Spectroscopy and chemistry of interstellar ice analogues

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Citation

Bouwman, J. (2010, October 12). *Spectroscopy and chemistry of interstellar ice analogues*. Retrieved from https://hdl.handle.net/1887/16027

CHAPTER 1

Introduction

The pressures in space are much lower than one can reach in the best vacuum chamber in a laboratory on Earth and the temperatures vary from extremely high to close to absolute zero. Despite these extreme circumstances there is a surprisingly active chemistry which enriches the vast regions in space, leaving a large puzzle for mankind to solve.

Most molecules detected in the interstellar medium (ISM) are unambiguously identified by their rovibrational (infrared), or purely rotational (microwave) fingerprint absorption or emission spectra. One particular family of molecules — the so-called Polycyclic Aromatic Hydrocarbons (PAHs) — is detected as a class by its characteristic mid-infrared (mid-IR) emission spectrum. Although these molecules have not been uniquely identified, because of their common spectral signature, their presence in photon-dominated regions (PDRs) is now widely accepted in the astrochemical community.

Besides gas phase species, molecules are also detected in solid form, as interstellar ices. Ices are formed in cold and dark regions in space, known as molecular clouds, by accretion of gas phase species on cold carbonaceous or silicate dust grains. The thin layers of ice contain rather simple molecules, such as H_2O, CO, CO_2, CH_3OH, CH_4, and NH_3. The constituents of icy grain mantles are further energetically processed by heat, cosmic rays, or ultraviolet (VUV) radiation, leading to more complex molecules. Interstellar ices are now regarded as important catalytic sites for the formation of complex (organic) molecules during the evolution of an interstellar cloud and are considered crucial in astrochemistry.

This thesis describes laboratory and observational studies which are aimed to understand physical interactions and abundances of species in, and the VUV induced chemical evolution of, interstellar ices in a laboratory setting using mid-IR and near-ultraviolet/ visible (near-UV/VIS) spectroscopic techniques. The remainder of the introduction is used to put the thesis work into context.

1.1 Astrochemistry

The formation and detection of polyatomic molecules in the interstellar medium had long been unexpected because of the harsh UV fields and low densities ($\sim$ 1–10^2 molecules

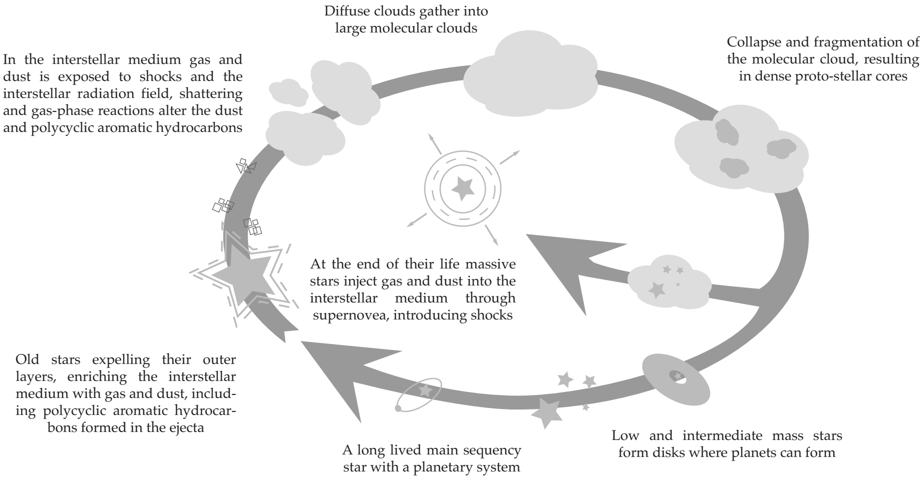

Figure 1.1 Cartoon of the Galactic life cycle. After Steven Simpson (Verschuur 1992, Sky & Telescope Magazine), by Christiaan Boersma.

cm^{-3}). However, in 1937 the first molecules, CH, CN, and CH$^+$ were detected in diffuse clouds [Swings & Rosenfeld 1937]. The detection of only transient species confirmed the idea that the unfavorable conditions would preclude the presence of more complex chemistry. The detection of more complex molecules in the ISM such as NH_3 and H_2CO in the 1960s opened up a new field in astronomy, astrochemistry, in which the abundances and reactions of chemical elements and molecules, and their interaction with light are studied. Up to now, as many as 152 molecules[1] have been detected in the gas of inter- and circumstellar clouds and every year some new species are detected. Amongst the detected molecules are simple species, such as H_2 and CO, but also rather complex and exotic species, such as $HC_{11}N$ [Bell et al. 1997] with the largest unambiguously detected molecules being C_{60} and C_{70}. The detection of a large variety of species in the strongly UV processed medium implies that chemical reactions are very efficient. It is mostly ion-molecule reactions that are responsible for the high production rates of these molecular species in the gas. In cold regions, such as dense clouds, chemistry is now known to proceed via grain catalyzed reactions in which species released from interstellar ices play a key role.

New ground-based and space-borne observatories with improved sensitivity and spectral resolution combined with advances in laboratory techniques shed new light on the molecular diversity. The detected species continue giving us insight in the complex chemistry that takes place in the vast regions of space and perhaps even clues to the formation of life on Earth, or even life outside of our own solar system.

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[1] `http://www.astrochymist.org`

1.2 The interstellar cycle of matter

Although what triggered the formation of the first stars in the Universe after the occurrence of the big bang about 14 billion years ago is still a big mystery, the life cycle of low-mass stars, such as our own sun, is now quite well understood [e.g. Evans 1999, van Dishoeck 2004, and references therein]. Disregarding the birth of the first stars, the evolution of gas and dust in the ISM from stellar birth to death can be depicted as a cyclic event as seen in Fig. 1.1. The building blocks of the newly formed stars are the remnants of the old dead stars; the diffuse interstellar medium is enriched by its previous inhabitants. Stellar remnants, however, are mostly destroyed by the omnipresent strong ultraviolet (UV) radiation, leaving only heavy elements, large molecules such as PAHs, and dust grains intact. New stars are formed from these basic ingredients and the complex chemistry involved in star-formation starts all over again.

