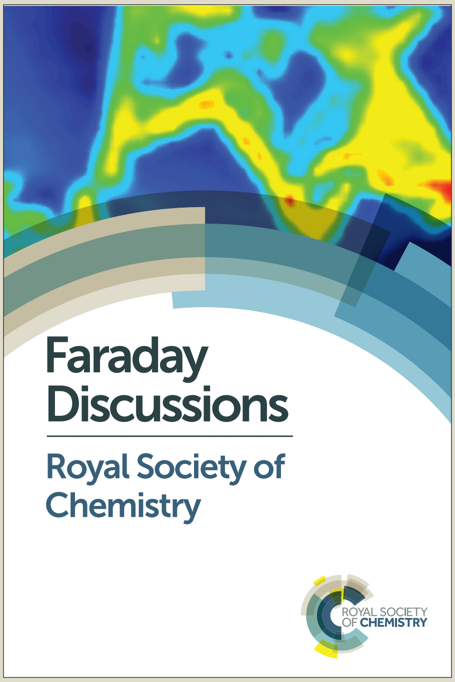
Faraday Discussions

Accepted Manuscript

This manuscript will be presented and discussed at a forthcoming Faraday Discussion meeting. All delegates can contribute to the discussion which will be included in the final volume.

Register now to attend! Full details of all upcoming meetings: http://rsc.li/fd-upcoming-meetings



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/faraday_d

PAPER www. rsc.org/faraday_d | Faraday Discussions

Astrochemistry of dust, ice and gas: introduction and overview

Ewine F. van Dishoeck[a,b]

Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
First published on the web Xth XXXXXXXXXX 200X
DOI: 10.1039/c000000x

A brief introduction and overview of the astrochemistry of dust, ice and gas and their interplay is presented. The importance of basic chemical physics studies of critical reactions is illustrated through a number of recent examples. Such studies have also triggered new insight into chemistry, illustrating how astronomy and chemistry can enhance each other. Much of the chemistry in star- and planet-forming regions is now thought to be driven by gas-grain chemistry rather than pure gas-phase chemistry, and a critical discussion of the state of such models is given. Recent developments in studies of diffuse clouds and PDRs, cold dense clouds, hot cores, protoplanetary disks and exoplanetary atmospheres are summarized, both for simple and more complex molecules, with links to papers presented in this volume. In spite of many lingering uncertainties, the future of astrochemistry is bright: new observational facilities promise major advances in our understanding of the journey of gas, ice and dust from clouds to planets.

1 Introduction

The space between the stars is not empty, but is filled with a very dilute gas, the interstellar medium (ISM). The ISM is far from homogeneous and contains gas with temperatures ranging from more than 10^6 K down to 10 K and densities from as low as 10^{-4} particles cm^{-3} to more than 10^8 cm^{-3}. The colder and denser concentrations of the gas are called interstellar clouds, and this is where molecules, dust and ice are detected. Even at the upper range of densities, interstellar clouds are still more tenuous than a typical ultra-high vacuum laboratory experiment on Earth. Thus, interstellar space provides a unique environment in which chemistry can be studied under extreme conditions. From an astronomical perspective, dense clouds are also important because they are the nurseries of new generations of stars like our Sun and planets like Jupiter or Earth. This combination makes astrochemistry such a fascinating research field, for both chemists and astronomers alike.

Traditional chemistry would predict that virtually no molecules are formed at typical densities of 10^4 cm^{-3} and temperatures of 10 K of dense molecular

---

[a] *Leiden Observatory, Leiden University, P.O. Box 9513, 2300 RA Leiden, the Netherlands; E-mail: ewine@strw.leidenuniv.nl*
[b] Max-Planck-Institute für Extraterrestrische Physik, Giessenbachstrasse 1, Garching, 85748, Germany

clouds, with 1000 times more hydrogen than any other chemically interesting element. The detection of nearly 180 different species over the past 45 years (not counting isotopologs) demonstrates the opposite: there is a very rich chemistry in space. Molecules like CO and H_2O have even been detected in distant galaxies out to high redshifts, when the Universe was less than 1 Gyr old[1]. Large Polycyclic Aromatic Hydrocarbon molecules (PAHs) are also detected across the Universe[2]. Closer to home, an increasing variety of molecules (no longer just the simplest ones) are found in luminous galaxies undergoing bursts of star formation at a rate up to 100 times higher than that in our own Milky Way[3,4]. In star-forming clouds within our Galaxy, a myriad of species has been found, some of which are prebiotic, i.e., molecules that are thought to be involved in the processes leading to living organisms. Fullerenes such as C_{60} have also been identified[5]. Finally, simple molecules including H_2O are being detected in the atmospheres of giant exo-planets[6,7].

Astrochemistry, also known as molecular astrophysics, 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' as stated by Dalgarno[8]. This definition includes not only the chemical aspects of the field, but also the fact that molecules are excellent diagnostics of the physical conditions and processes in the regions where they reside. This sensitivity stems from the fact that both the excitation and abundances of molecules are determined by collisions, which in turn are sensitive to gas temperature and density as well as to the radiation from nearby stars.

The main questions in the field of astrochemistry therefore include: how, when and where are these molecules produced and excited? How far does this chemical complexity go? How are they cycled through the various phases of stellar evolution, from birth to death? And, most far-reaching, can they become part of new planetary systems and form the building blocks for life elsewhere in the Universe?

The topic of this Symposium —dust, ice and gas— is at the heart of these questions. This brief overview is aimed at providing background information for non specialists on the conditions and ingredients in interstellar space (§2), the tools that are used in astrochemistry (telescopes, laboratory experiments, computer simulations) (§3), the main characters of this symposium (dust, ice and gas) (§4), the 'play' (chemical processes) (§5), and the 'plot' (evolution from clouds to planets (§6–11), followed by some concluding remarks (§12). There has been no shortage of excellent and much more detailed (and partly overlapping) reviews of the field over the last few years, see[9–14] for further information.

Throughout this talk the interdisciplinary aspect of this research will be emphasized as a two-way street: astrochemistry needs basic data on molecular spectroscopy and chemical processes, but also inspires new chemical physics through studies of different classes of molecules and reactions that are normally not considered on Earth. Indeed, astrochemistry is a 'blending of astronomy and chemistry in which each area enriches the other in a mutually stimulating interaction'[8].

Fig. 1 Blow-up of the Hubble Space Telescope optical image of the Carina nebula, showing dark molecular clouds as well as more diffuse ionized gas between the stars. The clouds are dark at visible wavelengths due to extinction by dust grains; young stars are embedded within them. In the colder regions, the dust particles are covered by ice mantles. Gas-phase molecules are present throughout the dark clouds. The distance to the cloud is 2.3 kpc, and the image covers a region of 0.94 pc in size. Colors: forbidden transitions of [O III] (blue), [N II] (green), and [S II] (red), together with hydrogen Hα (green). Credit: NASA/ESA/M. Livio.

2 The setting: interstellar clouds

2.1 Images of clouds

Figure 1 presents an *Hubble Space Telescope* image of a small part of the Carina star-forming cloud. The colorful nebulae are due to ionized gas at 10^4 K that emits brightly at optical wavelengths and consists of atomic hydrogen recombination lines (primarily Hα) and forbidden electronic transitions of atoms such as [O III], [N II] and [S II]. The dark areas are the dense molecular clouds which contain $\sim$0.1 μm-sized particles of dust composed of silicates and carbonaceous compounds which absorb and scatter the light. They also shield molecules from the dissociating ultraviolet radiation emitted by nearby stars. The dense cloud complexes can be quite large (tens of parsec* across) and massive (up to 10^5 solar masses†) but the process of star formation is quite inefficient and only a few % of the mass of the cloud is turned into stars.

The UV radiation absorbed by dust grains is converted to heat, raising their temperatures from $\sim$10 K in the most shielded regions to $\sim$50 K in more exposed

---

$*$ 1 parsec (pc)=3.1×10^{18} cm = 3.26 light year
† 1 $M_\odot$=2.0×10^{33} gr

gas. This heat is then radiated away through thermal emission in the far-infrared part of the spectrum as observed for example with the *Herschel Space Observatory*.

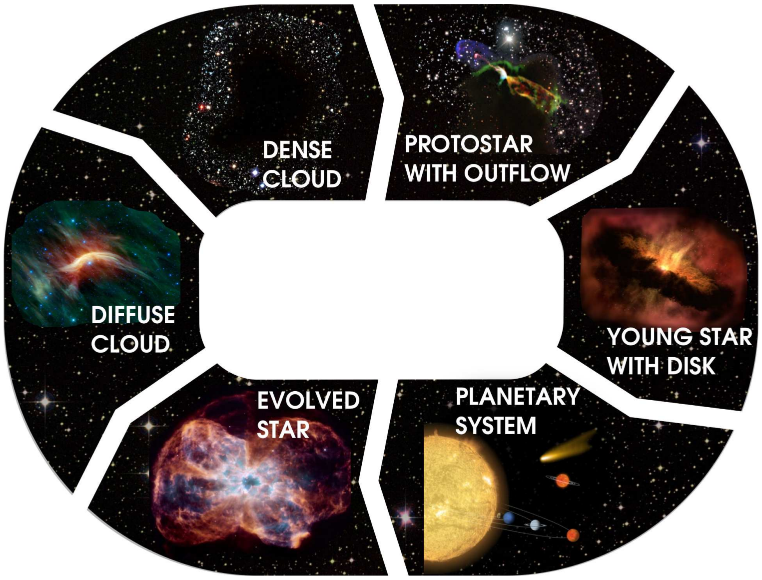


Fig. 2 Various stages in the lifecycle of gas, dust and ice in interstellar and circumstellar clouds.

