.61
	220.637	12 ₀ -11 ₀	69	1102.1	- ^d	0.44

^aThe 10_{2,9}-9_{2,8} and 10_{2,8}-9_{2,7} transitions for HNC are blended in source A. The flux given is the total combined flux for both lines. ^bBlended with the C₂H₅OH 13_{1,13}-12_{0,12} transition. ^cStrongly blended lines. ^dBlended with the main isotopic species CH₃CN.

Table 7.2. *Line parameters and fluxes from detected CH₂CO, CH₃CHO and C₂H₅OH transitions for the A and B components.*

Molecule	Freq. (GHz)	Transition	E_u (K)	$\mu^2 S$ (D ²)	$F\Delta V$ (Jy km s ⁻¹)	
					A	B
CH ₂ CO	220.178	11 _{1,11} -10 _{1,10}	76	65.4	3.98	3.30
CH ₃ CHO ^a	219.780	11 _{1,10,2} -10 _{1,9,2}	435	66.4	<0.66	0.43
	230.302	12 _{2,11,0} -11 _{2,10,0}	81	73.7	<0.66	2.23
	230.395	12 _{2,11,1} -11 _{2,10,1}	286	74.1	<0.66	1.01
	230.438	12 _{0,12,2} -11 _{0,11,2}	440	72.9	<0.66	0.66
	231.330	12 _{5,8/7,0} -11 _{5,7/6,0}	129	125.5	<0.66	2.66
C ₂ H ₅ OH	220.602	13 _{1,13} -12 _{0,12}	74	44.7	<0.66 ^b	0.88

^a3 σ upper limits are calculated assuming CH₃CHO has the same line widths as CH₂CO. ^bBlended with the CH₃CN 12₆-11₆ transition.

maps displayed in Fig. 7.1 are obtained by integrating over the width of the B component. Note that in the case of CH_2CO a large fraction of the flux from A is missed, because the line widths are different for both sources but the integrated intensities are similar (see Table 7.2). This effect is illustrated in Figure 7.2, where the maps for CH_2CO are shown integrated over both velocity ranges.

HNCO and CH_3CN clearly show much weaker emission at the B position, i.e. 8% and 18% respectively of that at the A position whereas CH_3CHO is only seen toward the B position. Tables 7.1 and 7.2 list the integrated line intensities for positions A and B. When there is no detection, 3σ upper limits to the intensity are given provided that there is no overlap with other species. Lines of isotopologues were also searched to check the optical depth. The HN^{13}CO lines were not detected leading to a lower limit for $\text{HNCO}/\text{HN}^{13}\text{CO}$ of about 10. Since even in high-mass objects no evidence for high optical depth is found (Zinchenko et al. 2000; Bisschop et al. 2007c), we assume for the remainder of this chapter that the emission from HNCO is optically thin. $\text{CH}_3^{13}\text{CN}$ has been detected toward both sources. Due to the large line widths and blends, it is difficult to determine optical depths for source A. For source B, however, clear detections are present. The $\text{CH}_3\text{CN}/\text{CH}_3^{13}\text{CN}$ ratio ranges from 2–6 with a relatively large uncertainty on the fluxes of 50% due to the low signal-to-noise. The ratio is much lower than the $^{12}\text{C}/^{13}\text{C}$ ratio of 77 ± 7 determined by Wilson & Rood (1994) for the local ISM and the estimated optical depth is ≈ 10 . In Table 7.3 the number of molecules for CH_3CN is estimated based on the $\text{CH}_3^{13}\text{CN}$ emission assuming the excitation temperature of $\text{CH}_3^{13}\text{CN}$ is 200 K and multiplying by 77. A high optical depth for CH_3CN was also found by Bottinelli et al. (2004b).

The $\text{C}_2\text{H}_5\text{OH}$ $13_{1,13}-12_{0,12}$ transition is detected toward source B. It is strongly blended with the $\text{CH}_3^{13}\text{CN}$ 12_3-11_3 transition at 220.600 GHz, and furthermore for source A with the CH_3CN 12_6-11_6 transition at 220.594 GHz (see Fig. 7.3 right). This makes the estimate of the number of molecules from this line very uncertain, but because of the very good overlap of the line position with the emission the presence of the line seems secure for source B.

7.3 Analysis

7.3.1 Disentangling compact and extended emission: fits in the (u, v) plane

One of the issues in dealing with interferometric observations of low-mass proto-stars is that a significant fraction of the emission may be resolved out, especially for low excitation transitions of molecules also present in the large scale cold envelopes. Furthermore, the emission may arise from both sources. Finally fits in the image plane suffer from the effects of the Fourier transformation and image deconvolution, in particular for sparsely sampled data.

Fits to the data were performed in the (u, v) plane to derive line intensities. This is shown in Fig. 7.4 for the observations of the lowest excitation transition

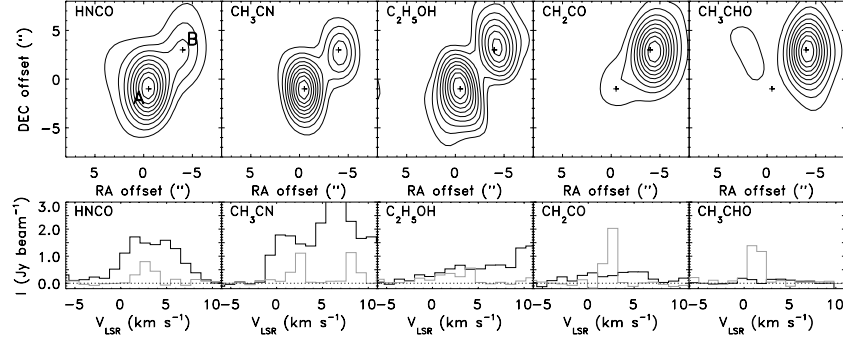


Figure 7.1. Maps and spectra of the $\text{HNCO } 10_{0,10} - 9_{0,9}$, $\text{CH}_3\text{CN } 12_0 - 11_0$, $\text{C}_2\text{H}_5\text{OH } 13_{1,13} - 12_{0,12}$, $\text{CH}_2\text{CO } 11_{1,11} - 10_{1,10}$ and $\text{CH}_3\text{CHO } 12_{5,8/7,0} - 11_{5,7/6,0}$ lines. The maps (upper panels) show the emission integrated over the width of the B component. The contour levels are at 10%, 20%, etc. of the peak in the maps. In the spectra (lower panels) the black line indicates the spectra toward A and the grey line the spectra toward B. Note that whereas species like CH_2CO are detected with a similar integrated intensity for both “A” and “B” components its broad line toward “A” makes it appear fainter in the contour map when only integrating over the channels where the “B” component is detected.