The process of low-mass star formation is schematically displayed in Fig. 1.2. In the first stage, the diffuse medium is disturbed by a process, such as a stellar wind or a supernova explosion. This causes dense clouds to form out of the material in the diffuse medium. Once formed, these dense cloud cores, mainly consisting of hydrogen, helium, heavier elements, dust and some larger molecules, are held together by gravitational forces. The densities in these clouds reach a point at which the core of the

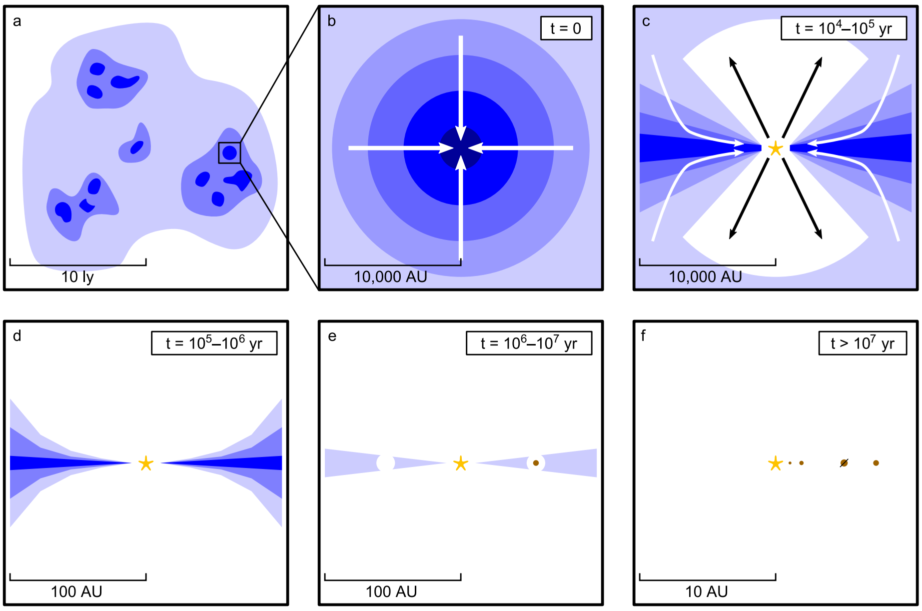

Figure 1.2 Schematic illustration of the different stages of low-mass star formation. Figure taken from Visser [2009].

cloud is completely shielded from intense UV radiation and molecules can form. The temperatures in these dense clouds are low (T ~10 K) and the densities rather high by interstellar standards (~ 10^4–10^5 molecules cm^{-3}), causing molecules to freeze out efficiently on nanometer sized dust particles or possibly on large PAH molecules or clusters of PAH molecules. Thin layers of ice which act as catalytic sites for chemical reactions are formed. Ice abundances, formation, and chemistry will be described in more detail in §1.3.

Within the dense molecular clouds, cores of even higher densities (>10^5 molecules cm^{-3}) are formed. If the density in such a core gets high enough, the core will collapse under its own gravity, forming a so-called protostellar core, i.e. a region of the cloud that will eventually become a star. The collapse releases a large amount of energy and the pressure building up in the core prevents it from collapsing further. At this stage, molecules play a key role in the process of star formation; they convert translational energy via collisions into IR radiation which is emitted at the molecule's specific wavelengths. Some of this radiation can escape the collapsing cloud, resulting in efficient cooling and a continuation of the collapse of the core.

In the next stage, the protostar starts losing angular momentum by expelling mass in bipolar outflows. Additionally, a protoplanetary disk is formed around the central object from which material continues to accrete onto the protostar. In this disk small grains coagulate, forming larger and larger rocks and eventually planets. The outside of the disk is processed by the strong UV irradiation from the new born star and becomes heated and chemically processed. The center of the disk, however, remains cold and the chemical evolution of matter in this part of the disk will be dominated by ice grain chemistry. For low-mass stars, the disk will slowly evolve into a planetary system such as our own.

The formation process of high-mass stars is not yet fully understood, but most likely has many similarities to the formation of low-mass stars. The final stages of the lifecycle of both high- and low-mass stars, on the other hand, are well understood. At the end of its life, the star enriches the interstellar medium by expelling its contents into its surroundings. Stars with a mass smaller than 2.5 Solar masses ($M \leq 2.5M_{\odot}$) such as our own Sun expel their mass in relatively gentle stellar winds, the so-called protoplanetary nebula phase, after which only the hot core of the star will remain; a white dwarf. Stars with a large mass ($M \geq 2.5M_{\odot}$) end their life in a less gentle manner. They return their mass to the ISM in a violent event, a so-called supernova explosion, which can again trigger the formation of new stars as described above.

1.3 Mid-IR absorption bands – Interstellar ices

The presence of ices in the interstellar medium was already proposed in 1937, even before the detection of the first interstellar molecule [Eddington 1937]. The detection of an interstellar ice absorption feature was a fact in 1973, nearly four decades after the presence of ices was proposed. A strong and broad mid-IR absorption band located at ~3 μm was detected and assigned to the H_2O ice stretching mode [Gillett et al. 1973]. The spectroscopic signatures of interstellar ices fall in the mid-IR as absorption profiles which are superimposed on the black body radiation curve of a background star, or embedded object. Since the molecules are confined within the ice, they do not have translational, nor rotational degrees of freedom and absorption of a mid-IR photon by a molecule results in vibration of the molecule only. While interstellar species in the gas phase can be detected in absorption or emission, ices are only detected in absorption. This comes from the fact that the temperature corresponding to mid-IR radiation is higher than the temperature of the ice.