2.2 Birth and death of stars

Figure 2 illustrates the cycle of material from clouds to stars and planets, and ultimately back to the interstellar medium. Diffuse clouds are low-density clouds ($\sim 100\ \mathrm{cm}^{-3}$) in which UV radiation can penetrate and destroy molecules. They are usually transient structures in the interstellar medium. Dense molecular clouds can be stable for millions of years due to support by turbulence and magnetic fields, but eventually gravity takes over and the densest part of the cloud collapses to form a new star. In the standard scenario, the collapse occurs inside out so the protostar at the center of the cloud continues to grow as material from the envelope accretes onto the star. Because of angular momentum conservation, the material that falls in at later times ends up in a disk around the star where the gas is in Keplerian rotation. Further accretion of material takes place in the innermost part of the disk in magneto-hydrodynamically (MHD) mediated funnel flows onto the star. The MHD processes near the disk-star boundary also result in jets and winds which can escape in a direction perpendicular to the disk. When they interact with the surrounding envelope and cloud, they create shocks and entrain material in bipolar outflows.

With time ($\sim$1 Myr=10^6yr), the opening angle of the wind increases and the envelope is gradually dispersed, revealing a young pre-main sequence star surrounded by a so-called protoplanetary disk. These disks are about the same size as the Solar System ($\sim$100 AU[‡]) and contain a few Jupiter masses of gas and dust (1 $M_{\rm Jup}$=1.9×10^{30} gr or about 0.1% of the mass of the Sun). Here densities can be as high as 10^{13} cm^{-3} in the inner regions of disks. The increased collision rates lead to gradual coagulation of dust grains to form pebbles, rocks and planetesimals, although the precise mechanisms are not yet understood[15]. The large particles settle to the midplane, where they can form kilometer-sized objects that interact gravitationally to form (proto)planets and eventually a full planetary system (up to 100 Myr). Comets and asteroids are remnant planetesimals that did not end up in one of the planets and were scattered and preserved in the cold outer regions of our Solar system. If they have not been heated during their lifetime, their composition reflects the conditions during the solar system formation.

The young star eventually becomes hot enough for nuclear fusion of hydrogen to ignite, at which stage it enters the stable main-sequence phase for several Gyr. Photospheric temperatures of low-mass stars are typically T_*=3000–5000 K so they emit most of their radiation at visible (as our Sun) and near-infrared wavelengths. High-mass stars have T_* up to 40,000 K so their Planck spectra peak at far-ultraviolet wavelengths, which are much more effective at destroying molecules.

At the end of the stellar life cycle, the nuclear fuel is exhausted, causing the low-mass stars to become larger and loose part of their mass (Fig. 2). These evolved Asymptotic Giant Branch (AGB) stars are surrounded by circumstellar envelopes, i.e., dense shells of molecular material driven by radiation pressure. Temperatures are high, 2000–3000 K near the stellar photosphere, dropping with radius down to 10 K at the outer edge. Because of the dense and warm conditions, they are a rich source of molecules. Such conditions are also favorable for the condensation of dust grains. Once the envelopes have been dissipated, the central star becomes very hot and emits copious UV radiation, illuminating the surrounding remnant gas producing a so-called ‘planetary nebula’ (not to be confused with a (proto)planetary disk). Massive stars explode after a much shorter lifetime ($\sim$10 Myr) as supernovae with their cores ending up as black holes or neutron stars.

2.3 UV radiation and cosmic rays

The UV radiation impinging on an interstellar cloud is often approximated by a scaling factor called G_o or $I_{\rm UV}$ with respect to the average radiation produced by all stars in the solar neighborhood from all directions. This interstellar radiation field (ISRF) I_0 has been estimated by Habing[16] and Draine[17] to have an intensity of about 10^8 photons cm^{-2} s^{-1}, with a relatively flat spectrum between the threshold at 912 Å and 2000 Å. Any photon with energies greater than 13.6 eV (wavelength $<$ 912 Å) is absorbed by atomic hydrogen outside the cloud and therefore does not affect the chemistry.

Dust particles absorb UV radiation and thereby shield molecules deeper into the cloud from the harshest radiation. The extinction at visual wavelengths, A_V, is defined as $1.086 \times \tau_d$ at 5500 Å, wit τ_d the optical depth of the dust. The intensity decreases as $I_{5500} = I_0 10^{-0.4A_V}$ with depth into a cloud. At UV wavelengths,

---

[‡] 1 AU = distance Sun-Earth = 1.5×10^{13} cm

the decline is much steeper but depends on the grain properties such as size, composition, shape and scattering characteristics[18].

Cosmic ray particles are another important ingredient of interstellar clouds. These are highly energetic atomic nuclei with >MeV energies. Cosmic rays penetrate much deeper into clouds than UV radiation and ionize a small fraction of atomic and molecular hydrogen needed to kick-start the gas-phase chemistry.

Cosmic rays also maintain a low level of UV radiation deep inside dense clouds[19]: the ionization of H and H_2 produces energetic secondary electrons which excite H_2 into the $B^1\Sigma_u^+$ and $C^1\Pi_u$ electronic states, which subsequently decay through spontaneous emission in the Lyman and Werner bands. The resulting UV spectrum consists of discrete lines and a weak continuum in the 900–1700 Å range[20]. The flux of internally generated UV photons is typically 10^4 photons cm^{-2} s^{-1} but depends on the energy distribution of the cosmic rays (see Fig. 4 of Shen *et al.*[21]) and the grain properties.

Interstellar clouds are largely neutral, since hydrogen-ionizing photons have been absorbed in the more diffuse surrounding gas. Of the major elements, only carbon can be ionized by the ISRF because its first ionization potential is less than 13.6 eV. Since the abundance of gas-phase carbon with respect to hydrogen is about 10^{-4} (see Table 1), this sets the maximum electron fraction in the cloud to about 10^{-4}. With depth into the cloud, the ionized carbon is converted into neutral atomic and molecular form. Around A_V=5 mag, cosmic rays take over as the main ionizing agent at a rate denoted by ζ in s^{-1}. The resulting ionization fraction depends on the detailed chemistry and grain physics but is typically 10^{-7} or lower, and scales as $(n/\zeta)^{-1/2}$.

3 The tools: telescopes, laboratory

3.1 Importance of multi-wavelength observations

The energy levels of a molecule are quantized into electronic, vibration and rotation states, with decreasing energy difference between two neighboring levels of the same type. Electronic transitions typically occur at optical and UV wavelengths, whereas those between two vibrational levels within the same electronic state take place at infrared wavelengths. Rotational transitions within a given electronic and vibrational state are found at (sub)millimeter and far-infrared wavelengths.

The advantages of optical and UV spectroscopy are that a number of key species, most notably H_2 and atoms, can be observed directly. The oscillator strengths of the transitions involved are large, so even minor species can be detected. The drawback is that only diffuse clouds and translucent clouds with less than a few mag of extinction can be observed along the line of sight toward a background source, since short wavelength photons do not penetrate thicker clouds.

The main advantage of infrared spectroscopy is that not just gases but also solids can be observed, both in absorption and emission. For the simplest case of an harmonic oscillator, the energy levels are given by $\omega_e(\mathrm{v}+1/2)$ where ω_e is the vibrational frequency and v the vibrational quantum number. Note the zero-point vibrational energy for v=0, which has important chemical consequences in cold dark clouds. The strongest vibrational bands of ices, silicates, oxides and PAHs occur at mid- and far-infrared wavelengths[22]. Some important gas-phase molecules without a permanent dipole moment, such as H_3^+, CH_4, C_2H_2 and CO_2, are also only observed through their vibrational bands. Disadvantages are relatively low spectral resolving power (up to $R = \lambda/\Delta\lambda = 10^5$) and moderate oscillator strengths, which means that in practice only a handful of molecules are detected at infrared wavelengths.

The bulk of the interstellar molecules have deen discovered at millimeter (mm) wavelengths. For the simplest case of a linear molecule, the rotational energy levels scale as $BJ(J+1)$ where J is the rotational quantum number and B the rotational constant, which is inversely proportional to the reduced mass of the molecule. Thus, the transitions of light molecules such as hydrides occur at higher frequencies (THz) than those of heavy molecules. The lowest levels have energies E_u/k_B (with k_B=Boltzmann constant) that range from a few to tens of K, and are thus readily excited at typical dense cloud conditions. The advantage of mm observations is high sensitivity to low abundance molecules (down to 10^{-11} with respect to hydrogen) and the fact that the emission can be mapped so that one is not limited to a single line of sight.

3.2 Telescopes

Progress in astronomy is very much driven by large telescopes equipped with highly sensitive detectors that allow investigation of clouds at a variety of wavelengths across the electromagnetic spectrum, each of which tells a different part of the story. In the last decade astrochemistry has been very fortunate to have had access to a number of new powerful telescopes with both imaging and high resolution spectroscopic instruments, the latter crucial for observing molecules. In particular, the *Herschel Space Observatory* was the largest astronomical telescope in space (3.5m diameter) operative from mid-2009 to mid-2013. Specifically, the HIFI instrument provided very high resolution (R up to 10^7) heterodyne spectroscopy covering the 490–1250 GHz (600–240 μm) and 1410–1910 GHz (210–157 μm) bands for a single pixel on the sky[23]. At mid-infrared wavelengths, the *Spitzer Space Telescope* had a low-resolution (R=50–600) spectrometer at 5–40 μm from 2003–2009, which was particularly powerful to study dust features and ices in large numbers of sources due to its high sensitivity, following on the pioneering results from the *Infrared Space Observatory* (ISO)[22].