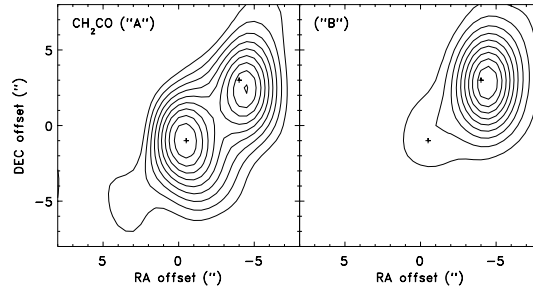


Figure 7.2. Maps for the $\text{CH}_2\text{CO } 11_{1,11} - 10_{1,10}$ line integrated over the width of the A component (left) and B component (right).

of $\text{HNCO } 10_{0,10} - 9_{0,9}$ at 219.798 GHz with $E_u = 58$ K. This is the only line to show a clear increase toward longer baselines in plots of interferometer baseline length vs. visibility amplitude. About a third of the flux for this line is observed at the longest baselines, due to compact emission. Thus two-thirds of the total flux recovered by the SMA for this line is due to extended emission. For each of the other species and lines the point source fits are therefore made simultaneously for both sources to baselines longer than $17 \text{ k}\lambda$ integrated over the velocity range of the lines of the A and B components. This results in the fluxes listed in Tables 7.1 and 7.2 respectively. These observations together with models by

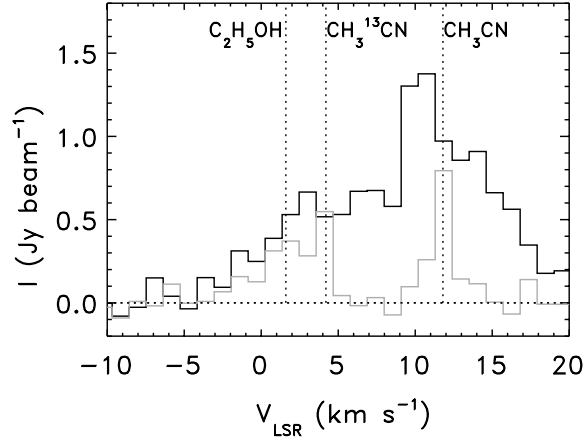


Figure 7.3. SMA spectrum of the C_2H_5OH $13_{1,13}-12_{0,12}$ line at 220.602 GHz (dotted line at 2.5 km s⁻¹). The black line indicates the emission spectrum toward A and the grey line toward B. The dotted vertical lines indicate the position of the $CH_3^{13}CN$ 12_3-11_3 transition at 220.600 GHz (4 km s⁻¹) and the CH_3CN 12_6-11_6 transition at 220.594 GHz (12.5 km s⁻¹).

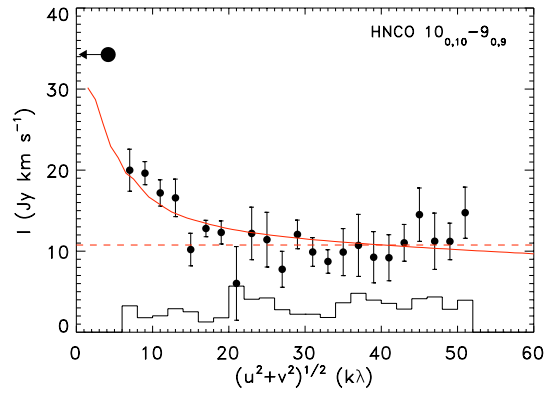


Figure 7.4. Visibility amplitudes of the emission for the $HNC O$ $10_{0,10}-9_{0,9}$ transition at 219.798 GHz observed with the SMA as a function of the projected interferometric baseline length with the phase center taken as the location of the continuum peak of the “A” component. The filled circle indicates the flux detected for the same line with the JCMT. The solid line represents a fit to the flux at different baselines using the Schöier et al. (2002) model and assuming a “jump” in the abundance for $HNC O$ at 90 K.

Schöier et al. (2002) show a break around 15 k λ with an almost constant amplitude, implying that there is unresolved emission at longer baselines. Fitting to these baselines therefore allows us to directly compare emission on similar spatial scales without worrying about presence of extended envelope material.

7.3.2 Rotation diagrams

When multiple transitions of a given molecule are observed spanning a large range in excitation energies it is possible to infer the physical properties of the emitting gas under various assumptions. The rotation diagram method (e.g., Goldsmith & Langer 1999) is often used for molecules of different excitation energies. Under the assumption that the emitting gas is optically thin a straightforward linear relationship exists between the integrated intensities, the column density of the molecule and its so-called “rotation temperature”. At high densities this will approach the kinetic temperature of the gas.

For single-dish observations one typically assumes that the source is compact with respect to the beam and that a specific beam filling factor (or source size) applies as a correction to the observed intensities. For the interferometric observations presented here we have additional information available, namely that the source is unresolved at a specific angular resolution. It is therefore more natural to work directly in units of flux densities. For an optically thin source, ignoring background radiation, the source brightness at a specific frequency, I_ν is given by:

$$I_\nu = \frac{A_{ul} N_u^{\text{thin}} hc}{4\pi \Delta V}, \quad (7.1)$$

where A_{ul} is the Einstein coefficient, N_u^{thin} the column density of molecules in the upper energy level and ΔV the emission line width. Assuming the source emits uniformly over a solid angle, Ω , we can also express the column density N_u^{thin} as the total number of molecules, Y_u^{thin} :

$$Y_u^{\text{thin}} = N_u^{\text{thin}} \Omega. \quad (7.2)$$

and since the definition of brightness of a uniform source is $I_\nu = S_\nu / \Omega$ where S_ν is the flux density, we can therefore write:

$$S_\nu = \frac{A_{ul} Y_u^{\text{thin}} hc}{4\pi \Delta V}. \quad (7.3)$$

Note that in contrast to the typical calculation for rotation diagrams, the source size does not enter the equation here - only the total number of molecules. The observed quantity from this expression is the integrated line intensity, $S_\nu \Delta V$, typically measured in Jy km s $^{-1}$.

From this expression it is straightforward to isolate the number of molecules in the energy level, Y_u^{thin} , and through the Boltzmann equation relate it to the

Table 7.3. Rotation temperature, Y_T and abundance x for HNC, CH_3CN and CH_3CHO derived from rotation diagrams for components A and B. For CH_2CO and $\text{C}_2\text{H}_5\text{OH}$ estimates for Y_T are given. The abundance x is determined relative to the number of molecules for HNC in either source. The notation $a(b)$ stands for $a \times 10^b$.

Molecule	Source A			Source B		
	T_{rot} (K)	Y_T (mol.)	x	T_{rot} (K)	Y_T (mol.)	x
HNC	277 ± 50	$8.9(14)$	1.0	237 ± 37	$7.5(13)$	1.0
CH_3CN^a	$<372 \pm 73$	$>5.6(14)$	>0.6	$<390 \pm 66$	$0.5\text{--}1.0(15)^b$	$7.2\text{--}13$
$\text{CH}_3^{13}\text{CN}$	—	—	—	—	$0.7\text{--}1.3(13)^b$	$0.1\text{--}0.2$
CH_2CO^c	—	$5.6(14)$	0.6	—	$4.7(14)$	6.3
CH_3CHO	—	$<6.6(13)^d$	$<0.07^d$	281 ± 47	$2.9(14)$	3.9
$\text{C}_2\text{H}_5\text{OH}^c$	—	—	—	—	$7.1(14)$	9.5

^aThe rotation temperatures are calculated assuming the main isotope is not optically thick, and are therefore upper limits to the temperature (see § 7.3.2), whereas the number of molecules is an underestimate. ^bThe values have been determined from the $\text{CH}_3^{13}\text{CN}$ lines assuming an excitation temperature of 200 K and a $^{12}\text{C}/^{13}\text{C}$ ratio of 77 (Wilson & Rood 1994). ^cThe number of molecules for CH_2CO and $\text{C}_2\text{H}_5\text{OH}$ are derived assuming they have the same temperature as CH_3CHO for the energy levels detected here (see Table 7.2). ^dThe upper limits are derived assuming the rotation temperature is identical to that in source B.

total number of molecules, Y_T :

$$\frac{Y_u^{\text{thin}}}{g_u} = \frac{Y_T}{Q(T_{\text{rot}})} e^{-E_u/T_{\text{rot}}}, \quad (7.4)$$

where g_u is the degeneracy of the upper energy level, Q the molecular partition function, T_{rot} the rotation temperature and E_u the energy of the upper energy level. As in the usual rotation diagram analysis, one can then plot Y_u^{thin}/g_u versus E_u , and derive the rotation temperature, T_{rot} , from the slope and the total number of molecules, Y_T , from the interpolation to $E_u = 0$. Column densities can be derived for interferometric observations through Eq. 7.2 but as for the single-dish observations an assumption for source size has to be made. Calculating abundances relative to H_2 is also complicated by the complex structure of IRAS 16293-2422. It is more direct to compare the relative abundances of molecules by comparing their total numbers, Y_T , or by comparing the numbers between the two sources. A source size is also required to determine the optical depth of a given transition.

