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Molecules during Stellar Formation and Death

Li, X.

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Author: Xiaohu Li

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Chapter 1

Introduction

THE universe is *huge*, but many of the objects that we see on the night sky —planets, stars, galaxies— actually have their origin in microscopic processes between atoms and molecules. These species also emit many lines that can be detected by sensitive telescopes, so nowadays astronomers explore much of the universe through the *small*—at the scale of molecules and their interactions. This requires knowledge from both *astronomy* and *chemical physics*, stimulating the rapid progress in *astrochemistry* which, in principle, can answer our questions about the universe from the level of *quantum mechanics*—How fascinating! The nature of the universe might be quantum.

1.1 Understanding the universe via astrochemistry

1.1.1 The molecular universe

WE live in an interesting universe, a ‘molecular universe’ (Tielens 2013). To date, nearly 180 different molecules (not counting isotopologues) have been identified in space via their rotational, vibrational and electronic spectra^a, including small molecules like CO and H₂O, and large molecules such as polycyclic aromatic hydrocarbons (PAHs), and fullerenes, e.g., C₆₀⁺, C₆₀, and C₇₀. Molecules are known to be abundant and widespread in all phases of the neutral interstellar medium, from diffuse clouds to dense star- and planet-forming regions, and from the envelopes of dying stars to the central regions of galaxies. The very rich chemistry of these species opens a window for exploring the history and future of stars, star clusters, galaxies, and interstellar matter, both chemically and physically. This is because the excitation and abundances of species are determined by collisions, which in turn are sensitive to gas density and temperature, as well as to the radiation field induced by their surroundings (van Dishoeck 2014). Thus, molecules can be used as ‘dyes’ of specific processes or conditions.

Complex, prebiotic interstellar molecules may represent the first steps toward life elsewhere in the universe. Human beings are not alone in the universe—at least from the perspective of their composition, since there is no big difference between the molecules that make us and those that make up the molecular clouds, planets, stars, nebulae, and many other objects in the universe. Astrochemistry can therefore help to better understand the origin and evolution of our own planet and Solar system, and ultimately ‘us’, thereby attracting an increasing research interest in recent years.

1.1.2 The golden time for astrochemistry

Astrochemistry, also known as molecular astrophysics, is the study of the rich and diverse chemistry that occurs throughout the universe (Herbst & Yates 2013). Specifically, it is the study of ‘the formation, destruction and excitation of molecules in astronomical environments and their influence on the structure, dynamics and evolution of astronomical objects’ (Dalgarno 2008). Thanks to the rapid progress in science and technology, we are now living in a golden time for studying astrochemistry.

Observationally, significant progress has been driven by new telescopes. For example, velocity-resolved spectra of many molecules, especially H₂O, at far-infrared wavelengths that are not accessible from the ground have recently been provided by the Heterodyne Instrument for the Far-Infrared (HIFI) aboard the Herschel Space Observatory (Pilbratt et al. 2010; de Graauw et al. 2010). The Atacama Large Millimeter/submillimeter Array (ALMA), is expected to lead to a brand new decade of astrochemistry due to an enormous increase in sensitivity and spatial resolution compared with earlier facilities. Together with other space missions, such as the James Webb Space Telescope (JWST), and, further into the future, 30–40m class telescopes such as the European Extremely Large Telescope (E-ELT), these facilities will allow for directly imaged astrochemistry on the relevant physical scales, both spatially and spectrally. There is no doubt that some progress will exceed our current imaginations, and one such an example is the Rosetta mission.

^a<http://www.astro.uni-koeln.de/cdms/molecules/>

Rosetta provides a milestone in astronomy that has been written into history. Rosetta is a robotic space probe built and launched by the European Space Agency, which is now performing a detailed study of comet 67P/Churyumov–Gerasimenko and sending back images and data on its composition, including the presence of complex organic molecules. Even expert astronomers were only convinced of Rosetta’s success when they saw the clear video and images made by the satellite and its lander Philae. Rosetta provides a unique view on the most primitive material in our solar system, and thus its origins.

From a chemical-physical perspective, accurate rate coefficients for many important reactions are needed by astronomers and these have been either measured experimentally and/or calculated theoretically. Computational methods include (quasi-)classical and quantum mechanical methods (or mixed methods), based on high accuracy *ab initio* potential energy surfaces. They have benefited enormously from the increase in computer power and availability of powerful (super) computers, as well as from new numerical methods.

Various chemical databases aimed at supporting different kinds of astrochemical models are now available online and are being kept up to date. For instance, the fifth release of the UMIST Database for Astrochemistry (UDfA, McElroy et al. 2013), hereafter RATE12, now contains 6173 gas-phase reactions involving 467 species. These kinds of databases are valuable for simulating the chemistry in different physical environments, such as dark clouds, protoplanetary disks and circumstellar envelopes.

Modern chemical physics and astrochemistry are actually supporting and inspiring each others progress, leading to a very bright and promising future for both fields.

1.1.3 The formation, evolution, and fate of stars

Stars are known to be formed in cool and dense molecular clouds. However, to form a normal star these clouds must collapse, which may be induced either by external forces or by their own gravity. For instance, if the cloud is close enough to a giant supernova the external pressure may lead to its collapse. Or two dense molecular clouds can collide with each other due to gravity. Several stars may be born immediately following the collision of two galaxies.

Fig. 1.1 shows a general picture for the evolution of a star. Once formed, its fate largely depends on the initial mass. Low-mass (small) stars, especially those with mass less than $8 M_{\odot}$, go through the red giant and planetary nebula phase before ending up as a white dwarf. High-mass (big) stars proceed through the red super-giant phase and end as supernova producing a neutron star or black hole. There are many questions surrounding these scenarios, especially about the route of high-mass star evolution which is known to occur in clustered environments. The discussion of this thesis is centered on the chemistry of molecules during the birth and death of low mass stars, which are better understood.

It is understood that the formation of low-mass star can be divided into four observationally defined ‘Classes’, which roughly correspond to various evolutionary stages (Robitaille et al. 2006; Evans et al. 2009). In the Class 0 phase, the parent molecular cloud fragments due to gravity or external forces, and forms first a prestellar core which then collapses into a protostar at its center. As the star-formation process continues, a disk of gas and dust forms around the protostar within the core (Class I object) and which conserves the initial angular momentum of the collapsing cloud. Meanwhile, out-