On the ground there have also been significant advances. The European Southern Observatory (ESO) -Very Large Telescope (VLT) and the Keck and Subaru Observatories provide the most powerful collection of 8–10m optical-infrared telescopes on Earth. At millimeter wavelengths the single-dish 10m Caltech Submillimeter Observatory, 15m James Clerk Maxwell Telescope, the 45m Nobeyama dish, the IRAM 30m telescope in Spain and the 12m Atacama Pathfinder Experiment (APEX) have opened up the (sub)millimeter regime and have been workhorses for astrochemistry over the past 30 years. To obtain higher spatial resolution, pioneering millimeter interferometers such as the IRAM Plateau de Bure and the CARMA array have provided a first glimpse. Astronomers usually express spatial resolution and scales in arcsec ($''$) [§]. The *Atacama Large*

[§] One arcsec ($''$) is 1/3600 of a degree or 1/206265 of a radian (π/180/3600). At a distance of $n\times100$

Millimeter/submillimeter Array (ALMA), located in north Chile on the Chajnantor plateau at an altitude of 5000 meter, became operational in 2011 and will be transformational for the field. It consists of 54 ×12m and 12×7m antennas which together can form images with a sharpness ranging from ∼0.01″ to a few ″ over the frequency range from 84 to 900 GHz, and with a sensitivity up to two orders of magnitude higher than any previous instrument.

3.3 Laboratory experiments

The most basic information that astronomers need from laboratory experiments is spectroscopy from UV to millimeter wavelengths, to identify the sharp lines and broad bands observed toward astronomical sources. Techniques range from classical absorption set-ups to the use of cavity ringdown spectroscopy to increase the sensitivity by orders of magnitude[24]. Transition frequencies and strengths of (sub)mm transitions are summarized in the Jet Propulsion Laboratory catalog (JPL)[25] and the Cologne Database for Molecular Spectroscopy (CDMS)[26,27] [¶]. Databases for vibrational transitions at infrared wavelengths include the HITRAN database[28] and the EXOMOL line lists[‖].

The spectroscopy of large samples of PAHs has been determined with matrix-isolation studies, with selected PAHs also measured in the gas phase[29]. Spectroscopic data bases of solids continue to grow and include the Heidelberg-Jena-St. Petersburg database of optical constants for silicates[30], various databases for ices[31–34] and carbonaceous material[35,36]. THz spectroscopy of ices is just starting, as reported by Ioppolo et al. in this volume.

The next step is to determine the rates for the various reactions that are expected to form and destroy molecules under space conditions are needed. Laboratory experiments for gas-phase processes have recently been summarized by Smith[37]. Developments include measurements and theory of gaseous neutral-neutral rate coefficients at low temperatures using techniques such as CRESU[38] or crossed molecular beams[39], branching ratios for dissociative recombination[40], and rates for photodissociation of molecules exposed to different radiation fields[41].

For ices, the combination of observations and associated modeling have stimulated the new field of solid-state laboratory astrochemistry, in which modern surface science techniques at ultra-high vacuum conditions are used to quantitatively study various chemical processes. A recent summary of activities across the world is given by Allodi *et al.*[42]. Temperature programmed desorption experiments now routinely probe thermal desorption of both pure and mixed ices, providing binding energies that can be used in models[43–45]. Surface chemistry experiments have demonstrated that solid CH_3OH[46–48] and H_2O[49–53] can indeed form at temperatures as low as 10 K, using beams of atomic H to bombard solid CO, O, O_2 and O_3, thereby confirming routes that were postulated more than 30 years ago by Tielens and Hagen[54]. The process of photodesorption has been measured quantitatively and found to be much more efficient than previously thought[55,56], and to depend strongly on the wavelength of the incident radiation field[57,58]. Details of the formation of complex organic molecules by UV irradi-

---

pc, 1 arcsec corresponds to $n\times100$ AU diameter, or $n\times$ 100× the Sun-Earth distance.

[¶] `spec.jpl.nasa.gov` and `www.astro.uni-koeln.de/cdms/catalog`

[‖] `www.cfa.harvard.edu/hitran` and `www.exomol.com` ation and by high-energy particle bombardment[59–64] continue to be elucidated by a variety of experiments. Finally, the techniques to analyze meteoritic and cometary material in the laboratory have improved enormously in the last decade, and now allow studies of samples on submicrometer scale using techniques such as ultra-L^{2}MS, nano-SIMS and NMR[65].

3.4 Theory and Computation

Theoretical studies can be equally important as laboratory experiments in providing information on astrochemically relevant questions. The most important example is that of collisional rate coefficients, needed to determine the excitation of interstellar molecules. Although laboratory experiments can provide some selected data, only theory can provide the thousands of state-to-state cross sections as function of temperature needed in astronomy. The process consists of two steps. First, *ab initio* quantum chemical methods are used to compute the multidimensional potential energy surface of the molecule and its collider (usually H_2). This surface is then fitted to a convenient functional or numerical form for use in the second step, the dynamics of the nuclei. Inelastic scattering calculations need to be computed over a large range of collision energies. Full quantum calculations are used at the lowest energies whereas quasi-classical methods are often employed at the highest energies. A large number of systems has been studied over the past two decades, as summarized in a number of reviews[66–68].

Theoretical studies are also important for computing cross sections and rates for other processes. A prime example is photodissociation rates of small radicals and ions through calculation of the excited electronic states and their transion dipole moments[69–71]. Other examples include radiative association reactions[72], rates and barriers for neutral-neutral reactions[73,74], state-selective reactions[75], and the structure[76] and infrared spectroscopy[77] of large molecules.

Molecular dynamics techniques can also be extended to solid-state processes, as demonstrated by the detailed study of the photodissociation and photodesorption of water ice and its isotopologs[78–80]. Another recent example is the attempt to model the formation of solid CO_2 ice[81].

4 The main players: dust, ice and gas

4.1 The ingredients: elemental abundances

The astronomers' view of the periodic table is fairly restricted. The local Universe consists primarily of 90% hydrogen with about 8% helium by number. All other elements are called 'metals' by astronomers even if they are obviously not a metal in a chemical sense. The next most abundant elements are oxygen, carbon, and nitrogen at abundances of only about 4.9, 2.7 and 0.7 $\times 10^{-4}$ that of hydrogen. The abundances summarized in Table 1 are those derived for the solar photosphere by Asplund *et al.*[82]. These abundances are thought to apply to the interstellar medium as well, although small variations are possible[83].

Table 1 Solar elemental abundances

Element	Abundance	Element	Abundance
H	1.00	Mg	4.0×10^{-5}
He	0.085	Al	2.8×10^{-6}
C	2.7×10^{-4}	Si	3.2×10^{-5}
N	6.8×10^{-5}	S	1.3×10^{-5}
O	4.9×10^{-4}	P	2.6×10^{-7}
Na	1.7×10^{-6}	Fe	3.2×10^{-5}

4.2 Interstellar dust

The size, composition, shape and other properties of interstellar dust have been studied through a wide variety of observational techniques, such as extinction, reflection and emission measurements, including polarization techniques, as well as spectroscopy (see reviews and books by Draine[84],[85] and Tielens[86]). It is clear that the bulk of the dust grains consist of a mix of amorphous silicates and carbonaceous material, which locks up nearly 100% of the Si, Mg and Fe, $\sim 30\%$ of the oxygen and about 70% of the available carbon. These materials are called 'refractory' since they do not vaporize until temperatures well above 1200 K. They are therefore not available for the 'volatile' gas or ice chemistry. Other types of solids such as iron oxides, carbides, sulfides or metallic iron are also present, but are at most a minor component.

Interstellar grains have a distribution of sizes a following roughly $a^{-3.5}$. This means that most of the surface area for chemistry is in grains that are smaller than the typcal 0.1 μm-sized grains that dominate the mass. These smaller grains, down to 0.001 μm or less, dictate the absorption and scattering of UV radiation. In dense cores and circumstellar disks, grain growth up to sizes of a few μm to a few cm has been found[87,88]. At low temperatures, grains in dense cores are covered with a thick ice mantle consisting primarily of H_2O ice. If the bulk of the 'volatile' oxygen is locked up in ice, a typical 0.1 μm-sized silicate grain core is surrounded by about 100 monolayers of water ice.

Polarization observations show that interstelar grains are not spherical but elongated. Whether or not they have a highly irregular and/or porous structure, such as seen in the larger Interplanetary Dust Particles (see Wikipedia for images), is still under debate. The bulk of the surface sites are suited for physisorption of atoms and molecules from the gas, but there are likely also some chemisorption sites available. Indeed, Jones *et al.*[89] (see also this conference) has suggested that grains in diffuse clouds are coated by a layer of amorphous hydrocarbon material a-C(:H) which will change the surface site properties.

More generally, interstellar grains are not thought to have an active role as catalysts in the chemical sense, in which surface molecules participate in promoting the reaction. Rather, they provide a reservoir where atoms and molecules from the gas can be stored and brought together for a much longer period than possible in the gas. They thus enable reactions with activation barriers that are too slow in the gas such as the hydrogenation of atomic O, C and N. Also, they act as a third body that absorbs the binding energy of a newly formed molecule, thereby stabilizing it before it can dissociate again.