7.4 Results

7.4.1 HNC and CH_3CN

The rotation diagrams are shown in Fig. 7.5 and the resulting rotation temperature and Y_T are given in Table 7.3 for source A and B. For source A the available single dish fluxes from the literature by van Dishoeck et al. (1995) have been

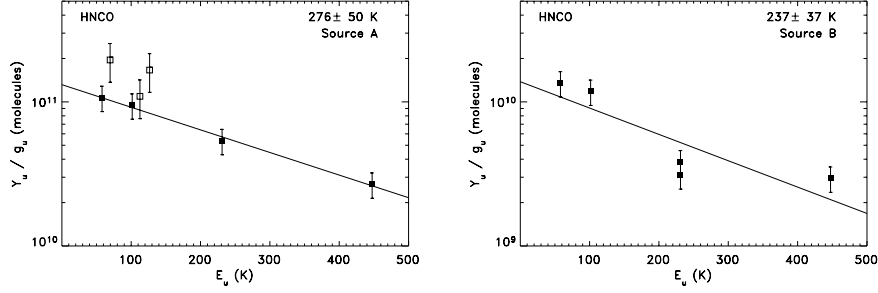


Figure 7.5. Rotation diagram for HNC0 transitions detected with the SMA (filled squares) toward sources A (left) and B (right). Emission lines detected with the single dish telescopes JCMT and CSO by van Dishoeck et al. (1995) are indicated with open squares ($\square$), but are not used for the fit.

over-plotted, but have not been used for the fit. The single dish covers both components, but because the flux from source A is significantly stronger than B (see § 7.2.2), we assume that most of the single dish flux is arising from source A. The single dish fluxes are consistent with the fluxes from the SMA, especially if the additional flux from the B source is taken into account. The rotation temperatures are the same for source A and B within the uncertainty and much higher than what is detected by van Dishoeck et al. (1995) of 135 ± 40 K. This discrepancy is due to the fact that van Dishoeck et al. (1995) include lines of low excitation levels in their fit. Similar to what is seen for the HNC0 $10_{0,10} - 9_{0,9}$ at 219.798 GHz with $E_u = 58$ K, it is likely that a large fraction of this emission is arising from the cold extended binary envelope (see § 7.3.1). When the model by Schöier et al. (2002) is used to fit the (u, v) -plot (see Fig. 7.4), the abundance (X) of HNC0 with respect to H_2 can be determined for the outer and inner envelope to be 6.0×10^{-11} and 4.0×10^{-9} assuming there is a jump in the abundance at 90 K. The inner abundance is somewhat uncertain, because the exact source size for the compact emission is not known.

For CH_3CN rotation diagrams are constructed for both sources (see Fig. 7.6). Less lines can be used for source A due to the larger line width and line-blending. The single dish detections by van Dishoeck et al. (1995) and Cazaux et al. (2003) are again over-plotted and consistent with the SMA data, except for the 6_5-5_5 transition at 110.329 GHz with $E_u = 197$ K which is clearly too high. This may be due to line blending with the $CH_3^{13}CN$ 6_0-5_0 transition at the same frequency. This transition has a larger line strength than that of the main isotope and has a very low excitation temperature of only ~ 19 K. It is thus likely that this transition is picked up in the single dish observations that are sensitive also to extended emission. The resulting rotation temperatures are the same within the uncertainty for source A and B (see Table 7.3). The fact that the data are rather scattered especially for source A points to high optical depths. The transitions of the isotopomer $CH_3^{13}CN$ are unfortunately

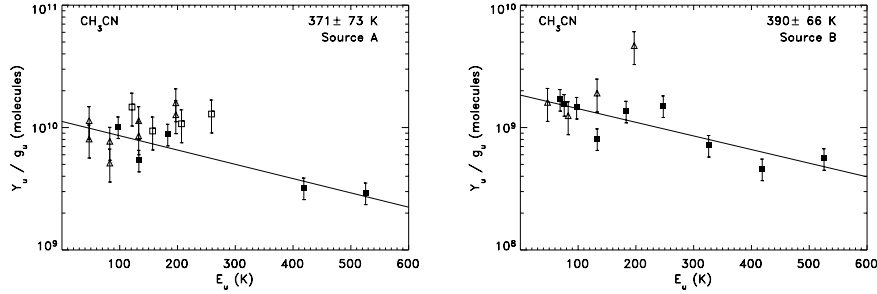


Figure 7.6. Rotation diagram for CH_3CN transitions detected with the SMA (solid squares) toward IRAS 16293-2422 for source A (left panel) and source B (right panel). Emission lines detected with single dish telescopes are over-plotted for source A. The JCMT observations by van Dishoeck et al. (1995) are indicated with open squares ($\square$) and by Cazaux et al. (2003) (IRAM 30 m) and Bottinelli et al. (2004b) (Plateau de Bure) with open triangles ($\triangle$), but are not used for the fit.

strongly blended in source A. From the detections of lines for $\text{CH}_3^{13}\text{CN}$ for source B it is clear that the emission is optically thick and it is likely that the same holds for source A, despite the larger line width for this source. The rotation temperatures are therefore overestimated and the number of molecules underestimated. For CH_3CN no extended emission can be inferred from the (u, v) -data. The lowest detected emission line has $E_u = 69$ K in our SMA data. Hence the non-detection of extended emission is not conclusive for lines with even lower excitation energies.

7.4.2 CH_2CO , CH_3CHO and $\text{C}_2\text{H}_5\text{OH}$

CH_2CO has previously been detected by van Dishoeck et al. (1995) who found only very weak lines with the JCMT and CSO. Their derived rotation temperature is 35 K and column density $4 \times 10^{13} \text{ cm}^{-2}$. Furthermore, Kuan et al. (2004) detected the CH_2CO $17_{2,15}$ – $16_{2,14}$ transition at 343.694 GHz ($E_u = 200$ K) only toward source B. The $11_{1,11}$ – $10_{1,10}$ transition ($E_u = 76$ K) detected here has a similar strength in both sources. A comparison with the single dish fluxes from van Dishoeck et al. (1995) shows that the SMA flux is lower by about a factor 2. This missing flux and the fact that it is often detected with low rotation temperatures toward high-mass star forming regions (Bisschop et al. 2007b; Ikeda et al. 2001) suggest that for CH_2CO a “jump” in abundance may also be present. Thus large scale emission from CH_2CO is resolved out with the SMA. Unfortunately, it is difficult to derive the presence of extended emission from the (u, v) visibility plots for the SMA observations, because the line strengths in source A and B are so similar leading to an oscillatory behavior in the plots from which compact and extended emission cannot clearly be separated.