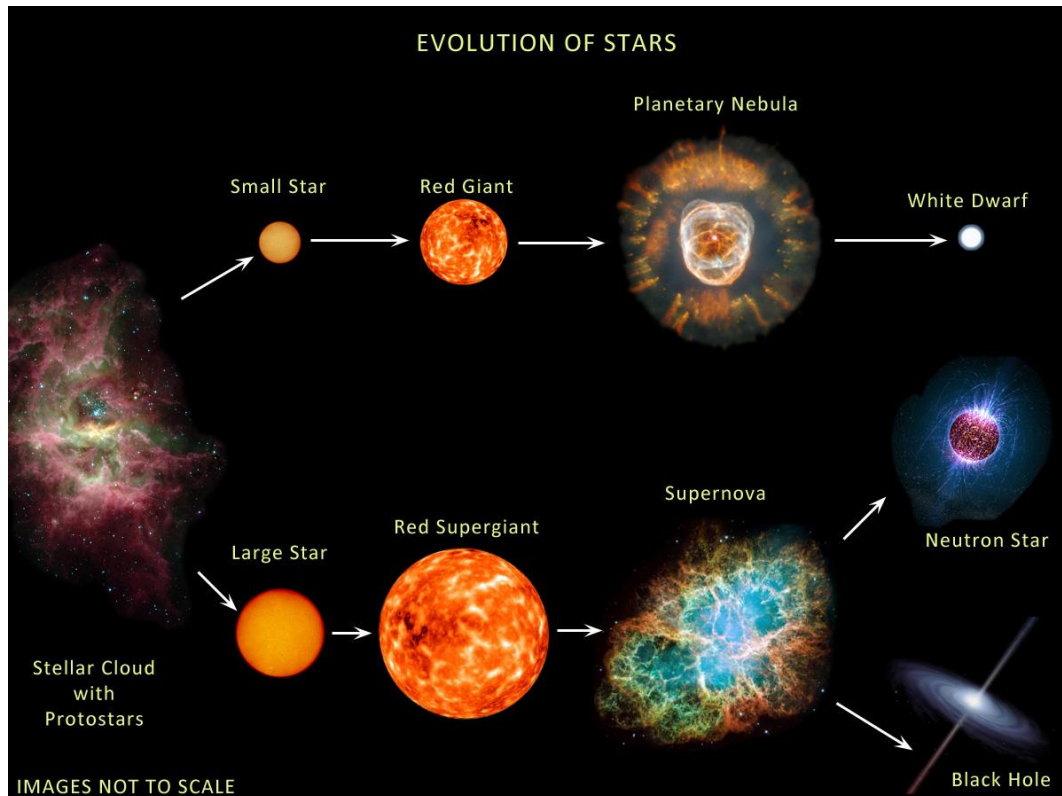


Figure 1.1 — The evolution of a star, determined largely by its mass. A low mass star eventually ends up as a white dwarf whereas a high mass one evolves to a neutron star or a black hole. Figure from E. Moravveji.

flows from the stellar poles eject material from the protostellar system and sweep up the surrounding cloud. Next, the envelope is dispersed and the dust grains stick together more and more, and grow to form pebbles, small rocks and eventually planetesimals in the disks (Class II object). Finally, a planetary system is born around a main sequence star after the remaining disk has been largely dispersed, with only some debris dust left (Class III). Basically, it takes about 10 million years to reach Class III from Class 0. Our solar system has gone through these phases and now, about 4.6 billion years later, still carries the memory of some of these processes.

The gravitational collapse of the cloud liberates heat that increases the temperature of the protostar and induces deuterium nuclear fusion (fast, a short time, ~ 1000 years), which is followed by hydrogen nuclear fusion (much later, $>$ few million yr) which keeps the star on the main sequence for a long period of stability. Low mass stars finally end up as a white dwarf after the material for nuclear fusion is exhausted. One of the most important phases during the late stages of evolution is the asymptotic giant branch (AGB) phase. AGB stars are of particular interest because they eject material into their surroundings, forming a warm and dense circumstellar envelope (CSE). This process leads to the formation of new molecules and the cores of dust grains, and recycles gas and dust to the ISM again for the next loop of star formation (Fig. 1.2).

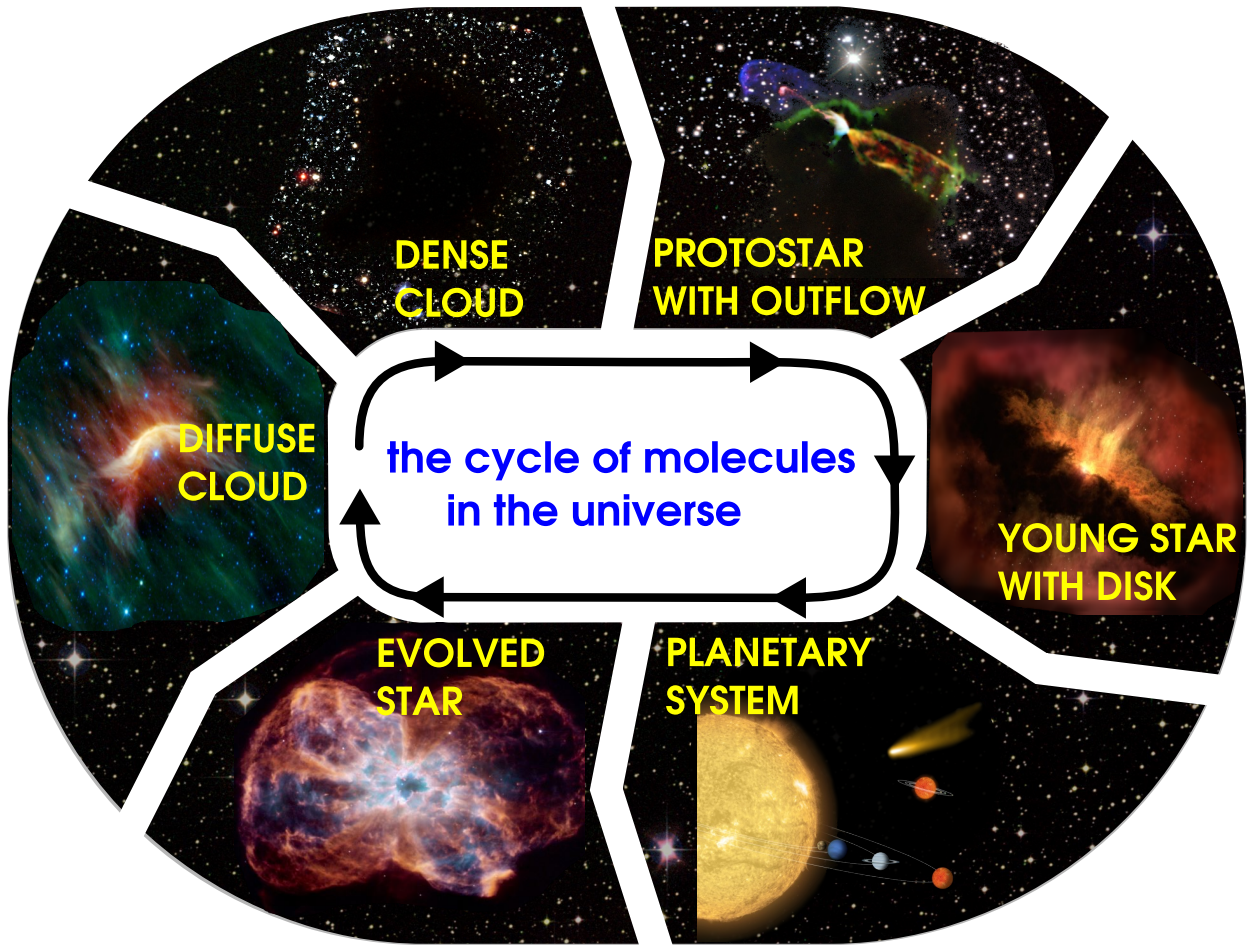


Figure 1.2 — The life cycle of molecules in the universe. Figure by M. Persson, adapted from van Dishoeck (2014).

1.2 The physical-chemical structure during star birth and death

1.2.1 Diffuse + translucent clouds

Denser concentrations in the ISM are called clouds. Key parameters, such as typical densities, temperatures and visual extinctions, of the various types of clouds studied in this thesis are summarized in Table 1.2 (van Dishoeck et al. 2013).

For a diffuse cloud, the gas density (mostly H_2) is rather low, around 10^2 cm^{-3} , with visual extinctions less than 1 mag, and temperatures between 30 and 100 K. Therefore, UV radiation can readily penetrate this kind of cloud and destroy many molecules, increasing the abundances of atoms and ions. The chemistry and physics of translucent clouds is similar to that of diffuse clouds. They have somewhat higher gas densities, around 10^3 cm^{-3} , larger visual extinctions (between 1 to 5 mag), and lower temperatures (15 – 50 K). Again, photodissociation is important in these clouds.