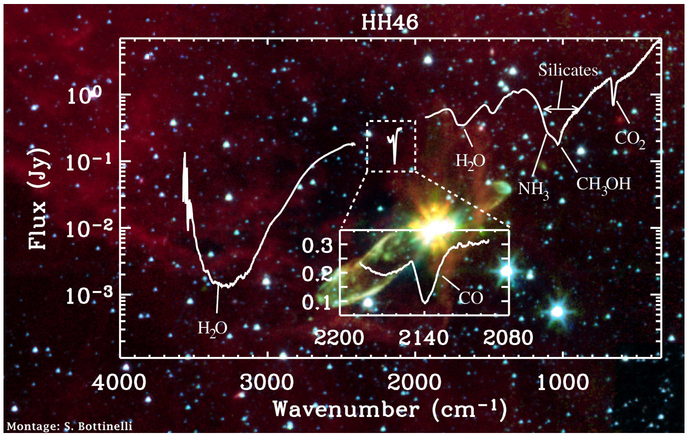


Fig. 3 Detection of ices toward the low-mass protostar HH46 IRS using *Spitzer* data at 5–20 μm and VLT-ISAAC data at 2–5 μm[90,91]. The strong solid CO_2 stretching band at 4.3 μm is missing since it cannot be observed from the ground. The insert shows a blow-up of the strong solid CO band; the weaker feature at 2167 cm^{-1} is due to OCN^-. Background: *Spitzer* composite 3 (blue, stars), 4.5 (green, shocked H_2), and 8 μm (red, PAHs) image, showing the embedded protostar with its outflow. Credit NASA/ESA/A. Noriego-Crespo.

4.3 Interstellar ices

Ices are primarily observed in absorption against bright mid-infrared sources, either embedded in the cloud or behind it (Fig. 3). The Kuiper Airborne Observatory and especially ISO opened up the field of infrared spectroscopy unhindered by the Earth's atmosphere, allowing the first full inventory of interstellar ices. The dominant ice species are simple molecules, H_2O, CO, CO_2, CH_4, NH_3 and CH_3OH, whose presence has been firmly identified thanks to comparison with laboratory spectroscopy[31,32]. These molecules are precisely the species predicted to be produced by hydrogenation and oxidation of the dominant atoms (O, C and N) and molecules (CO) arriving from the gas on the grains at low temperatures[54]. One ion, OCN^-, has also been convincingly detected along many lines of sight[92,93]. More recent *Spitzer* surveys have extended such studies to large samples of low-mass YSOs (Fig. 3). An important conclusion is that these sources have a remarkably similar overall composition as their high-mass counterparts within factors of two[94]. This implies that the formation mechanism of these 'zeroth generation' ice species is robust and universal across the Galaxy.

Interstellar ices are known to have a layered structure surrounding the silicate or carbonaceous cores: a water-rich and a water-poor layer (also called 'polar' and 'apolar' or 'non-polar' ices) (see Fig. 4). The observational evidence for different layers comes from the shapes of various ice bands, in particular the high-quality line profiles of solid CO[95,96]: a CO molecule surrounded by a H_2O molecule has a slightly different vibrational constant than a CO molecule embedded in CO itself, and these differences can be readily distinguished. The water-rich layer is thought to form early in the evolution of a cloud by hydrogeneration of atomic O, once the extinction is a few mag[97]. The bulk of solid CH_4 and NH_3 is likely also formed at this stage. In contrast, the water-poor, CO-rich layer is observed to form in much denser gas (typically $> 10^5$ cm^{-3}) when the freeze-out time, $\tau_{fo} \approx 2 \times 10^9/n_H$ yr, has become so short compared with the lifetime of the core that the bulk of the heavy elements are removed from the gas 'catastrophically'[98–100].

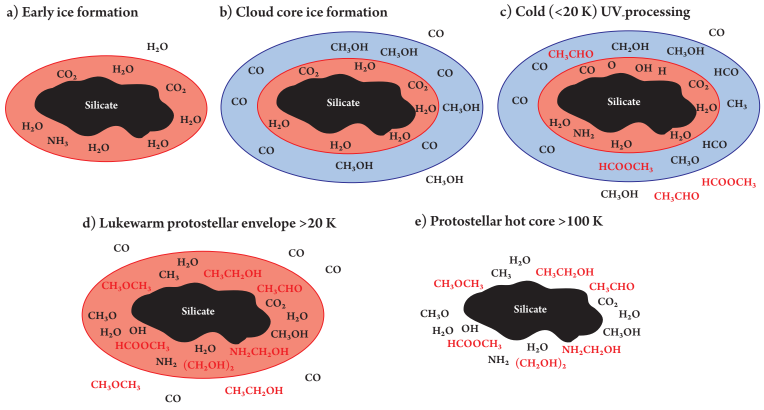


Fig. 4 Proposed evolution of ices during star formation and formation of complex molecules. Pink indicates an H_2O-dominated ('polar') ice and blue a CO-dominated ('non-polar') ice. Early during cloud formation (a) an H_2O-rich ice forms, with minor amounts of CH_4 and NH_3 through hydrogenation of O, C and N. Once a critical density is reached CO freezes out catastrophically (b), providing reactants for CH_3OH ice formation through hydrogenation of CO (0^{th} generation complex organic molecules). In the cold outer envelope (c), photoprocessing of the CO-rich ice results in the production of, e.g., $HCOOCH_3$ (1^{st} generation). Closer to the protostar (d), following sublimation of CO, other complex molecules become abundant. Finally, all ices desorb thermally close to the protostar >100 K (e) (2^{nd} generation). Figure from Öberg *et al.*[101], reproduced with permission.

4.4 Interstellar gas

About 180 different molecules have been detected in interstellar space, not counting isotopologs**. The bulk of the molecules are organic, i.e., they contain at least one carbon atom together with (usually) at least one hydrogen atom. Several molecules were first found in space before they were ever synthesized in a laboratory on Earth. This includes ions such as HCO^+ and N_2H^+ and radicals such as the long carbon chains HC_9N and C_6H. Only a few ring molecules have so far been found, with c-C_3H_2 the best known case. This does not necessarily imply that ring molecules are less abundant than linear chains: it may simply be an observational effect since the energy level structure and hence the partition function are less favorable for cyclic molecules. Several of the organic molcules are isomers, i.e., molecules with the same atomic constituents but different structures. Well known examples are HCN and HNC, methyl formate

---

** See `www.astro.uni-koeln.de/cdms/molecules` or `www.astrochemystry.org` for summaries

($HCOOCH_3$), acetic acid (CH_3COOH)[102] and glycolaldehyde ($HCOCH_2OH$), and most recently HNCO versus HCNO, HOCN and HONC[103].

The saturated organic molecules are found primarily in hot cores associated with star formation. In contrast, the unsaturated long carbon-chain molecules are found predominantly in cold dark clouds prior to star formation. Molecules involving metals such as MgCN, AlOH, and FeCN and phospor-containing molecules like HCP are primarily identified in the envelopes around evolved stars.

The rate of detections is still on average 3 new molecules per year. Recent highlights include the detection of new hydrides, such as H_2O^+[104,105], HCl^+[106], H_2Cl^+[107], SH^+[108] and SH[109]. Particularly exciting is the recent discovery of the first interstellar noble gas molecule, $^{36}ArH^+$, in the gas associated with the Crab nebula[110], the remnant of a supernova that exploded in 1054 AD. This identification was facilitated by the realization that in space, ^{36}Ar is more abundant than the ^{40}Ar isotope commonly found on Earth. $^{36}ArH^+$ is now also seen in diffuse clouds along the line of sight to the Galactic Center and other distant sources[111].

At the opposite end of the size range of interstellar molecules, C_{60} and C_{70} have recently been identified in a young planetary nebula through infrared spectroscopy[5]. Other large molecules such as PAHs are also inferred to be present based on the ubiquitous set of mid-infrared bands that are observed throughout the Universe and which can be ascribed to aromatic C=C and C-H bonds[2]. However, in contrast with all other molecules mentioned above, no individual PAH molecule has yet been identified; likely a complex mix of PAH species makes up the observed features[112].

5 Interstellar chemistry

5.1 Basic types of processes

Table 2 summarizes the basic types of reactions in space. Because of the low densities, only two-body processes are thought to be important. The rate of a reaction between species X and Y is given by $kn(\mathrm{X})n(\mathrm{Y})$ in cm^{-3} s^{-1}, where k is the reaction rate coefficient in cm^3 s^{-1} and n is the concentration in cm^{-3}. Three-body reactions only become significant at densities above 10^{13} cm^{-3} such as encountered in the atmospheres of AGB stars, the inner midplanes of protoplanetary disks, and in the formation of the first stars in the Universe.

5.1.1 Formation. There are two basic processes by which molecular bonds can be formed. The first one is radiative association of atoms or molecules, in which the binding energy of the new molecule is carried away through the emission of photons. The second process involves formation on the surfaces of grains, in which the dust particle accomodates the released energy (see § 5.2). Both of these processes are intrinsically slow. For radiative association, typical timescales for infrared emission are 10^{-3} s^{-1}, about 10 orders of magnitude slower than collision timescales of 10^{-13} s^{-1} making the process intrinsically very inefficient. Only for specific cases, such as $C^+ + H_2 \rightarrow CH_2^+ + h\nu$, or for large molecules are the rate coefficients increased by a few orders of magnitude. Radiative association is so slow that it is very difficult to measure properly in a laboratory on Earth, where three-body processes often dominate[113].