Interstellar ices have been detected either using ground-based, airborne, or space based observatories. Ground based mid-IR observatories, such as the powerful Very Large Telescope (VLT), have a limited spectral window because nearly half of the mid-IR spectrum is blocked by telluric absorptions, primarily H_2O and CO_2. Sophisticated observatories were built to extend wavelength coverage, push the detection limit and to obtain higher resolution spectra. First, the Kuiper Airborne Observatory (KAO) was constructed. Observations with the KAO were conducted at high altitude (40,000 to 45,000 feet), well above most of the H_2O in the atmosphere. This opened up a very important 5 to 10 μm portion of the infrared fingerprint region [Haas et al. 1995]. The combination of airborne with ground based observations provided the first access to nearly all of the mid-IR spectrum for a handful of objects. By the early 1990s, interstellar ices were known to be water-rich mixtures containing species such as CH_3OH, NH_3, H_2CO, etc. The complete mid-IR spectrum of the cosmos was opened up with the launch of the Infrared Space Observatory (ISO), an observatory that revolutionized our understanding of interstellar ices. Free of telluric absorptions, the eyes of ISO revealed many secrets of ices in dense clouds and around star forming regions. The number of detected interstellar ices nearly doubled. While ISO probed quiescent lines of site as well as star forming regions, due to its low sensitivity, however, ISO was limited to observing bright, high-mass, star-forming regions [e.g., van Dishoeck 2004, and references therein]. Its successor, NASA's very sensitive *Spitzer Space Telescope*, opened up the window of opportunity further. It offered the high sensitivity needed to observe faint objects such as low-mass protostars, without being limited by the transmission of the Earth's atmosphere [Chapter 3, Pontoppidan et al. 2008, Boogert et al. 2008, Öberg et al. 2008]. These very successful observatories offered a sensitive view into the kitchen of newborn high- and low-mass stars.

1.3.1 Composition of interstellar ices

It is now established that water is the first molecule to form and freeze out on interstellar grains in the evolution from a diffuse cloud to a dense cloud and that H_2O is the most abundant species in ice toward most sources [e.g. Sonnentrucker et al. 2008]. Typical *Spitzer* absorption spectra combined with L and M band VLT data toward two low-mass protostars with the identified ice absorption bands marked out is shown in Fig. 1.3. The ice absorption profiles are always accompanied by a feature at 10 μm which is typical for the silicate Si–O stretching mode originating from the grain core. Table 1.1 gives an overview of ice abundances with respect to H_2O ice detected towards the high-mass object W33A.

Besides the identified species indicated in Fig. 1.3, the detections of some other molecules based on absorptions in the 5 to 8 μm spectral region have been suggested and are given in parenthesis in Table 1.1. The dominant absorption profile in this region is the 6 μm H_2O bending mode on which a substructure is superimposed. Besides the H_2O bending mode and an absorption band at 7.68 μm, which can confidently be attributed to the CH_4 deformation mode. Assignments of other bands in this spectral region remain controversial. For example, the detection of species such as formaldehyde (H_2CO), formic acid (HCOOH) and the ammonium ion (NH_4^+) have been claimed. Experiments on the formation route of these molecules indeed point out that these molecules are the likely formed under interstellar conditions and thus these species are plausible carriers of these absorption bands [Fuchs et al. 2009, Ioppolo et al. 2010]. An absorption located at 6.2 μm has been tentatively assigned to the CC stretching mode of aromatic molecules trapped in the interstellar ice based on proximity to an interstellar emission band attributed to aromatic species [Keane et al. 2001a]. Experimental data on the spectroscopy of these species in interstellar ice analogues, however, is lacking in the literature. Chapter 4 deals with the spectroscopy of aromatic molecules in ices and their possible contribution to several absorption features in the 5 to 9 μm region.

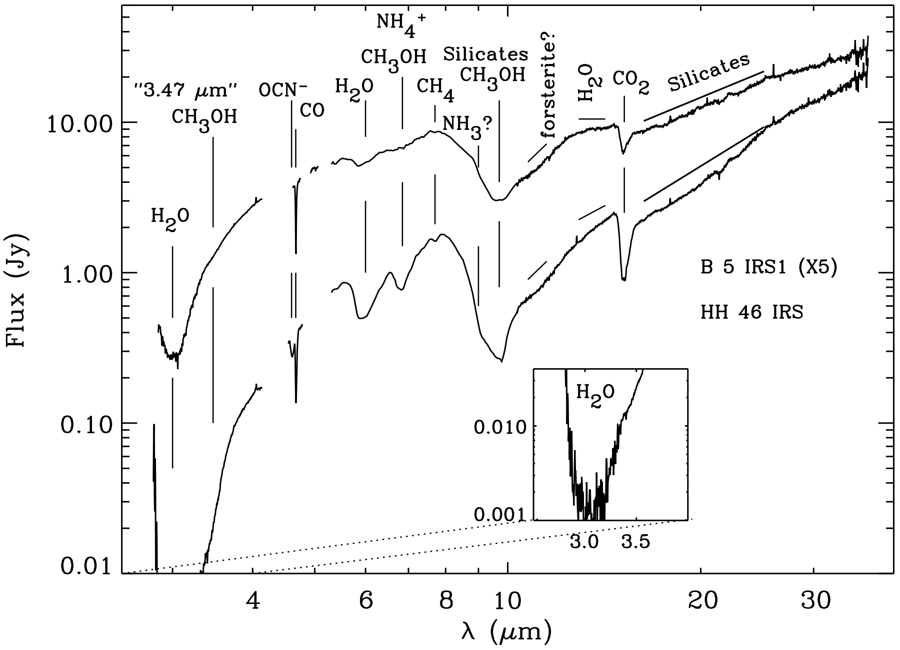

Figure 1.3 *Spitzer* infrared absorption spectrum combined with L and M band observations of low-mass embedded protostars B5 IRS1 (top, multiplied by factor of 5 for clarification) and HH46 IRS (bottom). Identifications and possible identifications are indicated. Spectrum is adopted from Boogert et al. [2004]

Table 1.1 Ice abundances with respect to H_2O ice towards the high-mass protostar W33A taken from Gibb et al. [2000]. The NH_4^+ abundance is taken from Boogert & Ehrenfreund [2004].

Species	Abundance % of H_2O	Species	Abundance % of H_2O
H_2O	100	(HCOOH)	7
CO (polar)	6	(H_2CO)	6
CO (non-polar)	2	(NH_3)	15
CO_2 (polar)	11	(NH_4^+)	12
CO_2 (non-polar)	2	OCN^-	3.5
CH_4	1.5	(SO_2)	2.4
CH_3OH	18	OCS	0.2

The detection of NH_3 ice has been claimed in some studies [e.g. Gibb et al. 2000, Lacy et al. 1998] and upper limits of its abundance towards massive YSO's have been reported in others [e.g. Dartois & d'Hendecourt 2001]. Detections towards low-mass Young Stellar Objects (YSO's), however, remain controversial [Taban et al. 2003]. Most of the NH_3 vibrations overlap with other prominent bands in the spectrum. The most isolated band, the umbrella mode at ~9 μm, overlaps with the strong 10 μm silicate absorption band. The detection of NH_3 in low-mass star forming regions is confirmed and investigated in detail in Chapter 3 of this thesis.