An example of a well-studied diffuse cloud is that toward the bright star ζ Oph, whereas the HD 124314 cloud studied in Chapter 2 is a borderline translucent cloud. Nowadays, these objects can be well-modelled and observed, therefore these clouds are very good candidates for testing and illustrating the importance of new improvements in

Table 1.1 — Different astrochemical environments and their typical physical parameters, adapted from van Dishoeck et al. (2013).

Name	Density (cm ⁻³)	Temperature (K)	A _V (mag)	Examples
Diffuse cloud	10 ²	30–100	≤ 1	ζ Oph
Translucent cloud	10 ³	15–50	1–5	HD 124314
Dense PDR	10 ⁴ – 10 ⁵	50–500	< 10	Orion bar
Cold dense cloud	10 ⁴ – 10 ⁵	10–20	> 10	Taurus cloud
Prestellar core	≥ 10 ⁵	8–15	10–100	L1544
Protostellar envelope				
Cold outer	10 ⁴ – 10 ⁷	8–100	10–100	NGC 1333 IRAS4A
Warm inner / hot core	10 ⁷ – 10 ⁹	≥ 100	100–1000	W3 IRS5 / Orion hot core
Shock	10 ⁴ – 10 ⁵	200–2000	≤ few	L1157 B1
Protoplanetary disk				
Outer	10 ⁶ – 10 ¹⁰	10–500	1–100	TW Hya HD 100546
Inner	10 ⁹ – 10 ¹⁵	100–3000	1–1000	AS 205
AGB envelope				
Outer	≤ 10 ⁸	10–100	1–50	IRC+10216(C-rich)
Inner	10 ¹⁰ – 10 ¹³	100–2000	50–1000	VW CMa(O-rich)

astrochemical models.

1.2.2 Photodissociation regions (PDRs)

Photodissociation regions (PDRs), also called photon-dominated regions, are defined as any interstellar cloud in which UV radiation dominates the chemistry and temperature structure. Traditionally, the term PDR refers to dense clouds located close to a bright star (such as in Orion) but the definition includes the diffuse and translucent clouds discussed above. All of the neutral atomic and most of the molecular gas in the Milky Way galaxy and external galaxies is in PDRs. Moreover, most of the non-stellar infrared and the millimeter ¹²CO emission from a galaxy originates in PDRs (Hollenbach & Tielens 1997). Thus, the study of PDRs can help us to understand the structure, chemistry, thermal balance, and evolution of the neutral interstellar medium of galaxies illuminated by far-ultraviolet (FUV, 6 eV < hν < 13.6 eV) photons.

One of the most important chemical processes in PDRs is photodissociation, which is sensitive to the extinction of UV radiation by dust grains. Astronomers use the extinction at visual wavelengths, A_V, as a reference point to quantify the decrease of the UV radiation with depth into a cloud. Therefore, A_V can be used to characterize the physical structure of PDRs, as illustrated in Fig. 1.3. In this figure, the ultraviolet flux from the interstellar radiation field (ISRF) or nearby hot stars is incident on one side of a cloud, and the physical conditions and chemical composition then depend on visual extinction. For example, at the surface where A_V < 1 mag, the temperature is between 10² – 10³ K. Atoms and ions are dominant, among which H, C⁺, O, N are the most abundant, whereas ices cannot survive.

Deeper into the cloud, e.g., 1 < A_V < 10 mag the temperature is within 10 – 10² K,

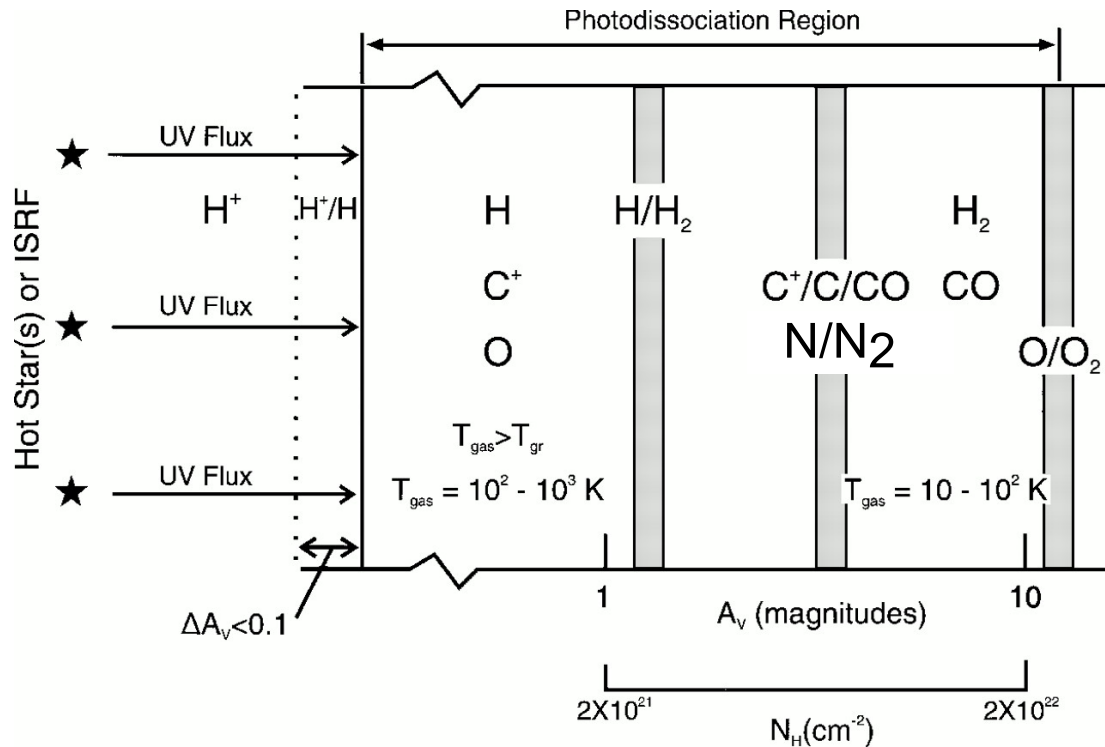


Figure 1.3 — A schematic view of a photodissociation or photon-dominated region. The PDR is illuminated from the left by a strong FUV field. The PDR extends from the H^+/H transition region through the H/H_2 , $\text{C}^+/\text{C}/\text{CO}$ and N/N_2 transitions, until the O/O_2 boundaries. It thus includes the predominantly neutral atomic surface layer as well as large columns of molecular gas. Figure adapted from Hollenbach & Tielens (1997).

and a transition from atoms/ions enriches the fractional abundances of molecules. The transitions forming the most abundant molecular species are $\text{H} \rightarrow \text{H}_2$, $\text{C}^+ \rightarrow \text{C} \rightarrow \text{CO}$, and $\text{N} \rightarrow \text{N}_2$. Ices start to form on grains in this zone. In the innermost region of the cloud where $A_V > 10$ mag, the temperature falls to 10 K, the transition of atoms/ions to molecules is complete, and gas-phase molecules and ices are abundant.

In cold and shielded cloud regions, chemistry is stopped in the gas-phase but can continue in the ice phase when triggered by UV photons penetrating from outside the cloud or produced internally by the interaction of cosmic rays with H_2 . Large PAH molecules can also survive in PDRs (Visser et al. 2007). The highest extinguished objects are called dark clouds.

PDRs occur almost everywhere during stellar evolution. For instance at the surface of protoplanetary disks, at the edge of circumstellar envelopes around AGB stars, and elsewhere. Therefore it is of particular importance to understand the chemistry in PDRs, especially photodissociation of some key species like H_2 , CO , and N_2 .