Table 2 Types of Molecular Processes

Bond Formation Processes		Typical rate coefficient ($cm^3\ s^{-1}$)
Radiative association	$X + Y \rightarrow XY + h\nu$	$10^{-17} - 10^{-14}$
Grain surface formation	$X + Y{:}g \rightarrow XY + g$	$\sim 10^{-17}$
Associative detachment	$X^- + Y \rightarrow XY + e$	$\sim 10^{-9}$
Bond Destruction Processes		
Photodissociation	$XY + h\nu \rightarrow X + Y$	$10^{-10} - 10^{-8}\ s^{-1}$
Dissociative recombination	$XY^+ + e \rightarrow X + Y$	$10^{-7} - 10^{-6}$
Collisional dissociation	$XY + M \rightarrow X + Y + M$	$\sim 10^{-26}\ cm^6\ s^{-1}$
Bond Rearrangement Processes		
Ion–molecule exchange	$X^+ + YZ \rightarrow XY^+ + Z$	$10^{-9} - 10^{-8}$
Charge–transfer	$X^+ + YZ \rightarrow X + YZ^+$	10^{-9}
Neutral–neutral	$X + YZ \rightarrow XY + Z$	$10^{-11} - 10^{-9}$

A third process, called associative detachment, is fast but requires the presence of negative ions, the formation of which is the rate limiting step. It plays a minor role in dense cloud chemistry but is important, for example, in the chemistry of the early Universe.

5.1.2 Destruction. Diffuse clouds are permeated by intense ultraviolet radiation, which destroys molecular bonds through the process of photodissociation[114,115]. If the molecule has dissociative excited electronic states below 13.6 eV, photodissociation is very rapid, with typical molecular lifetimes of only ∼100–1000 yr in the standard ISRF. Photodissociation can also take place by absorption into excited states that are initially bound, but which are subsequently either pre-dissociated or decay through emission of photons into the vibrational continuum of the ground state. The photodissociation of three of the most important interstellar molecules, H_2[116], CO[117] and N_2[118,119], is controlled by these indirect processes. Because the UV absorption lines by which the photodissociation is initiated can become optically thick, these molecules can shield molecules lying deeper into the cloud through 'self-' or 'mutual' shielding[120].

Molecular ions are efficiently destroyed by the process of dissociative recombination with electrons, which is very rapid at low temperatures. Rate coefficients in 10–30 K gas are typically 10^{-7} to 10^{-6} $cm^3\ s^{-1}$. The dissociative recombination of H_3^+, a key species in the chemistry, has been subject to considerable discussion in the last three decades, but experiments appear to converge on a rapid value of $\sim 10^{-6}$ $cm^3\ s^{-1}$ at low temperatures[121].

In contrast with the absolute rate coefficients, the branching ratios to the various products are a major uncertainty. Experiments and theory have produced different results. Experiments indicate that three–body product channels (e.g.,

H_3O^+ + e → OH + H + H) have a much larger probability than thought previously. The fraction of dissociations leading to the largest stable molecule is often small. For example, the probability of forming H_2O in the dissociative recombination of H_3O^+ is only 17%[122] and that of CH_3OH in the recombination of $CH_3OH_2^+$ only ~6%[123].

In dense clouds, destruction of neutral molecules can also occur through chemical reactions (see below). The He^+ ion, formed by the cosmic–ray ionization of He, is particularly effective in breaking bonds since 24 eV of energy is liberated in its neutralization (e.g., $He^+ + N_2 \rightarrow He + N^+ + N$ or $He^+ + CO \rightarrow He + C^+ + O$). Collisional dissociation of molecules is only important in regions of very high temperature (>3000 K) and density such as shocks in the vicinity of young stars.

5.1.3 Rearrangement. Once molecular bonds have been formed, they can be rearranged by chemical reactions leading to more complex species. Initially mostly ion–molecule reactions were considered in the models, primarily because the vast majority of them are very rapid down to temperatures of 10 K[124]. If the reaction is exothermic, the simple Langevin theory states that the rate coefficient is independent of temperature, and depends only on the polarizability of the neutral molecule and the reduced mass of the system, leading to typical values of $\sim 10^{-9}$ cm^{-3} s^{-1}. It was subsequently realized that reactions between ions and molecules with a permanent dipole (e.g. $C^+ + H_2O$) may be factors of 10–100 larger at low temperatures, because of the enhanced long–range attraction. The ions are produced either by photoionization (C^+) or by cosmic rays producing H^+ or H_2^+. H_2^+ reacts quickly with H_2 to form H_3^+, whereas H^+ can transfer its charge to species like O. These ions subsequently react rapidly with neutral molecules down to very low temperatures, as long as the reactions are exothermic and have no activation barrier.

Over the last two decades, experimental work has demonstrated that radical–radical (e.g. $CN + O_2$) and radical–unsaturated molecule (e.g. $CN + C_2H_2$) reactions have rate coefficients that are only a factor of ~5 lower than those of ion–molecule reactions at low temperatures. Even some radical-saturated molecule reactions can occur in cold clouds (e.g. $CN + C_2H_6$). Also, reactions between radicals and atoms with a non–zero angular momentum (e.g. $O(^3P_2) + OH$) are fast at low temperatures[125].

In deciding which reactions are most important in the formation of a certain species, a few simple facts should be kept in mind. First, the abundances of the elements play an important role (see Table 1). Because hydrogen is so much more abundant than any other element, reactions with H and H_2 dominate the networks if they are exothermic. This is only the case for small ions. Most reactions of neutrals and large ions with H or H_2 have substantial energy barriers or are endothermic, and therefore do not proceed at low temperatures. Reactions with the next most abundant species then become important, especially with ions because of their large rate coefficients. The ions are produced either by photoionization by the ISRF at the edges of clouds (e.g., C^+) or by cosmic rays deep inside clouds (e.g., H_3^+). Because the ionization potentials of O and N are larger than 13.6 eV, these elements cannot be photoionized by the ISRF and are therefore mostly neutral in interstellar clouds.

Compilations of reaction rate coefficients together with codes that solve the coupled differential equations include the UMIST 2013 database[126] and the KIDA database[127] ††. The latter website includes the Nahoon (formally known as Ohio State) gas-grain chemistry code by Herbst and co-workers.

5.2 Gas-grain chemistry models

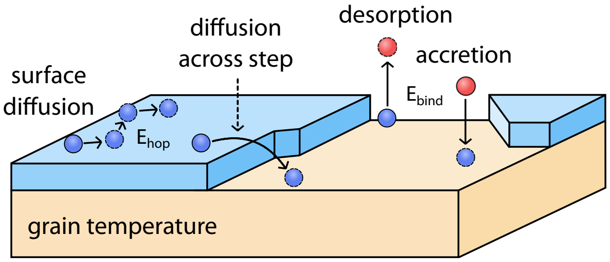


Fig. 5 Illustration of different binding sites on a rough surface.

5.2.1 Surface chemistry. The overall efficiency of surface reactions depends on the probability that the atoms or molecules stick to the grains upon collision, their mobility on the surface, the probability that molecule formation occurs, and finally the probability that the molecule is released back into the gas phase.

The bulk of the surface reactions are assumed to proceed by diffusion of at least one of the two reactants on the surface to find the other partner. This requires a prescription of the diffusion of the reactant to hop from one surface site to another. Usually, this is described by a standard reaction rate coefficient $K_{\rm hop} = \nu \exp(-E_{\rm hop}/kT_s)$ where ν is the vibrational frequency of the reactant to the surface, $E_{\rm hop}$ is the energy barrier to hop from one site to another and T_s is the surface temperature. In most models, this barrier is taken to be a constant fraction of the binding energy, $E_{\rm hop} = c^{\rm st} \times E_{\rm bind}$ with $c^{\rm st}$ varying from 0.3 to 0.7 in different models[128]. However, this prescription does not take into account that the surface is rough and that the hopping barriers change from site to site[129] (see Fig. 5). Also, the importance of tunneling at the lowest temperatures is still debated and the formulation for the competition between diffusion and reaction is not clear.

The competing Ely-Rideal mechanism, in which an atom or molecule from the gas lands directly on top of the reactant on the surface can also play a role under some conditions, as do ‘hot atom’ reactions in which the atom lands on the surface with excess energy that can be used to overcome barriers. Regardless of the precise process, it is clear that surface temperature plays a critical role in the ability of species to react. Light species such as H, H_2, C, N and O can likely hop over the surface to find a reaction partner even at $T_D \approx 10$ K, whereas heavier species are immobile at low dust temperatures. Reactions of these atoms with CO can produce a number of ‘cold’ complex molecules (see § 8)[130].

Chemistry occurs not only on the surface of the grains but also deep inside the ice. UV photons can penetrate at least 50 monolayers and dissociate molecules

---

†† `www.adfa.net` and `kida.obs.u-bordeaux1.fr`

both on top and deep inside the ice. The resulting atoms and radicals are initially highly mobile because of the excess energy from the dissociation process but quickly loose this energy on pico-second timescales and become trapped[78]. A second route to producing complex organic molecules invokes that these radicals become mobile and find each other once the ice temperature increases from $\sim$10 K to 20–40 K[131,132].