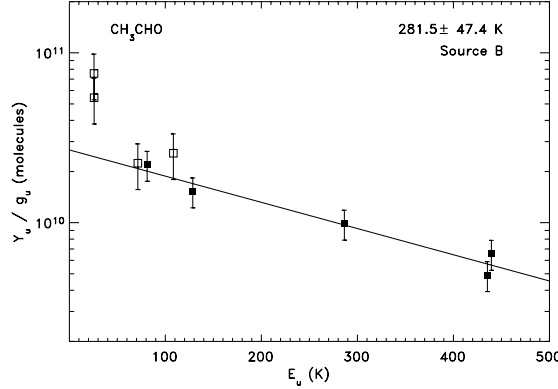


Figure 7.7. Rotation diagram for CH_3CHO emission detected with the SMA toward source IRAS 16293-2422B. The single dish data by Cazaux et al. (2003) are over-plotted with open squares ($\square$), but not used for the fit.

Figure 7.7 shows the rotation diagram of the CH_3CHO lines detected with the SMA and the resulting values for T_{rot} , Y_{T} and x , the abundance with respect to HNC are given in Table 7.3. The single dish data by Cazaux et al. (2003) are over-plotted but are not used for the fit. They are consistent with the SMA fluxes for $E_{\text{u}} > 50$ K. The rotation temperature calculated from the SMA data is 281 ± 47 K. Cazaux et al. (2003) find a rotation temperature of ≤ 40 K, and furthermore their lower excitation lines lie significantly above the fit to the rotation diagram. This implies that the emission with $E_{\text{u}} < 30$ K originates from cold extended material. This is also consistent with interferometric observations of CH_3CHO in the high-mass star forming region Sgr B2(N) (Liu 2005), where the CH_3CHO emission is largely extended. Thus in single dish data alone the “hot” component of CH_3CHO emission cannot be detected. The limit to the CH_3CHO abundance in source A is an order of magnitude lower than the detection in source B.

Previously, van Dishoeck et al. (1995) suggested that $\text{C}_2\text{H}_5\text{OH}$ could be present in the spectra of this source, but were not able to make a firm identification based on strong line-blends. Huang et al. (2005) made the first conclusive detection of compact emission for $\text{C}_2\text{H}_5\text{OH}$ toward source A for the $20_{3,17}-19_{3,16}$ transition at 354.757 GHz with $E_{\text{u}} = 249$ K. The detection here seems secure, but is blended with other lines (see § 7.2.2). The previous detection by Huang et al. (2005) gives additional weight to the assignment of $\text{C}_2\text{H}_5\text{OH}$, however.

The emission of CH_2CO , CH_3CHO and $\text{C}_2\text{H}_5\text{OH}$ behaves spatially very different, also with respect to HNC and CH_3CN . Both CH_2CO and $\text{C}_2\text{H}_5\text{OH}$ have emission that is similar in strength for source A and B, whereas the limit on Y_{T} for CH_3CHO is a factor of three lower than the detection toward source B. The emission from CH_2CO and $\text{C}_2\text{H}_5\text{OH}$ may arise from similar regions, but

more transitions are required for a determination of the rotation temperatures.

7.5 Discussion

In this section the chemical implications of the observations are discussed. To compare the abundances of the species studied here with other sources, they are determined relative to the CH_3OH abundance with respect to H_2 of 7×10^{-7} for source A and 3×10^{-7} for source B derived by Kuan et al. (2004) with the SMA (see Table 7.4). CH_3OH is taken as a reference because it is one of the most abundant grain-surface products.

7.5.1 HNCO and CH_3CN

It is striking that even though the line widths are significantly different between the A and B components, their excitation is similar for HNCO and CH_3CN . When optical depth is taken into account it is very probable that both species are present in the same environment. IRAS 16293-2422 emits at mid-infrared wavelengths (Jørgensen et al. 2005c), and thus infrared pumping of HNCO is possible. In that case the excitation temperature of HNCO would be higher than the gas kinetic temperature - and thus than rotation temperatures determined for other molecules.

The emission for both species is much stronger for source A than source B. This is compared to other sources in Table 7.4. Clearly, these relative abundances are much lower than in Sgr B2(N) (Nummelin et al. 2000), but similar to the Orion A source (Sutton et al. 1985) and the high-mass survey by Bisschop et al. (2007c). It is unclear what causes this large variation. The most likely formation mechanism for HNCO is OCN^- evaporation from grains (Allamandola et al. 1999; van Broekhuizen et al. 2004), whereas CH_3CN is commonly thought to form in the gas phase from reactions of grain mantle products (Charnley et al. 1992). The similarity for HNCO and CH_3CN emission suggests that their formation mechanisms are linked. The difference between the nitrogen-bearing and the oxygen-bearing species may be explained by a higher solid state abundance of NH_3 similar to what is observed for the Orion Hot Core versus the Compact Ridge (Caselli et al. 1993). Alternatively source A may have a higher solid state abundance of OCN^- : variations of about an order of magnitude have been observed for sources that are only 400 AU apart (van Broekhuizen et al. 2005), similar to the distance between sources A and B. Naturally, both effects could also occur simultaneously. This may result in enhanced ice abundances of nitrogen-bearing species. The gas phase abundances of HNCO will increase after grain-mantle evaporation. Additionally, CH_3CN may form in the gas phase from radiative association of CN with CH_3^+ or reaction of HCN with CH_3^+ followed by dissociative recombination. It is thus possible that the desorption of an enhanced amount of nitrogen-bearing grain-surface molecules also enhances the CH_3CN gas phase abundance toward source A.

7.5.2 CH₂CO, CH₃CHO and C₂H₅OH

In high-mass sources CH₂CO and CH₃CHO are typically detected in cold gas and C₂H₅OH in hot gas (Bisschop et al. 2007c, also Chapter 2). A comparison of the abundances of these species in hot gas is given in Table 7.4. The CH₂CO and C₂H₅OH abundances relative to CH₃OH are similar to those found in high-mass sources, except for the C₂H₅OH abundance toward Sgr B2(N) which is significantly higher. The relatively similar ratios in high- and low-mass sources imply that the formation mechanisms are the same for CH₂CO and C₂H₅OH in both types of sources. In contrast, the CH₃CHO abundance differs about an order of magnitude between sources A and B. This difference arises from the fact that the limit on the number of molecules is a factor of three lower toward source A compared to B, whereas the CH₃OH abundance is a factor of three higher toward source A.

Tielens & Charnley (1997) explained the presence of these molecules through successive hydrogenation of HCCO. It is, however, puzzling how this can be the case with the different spatial behavior of the three species. For this scheme there are three possibilities, i) hydrogenation is complete; ii) hydrogenation is incomplete or iii) CH₃CHO is very efficiently destroyed to molecules other than C₂H₅OH at high temperatures in the ice or right after evaporation from the grain surface. For scenario (i) behavior such as observed for high-mass sources is expected with only C₂H₅OH seen in the hot gas. However, the detection of hot compact emission for CH₂CO and CH₃CHO implies that this cannot be the case. Recently Bisschop et al. (2007b) have shown through laboratory experiments that CH₃CHO is indeed partially converted to C₂H₅OH and another fraction leads to CH₄, H₂CO and CH₃OH. Whether CH₃CHO is incompletely converted as proposed in scenario (ii) depends on time or rather the total number of H-atoms the ice is exposed to, but also on the ice thickness: for ices of a few monolayers some CH₃CHO molecules can be hidden from impinging H-atoms. In such a scenario it is difficult to predict the exact ratio between the abundances of CH₂CO/CH₃CHO/C₂H₅OH. This ratio may vary strongly per source if the density and thus the freeze-out rate was higher. The presence of CH₂CO and C₂H₅OH toward source A could for example suggest that the conversion of CH₂CO to CH₃CHO was incomplete, whereas the CH₃CHO to C₂H₅OH conversion was complete. One way to test this scenario is to compare C₂H₅OH/CH₃CHO to CH₃OH/H₂CO (see Fig. 7.5.2), because these ratios are expected to be sensitive to the same ice properties when grain-surface hydrogenation is the main formation mechanism (Watanabe et al. 2004; Fuchs et al. 2007). The CH₃OH/H₂CO ratio is ~ 5 from the single dish observations towards IRAS 16293-2422 and high-mass sources, whereas C₂H₅OH/CH₃CHO is about an order of magnitude lower. The estimated abundance ratio C₂H₅OH/CH₃OH for source B is 0.01 (Table 7.4) and is comparable to what was found by Bisschop et al. (2007c) and Requena-Torres et al. (2006) for high-mass star forming regions and galactic clouds within the uncertainties. The similar relative abundances of H₂CO, CH₃OH and C₂H₅OH indicate that their formation mechanisms are linked and likely the same as in high-mass star forming regions.