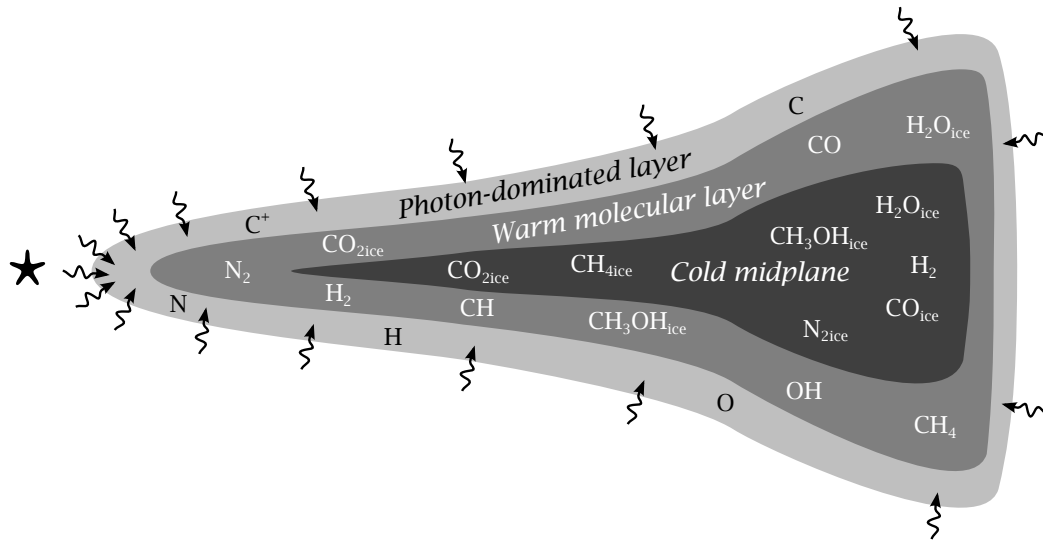


Figure 1.4 — Schematic representation of the three chemical regimes in a circumstellar disk: the photon-dominated layer (irradiated by the protostar and the interstellar UV field), the warm molecular layer, and the cold midplane. Typical species for each regime are indicated. Figure from Visser et al. (2009).

1.2.3 Protoplanetary disks

Disks around young stars are the birthplace of planets and are therefore particularly important targets for astrochemistry. Disks that are rich in gas and dust are called protoplanetary disks, in contrast with the gas-poor debris disks which represent a later evolutionary stage. As shown in Fig. 1.4, a circumstellar disk consists of three different chemical layers: the photon-dominated layer, the warm molecular layer, and the cold midplane (Aikawa et al. 2002; Bergin et al. 2007; Henning & Semenov 2013). The surface of the disk is heated by the protostar and the interstellar radiation field, therefore it forms a PDR with a strong UV field where molecules are dissociated into atoms. Deeper in the disk, molecules are shielded enough from the UV to survive in a warm layer where they are not frozen out. CO, H₂O and other species start to stick to dust grains and form icy layers when the dust temperature drops, leading to ‘snow-lines’. A snow-line is an annulus in a protoplanetary disk where molecules freeze-out from the gas (Sasselov & Lecar 2000). Deep in the cold disk midplane most molecules except H₂, H₃⁺ and their isotopologs are frozen out onto grains. No single instrument or wavelength regime probes the entire and variable disk reservoir. A combination of near-, mid-, and far-infrared spectroscopy combined with spatially resolved interferometric data is needed to explore the physics and chemistry in these objects.

Photodissociation plays an important role in controlling the chemistry of the molecules that are observed in the upper and midplane layers of disks. Moreover, isotope-selective processes have been invoked to explain some of the anomalies found in meteorites formed in the early solar nebula disk (Lyons & Young 2003).

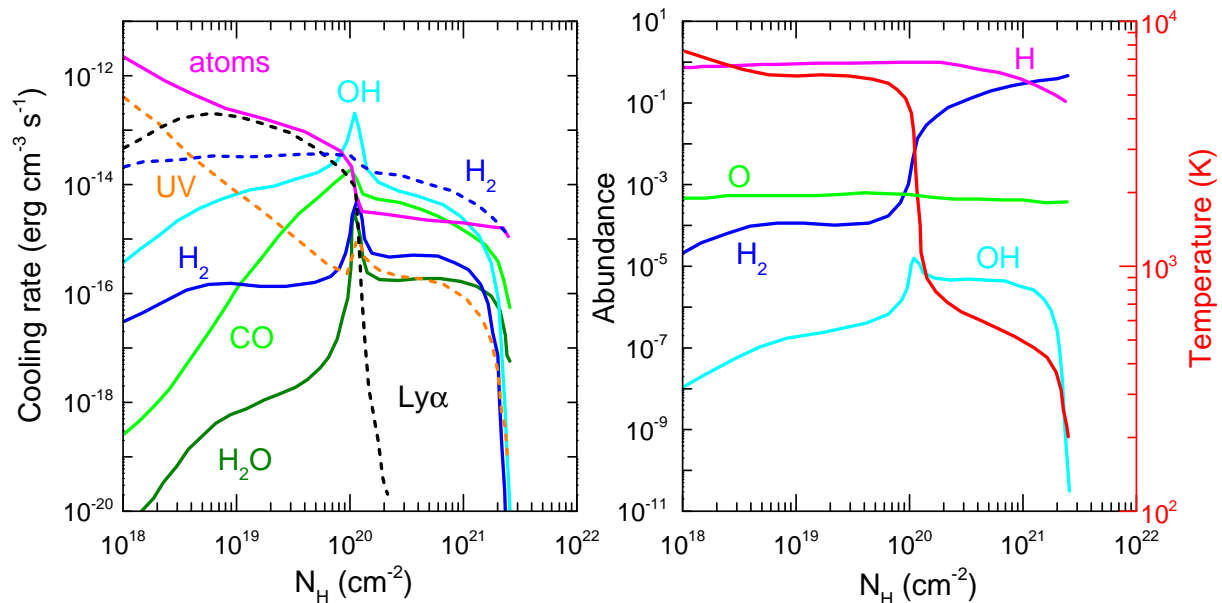


Figure 1.5 — Left panel: Rates of heating and cooling processes in dissociative shocks for a few species. Solid lines, cooling processes; dashed lines, heating processes. Right panel: Abundance profiles of H, OH, O, and H₂, as well as the temperature profile. For both panels, the shock velocity is 80 km s⁻¹, and the preshock density is 10⁵ cm⁻³. Data extracted from Neufeld & Dalgarno (1989).

1.2.4 Shocks

Shock waves provide another interesting observational signal for astrochemists, and occur in compressible media when pressure gradients are large enough to generate supersonic motions. Shocks compress, heat, and accelerate the ISM material. Most shocks in the ISM are thought to be produced by stellar winds or outflows and the strongest originate from supernovae. Interstellar shocks can also result from the collision of two interstellar clouds. Detailed discussions on shocks can be found in reviews, e.g., McKee & Hollenbach (1980).

Generally, shocks are divided into two types: C-type and J-type. For a C-type shock, the shock velocity is less than ~ 50 km s⁻¹ (value depending on the magnetic field strength) (Neufeld & Dalgarno 1989), which is not fast enough to dissociate molecules. Because ions couple with the magnetic field, they receive information about the shock ahead of time and can transmit this information to neutral species. Thus, physical parameters (e.g., temperature, gas density, etc.) in the shocked gas change gradually or ‘continuously’ across the shock front. For a J-type shock, the shock velocity is greater than ~ 50 km s⁻¹, which results in such high temperatures that molecules are destroyed. They are, therefore, also called dissociative shocks or fast molecular shocks. The temperature and density in this kind of shock changes discontinuously at the shock front, like a ‘jump’. J-type shocks may be generated during the birth, throughout the life, and by the explosive death of stars.