Apart from the identification of frozen out species, mid-IR absorption spectra also allow one to obtain information on physical properties of the ice, such as ice temperature, degree of mixing, and interactions between species. Precise peak positions and band profiles directly reflect the composition and complex physical interplay between the species in ices. This allows observers to discriminate, for example, between polar ices (H_2O-rich) and non-polar ices (H_2O-poor) [Sandford et al. 1988] ice composition, in turn, reflects the formation mechanisms and accretion history of molecules on cold grains. To this end, the interaction between CO and H_2O in binary ices and the effect of mixing rations on band shapes and band strengths is studied in detail in Chapter 2. A similar extensive laboratory study on the effects of mixing H_2O, NH_3, CH_3OH , CO_2 and CO is presented in Chapter 3, where the data are used to interpret *Spitzer* spectra towards 41 low-mass objects.

1.3.2 Ice formation and grain chemistry

Ice covered grains are crucial for the interstellar chemistry leading to the formation of complex molecules. As the embedded object starts nuclear fusion, the ices in the surrounding region are processed energetically by heating, by cosmic ray induced processes and by ultraviolet processing. The rather simple mixtures of ices evolve to more complex ices. When the temperature reaches a high enough value the ices are desorbed and molecules are brought back into the gas phase. Gas phase observations of this stage of star formation indeed exhibit a large variety of complex species that originate from interstellar grains and thus confirm the importance of chemical reactions catalyzed on very cold ices. Chemistry in the gas phase and on grains are thus strongly coupled.

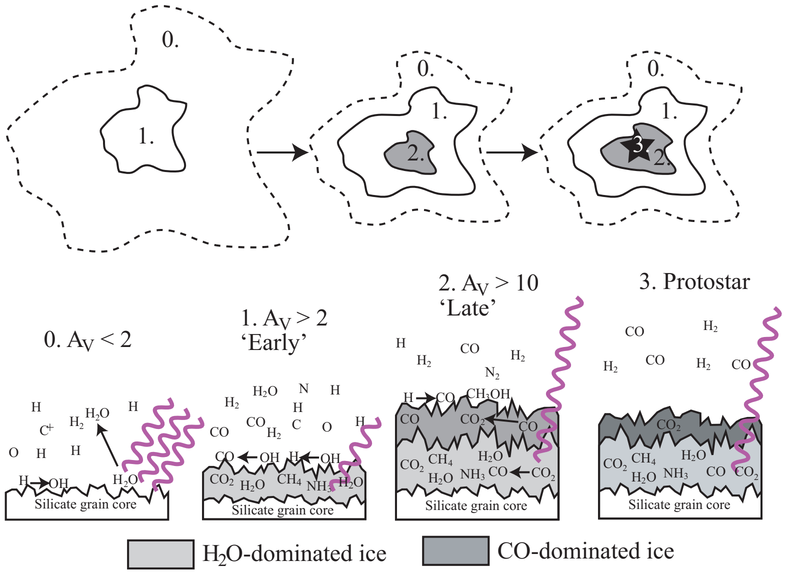

Figure 1.4 A proposed route of ice formation in the evolution from a diffuse to a dense cloud. Figure is taken from Öberg [2009].

The formation of ices in the evolution from a diffuse cloud toward a protostar is illustrated in Fig. 1.4. Tielens & Hagen [1982] proposed a chemical network in which molecules are formed from atoms which are accreted to the grain surface. In their model, the desorption energy of the atom is larger than the energy needed for the atom to hop from one site on the surface to the next. The atom scans the grain surface for a certain amount of time, depending on the grain temperature and desorption energy of the atom. Meanwhile the atom may find a (radical) reaction partner on the surface, react, and form a new species. Since hydrogen atoms are the most mobile species present on the grain, simple H-rich species such as H_2O, CH_4, NH_3 can be formed. Observations towards protostars and dense clouds indeed point to ice layers containing H-rich molecules, dominated by H_2O (polar ices).

Carbon monoxide is, as opposed to the other species mentioned above, efficiently produced in the gas phase. Therefore, CO ice is formed by the freeze-out of CO directly from the gas phase, rather than by reactions on the surface [Pontoppidan 2006]. The CO ice forms on top of the other species in a rather pure layer, forming the so-called non-polar ice. On the grain CO can be further processed by hydrogen addition reaction, resulting in formaldehyde (H_2CO) and eventually methanol (CH_3OH) [Watanabe & Kouchi 2002, Fuchs et al. 2009].

This is not the end of the ice chemistry. Ice species, such as CH_3OH, are also subjected to VUV radiation powerful enough to photodissociate the molecules, leading to radical species in the ice layer [e.g. Öberg et al. 2009c]. The fragments can diffuse on the surface of the ice and react with other radical species or molecules. This system is thought to be responsible for the formation of larger organic molecules such as methyl formate ($HCOOCH_3$), formic acid (HCOOH) and (CH_3OCH_3) [e.g. Garrod & Herbst 2006]. These species have been detected in the gas phase in regions where ices are released in the gas phase by thermal or photo-desorption.