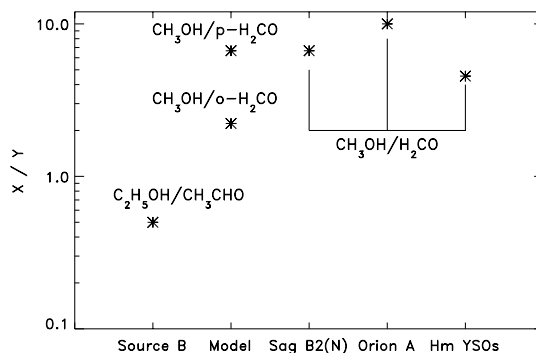


Figure 7.8. Comparison of the $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{CHO}$ abundance ratio detected here for source IRAS 16293-2422 B with the $\text{CH}_3\text{OH}/\text{H}_2\text{CO}$ abundance ratio of a spherical model of the envelope of IRAS 16293-2422 by Schöier et al. (2002) and of the high-mass sources Sgr B2(N) (Nummelin et al. 2000) and Orion A (Sutton et al. 1985) as well as a survey of 7 high-mass sources (Hm YSOs) (Bisschop et al. 2007c).

The lower $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{CHO}$ ratio suggests that if CH_3CHO and $\text{C}_2\text{H}_5\text{OH}$ are chemically related in IRAS 16293-2422, the relation is different from H_2CO and CH_3OH .

One explanation for this difference is scenario (iii) where CH_3CHO is rapidly destroyed in the solid state or in the gas phase right after evaporation, while CH_2CO and $\text{C}_2\text{H}_5\text{OH}$ are more stable. If this scenario is correct, the determining factor for CH_3CHO destruction is absent or less strong for source B compared to A. This could be an effect of e.g. UV-photolysis. The more quiescent nature of source B compared to A may also play a role. Alternatively, CH_2CO , CH_3CHO and/or $\text{C}_2\text{H}_5\text{OH}$ are formed via other solid state or even gas phase formation mechanisms, through which they are not directly related. In such a case, the abundances of these species are not at all expected to peak at the same locations such as observed in the IRAS 16293-2422 region.

7.6 Summary and conclusions

We have performed an interferometric study of the complex organic species HNCN, CH_3CN , CH_2CO , CH_3CHO and $\text{C}_2\text{H}_5\text{OH}$ toward the low-mass protostar IRAS 16293-2422 with the SMA. Previously published data from Kuan et al. (2004) are used to determine relative abundances with respect to CH_3OH . The main conclusions of this work are:

- ▷ The emission from both HNCN and CH_3CN is compact and is seen toward both sources in the binary, with only 10–20% arising from source B.

Table 7.4. Comparison of the summed abundances for source “A” and “B” normalized to the CH_3OH abundances by Kuan et al. (2004), assuming the emission arises from a compact region with an excitation temperature of 200 K. Interferometric SMA data are presented as well as previously published single dish data by van Dishoeck et al. (1995), observations of the high-mass sources Sgr B2(N)^b and Orion A^c and the single dish survey^d presented in Chapter 6.

Molecule	“A”	“B”	“A” + “B”	Single Dish ^a	Sgr B2(N) ^b	Orion A ^c	High-mass survey ^d
HNCO	0.03	0.005	0.02	0.04	0.17	0.01	0.0084
CH ₃ CN	>0.02	0.03 – 0.06	>0.02	0.04	63	0.04	0.045
CH ₂ CO	0.02	0.03	0.02	0.04	0.07	0.01	–
CH ₃ CHO	<0.002	0.02	<0.007	<0.02	0.044 ^e – 3.2 ^f	–	–
C ₂ H ₅ OH	–	0.01	–	≤0.05	0.42	–	0.025
H ₂ CO	–	–	–	0.24	0.15	0.1	0.22

^avan Dishoeck et al. (1995), ^bNummelin et al. (2000), ^cSutton et al. (1985), ^dBisschop et al. (2007c), see also Chapter 6,

^eA-type, ^fB-type.

Additionally, the lowest excitation line of HNC shows extended emission suggestive of its presence in a cold extended envelope. Such a component cannot be ruled out for CH₃CN either. The relatively higher abundances in source A with respect to CH₃OH may originate from higher initial abundances of NH₃ and/or OCN⁻ in the ice.

- ▷ For CH₂CO and C₂H₅OH only one emission line is detected. These lines are detected with similar strength toward both sources and the emission is compact. Compact hot emission for CH₃CHO is detected only toward source B, in contrast to previous single dish observations of high and low-mass sources where CH₃CHO consistently has temperatures below 100 K. Comparison with previous single dish observations by Cazaux et al. (2003) suggests that a cold extended component is potentially present as well. If CH₂CO, CH₃CHO and C₂H₅OH are related through successive hydrogenation on the surfaces of grains, the same spatial behavior is expected for all three species. Since this is not observed, it suggests that hydrogenation reactions on grain surfaces alone cannot account for the observed gas phase abundances, but that CH₃CHO is likely selectively destroyed right before or after grain-mantle evaporation.

The discussion in this chapter demonstrates the strength of clearly resolved interferometric observations for studies of the chemistry in star forming regions. First, molecules that have both extended and compact emission can easily be identified based on (u, v) -visibility analysis. In single dish observations these components will be averaged together giving rotation temperatures in between that of the hot and cold component. Additionally, compact emission arising from different components in the same single-dish beam can be separated, which leads in some cases to very different abundance ratios for the different sources as exemplified in Table 7.4 for HNC and CH₃CHO. For HNC the presence of a cold extended component could not be derived from the single dish observations, whereas for CH₃CHO it is the hot component that is not detected. Further interferometric studies are needed to elucidate the chemical relations between complex organics.