Dissociative shocks can be subdivided into two regions: a hotter region ($T > \sim 10^4$ K) containing atoms and ions, and a cooler region ($\sim 10^2$ K $< T < \sim 10^4$ K) containing atoms, ions, and molecules. The heating of gas in shocks is initially dominated by the

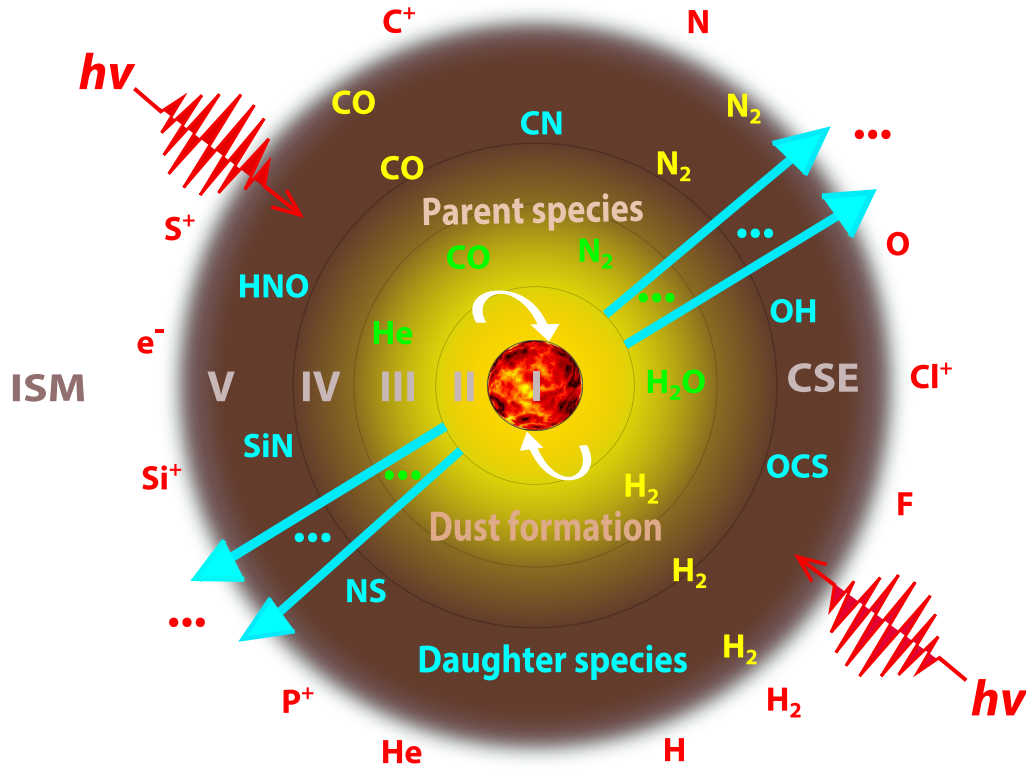


Figure 1.6 — Schematic structure of the CSE for an O-rich AGB star, which is divided into 6 regions for modelling purposes. (I): A degenerate C/O core and He/H burning shell, (II): A convective shell, (III): A stellar atmosphere in which parent species are formed, (IV): A dust formation shell with an expanding envelope, (V): An outer CSE where daughter species are formed primarily by photodissociation, (VI): The interstellar medium (ISM).

conversion of kinetic energy into heat, but absorption of radiation emitted by warmer up-stream gas, and the release of chemical energy during the (re-)formation of molecules also play a role. Cooling of the hottest shocked gas is controlled by the excitation and subsequent emission from electronic levels of the most abundant atoms, and by ro-vibrational emission of molecules further downstream where the shock has cooled. Here we address the importance of molecular reactions during the cooling process.

Fig. 1.5 presents the cooling rates and abundances of a few key species in a dissociative J-type shock. Initially the gas is cooled by atoms, until the temperature decreases to about 3×10^3 K. Then, it is the excitation of molecules that contributes most to the cooling, e.g., H_2 , H_2O , CO , and OH . Among these molecules, OH has the initially-largest cooling rate. In shocked layers, atomic H is more abundant than H_2 until the temperature of the gas decreases to 500 K. Collisions between H and OH in various ro-vibrational states is therefore one of the key processes affecting the chemistry and cooling, and state-selective rate constants between them, as calculated in Chapter 5, are of particular importance.

1.2.5 AGB stars

AGB stars are dying stars of low- to intermediate-mass (from $0.8 M_{\odot}$ to $\sim 8 M_{\odot}$). These stars are in the last nuclear-burning phase having exhausted their supply of H and He, and eject dust and molecules into the surrounding region, creating CSEs. These gas and dust envelopes eventually merge with the ISM and enrich molecular clouds in which new stars may be born. What remains after the AGB phase is a hot C/O core, which illuminates the expanding CSE for a short while and forming a proto-planetary nebula (Fig. C.1). AGB and post-AGB stars, in addition to proto-planetary nebulae, are important sources of dust and several elements and isotopes in the universe. Therefore understanding the composition and evolution of the material they emit is of wide interest.

There are three types of AGB stars: C-rich ($C/O > 1$), O-rich (M-type) ($C/O < 1$), and S-type ($C/O \approx 1$). The Sun will eventually become an O-rich AGB star. As shown in Fig. 1.6, the molecules in the outer expanding envelopes are called ‘daughter’ species, which are driven by hot (1000 – 2000 K) and shocked processes in the inner CSE where ‘parent’ species are formed. The composition of the parent molecules depends on the C/O ratio and is thus different for the various types of AGB stars. This in turn leads to rather different distributions and chemistry of the corresponding daughter species.

Generally, C-bearing molecules are abundant in C-rich AGB stars, from simple CO to large polycyclic aromatic hydrocarbons (PAHs, e.g., Boersma et al. 2006; Cherchneff 2011). The best-investigated AGB star both observationally and theoretically is the nearest C-rich star, IRC +10216 (e.g., Cordiner & Millar 2009; Decin et al. 2010; De Beck et al. 2012; McElroy et al. 2013; Li et al. 2014). To date, nearly half of the 180 identified species in inter- or circumstellar media have been detected around this star, with some being the first detections in any astrophysical environment, e.g., the cyanide anion CN^- (Agúndez et al. 2010b) and FeCN (Zack et al. 2011).

A relatively small, but increasing, number of investigations have been made into S-type AGB stars (e.g., Schöier et al. 2011; Danilovich et al. 2014). The central star in S-type AGB objects is undergoing a transition from an O-rich to a C-rich phase, therefore a mixed chemistry may occur because O-rich material is stored in a stable disk around the central star for some period of time (Willems & de Jong 1986; Szczerba et al. 2007). This interesting dual chemistry may continue to post-AGB stars and even proto-planetary nebulae (see Gielen et al. 2011, and the references therein).

For the case of O-rich AGB stars, OH and H_2O are the dominant species and important progress has been driven by new telescopes (Tenenbaum et al. 2010; Decin 2012), especially the HIFI instrument aboard Herschel (de Graauw et al. 2010), which could provide velocity-resolved spectra at far-infrared wavelengths. Not only ‘small’ and ‘common’ species have been observed, e.g., CO, H_2O , HCN, HNC, CN, OH, NO, SiS, and SiO (e.g., Decin et al. 2010a), but also inorganic molecules, e.g., AlO and AlOH (Tenenbaum & Ziurys 2010). Moreover, surprising emission from PAHs and fullerenes, e.g., C_{60} , have also been found in O-rich post-AGB sources (Gielen et al. 2011).

The outer region of the CSE around an AGB star is a PDR, where photodissociation is important. Therefore, as demonstrated in Chapters 3 and 4, treating properly the photodissociation of parent species is necessary when modelling the distributions and chemistry of daughter species, especially for high-abundance parent species, like CO and

Table 1.2 — Important molecular processes (van Dishoeck 1998).