Alternatively, cosmic rays can penetrate ices and create a wealth of chemical complexity, and there is a rich literature on laboratory experiments bombarding ices with high energy particles[59,62,64]. The relative importance of UV vs cosmic ray processing in creating complex organic molecules is still under discussion. Shen *et al.*[21] have argued that UV radiation is more important since it deposits 10× more energy per molecule in the ice than cosmic rays for typical cosmic ray fluxes (see their Table 3). On the other hand McCoustra argues in this volume that each cosmic ray triggers multiple events compensating for the lower energy deposition rate. Overall, the chemical consequences of UV and high-energy particle processing of ices may be rather similar[34], although the very strong CO and N_2 bonds are usually not broken in the UV irradiation case. A new aspect discussed at this conference in papers by Mason, Boamah, Siemer and Maity et al. is to what extent electron bombardment and charged species in ices can affect the production of complex molecules.

While there is a growing set of laboratory experiments studying reactions in ices of the types described above, it is not yet clear how to translate the laboratory data to astronomical model parameters. Timescales are also an issue: individual processes occur on picosecond timescales but lab experiments usually measure changes of bulk ice as function of fluence over a period of hours. Astronomical applications involve timescales of $> 10^5$ yr, and further modeling is needed to translate laboratory results to these different regimes[133,134].

5.2.2 Gas-grain interactions. The standard treatment of the interplay between gas phase and grain surface chemistry is through rate equations[135], the basics of which are described in more detail elsewhere[10,11]. The standard rate equation approach is known to be inadequate under some conditions, however, especially for models with very small grains and only a few species per grain. Many alternative approaches are being considered such as the modified rate equations, Monte Carlo, Master equation, and hybrid methods, each with their advantages and drawbacks.

The terms coupling the two regimes are accretion of gas-phase species onto the grains and desorption of molecules from the grains back into the gas. The accretion basically involves the rate of collisions of the gas-phase species with the grain and the probability that the species then sticks on the grain. This term is in principle straight-forward to implement and depends on the geometrical surface area of the grains as well as the sticking coefficient S as function of temperature. Usually, S is taken to be 1 for heavy species at low temperatures, as also suggested by laboratory experiments[44]. For the important case of atomic H sticking to ice, the temperature dependence of $S(T)$ has been computed[136] and is now also being measured[137]. Older models have often adopted a value of S less than unity, say 0.8 or 0.9, as a ‘fudge factor’ to implicitly prevent all species from freezing out onto the grains within 10^5 yr, rather than treating the desorption processes explicitly.

In terms of desorption, there is a growing list of mechanisms that can return molecules from the ice into the gas. These include (i) thermal sublimation[43,138]; (ii) UV photodesorption[56]; (iii) cosmic-ray induced spot heating[139]; (iv) cosmic-ray whole grain heating[139]; (v) exothermicity from chemical reactions[140,141]; and (vi) ice mantle explosions[142]. Process (i) is well measured in the laboratory for many species but is clearly not operative in cold dark clouds where dust temperatures are only 10 K. Process (iii) may be effective for weakly bound molecules like CO but not for strongly bound species like H_2O, whereas process (iv) is generally negligible except for the smallest grains. Processes (v) and (vi) may contribute but are still poorly characterized experimentally.

This leaves process (ii), UV photodesorption, as a prime non-thermal mechanism for getting molecules off the grains in cold dense clouds. The UV radiation is provided not only by the external ISRF but also has contributions from the internally produced UV photons by the interaction of cosmic rays with H_2 (§ 1). Thanks to a series of molecular dynamics simulations[78,79] and laboratory experiments[56,57], the photodesorption yields are now being quantified for the main ice species like CO and H_2O (see also Fillion et al., this volume). The process is induced by absorption into excited electronic states (either directly dissociative or indirectly through an exciton state), so the photodissociation cross section or yield is wavelength dependent just as for gas-phase molecules. It is also possible that UV excitation of one molecule kicks out a neighboring molecule, as demonstrated experimentally for the case of N_2 by CO[55,58].

Basic input parameters for any gas-grain model are the overall elemental abundances, the initial molecular abundances at $t = 0$ in the case of time-dependent models, the primary cosmic ray ionization rate ζ_H and the grain size distribution. The models then provide number densities or concentrations n (in cm^{-3}) of a certain molecule as function of time and/or position within a cloud. The fractional abundance of the molecule AB with respect to H_2 is given by $n(\mathrm{AB})/n(\mathrm{H_2})$. Observers measure column densities in cm^{-2}, i.e., the number density n in cm^{-3} of a species integrated along a path, $N = \int n\, dz$. An empirical relation between extinction and the column density of hydrogen nuclei has been found[143,144] $N_H = N(\mathrm{H}) + 2N(\mathrm{H_2}) = 1.8 \times 10^{21}\ A_V\ \mathrm{cm}^{-2}$, which is often used to present model results as a function of A_V rather than pathlength z. For diffuse clouds or PDRs proper integration along the line of sight is done, but for dark clouds local model concentration ratios are usually compared with observed column density ratios.

5.2.3 Water as an example. An illustrative example of how different routes contribute to the formation of a particular molecule under different conditions is provided by the networks leading to interstellar water[10] (Fig. 6). At low temperatures and densities, the ion-molecule reaction route dominates and produces a low fractional abundance of water around 10^{-7}. At high temperatures such as encountered in shocks, reaction barriers of O and OH with H_2 can be overcome and H_2O is rapidly formed by neutral-neutral reactions. Finally, in cold dense clouds, formation of water ice is very efficient and locks up the bulk of the oxygen not contained in CO. Water can be brought from the ice into the gas phase by photodesorption in cold clouds and by thermal desorption at high temperatures.

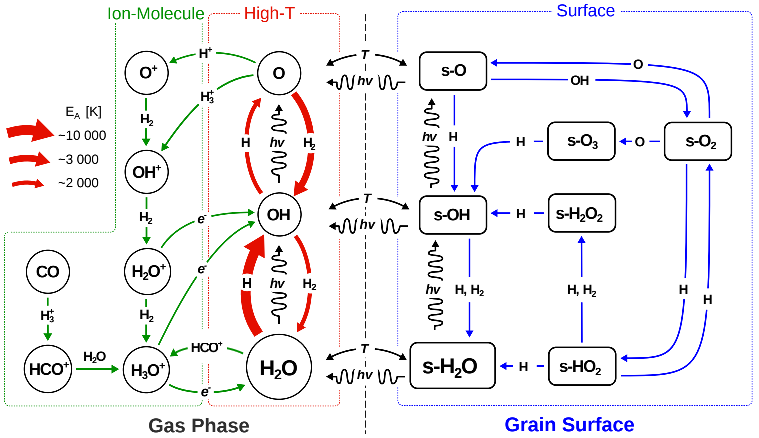


Fig. 6 Simplified water chemistry illustrating the different routes to water through (left) low temperature gas-phase ion-molecule chemistry; (middle) high temperature gas-phase chemistry; and (right) surface chemistry. Reproduced with permission from van Dishoeck *et al.* [10].

5.3 Model results: managing expectations and 'back to basics'

The reliability of the results of any chemical model depend on the accuracy of the rate coefficients of the hundreds or thousands of reactions contained in the databases. The rate coefficients, in turn, are provided by chemical physics experts carrying out the relevant experiments or calculations. Ideally, each rate coefficient in a database should be motivated by a critical evaluation of the chemistry literature on that particular reaction by an independent expert: the latest measurement is not necessarily the best or the most appropriate value for astrochemical applications. Also, often extrapolations beyond measured temperature regimes have to be made and motivated. This is a time consuming process and one that is not highly valued by funding agencies nor by universities in terms of career paths.

It is therefore important to recognize that astrochemical databases are put together and updated on a 'best effort' basis. Following the good example of atmospheric chemistry, where a two decade long effort has resulted in a set of critically evaluated and motivated rate coefficients [125], the KIDA database has an (estimated) uncertainty associated with each rate coefficient which can then be propagated in the network. Wakelam *et al.* [145] show examples of such sensitivity analyses for a pure gas-phase chemistry network, demonstrating that even the abundances of simple molecules like H_2O, SO or CH, have an uncertainty of a factor of $\sim$3 just from the uncertainties in individual rate coefficients. For larger molecules, the cumulative effect of uncertainties in many more rates easily results in an order of magnitude overall uncertainty. Such differences are comparable to those found when two independent networks are run for the same physical model.

So what constitutes good agreement between models and observations? For diffuse clouds, the column densities of simple molecules like CH, C_2, CN, OH, H_2O and HCl can be reproduced within a factor of 2 or better if the physical conditions of the cloud are independently constrained [146–148]. Even for such relatively simple clouds with well constrained temperatures and densities, there are well-known exceptions like CH^+ that require different physical processes to be added to the model such as turbulence (see § 6.1). Nevertheless, diffuse clouds and PDRs are still he best laboratories for 'precision astrochemistry'.

For dense clouds, the agreement between models and observations is generally much worse. The chemically-rich dark cloud TMC-1 has served as one of the main testbeds for decades and here agreement within an order of magnitude for 80% of the observed species is considered good[149]. In spite of considerable laboratory effort, there has not been much progress in this comparison over the past few decades. Should we aim to do better as a community? Or is this uncertainty the inevitable consequence of the cumulative effect of uncertainties in many individual rate coefficients with little hope for improvement? Or do these dicrepancies point to other ingredients that are missing in the models, such as the physical and dynamical evolution of the source or small scale unresolved structure?