1.4 Mid-IR emission bands – Polycyclic Aromatic Hydrocarbons

The initial ground-based detection of the first of a family mid-IR emission features that are now attributed to polycyclic aromatic hydrocarbons (PAHs) dates back to 1973, when Gillett et al. discovered an unexpectedly broad emission feature peaking near 11.3 μm. Over the next twenty years it was found that this family of bands was surprisingly widespread and associated with a wide variety of different types of astronomical objects including galactic HII regions, reflection nebulae, young stellar objects, planetary nebulae, and post-asymptotic giant branch (AGB) objects. With the launch of ISO, and later *Spitzer*,

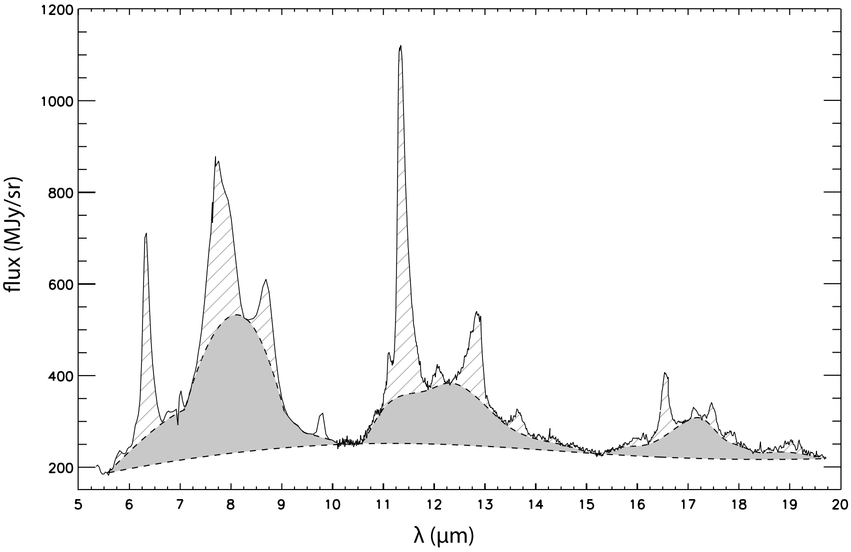

Figure 1.5 Mid-infrared spectrum of the reflection nebula NGC 7023 observed by NASA's *Spitzer* space telescope, illustrating the richness and dominance of the UIR bands. The hatched areas are the distinct UIR bands, the shaded area are UIR plateaus. (Spectrum from Sellgren et al. [2007], shadings courtesy Boersma)

mapping of these features in extended objects became possible and their detection was pushed out to galaxies across the Universe [Peeters et al. 2004b, van Dishoeck 2004, Tielens 2008].

The most prominent of these mid-IR emission bands occur at 3.3, 6.2, 7.7, 8.6, 11.2, and 12.7 μm and are often superimposed on broad plateaus (see Fig. 1.5). The bands originate from regions where material is too cold to be emitting mid-IR radiation. This requires that the carrier emits the bands upon excitation by a single photon of higher energy (UV–near IR) and that the molecules are free gas phase species. Strong correlation between the mid-IR emission bands and the available carbon suggests that carbon is the main building block of the carrier. Additionally, the emission bands also originate from regions which are dominated by harsh UV radiation, implying that the carrier must be highly photostable. The origin of the emission features was long debated, but after more than two decades the hypothesis that they are emitted from highly vibrationally excited PAHs [Allamandola et al. 1989, Puget & Leger 1989] is gaining wide acceptance [e.g. van Dishoeck 2004, Tielens 2008].

PAHs are the largest molecules known in space and contain about 10–20% of the total available cosmic carbon. They have been found in objects, such as meteotites, and in interplanetary dust particles, indicating their prescence in the early stages of the formation of our solar system. PAHs may even play an important role in the formation and evolution of life on Earth [Bernstein et al. 1999, Ehrenfreund et al. 2006].

1.4.1 The PAH building block – Carbon

Carbon is abundantly produced in stars by the triple alpha nuclear fusion process of helium, making it the sixth most abundant species in the ISM. The ability to form 4 bonds makes carbon an important material both in a terrestrial setting as well as in space; carbon acts as a building block from which complex organic molecules can be formed. The carbon atom contains 4 electrons which can participate in molecular bonding; two electrons reside in the 2s atomic orbital and two electrons reside in the atomic 2p orbitals. These atomic orbitals can mix, forming the hybridised orbitals sp, sp^2 and sp^3. In the case of the sp^3 bonded form, one of the 2s electrons is promoted to the empty 2p orbital. The 2s and three 2p electron atomic electron wavefunctions mix to form sp^3 atomic orbitals, giving rise to a tetrahedral structure with the ability to form four covalent σ bonds. This form of hybridisation is found in structures such as diamond, or in molecules such as diamondoids (diamantane, iceane, adamantane, etc.), and alkanes (methane, ethane, etc.). In the sp^2 hybridised form only two of the three 2p orbitals mix with the 2s orbital, resulting in the ability to form three σ bonds and one π bond. This type of bonding occurs in nanotubes, graphene, or PAHs. In the last hybridised form, sp hybridisation, the 2s electron wavefunction only mixes with one of the p electrons. The C atom can form two σ bonds and two π bonds. This occurs in the ethynes, such as acetylene (C_2H_2), or carbon chain radicals (e.g. C_6H). Summarizing, carbon can reside in many different forms, ranging from very stable configurations to highly reactive molecules. Figure 1.6 shows some examples of the forms in which carbon atoms can be found.

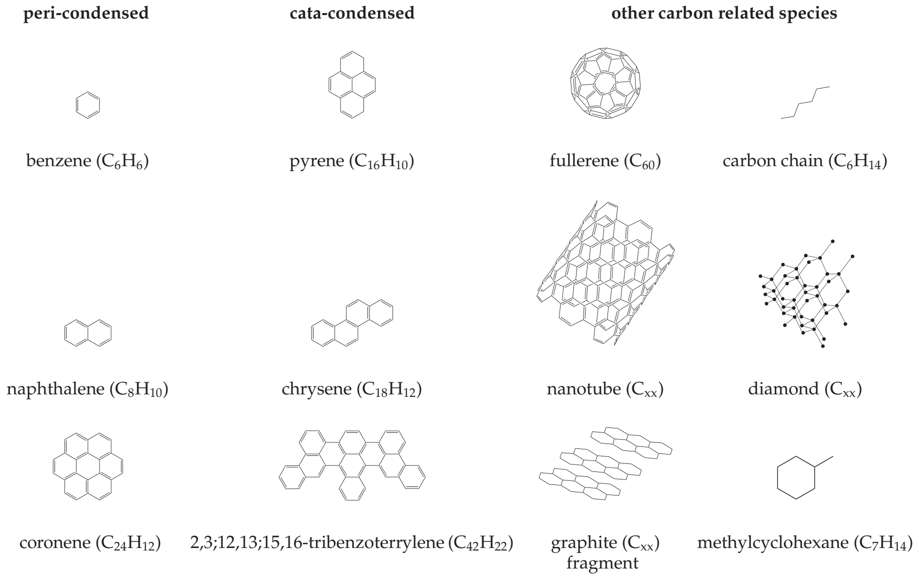

Figure 1.6 Some examples of the various types of carbon containing material. (Figure taken from Boersma [2009])