<i>Bond formation processes</i>	
Radiative association	$X + Y \longrightarrow XY + h\nu$
Grain surface formation	$X + Y:g \longrightarrow XY + g$
Associative detachment	$X^- + Y \longrightarrow XY + e$
<i>Bond destruction processes</i>	
Photodissociation	$XY + h\nu \longrightarrow X + Y$
Dissociative recombination	$XY^+ + e \longrightarrow X + Y$
Collisional dissociation	$XY + M \longrightarrow X + Y + M$
<i>Bond rearrangement processes</i>	
Ion-molecule exchange	$X^+ + YZ \longrightarrow XY^+ + Z$
Charge-transfer	$X^+ + YZ \longrightarrow X + YZ^+$
Neutral-neutral	$X + YZ \longrightarrow XY + Z$

N_2 .

1.3 Astrochemical models

1.3.1 Types of reactions: photodissociation

Astrochemical models may include thousands of reactions, but which belong to only a few different types of processes as summarised in Table 1.2. Understanding the mechanisms behind these basic processes is very important for determining the nature and abundance of molecules observed in the ISM. Detailed discussion on these processes can be found in many reviews (e.g., Smith 2011; van Dishoeck 2014). Among the different types of reactions, photodissociation is the dominant destruction process of molecules in any region exposed to intense UV radiation.

Simply speaking, photodissociation is a process in which a molecule absorbs a UV photon into an excited electronic state and then dissociates to smaller molecules or atoms. Here we take a diatomic molecule AB as an example, see Fig. 1.7. If AB absorbs a photon into an excited electronic state that is repulsive with respect to the nuclear coordinate, then the molecule simply breaks into two atoms, $A + B$. This kind of process is called *direct photodissociation*, and results in a broad cross section as a function of photon energy, with the width of the cross section determined by the steepness of the repulsive potential: the steeper the curve, the broader the cross section.

If AB is excited into a bound electronic state which couples with a nearby repulsive electronic state and then dissociates to atomic form along the repulsive state, the process is called *predissociation*. This kind of photodissociation produces a cross section consisting of a series of discrete peaks or lines, the width of which depends on the sum of the radiative and predissociation rates. If AB is excited into an upper electronic state which does not couple with a lower-lying repulsive state or the vibrational continuum of the ground electronic state, spontaneous emission of photons into the ground state continuum

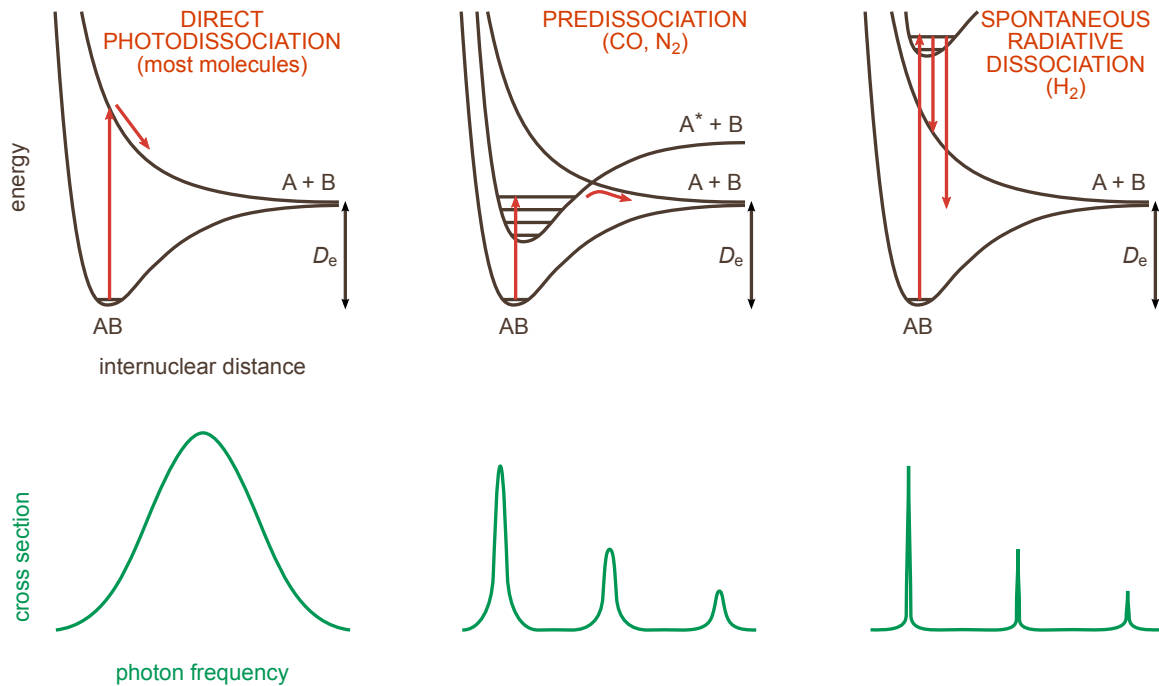


Figure 1.7 — Three types of molecular photodissociation, together with their corresponding cross sections, adapted from van Dishoeck & Visser (2011).

can occur leading to dissociation to $A + B$. This process is called *spontaneous radiative dissociation*. Photodissociation of most molecules, e.g., H_2O , OH , CH^+ , and NH , goes through direct photodissociation. The photodissociation of CO and N_2 is dominated by predissociation. Spontaneous radiative dissociation is important for H_2 . A more detailed discussion of these processes can be found in van Dishoeck & Visser (2011).

Accurate photodissociation rates of molecules are hard to obtain because a molecule can be excited to many electronic states but only some of these states lead to photodissociation. Furthermore, the photodissociation rate depends on the intensity and shape of the radiation field in PDRs. Moreover, there are many possible photodissociation product channels, but their branching ratios are not straightforward to determine. Therefore, it may take a long time to finally fully understand the photodissociation of a molecule. For example, the photodissociation of even the simple diatomic molecule N_2 took more than two decades to finally fully understand, as summarised in Chapter 2. The situation is similar for CO (Visser et al. 2009).

The photodissociation rate of a molecule decreases with depth into a cloud due to UV extinction by dust. For abundant molecules whose photodissociation is dominated by discrete absorption, the UV lines can become saturated for sufficiently large column densities. Thus, molecules lying deeper into clouds are shielded from the dissociating radiation. This ‘self-shielding’ is particularly important for H_2 and CO , and, as shown in Chapter 2, also for N_2 . In the inner planet-forming regions of disks around young stars (inside the H_2O snow-line), the column densities of H_2O become so high that this molecule also becomes self-shielding even though its photodissociation is controlled by broad absorptions due to direct photodissociation (Bethell & Bergin 2009).

1.3.2 Astrochemical models

Astrochemical models are used to simulate the abundances of molecules in various astrophysical environments, including their variation as a function of time or distance. In the ISM, the chemistry is governed by gas-phase reactions together with interactions on grain surfaces. The development of these models started with relatively simple and small chemical networks of gas-phase reactions and was then extended piece-by-piece, taking into account more complex factors step-by-step. Nowadays, both gas-phase and grain-surface reactions are considered in many models.

Depending on the lifetime of the physical environment, models may assume equilibrium chemistry or include its time-dependence. The physical conditions in models can also vary with time. In some cases the main physical conditions are temperature, gas density, and visual extinction, and are held fixed while considering the chemistry as it evolves with time, e.g., in so-called single-point models. It is possible to obtain a full picture of the possible range of chemical evolution by running single-point models for many different fixed physical conditions. Models which consider a gradient of temperature, density, or visual extinction as a function of distance and time, or include dynamical movement, are more realistic but more complex. A detailed discussion of these matters centered on dark cloud models can be found in a recent review (Agúndez & Wakelam 2013).