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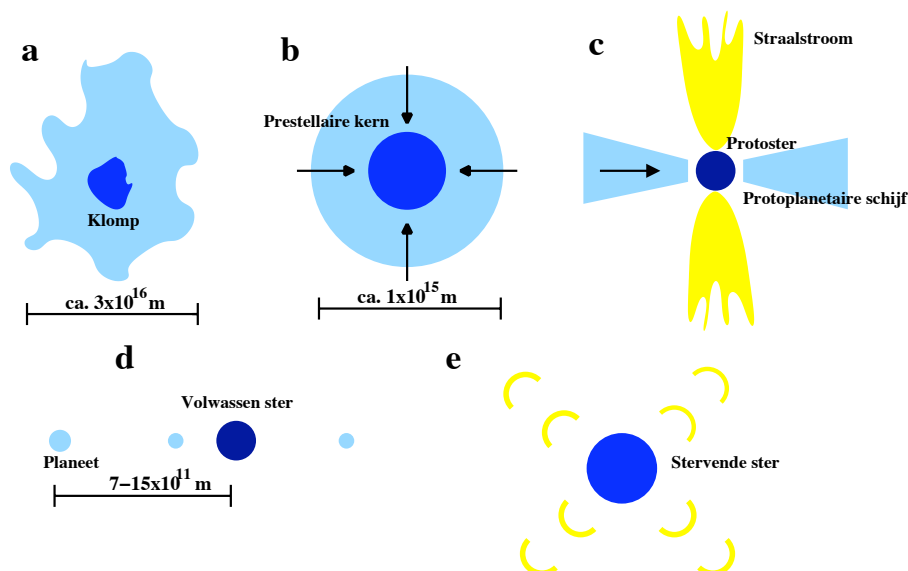
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Nederlandse samenvatting

“Chemie overal” is het boek dat op Nederlandse middelbare scholen voor het scheikunde onderwijs wordt gebruikt. Op een paar uitzonderingen na is deze titel inderdaad niet alleen op aarde maar ook ver daarbuiten van toepassing. In het begin van de vorige eeuw verwachtte men niet dat scheikundige reacties plaats konden vinden in “interstellaire wolken” vanwege de lage dichtheden (ca. 100 waterstofatomen per kubieke centimeter) en zeer lage temperaturen van -263°C (10 K). In 1937 werd echter voor het eerst het gasvormige radicaal koolstof hydride (CH) ontdekt in de ruimte. Sindsdien is het aantal detecties van interstellaire chemische verbindingen toegenomen tot 149¹. Sommige van deze materialen zijn heel alledaags zoals bijvoorbeeld water (H_2O) en koolstofdioxide (CO_2). Andere bestaan uit lange koolstofketens. Ook zijn “complexe organische moleculen”² zoals methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$) en methyl formaat (CH_3OCHO) ontdekt. Zelfs positieve ionen zoals geprotoneerd stikstof (N_2H^+) en geprotoneerd koolstofmonoxide (HCO^+) zijn waargenomen en zeer recent zijn ook negatief geladen koolstofketens geïdentificeerd. Bovendien worden niet alleen gassen aangetroffen maar ook vaste stoffen op de oppervlakken van interstellaire stofdeeltjes. Water is het eerste materiaal dat in die hoedanigheid werd gedetecteerd, maar vele andere moleculen zoals koolstofdioxide, koolstofmonoxide en mierenzuur zijn ook als ijs waargenomen. De interstellaire stofdeeltjes waarop dit “interstellair” ijs is vastgevroren, bestaan voornamelijk uit zwaardere chemische elementen en zijn zichtbaar doordat ze het licht van achterliggende sterren op infrarode golflengten absorberen. Het is nog niet precies bekend uit welke materialen “interstellair” stof bestaat, maar de infrarood emissie en absorptie duidt op zandachtige materialen (silicaten), amorf koolstof of grafietachtige materialen en polycyclische aromatische koolwaterstoffen. Er zijn zelfs aanwijzingen voor kleine diamanten. Het is de wetenschap “astrochemie” die bestudeert hoe deze gassen, ijs- en stofdeeltjes worden gevormd en hoe deze materialen bijdragen aan de chemische evolutie van het heelal.

¹ <http://www.astrochymist.org/astrochymist.ism.html>

² Moleculen worden in de sterrenkunde “complex” genoemd wanneer ze bestaan uit meer dan 4 atomen en “organisch” wanneer ze opgebouwd zijn uit koolstof- en waterstofatomen. Daarnaast kunnen organische stoffen ook andere atomen bevatten.



Figuur 1. Overzicht van de levenscyclus van een ster met in a) interstellair gas en stof is aanwezig in klompen materiaal met hogere dichtheden ook wel wolken genoemd, b) het materiaal in een klomp slaat neer op een centraal object, de prestellare kern, c) het verder “groeien” tot een protoster vindt plaats via een schijf van gas en stof en tegelijkertijd blazen straalstromen materiaal vanaf de polen weg, d) in de schijf rondom de ster vormen zich planeten en uiteindelijk in e) sterft de ster, waarbij het veel van zijn massa uitstoot en het interstellair medium wordt verrijkt met zwaardere elementen die door nucleosynthese in de ster zijn gevormd.

De cyclus van gas en stof

De astrochemische cyclus van gas en stof is weergegeven in Figuur 1. Het merendeel van het gas en stof in de ruimte is aanwezig in kleine compacte gebieden (Fig. 1a). Het materiaal in zo'n gebied kan door zijn eigen zwaartekracht of door krachten van buitenaf instorten om een prestellare kern te vormen (Fig. 1b). Later in de cyclus kan het materiaal niet meer direct vanuit de omgeving op de protoster vallen, maar wel via een protoplanetaire schijf (Fig. 1c). Tegelijkertijd wordt er materiaal vanaf de polen van de protoster de ruimte ingespuwd door “straalstromen” die ook het omliggende omhulsel van de protoster wegblazen. Uiteindelijk ontstaan vanuit de protoplanetaire schijf planeten (Fig. 1d). Wanneer de ster na een lang leven sterft en daarbij een groot deel van zijn massa uitstoot (Fig. 1e) begint het hele proces opnieuw. Het is echter geen perfecte recycling die plaatsvindt. Ten eerste wordt door kernfusie in sterren waterstof voornamelijk omgezet in zwaardere elementen en wordt een deel van de massa omgezet in energie. Ten tweede blijven er na het uitdoven van de ster heel compacte objecten achter. In het geval van de meest massieve sterren is dit

een neutronenster of een zwart gat. Dit proefschrift richt zich op de chemie in stervormingsgebieden (Fig. 1a–c).

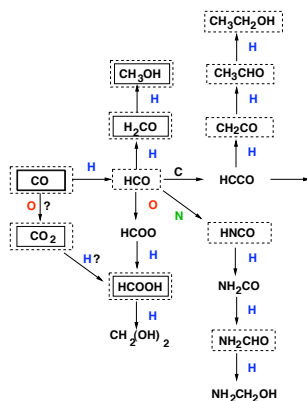
Chemische processen tijdens stervorming

De fysisch-chemische processen die plaatsvinden tijdens de stervorming omvatten vier verschillende fasen die hieronder kort zijn samengevat:

- I. Bij lage temperaturen en dichtheden vinden vooral zogenaamde “ion-molecuul” reacties plaats, waarbij een molecuul met een ion reageert.
- II. Wanneer de dichtheden toenemen vriezen atomen en moleculen vast op interstellair stofdeeltjes. Bij deze lage temperaturen kunnen alleen de H-atomen bewegen over het oppervlak wat resulteert in veel waterstofrijke materialen.
- III. De protoster warmt de ijslagen op de stofdeeltjes op. Dit zorgt ervoor dat ook andere atomen en radicalen die zwaarder zijn dan waterstof mobiel worden zodat meer complexe organische moleculen ontstaan.
- IV. Als de temperatuur van het ijs boven 90 K komt, verdampt al het ijs van de stofdeeltjes. In de gasfase reageren de moleculen die op de stofdeeltjes zijn gevormd waarbij zogenaamde “tweede generatie” moleculen ontstaan.