For this reason, several groups have started to go 'back to basics' and to ask more specialized questions that can be addressed with more limited networks in order to isolate the critical chemical processes at work. For example, detailed models of well characterized dark cores like B68 or L1544, for which the physical structure is well determined independently, demonstrate that impressive agreement with observations can be achieved for selected species, even on a linear scale[100,150–152]. Similarly, the water abundance profile in low-mass pre- and protostellar cores is well described by a simple network[153–156].

This leads to two different approaches for modeling observational data[157]. On the one side is the 'forward model' in which a full-blown chemical model is applied to a physical structure of the source and the output is then compared with observations. Such a model can turn many knobs to improve comparison with the data and the question is what one has learned if good agreement is finally obtained. The alternative approach is the 'backward' or 'retrieval' model in which a trial abundance of a molecule is taken within a physical model of the source, and this abundance is then varied to obtain best agreement with observations. A more sophisticated case of 'retrieval' is where the trial abundance is inspired by the full chemical models (e.g., by applying abundance jumps at certain locations or adopting a functional form). The hybrid 'back to basics' method described above uses a simple or minimal chemical network of the particular molecule under study to isolate the principal chemical routes. As deeper and higher angular resolution data are becoming available with ALMA, this approach of addressing more focused questions may be key to progress in the field.

In the following, major developments in observations and models of specific regions in the lifecycle from clouds to planets are discussed.

6 Diffuse clouds and dense PDRs

6.1 Diffuse and translucent clouds

The study of diffuse and translucent clouds with visual extinctions of a few mag has obtained a large boost with the recent *Herschel*-HIFI data[158]. Rotational lines of molecules are seen in absorption in diffuse clouds throughout the Galaxy along the lines of sight toward distant far-infrared sources. Usually only the lowest $J = 1-0$ line is observed because higher levels do not have sufficient population under these tenuous conditions. These far-infrared data complement continued studies of other molecules like H_2, C_2, C_3 which can only be observed by traditional optical and UV absorption lines toward bright stars[144,159]. Only a few molecules, most notably CH and CH^+, can be observed by both techniques, although not for the same lines of sight.

Because H_2 cannot be observed directly toward far-infrared sources, the use of other molecules as tracers of H_2 have been investigated. CH is a good candidate[160], but one of the best options has proven to be the HF molecule[161,162]. Even though the elemental abundance of fluor is only 4×10^{-8}, the fluorine chemistry is particularly simple because the $F + H_2 \rightarrow HF + H$ reaction is exothermic and has been very well studied by the chemical physics community. The reaction of HF with C^+ produces CF^+ which has also been detected, further confirming its chemistry.

A summary of the state of the observations and models prior to *Herschel* has been given in a number of reviews[146,163]. The recent detections of OH^+ and H_2O^+ point toward the existence of a new type of diffuse clouds with only a small molecular fraction[158]. The H_2/H ratio must be low, of order 10%, because both ions react rapidly with H_2 to form eventually H_3O^+. This mixed H/H_2 phase must be ubiquitous in the interstellar medium since it is seen in absorption along nearly every line of sight in the Galaxy, and even in emission throughout entire galaxies in the local and distant Universe[1,164]. For the same reason, ArH^+ probes nearly pure atomic hydrogen gas, with an even lower H_2/H ratio of 10^{-4}.

The long-standing puzzle of the high abundance of CH^+ in diffuse clouds, first detected nearly 80 years ago[165], is still not fully solved, although models of the chemistry in turbulent clouds, where the dissipation of turbulent energy provides the heat to overcome the $C^+ + H_2$ endothermicity of 4640 K, is a plausible explanation[166,167]. The physics of interstellar turbulence is not yet understood from first principles, however, and non-Maxwellian motions between ions and neutrals need to be taken into account in the presence of magnetic fields. Similarly, the formation of SH^+, detected both with ground-based telescopes and with *Herschel*-HIFI, requires extra energy for the $S^+ + H_2$ reaction (+9860 K) to proceed[108,168]. Both species have somewhat larger line widths than those of CH and CN, $\sim$4 vs $\sim$2 km s^{-1}, further justifying that additional physical processes need to be invoked to drive the reactions.

6.2 Photon-dominated regions

Photon-dominated or photodissociation regions (PDRs) are dense clouds exposed to intense UV radiation, which controls both the chemistry and heating of the gas. They are the high $I_{\rm UV}$ ($> 10^3$), high $n_{\rm H}$ ($> 10^4$ cm^{-3}) versions of the diffuse clouds discussed above. At the edge of the cloud, the gas temperature becomes so high ($\sim$ 1000 K) that endothermic processes and reactions with energy barriers can proceed, most notably the $C^+ + H_2 \rightarrow CH^+ + H$ and the $O + H_2 \rightarrow OH + H$ reactions[169]. Subsequent reactions with C^+ lead to other characteristic PDR tracers such as CO^+.

The Orion Bar PDR and the Horsehead nebula are prototype examples of dense PDRs which have been studied in great detail observationally. The Orion Bar is the clearest case exhibiting the layered chemical structure: C^+ and PAH emission (pumped by UV) is seen close to the star, followed by warm H_2 emission and then cool CO[170]. This structure is also reflected in the chemistry of other species, with radicals such as C_2H, C_4H and C_3H_2, whose formation benefits from the presence of free atomic carbon, peaking ahead of molecules like $C^{18}O$[171–174]. Deep searches are now starting to reveal more complex organic molecules in PDRs, mostly those belonging to the 'cold' complex type (see § 5.2.1 and 8) (Guzmán et al, this volume).

Because of exposure to intense radiation and high temperatures, excited ro-vibrational levels of molecules can be pumped. The resulting populations are large enough that *state-to-state* processes become significant in dense PDRs. The most prominent example is that of CH^+ formation through reactions of C^+ with $H_2(v,J)$, where the H_2 ro-vibrational levels are pumped by UV radiation. These state-specific reactions were included in PDR models developed in the 1980s and 1990s but have recently been revived in the context of dense PDRs and the surface layers of protoplanetary disks[175–177].

A second example is *formation pumping*, in which the reaction produces a molecule in an excited ro-vibrational level which then radiates before it collides with H_2. This process must dominate the excitation of those species that react on every collision[178]. Examples are $C^+ + H_2 \rightarrow CH^+(v,J) + H$[177], $C^+ + OH \rightarrow CO^+(J) + H$[179] and the processes leading to the formation of H_3O^+ (J)[180].

Finally, excitation by electrons rather than H_2 or H can become significant in PDRs. It explains why the HF line can be seen in emission in the Orion Bar rather than absorption[181].

7 Cold molecular cores

7.1 H_2D^+ and extreme deuteration

Cold molecular clouds have long been known to harbor high abundances of deuterated molecules such as DCO^+ and DCN[182], with DCO^+/HCO^+ and DCN/HCN ratios at least three orders of magnitude higher than the overall [D]/[H] ratio of $\sim 2 \times 10^{-5}$. More recently, even doubly- and triply-deuterated molecules such as D_2CO and ND_3 have been detected[183]. The observed ND_3/NH_3 ratio is about 10^{-3}, indicating an extreme deuterium enhancement of a factor of $\sim 10^{12}$.

This huge fractionation has its origin in two factors. First, the zero-point vibrational energy of deuterated molecules is lower than that of their normal counterparts because of their higher reduced mass. This makes their production reactions exothermic. In cold cores, most of the fractionation is initiated by the $H_3^+ + HD \rightarrow H_2D^+ + H_2$ reaction which is exothermic by about 230 K. H_2D^+ then transfers a deuteron to CO or N_2 or another species. Proof of this mechanism comes from direct observations of H_2D^+ in cold clouds[184,185]. Even D_2H^+ has been observed toward these sources[186,187]. Correct calculation of their abundances requires explicit treatment of the nuclear spin states (ortho and para) of all the species involved in the reactions[188–191].

The extreme fractionations observed in some clouds require an additional explanation beyond just gas-phase reactions. In the centers of cold cores, there is now convincing observational evidence that most of the heavy elements, including CO, are frozen out onto the grains (see § 4.3). Since CO is the main destroyer of both H_3^+ and H_2D^+, their abundances are even further enhanced when CO is removed from the gas. Indeed, HD then becomes the main reaction partner of H_3^+ and the chemistry rapidly proceeds to a highly deuterated state in which even D_3^+ can become comparable to H_3^+ in abundance[192]. At slightly elevated temperatures, the CH_2D^+ ion, formed by reaction of CH_3^+ + HD, becomes more effective in controlling the DCN/HCN ratio, consistent with observations of somewhat warmer PDRs and protoplanetary disks[193,194].

H_3^+ and HCO^+ are among the most abundant ions in dark clouds and thus set the level of ionization in the cloud. This, in turn, controls the coupling of the gas to the magnetic field which slows down the collapse of the cloud. Since H_3^+ cannot be observed directly in these clouds, the DCO^+/HCO^+ abundance ratio is commonly used to infer the ionization fraction of cold cores. Typical values are 10^{-9} – 10^{-8} in the densest regions Bergin and Tafalla[195].