It is primarily the physical conditions of the object under study that determine the requirements of an astrochemical model. The model is just a tool. The aim of using it is to understand the chemistry of the environment without delving into the maximum-possible complexity. For example, grain-surface reactions are very important in simulating the processes in protoplanetary disks because there is a large amount of ice-coated dust there. However, in hot CSEs the dust temperature is high in the inner shells and the radiation field strong enough in the outer CSE so that it is hard for ice to survive. Therefore, pure gas-phase chemical modeling can already give good predictions. Nevertheless, since the gas density is relative high at the inner radii of CSEs, the interaction of gas and bare-grains could potentially play a minor role there.

Another very important point in astrochemical simulations is the description of the radiation field, which depends on the location of interest. In the CSEs of AGB stars, the photospheres of the central stars typically have effective temperatures around 3000 K and cannot cause the photodissociation of molecules, thus one only has to take into account photons from the ISM. However, in post-AGB or protoplanetary nebulae, the central stars are very hot, up to $T_{\text{eff}} \approx 100\,000$ K, and their radiation can destroy molecules rapidly, therefore one must consider these effects. Cosmic ray interactions with H_2 lead to another, weaker source of radiation which is important in the most shielded parts of dark cloud cores and protoplanetary disks.

Once the physics of the environment are well understood and the basic model has been built, the chemical evolution is modelled through reaction networks and a reliable chemical database is needed. To prevent the use of inappropriate or obsolete data and extrapolations, the best way is for experts to build such a database, and more importantly, maintain it. This in turn requires close interaction between astrochemists and chemical physicists. Fortunately, much hard work has already been done by some pioneer astrochemists. Three main chemical databases currently exist for interstellar gas-phase

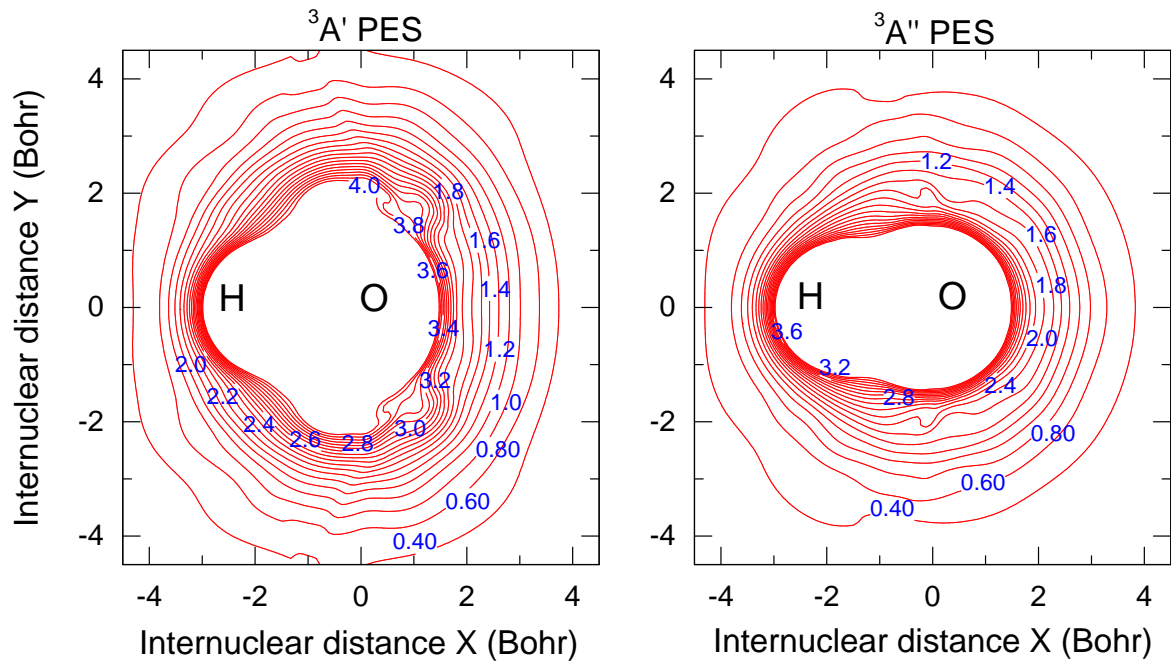


Figure 1.8 — Potential energy surface of the $\text{O}(^3\text{P}) + \text{H}_2$ system. Atomic O and H are fixed at the (X, Y) positions of (0, 0) and (-2, 0), whereas another H is free to approach them from all directions, causing different total potential energies (in units of eV). Figure from Li et al. (2014).

chemistry. The UDfA (UMIST Database for Astrochemistry) database (previously called the UMIST database, created by Tom Millar) is the best-known and most widely used. A second is the OSU database initially developed by Prasad & Huntress (1980), updated by Chun Leung and Eric Herbst, and then revised over the last twenty years by Herbst and collaborators. Recently, a third, the KInetic Database for Astrochemistry (KIDA, see Wakelam et al. 2012), has been built and is starting to be used. The simulated results may be different depending on the database used in the model calculation. A comparison between the results obtained by using UDfA and KIDA is included in the review by Agúndez & Wakelam (2013). In this thesis, we employ the UDfA database for our astrochemical simulations.

1.4 Basic chemical physics

The molecular data used in astrochemical models, such as collision rates, reaction rate coefficients and photodissociation cross sections, come from chemical physics (sometimes called physical chemistry) and are studied both experimentally and theoretically. Experimental techniques, which have heavily relied on lasers over the past 50 years, can provide information on the reaction cross sections, products and their energetics, branching ratios, and reaction mechanisms, amongst other things. These experiments, such as those using crossed molecular beams with mass spectrometric detection, chemiluminescence, and laser induced fluorescence, are very expensive and time consuming, and sometimes dangerous or difficult to conduct. Alternatively, computational chemistry, which is based on strict quantum mechanics or classical approximations, can provide similar or even

more-accurate information on chemical properties and molecular processes than can experiments, especially for radicals and ions which are difficult to prepare in the lab. This is thanks to the progress with multicore (super-)computers. Data from experiments can then be used to benchmark the chemical-physics models.

Within the Born-Oppenheimer approximation, it takes two steps to model a molecular process such as photodissociation or a collision. First, one needs to solve for the eigenvalues of the electronic Hamiltonian while keeping the nuclear positions fixed. For a diatomic system, this results in a potential energy curve for each bound or unbound electronic state (see Fig. 1.7), whereas for a tri- or poly-atomic molecule, the solutions are depicted as potential energy surfaces (PES). These PESs can be determined by first computing the energy of a large number of geometrical configurations using *ab initio* calculations from first principles of quantum mechanics or some approximate method. These points are then fitted to a convenient functional form. For a polyatomic system, accurate potential energy surfaces are very hard to compute and impossible to derive from experiments. The computation of the many excited electronic states of a triatomic molecule, or the ground electronic state of a polyatomic system typically takes years of hard work before the construction of reliable PESs.

After the calculation of a PES, the dynamics of the nuclei on it need to be solved, with the specific method depending on the application. In this thesis, the main applications are photodissociation and state-to-state reaction rates. Obtaining photodissociation cross sections may involve solving the coupled-channels nuclear Schrödinger equations, whereas other techniques may be more appropriate for solving the dynamics on the ground state potential surface to determine inelastic collision rates or reaction rate coefficients. Despite the differences between employed methods, such as for these two processes, the underlying idea is the same.