In fase I vinden reacties bij heel lage dichtheden plaats in koude dichte wolken. Deze reacties zijn heel anders dan de op aarde voorkomende reacties. Bij de zeer lage temperaturen van ongeveer $-263\text{ }^{\circ}\text{C}$, maar net boven het absolute nulpunt, hebben de moleculen heel weinig bewegingsenergie en zijn reacties tussen verschillende atomen of moleculen alleen mogelijk wanneer er geen energiebarrières zijn die moeten worden overbrugd. Op aarde is de bewegingsenergie echter veel hoger en zijn de dichtheden zo hoog dat vaak drie of meer moleculen tegelijkertijd tegen elkaar botsen. Dit is van belang omdat bij chemische reacties tussen twee deeltjes vaak een derde deeltje nodig is om de energie die vrijkomt te absorberen. In de ruimte zijn de dichtheden zo laag dat bij elke botsing maar twee moleculen betrokken zijn, waardoor sommige “aardse” reacties niet kunnen optreden. Vooral reacties met ionen zijn belangrijk in de ruimte vanwege de grotere aantrekkingskracht van geladen deeltjes. Het gevolg hiervan is dat de moleculen die in de ruimte voorkomen vaak heel anders zijn dan die op aarde.

In fase II nemen de dichtheden toe wanneer de koude wolk in elkaar stort door zijn eigen zwaartekracht of door druk van buitenaf. Het gevolg is dat botsingen tussen verschillende atomen en moleculen vaker voorkomen. Vanwege de lage temperaturen zullen moleculen en atomen die met een stofdeeltje botsen hierop vastvriezen. Hierdoor ontstaan kleine ijslaagjes op de oppervlakken. Het resultaat hiervan is dat heel andere stoffen gevormd worden dan in de vorige fase. Vooral reacties met waterstofatomen zijn zeer talrijk. Deze atomen zijn namelijk als enige licht genoeg om over het oppervlak van de stofdeeltjes te bewegen en



Figuur 2. Reactieschema van de vorming van complexe organische materialen beginnend bij koolstofmonoxide en waterstof. Vervolgens kunnen door reacties met andere atomen nog “complexere” moleculen worden gevormd. De rechthoeken met doorgetrokken lijnen geven aan dat moleculen zijn waargenomen in vaste vorm en rechthoeken met niet-doorgetrokken lijnen dat ze gedetecteerd zijn in de gasfase.

kunnen zo andere atomen of moleculen tegenkomen waarmee ze kunnen reageren. Het gevolg hiervan is dat veel scheikundige verbindingen die in deze fase gevormd worden, verzadigd zijn met waterstofatomen. Een voorbeeld van de specifieke reacties die kunnen plaatsvinden en de daarbij gevormde moleculen wordt getoond in Fig. 2.

In fase III neemt de intensiteit van de straling van de jonge ster toe waardoor de omringende wolk opwarmt. In eerste instantie wordt dit veroorzaakt door accretie van materiaal op de ster, waardoor potentiële energie in straling en warmte wordt omgezet. Daarna zal ook kernfusie in de ster op gang komen, waardoor de ster zelf gaat stralen. Door deze hogere temperaturen zullen in het ijs ook zwaardere atomen en zelfs radicalen over het oppervlak van stofdeeltjes kunnen bewegen en verder zorgt UV-straling van de ster ervoor dat sommige moleculen in het ijs worden afgebroken. Het gevolg is dat nog complexere organische materialen gevormd kunnen worden. Tegelijkertijd kunnen vluchtige moleculen ook verdampen.

In fase IV zijn alle ijsmoleculen boven ca. 90 K verdampt, waardoor scheikundige reacties in de gasfase nu bij veel hogere temperaturen en dichtheden plaatsvinden. Dit zorgt ervoor dat in de ijsmantel gevormde moleculen worden omgezet in andere moleculen. Een deel van deze materialen kan in een protoplanetaire schijf rondom de jonge ster terecht komen en er worden inderdaad veel van dezelfde stoffen in komeetstaarten en meteorieten gevonden. Het is nog niet duidelijk of deze verbindingen in ons zonnestelsel afkomstig zijn uit het omringende gas van de protoster of dat deze materialen in de protoplanetaire schijf op een vergelijkbare manier gevormd worden. In beide gevallen zijn het deze organische materialen waaruit nieuwe planeten ontstaan en die wellicht de bouw-

stenen zijn van prebiotische moleculen zoals aminozuren en kernzuren.

Dit proefschrift

In bovenstaande paragrafen zijn de fysisch-chemische processen besproken die plaatsvinden in stervormingsgebieden. Er is over deze processen nog een groot aantal open vragen:

- ▷ Hoe complex zijn de organische materialen die worden gevormd in de ruimte?
- ▷ Welke moleculen worden op de oppervlakken van ruimte-stof gevormd en welke in de gasfase?
- ▷ Wat zijn de structuren van het interstellair ijs op de stofdeeltjes? Beïnvloeden deze structuren de scheikundige reacties?
- ▷ Wat zijn de effecten van UV-straling en waterstofatomen op het ijs? Kunnen complexe moleculen overleven in het ijs tot ze van de stofdeeltjes verdampen?

In dit proefschrift wordt een aantal van deze vragen behandeld. Aangezien het niet mogelijk is het materiaal in de ruimte direct te bestuderen, zijn in dit proefschrift twee verschillende indirecte methoden gebruikt. Ten eerste zijn hoog vacuüm (10^{-7} mbar) en ultra-hoog vacuüm (10^{-10} mbar) experimenten verricht waarin de omstandigheden in de ruimte worden nagebootst (Hoofdstukken 2 t/m 5). In deze experimenten worden processen in puur, gelaagd en gemengd ijs bij verschillende temperaturen bestudeerd. Mogelijke processen die in het ijs plaatsvinden, zijn zowel het zich mengen of van elkaar scheiden van verschillende materialen als het verdampen en reageren met waterstofatomen. Bovendien zijn infrarode spectra gemeten in het laboratorium die vervolgens zijn vergeleken met waarnemingen van interstellaire gebieden. Met de resultaten van deze experimenten worden voorspellingen gedaan over hoe verschillende materialen zich gedragen in de ruimte.

Ten tweede zijn er waarnemingen gedaan op submillimeter golflengten van moleculen in de gasfase (Hoofdstukken 6 en 7). Het is niet mogelijk om moleculen met lage abundanties in het ijs bij infrarode golflengten direct waar te nemen. Om te weten of deze moleculen aanwezig zijn en eventueel gevormd worden in het ijs, is het nodig ze in de gasfase na verdamping te detecteren. Uit de waarnemingen wordt informatie verkregen over de temperatuur van het gas waarin de moleculen zich bevinden en welke hoeveelheden er aanwezig zijn. Deze informatie is belangrijk voor het bepalen van de meest waarschijnlijke vormingsmechanismen van deze moleculen. De vraag is namelijk of deze worden gevormd op de oppervlakken van stofdeeltjes of in de gasfase. Een aantal reacties op ruimte-stof (zie Fig. 2) is in dit onderzoek vervolgens in het laboratorium getest.

Conclusies proefschrift

Hieronder worden de voornaamste conclusies van alle hoofdstukken kort samengevat.

Hoofdstuk 2: Onder ultrahoge vacuüm condities is nagegaan of waterstof-atomen (H) met koolstofdioxide (CO_2), mierenzuur (HCOOH) of acetaldehyde (CH_3CHO) reageren. De resultaten van deze studie zijn dat de reactiesnelheden met CO_2 en HCOOH heel laag zijn. Dit betekent dat deze reacties waarschijnlijk geen grote rol in interstellair ijs zullen spelen. CH_3CHO reageert echter wel met H-atomen waarbij of ethanol ($\text{C}_2\text{H}_5\text{OH}$) wordt gevormd of waarbij de koolstofbinding breekt en methaan (CH_4), formaldehyde (H_2CO) en methanol (CH_3OH) ontstaan. De reactiesnelheid die in dit experiment is gevonden voor de vorming van $\text{C}_2\text{H}_5\text{OH}$ is hoog genoeg om de hoeveelheden alcohol die in de ruimte gevonden worden te verklaren.