Aromatic molecules are planar structures with the atoms arranged in one or more rings and a conjugate π-system which consists of a number of delocalized π-electrons given by Hückels rule ($4n + 2$, where $n = 0, 1, 2..$). Polycyclic aromatic hydrocarbons, a class of aromatic molecules, are characterized by carbon atoms arranged in chickenwire shaped ring structures of 6 carbon atoms with 3 electrons participating in sigma-bonds and the left over electron participating in a delocalized π-bond, resulting in a highly stable structure. The simplest member of the stable aromatic family is benzene (C_6H_6). The 6 carbon atom containing hexagon of the benzene molecule forms the building block of larger aromatic molecules consisting of 2 or more rings fused together, the PAHs. PAHs can exist in two main forms; the peri-condensed and cata-condensed PAHs. Peri-condensed PAHs are those which contain C atoms that are part of three fused rings of the aromatic network. Peri-condensed PAHs are therefore centrally condensed and allow for full delocalization of the π electron, resulting in highly stable molecules. Cata-condensed PAH molecules do not have any carbon atoms bonded to more than two rings and therefore have a more open structure which restricts electron delocalization making them less stable.

1.4.2 The origin of interstellar PAHs

In the ISM, PAH molecules are most likely formed in carbon-rich Asymptotic Giant Branch (AGB) stars [Latter 1991, Cherchneff et al. 1992]. Until recently, direct evidence for this was lacking. In general, carbon-rich AGB stars are namely too cold to efficiently excite the PAHs and therefore no strong PAH mid-IR emission is found towards these objects. However, the presence of PAHs in planetary nebulae and post-AGB carbon-rich stars, objects sampling the next stage of stellar ejecta, is unequivocal [Cerrigone et al. 2009]. Stars at this stage of their life are hotter and brighter in the near-UV and hence pump the PAHs more efficiently, making them fluoresce in the mid-IR. Recently, *Spitzer* observations of carbon-rich AGB stars have shown emission from what appears to be a mixture of aromatic species. This mixture seems to include less stable PAH related species that have not yet been 'weeded out' to the more robust PAH forms which can survive the rigors of the UV rich radiation from the hotter stars and general ISM and which produce the well-known emission spectra.

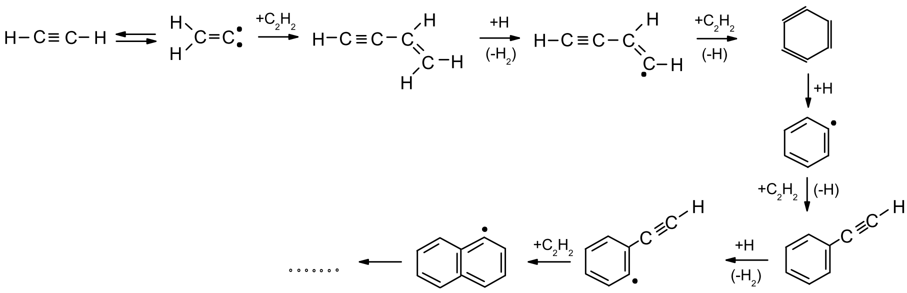

Figure 1.7 Chemical reaction scheme thought to be responsible for the production of the first aromatic ring, from which larger PAH species grow. Figure is reproduced from Frenklach & Feigelson [1989].

The formation process of interstellar PAHs is thought to be similar to the formation of soot in a terrestrial setting [Frenklach & Feigelson 1989, Allamandola et al. 1989, and Fig. 1.7]. The carbon in the outflow of carbon-rich AGB stars is mainly locked up in CO and acetylene (C_2H_2). Since CO is highly stable, the molecule that is most likely responsible for the formation of PAHs in the the outflow of these stars is acetylene and its radical derivatives. The creation of the first aromatic ring is the most problematic step in the formation of PAHs. Hydrogen addition to a C_2H_2 molecule yields the C_2H_3 radical, which can react with a second C_2H_2 molecule, forming C_4H_5. Two reactions involving H abstraction followed by reactions with two acetylene molecules yields C_6H_5, which after a reaction of the remaining triple bond and the unpaired electron forms the first fused ring. From here, more rings can be fused to the aromatic ring by similar acetylene addition reactions. After their formation, they are brought into the ISM by dust-driven winds [Speck & Barlow 1997, Boersma et al. 2006]. They can be regarded as an extension of the grain-size distribution into the molecular (sub nanometer size) domain and are the building blocks from which larger agglomerations — soot particles — of PAHs can be formed.

1.4.3 PAHs in interstellar ices?

The mid-IR emission bands are omnipresent in space, however, the strength of these bands varies strongly. Towards dense clouds the bands have much lower intensity. There are two contributing factors for the quenching of the emission bands as one probes deeper into dense clouds. The first being that the emission bands lose intensity in dense clouds because the extinction increases and there are not enough high energy photons to excite the PAH. The second is that the highly non-volatile PAHs condense out on grains and are incorporated in interstellar ices.

PAHs are not expected to fluoresce in their typical mid-IR modes when incorporated in ices, since the energy is quickly dissipated into the phonon modes of the ice lattice [Allamandola et al. 1985, 1989]. Thus, when trapped in ices PAHs are expected to exhibit mid-IR absorption bands instead. There are lines of evidence that support the existence of PAHs in ices covering interstellar grains. Absorption bands *likely* caused by PAH feature have been reported [Smith et al. 1989, Chiar et al. 2000, Bregman et al. 2000], but extensive laboratory studies are still lacking in the literature. Chapter 4 of this thesis describes a study of the mid-IR spectroscopy of PAH species trapped and photolyzed in H_2O ice with the aim to understand: 1) the roles that PAHs might play in ice processing and astrochemistry, 2) the signature PAHs add to the mid-IR spectra of embedded protostars, and 3) identify PAH:H_2O ice photoproducts and to obtain first order estimates of their abundances in the ices surrounding both low- and high-mass protostars.