Taking the reaction between H and OH as an example, a high-accuracy potential energy surface for the reaction between $O(^3P)$ and H_2 , constructed by Rogers et al. (2000b), is shown in Fig. 1.8. These same PESs can also be used to study its reverse reaction, $H + OH$, which is experimentally difficult to measure because it is hard to prepare coincident beams of pure OH and H. To accurately evaluate a thermal rate coefficient of a reaction theoretically one has to know the contributions from the most important reactant rovibrational states. This requires individual state-to-state cross sections and reaction rates, each of which may take a long time to calculate. Full quantum mechanical calculations (QM) provide the most accurate method when solving the nuclear equations, but become computationally prohibitive at high temperatures. For the case of $H + OH$, the best compromise solution are Quasi-Classical Trajectory calculations (QCT), which are based on Newton's equations of motion and are more efficient than QM. Transition State Theory (TST) is another useful tool for calculating approximate rate constants for reactions occurring in the gas phase and in the condensed phases (Truhlar & Garrett 1984) and assumes that a reaction proceeds along the path of least potential energy. This method becomes especially important when the reaction system is large.

1.5 Contents of this thesis and outlook

This thesis explores the chemistry of interstellar and circumstellar molecules during star formation and death. The subjects of the next four chapters and the main questions they address are outlined below. From the perspective of chemical physics, the most important outcome of this thesis lies in that the rates for two important reactions are determined accurately for the first time: N_2 photodissociation and reaction rates (both state-to-state and thermal) of OH with H.

In Chapter 2, the photodissociation rate of interstellar N_2 is determined. Nitrogen is one of the most abundant elements in the universe, and the partitioning of nitrogen between N and N_2 controls the formation of more complex prebiotic nitrogen-containing species. Photodissociation is the primary destruction route of N_2 in any region where UV photons are present. Based on a highly-accurate spectroscopic model of the molecule, new photodissociation rates and shielding functions for N_2 are computed. The $\text{N} \rightarrow \text{N}_2$ transition in PDRs and other astrophysical environments is then modeled, and some interesting questions are raised about a previous marginal detection of N_2 in the absorption spectrum of a translucent cloud.

In Chapter 3, the newly derived N_2 photodissociation rates from Chapter 2 are applied to the chemistry in the circumstellar envelope of a C-rich AGB stars, IRC +10216. This source is the nearest asymptotic giant branch star and the brightest object in the sky at far-infrared wavelengths, and one of the richest molecular sources in the sky. According to a sensitivity analysis of the entire chemical network, the process $\text{N}_2 + h\nu \rightarrow \text{N} + \text{N}$ is one of the most significant reactions in the outer CSEs, but has never been treated properly. In addition to using the latest reported photodissociation rates and shielding functions of N_2 and CO in our models, a new fully-3D spherical model of an isotropic interstellar radiation field has been employed. Using the RATE12 gas-phase reaction network with our improved photodissociation treatment, it is found that the abundances of many N- and C-bearing species are affected. The new results are compared with observational data.

In Chapter 4, the chemistry of O-rich AGB stars is studied using a similar approach as in Chapter 3, with our updated photodissociation treatment of N_2 and CO. The specific CSE modeled is that of the AGB star IK Tau for which many new data exist. Our improved model of CSE chemistry from Chapter 3 is combined with a new appraisal of the critical ‘parent species’, i.e., the products of high-temperature and shocked chemistry in the inner CSE which seed our model of the cooling outer-CSE. The important formation and destruction pathways of molecules in IK Tau are identified, this time finding higher abundances of O-bearing species relative to Chapter 3, such as H_2O , OH, and NO. The appearance of several species formed in the outer-CSE model can be linked to the abundances of parent species, and can thus put constraints on their abundances through comparison with observations of IK Tau.

In Chapter 5, state-dependent rate coefficients for the experimentally-difficult reaction, $\text{H} + \text{OH} \longrightarrow \text{O} + \text{H}_2$, are computed. The reverse $\text{O} (^3\text{P}) + \text{H}_2$ system has attracted interest for more than half a century since it is known to be a participant in combustion processes and plays an important role in warm interstellar gas such as shocks, clouds exposed to intense UV radiation, and the inner regions of protoplanetary disks. Despite

extensive theoretical and experimental investigations on $\text{O} (^3\text{P}) + \text{H}_2$, few studies have been done for the forward reaction, $\text{H} + \text{OH} (v, j) \rightarrow \text{O} + \text{H}_2$. In particular, accurate state-specific rate constants of this reaction, which are needed in astrochemical models of dissociative shocks and disks, are lacking. In this chapter, highly-accurate *ab initio* potential energy surfaces are used to perform quasi-classical trajectory calculations as well as transition-state theory methods. The computed state-to-state cross sections over a range of collision energies and internal ro-vibrational excitation states are then used to determine state-to-state and thermal rate constants, including their temperature dependencies.

The main results of this thesis are:

- Chapter 2. The new interstellar N_2 photodissociation rate has been determined with an uncertainty of only 10%, down by an order of magnitude compared with the previous uncertainty. Self-shielding and shielding by H_2 and dust are more effective than that by H and CO . The transition of $\text{N} \rightarrow \text{N}_2$ occurs at nearly the same depth into a cloud as that of $\text{C}^+ \rightarrow \text{C} \rightarrow \text{CO}$.
- Chapter 3. N_2 and CO are more abundant at the edge of a circumstellar envelope than predicted by previous models due to a proper treatment of their self- and mutual shielding. The new photodissociation treatment induces large changes in the predicted column densities (factor of 10) and peak radii of some species (e.g., C_nN and C_nN^- carbon chains) in the IRC +10216 carbon-rich AGB star model. The new models can be tested directly by future ALMA observations.
- Chapters 4. The most abundant daughter species suitable as targets for future observations in the AGB star IK Tau were identified, quantified, and analysed, including all C-, N-, O-, Si-, S-, P-, Cl-, and F- bearing molecules. Key molecular processes in O-rich AGB envelopes are photoionization/photodissociation, ion-molecule reactions, and dissociative recombination. The upper limit on the potential parent species CH_4 is $< 2.5 \times 10^{-6}$, based on the observed upper-limits of two daughter species, C_2H and CH_3OH . Future observations of NS and N_2H^+ can be used to constrain the abundances of parent species S and N_2 . Finally, the stellar mass-loss rate has a large impact on the calculated abundances, which is usually difficult to obtain from observations directly.
- Chapters 5. Rate constants for OH in excited vibrational and rotational states are orders of magnitude larger than the thermal rate constants, which needs to be taken into account in astrochemical models. An effective barrier may be induced by the rotational excitation at lower collision energies (< 0.6 eV).

The future outlook of astrochemistry is bright. This is evident in the rapid progression of observational techniques as well as theoretical and laboratory physics and chemistry, and their combination into sophisticated models of real astrochemical objects. This thesis attempts to cover a range of these astrochemical aspects. There are many interesting topics which are the subject of ongoing efforts in the field of astrochemistry. Here, I would like to mention a few possible projects that are a natural extension of current work in the coming years. Evolved stars are of particular interest and raise a few important questions which are yet to be solved. For example, what is the chemistry in S-type AGB stars? How to correctly simulate the chemistry in post-AGB objects like protoplanetary nebulae with increased central UV radiation? Which of the predictions made in this

thesis will stand up best to future observational tests made possible by spatially resolved observations with ALMA? Questions also remain about the parent species in AGB CSEs, including the abundances of elemental N and S: how well are those predicted by shock-induced non-LTE chemical models? In a broader context, in what form do the gas and dust ejected from evolved stars eventually get transferred to another generation of forming stars? More observations will raise even more questions, and with improved models some will also be answered. But, understanding these observations will undoubtedly require further efforts from chemists determining accurate rate coefficients.

One also needs to look much further into the future. Take again the Rosetta mission as an example. Planned more than 30 years ago, this mission not only helped in answering many interesting astrochemical questions but it also proved that (nearly) anything is possible in the future as long as one has a long-term vision! This holds in particular for the field of astrochemistry.