Hoofdstuk 3: Het infrarood spectrum van koolstofmonoxide (CO) in puur, gelaagd ijs en in gemengd ijs van methanol (CH_3OH), methaan (CH_4), koolstofdioxide (CO_2) en mierenzuur (HCOOH) is bestudeerd in hoog vacuüm. Het pure ijs en het gelaagde ijs blijken sterk op elkaar gelijkende spectra te hebben. Alleen de mengsels hebben bredere absorptiebanden. De absorptieband die gedetecteerd wordt in waarnemingen van “interstellair” ijs kan voornamelijk worden toegeschreven aan CO in puur of gelaagd ijs maar er zijn ook absorptiebanden van CO die afkomstig zijn van CO moleculen in de nabijheid van water (H_2O) of andere materialen die waterstofbruggen vormen zoals CH_3OH . Bovendien kan CO door CH_3OH en HCOOH vast worden gehouden in de vaste fase boven de normale verdampingstemperatuur. Het gevolg hiervan is dat op hogere temperaturen CO kan reageren met andere moleculen/atomen in het ijs.

Hoofdstuk 4: Het infrarood spectrum van mierenzuur (HCOOH) is bestudeerd in puur en gemengd ijs met water (H_2O), koolstofmonoxide (CO), koolstofdioxide (CO_2) en methanol (CH_3OH) in hoog vacuüm. De experimentele spectra van puur HCOOH -ijs en mengsels met één andere component kunnen de waargenomen spectra van “interstellair ijs” slecht reproduceren. Het zijn de complexe mengsels van HCOOH , water met CO, CO_2 en in het bijzonder met CH_3OH die goed met de waarnemingen overeen komen. De conclusie is dat HCOOH waarschijnlijk aanwezig is in interstellaire ijsmengsels, en dat deze omgeving consistent is met de meest waarschijnlijke vormingsmechanismen.

Hoofdstuk 5: Verdampingsexperimenten van puur, gelaagd en gemengd ijs van koolstofmonoxide (CO) en stikstof (N_2) zijn uitgevoerd in ultrahoog vacuüm. De resultaten hiervan zijn dat de bindingsenergieën voor N_2 hoger en meer vergelijkbaar met CO zijn dan voorheen werd gedacht. Bovendien plakken beide materialen ook met dezelfde efficiëntie aan stofdeeltjes vast bij lage temperaturen. Deze resultaten zijn belangrijk om

waarnemingen van CO en geprotoneerd stikstof (N_2H^+) in koude klompen in de ruimte te verklaren.

Hoofdstuk 6: Submillimeter waarnemingen van complexe organische materialen van zeven hoge massa stervormingsgebieden genomen met de “James Clerk Maxwell Telescoop” zijn geanalyseerd. Deze moleculen zijn gekozen omdat ze naar verwachting gevormd worden door reacties van waterstofatomen met andere atomen en moleculen in “interstellair” ijs. Ook een groot aantal “tweede generatie” moleculen is gedetecteerd, waarvan gedacht wordt dat ze vormen in de gasfase na verdamping uit het ijs. Uit de analyse van het uitgezonden licht blijkt dat sommige materialen aanwezig zijn in koud gas en andere in warmer gas. Bovendien zijn de relatieve hoeveelheden van zuurstofhoudende moleculen, waaronder een aantal “tweede generatie producten” onderling constant tussen de verschillende objecten. Dit impliceert dat de zuurstofhoudende stoffen verwante vormingsmechnismes hebben en dat ook de zogenaamde “tweede generatie” zuurstofhoudende materialen op de oppervlakken van interstellaire stofdeeltjes, waarschijnlijk in de prestellaire fase, worden gevormd. Hetzelfde geldt voor de stikstofhoudende materialen.

Hoofdstuk 7: Interferometrische submillimeter waarnemingen van een aantal organische materialen zijn verricht met de “Submillimeter Array” van het lage massa stervormingsgebied IRAS 16293-2422. Dankzij het hoog oplossend vermogen van de telescoop kan de ruimtelijke verdeling van deze stoffen rond de jonge dubbelster (bestaande uit ster A en ster B) worden bepaald. Het is duidelijk dat sommige stoffen zowel aanwezig zijn in een koude omgeving rond de ster als in het hete gas dichtbij de ster. Bovendien komen sommige materialen, met name de stikstofhoudende, meer voor rondom ster A. Het verschil tussen de twee objecten kan worden veroorzaakt door een hogere ijsabundantie van ammonia (NH_3) of het cyanaat ion (OCN^-), waardoor een grotere hoeveelheid stikstofhoudende materialen wordt gevormd. Van de zuurstofhoudende stoffen wordt acetaldehyde (CH_3CHO) exclusief gedetecteerd rondom ster B. De andere stoffen keteen (CH_2CO) en ethanol ($\text{C}_2\text{H}_5\text{OH}$) worden in beide objecten aangetroffen met vergelijkbare hoeveelheden. Het verschillende gedrag van respectievelijk acetaldehyde, keteen en ethanol impliceert dat deze materialen alleen gevormd kunnen worden door opeenvolgende toevoegingen van waterstofatomen op de oppervlakken van stofdeeltjes wanneer acetaldehyde selectief vernietigd wordt na verdamping in ster A.

Nederlandse samenvatting

Curriculum vitae

I was born September 2nd 1980 in Utrecht, the Netherlands. I grew up in Maarssenbroek, close to Utrecht, where I went to high school at “Het Utrechts Stedelijk Gymnasium” from 1992–1998.

After high school, I studied chemistry at Utrecht University and received a scholarship from the Organization for the Dutch Chemical Industry (VNCI) for excellent study results in the first year. In 2000–2001, I was a member of the board of Chemistry students in Utrecht, the “Utrechtse Scheikundige Studentenvereniging Proton”, and I have been actively involved in a number of its committees throughout my studies. Late 2001, I learned about the astrochemistry group of Prof. dr. Ewine van Dishoeck at Leiden University and I ended up doing my masters research project in her group. Most of my research consisted of experimental work in the “Raymond and Beverly Sackler Laboratory for Astrophysics” at Leiden Observatory with Dr. Helen Fraser. I finished my studies by going abroad for half a year to work in the groups of Prof. dr. Geoffrey Blake and Prof. dr. John Eiler at “The California Institute for Technology” in Pasadena, California. I received my masters degree in Chemistry in November 2003 with the *judicium Cum Laude*.

I returned to start my Ph.D. at Leiden University. My research was a combined project working on both observations with Prof. dr. Ewine van Dishoeck and laboratory work with Prof. dr. Stephan Schlemmer and later on dr. Harold Linnartz. During my Ph.D. I have frequently given public lectures for amateur astronomy societies and have been a member of the computer committee of Leiden Observatory. I supervised a master student research project for Evelyn de Wachter and the bachelor student project of Laura van Kempen-Helmsing and Casper Schönau. During my Ph.D. I presented my research in the form of posters or talks at several national and international conferences in Switzerland, U.S.A., Denmark, U.K. and France. After my Ph.D. defense I will continue in Bonn as a postdoctoral researcher.

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