Additional spectroscopic studies are performed in the near-UV/VIS regime on PAH containing H_2O and CO ice in order to obtain rate constants for photoreactions of PAHs in ices as a function of temperature. These studies are presented in Chapter 5–7. The studies indicate that PAH are efficiently ionized and react with other ice constituent photoproducts. PAHs are thus shown to have a great impact on the interstellar ice radical budget and charge state, particularly during the early stages of star formation and possibly also in later stages. Although much is now known about the formation of organic molecules on interstellar ices, very little is known about the chemical processes involving the abundantly present and largest organic molecules in the ISM, the PAHs.

1.5 Laboratory spectroscopic ice studies

Laboratory astrophysics aims to understand the physical interactions between and chemical evolution of molecular species in the interstellar medium. The physical interplay of mixed molecular ices and their chemistry have been studied for some decades and are reasonably well understood. The first experiments were extensions of a technique called “Matrix Isolation Spectroscopy” [e.g. Hagen et al. 1979, 1980, Hudgins et al. 1993] and aimed to measure band positions, FWHM and band strengths of the simplest molecular species at cryogenic temperatures. Quickly the field evolved and more realistic “dirty ices” — ice mixtures consisting of 2 or more species with specific mixing ratios — were studied with the aim to understand the complex mid-IR spectra that new observatories were discovering. Even now, these rather simple experiments still offer a wealth of infor-

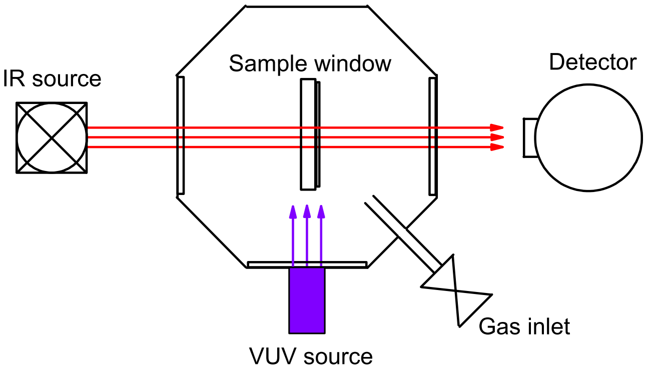

Figure 1.8 A schematic of the high vacuum setup used for monitoring physical interactions and VUV induced chemical reactions in interstellar ices with mid-IR spectroscopy.

mation on the physical interactions between molecules condensed on a cold surface and gain insight in physical parameters — such as temperature and composition — in actual interstellar ices.

Since molecules are brought in close contact in interstellar ices, the grains act as catalytic sites for chemical reactions. These reactions are important for the overall chemistry in the ISM. Many laboratory studies have been devoted to understanding the chemical evolution of ices upon energetic input. Up to date, most experimental studies have employed mid-IR absorption spectroscopy on ice covered cryogenic sample windows or gold surfaces suspended in either high- or ultrahigh vacuum systems. Recently, experimental setups employing near-UV/VIS absorption spectroscopy have become available [Gudipati & Allamandola 2003, and Chapter 5 of this thesis]. Both the mid-IR and near-UV/VIS spectroscopic techniques are the subject of this thesis work and will be described shortly in this section.

1.5.1 Mid-IR ice spectroscopy

A typical mid-IR spectroscopic setup is schematically depicted in Fig. 1.8. A sample window is suspended in the center of a vacuum chamber, which is pumped down by a turbomolecular pump to a pressure of 10^{-7} mbar. The sample window is cooled down by a closed-cycle Helium refrigerator and the sample window temperature can be controlled by means of resistive heating. The (mixed) gas sample is prepared off-line in a glass bulb which can be connected to the vacuumchamber gas inlet. Ice samples are grown by vapor depositing this gas sample onto the cold window. Subsequently, spectra are taken with a Fourier Transform InfraRed (FTIR) spectrometer on samples of different mixing ratios and sample window temperatures. For some of the mid-IR experiments in this thesis, energetic H_2 emission is generated using a Hydrogen flow microwave (MW) discharge lamp, to simulate energetic processing of the ices in the ISM. The resulting vacuum ultraviolet

(VUV) photons at 121.6 nm (Ly-α 10.2 eV) together with a broad molecular H_2 emission band at 160 nm (7.8 eV). Ices are subject to photons of high energy which may alter their chemical identity and the chemical evolution of the photoproducts is tracked as a function of VUV photolysis time. Typically, the FTIR spectroscopic technique has a time resolution of roughly 1 spectrum per 20 minutes for good signal to noise and a resolution of 0.5 cm^{-1}. Furthermore, the sample window needs to be rotated by 90° when changing from the performing spectroscopy to the VUV photolysis position. Thus, this experiment does not allow the possibility of monitoring changes in real-time nor without disturbing the optics; requirements that must be met to fully understand the photochemistry and determine reaction rates. This mid-IR system, however, is ideal for the identification of functional groups in the newly formed photoproducts.

1.5.2 Near-UV/VIS absorption ice spectroscopy

Although some gas phase spectra of small PAH members are available, most of our knowledge on PAHs and related species is based on matrix isolation experiments in which the species of interest are doped in an argon or neon matrix at low temperature, after which the spectra — in both the mid-IR and near-UV/VIS — of the cryogenic samples are taken. These experiments have allowed for comparison of experimental data with theoretical calculations. In addition, the experiments mentioned above using a H_2 microwave powered discharge VUV sources also allow for measuring the spectra of cationic and an-

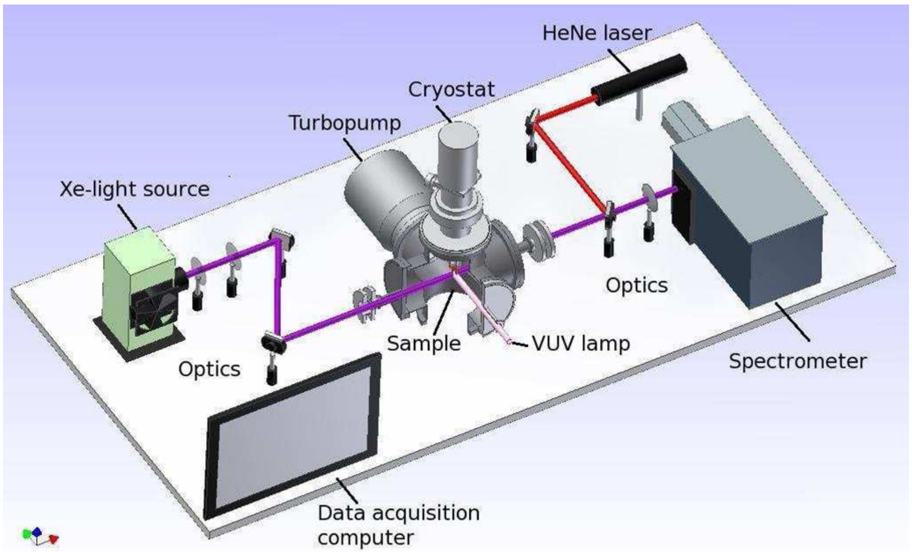

Figure 1.9 A schematic of *OASIS*; the experimental setup for measuring spectroscopy and chemical kinetics of VUV processed PAH:H_2O ice mixtures.

ionic species. Recently, researchers realized that in the ISM PAHs should also condense on cold grains and should be incorporated in ices. Subsequently, they can participate in VUV induced chemical reactions and form more complex species.

The field of PAH photochemistry in realistic interstellar ice analogues was opened by Bernstein et al. in 1999. However, it was soon realized that because PAHs have very weak bands compared to the bands of dominant interstellar species such as, e.g., H_2O, it was difficult to disentangle their chemistry in the laboratory with traditional IR techniques and equally difficult to interpret the role PAHs played in the spectra of astronomical observations. The dominant interstellar ice species, however, do not have electronic transitions and are thus largely transparent in the near-UV and visible spectral range. PAHs on the other hand, because of their delocalized π-electrons, exhibit very strong transitions in this part of the electromagnetic spectrum. Subsequently, an experimental setup — Optical Absorption Setup for Ice Spectroscopy (*OASIS*) — aimed to study PAH electronic transitions in interstellar ice analogues was developed. A schematic the setup is displayed in Fig. 1.9.

The new measurement technique has two major advantages compared to measurements made using mid-IR FTIR spectroscopic techniques. The first is that PAH absorptions in this wavelength regime are much stronger compared to the (very) weak PAH absorptions in the IR (band strengths of $\sim 10^{-13}$ cm molecule^{-1} for near-UV/VIS compared to $\sim 10^{-17}$ cm molecule^{-1} for mid-IR bands). The other advantage of near-UV/VIS studies of ices compared to IR studies is in the time resolution of the spectroscopic measurement. *OASIS*, on the other hand, is capable of measuring one spectrum per 5 ms. The technique is described in more detail in Chapter 5.

1.6 Outline of this thesis

In the work presented here, two laboratory methods are employed to investigate the physical interactions and chemistry in laboratory analogues of astrophysical ices. The first measurements are performed by FTIR studies of ices. These data are almost one-to-one comparable to observational spectra and give good insight in the physical state of the interstellar ice, i.e., its mixing ratio and temperature. Additionally, measurements are performed in the near-UV/VIS spectral regime. This type of spectroscopy is perfectly suited to investigate the fast chemical reactions taking place within laboratory ice analogs of interstellar ices with in situ VUV photolysis. This thesis is thus divided into two parts. Part I of this thesis aims to interpret infrared laboratory measurements to explain the detection, or non-detection, of absorption bands in observational spectra. Part II aims to qualitatively and quantitatively understand VUV driven chemical processes in PAH containing interstellar ices by means of near-UV/VIS absorption spectroscopy.

Part I: Mid-IR absorption spectroscopy

- **Chapter 2** Absorption profiles and band strengths of the H_2O fundamental vibrations change in a mixed H_2O:CO ice. These changes are investigated as a function of the amount of mixed in CO. Additionally, the appearance of a CO stretching mode band at 2152 cm^{-1} is quantified as a function of two physical parameters; the amount of mixed in H_2O and the sample temperature.

- **Chapter 3** The detection of NH_3 ice towards low-mass protostars has long been debated. This chapter aims to detect the NH_3 umbrella mode in a set of 41 *Spitzer* spectra and to derive the abundance of NH_3 with respect to H_2O. Additionally, the CH_3OH abundance is also determined from the CO stretch mode. The obtained CH_3OH abundances are compared to previously obtained data based on the CH_3OH ν_2 C-H stretching mode.

- **Chapter 4:** PAHs are known to be ubiquitous in many phases of the ISM. Spectroscopy and chemistry of PAHs in H_2O ices, however, is poorly understood. This chapter aims to obtain mid-IR spectroscopic information on PAHs trapped in H_2O and to identify the photoproducts resulting from VUV processing of these ices. The data are used to derive upper limits of PAH abundances in interstellar ices towards a low- and high-mass protostar.

Part II: Near-UV/VIS absorption spectroscopy

- **Chapter 5:** This chapter describes a new experimental setup for performing near-UV/VIS spectroscopy on VUV processed interstellar ice analogues. The spectral and temporal performance of the experimental setup is described by means of measurements on pyrene trapped in water ice.

- **Chapter 6:** The system, pyrene trapped and photolyzed in H_2O and CO ice, is described in detail in this chapter. The chemical reactions are quantified by fitting rate constants to the experimental data. The data are used to calculate the limit for detecting Pyrene:H_2O ice and its photoproducts in near-UV/VIS spectra towards dense clouds.

- **Chapter 7:** A set of four PAH:H_2O ice mixtures is investigated spectroscopically. Rate constants are fitted to the experimental and a general conclusion is drawn on the ionization of PAHs in interstellar ices. The findings are incorporated in an astrochemical model demonstrating the importance of these processes in interstellar environments.

- **Chapter 8:** This chapter is dedicated to the future prospects of the experiments on PAH:ice spectroscopy in the Sackler Laboratory for Astrophysics and the future prospects of the near-UV/VIS absorption spectrometer in particular. Open research questions and possible future measurements are briefly discussed.