7.2 H_2O, O_2 and the importance of solid-state chemistry

In the shielded regions of cold cores, the bulk of the heavy elements are in ice mantles (see § 4.3). The laboratory confirmation of the low temperature production of H_2O ice through hydrogenation of O, O_2 and O_3 forms a highlight of solid-state astrochemistry[49–52,196,197]. In low density regions the route through atomic O dominates, but at higher densities the O_2 route becomes more important, with O_2 formed on the grains rather than frozen out from the gas. This simple chemistry reproduces well the *Herschel*-HIFI observations of water in pre-stellar cores[153] and protostellar envelopes[154], provided that cosmic-ray induced UV photodesorption is included in the models to get water off the grains in the central part pf the core.

The O_2 route forms solid HO_2 and H_2O_2 as intermediates. The success story of combined laboratory and observational studies became complete with the detection of gas-phase HO_2[198] and H_2O_2[199] with abundances consistent with their grain surface formation[200]. However, both species have so far been detected in only one cloud, ρ Oph A, with searches in other clouds unsuccessful (Parise et al., this volume).

Interestingly, ρ Oph A is also one of only two positions where interstellar O_2 gas has been firmly detected through multi-line observations with the Odin and *Herschel* satellites[201,202]. Deep limits in other cold cores confirm the scenario in which most of the O and O_2 must be converted into H_2O ice on the grains before the protostar starts to heat its surroundings[203,204]. Perhaps the grain temperature in ρ Oph A, around 30 K, is just optimal to prevent atomic oxygen from freezing out and being converted into water ice. A critical parameter in these models is the binding and diffusion energy of atomic O to silicates and ices. The papers by Congiu, Lee and He et al. discuss recent laboratory experiments which may suggest somewhat higher values than used before[205]. They also highlight the difficulties in providing a proper formulation for diffusion and desorption of atoms at very low temperatures.

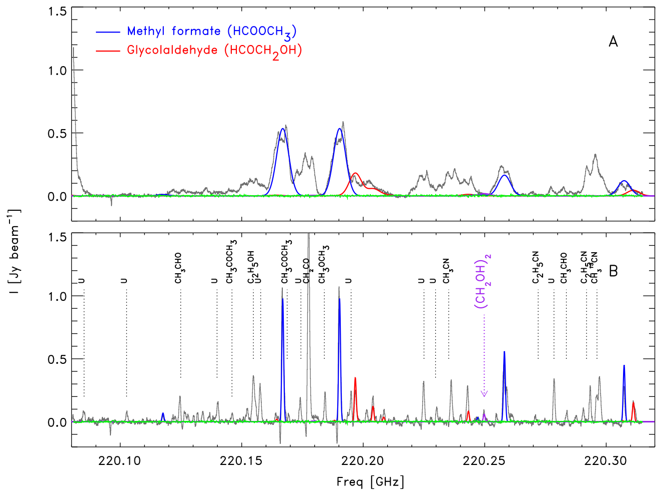


Fig. 7 ALMA data toward the low-mass binary protostar IRAS16293A (upper) and IRAS16293B (lower) obtained with 16 antennas. Fits from LTE models of the methyl formate (blue) and glycolaldehyde (red) emission are overplotted. The purple line indicates the model fit to the possible ethylene glycol transition. Note the high density of lines, including several unidentified features, even in these early ALMA science data. Reproduced with permission from Jørgensen *et al.* [206].

8 Protostars and hot cores: complex molecules

Saturated complex organic molecules such as CH_3OCH_3, $HCOOCH_3$ and CH_3CN are prominently observed toward many (but not all) high-mass protostars as well as toward some low-mass sources [12,14] (Fig. 7). Three generations of complex molecules are distinguished [14]: zeroth generation ice formation in cold dense cores prior to star formation, which leads primarily to CH_3OH through hydrogenation of CO. First generation organics are then formed during the subsequent protostellar warm-up phase when radicals produced by photodissociation of species like CH_3OH become mobile in and on the ices (first generation, e.g., $HCOOCH_3$). Second generation organics result from high temperature gas-phase reactions involving evaporated molecules (Fig. 4).

As the protostar heats the envelope, molecules sublimate from the ice mantles, starting with the most volatile molecules like CO and N_2 in the outer envelope, and followed by species with larger binding energies like CO_2. Once the grain temperature reaches 100 K close to the protostar, even the most strongly bound molecules like H_2O and CH_3OH sublimate from the grains, including any minor species that are trapped in their matrices. These evaporated species then drive a high temperature gas-phase chemistry producing second generation complex molecules for a period of $\sim 10^5$ yr after sublimation [207]. Recent determinations of reaction rate coefficients and branching ratios for dissociative recombination show that this gas-phase route is less important than thought before, however (see § 5.1).

This scenario can soon be tested in great detail with high angular ALMA observations which can spatially resolve the hot cores and map the different molecules. A 'sweet taste' of what to expect is the recent detection of the simplest sugar, glycolaldehyde ($HCOCH_2OH$), in the low-mass protostar IRAS 16293-2422B (Fig. 7). The emission comes from a region of only 25 AU in radius, i.e., comparable to the orbit of Uranus in our own solar system[206]. Its abundance with respect to related complex molecules like methyl formate and ethylene glycol is consistent with laboratory experiments of mild photoprocessing of methanol-rich ice mantles[61], although other reaction routes such as discussed by Boamah et al, this volume, are not excluded.

The above scenario requires that the grains spend some time at elevated temperatures so that the radicals become mobile (see § 5.2). The recent detection of some complex organic molecules in very cold sources that have never been heated much above 10 K therefore came as a surprise[101,208–210]. Most of these species are the same as those identified as 'cold' complex molecules in the survey of hot cores by Bisschop *et al.*[211], i.e., molecules with excitation temperatures below 100 K originating in the colder outer envelope rather than the hot core. The papers by Öberg et al. and Guzmán et al. image these molecules in protostellar envelopes[212] and PDRs, respectively. Possible explanations that have been put forward include enhanced radiative association rate coefficients for these species or using the exothermicity of the reactions[213]. Alternatively, low temperature surface reactions of atomic C and H with CO can naturally lead to these species, if the binding energy of C to ice is low enough (see Guzmán et al.). Similarly, reactions with N and H with CO could lead to nitrogen-bearing species like HNCO and even NH_2CHO.

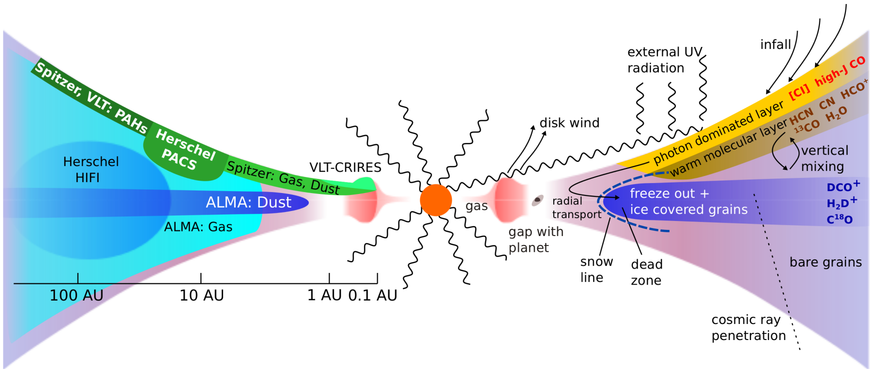


Fig. 8 Cartoon illustration of the various physical and chemical processes taking place in protoplanetary disks (right) that are probed by different observational facilities (left).

8.1 Protoplanetary disks

Disks around young stars are the birthplaces of planets and are therefore particularly important targets for astrochemistry. However, disks are at least a factor of 1000 smaller than the clouds in which they are formed and they contain only $\sim 1\%$ of the mass. Thus, their emission is readily overwhelmed by that of any cloud and they can only now be properly studied with the new generation of high angular resolution and high sensitivity instruments. Disks are heated by the radiation of their parent star so they have a radial and vertical temperature gradient in both the gas and dust. No single instrument or wavelength probes the entire disk reservoir: a combination of near-, mid-, far-infrared spectroscopy combined with spatially resolved ALMA data is needed (Fig. 8). As a result of this physical structure, disks consist of different chemical layers[214]: at the surface, molecules are dissociated into atoms by the strong UV radiation. Deeper in the disk, the grains are still warm enough to prevent freeze-out and molecules are shielded enough from the UV to survive. Deep in the cold miplane most molecules except H_2, H_3^+ and their isotopologs are frozen out onto the grains.

There has been enormous observational and model activity in this field in recent years, see recent reviews[195,215–218]. Highlights include the *Spitzer* and ground-based detections of hot ($\sim 300-800$ K) C_2H_2, HCN, H_2O and CO_2 originating in the inner ~1 AU of disks[219–225]. CH_4 has been found in one disk[226], but no detection of NH_3 has yet been reported[227]. This rich array of lines of simple molecules is primarily seen in disks around low-mass stars that are cooler than the Sun; they are absent toward higher mass stars with $T_{\rm eff} \approx 10,000$ K. This points again to the importance of the wavelength dependence of the radiation field and associated photodissociation[228]. The implications for the elemental C and N budget in disks is discussed in the papers by Bergin and Pontoppidan et al. in this volume.

Cooler H_2O and OH have been detected somewhat further out and deeper into the disk with *Herschel*-PACS in a few sources[229,230]. The bulk of the cold water reservoir has been revealed by *Herschel*-HIFI in two disks. Because the observed water gas is produced primarily by UV photodesorption of ice, it points to the presence of a large reservoir of underlying water ice[231].

Another related highlight is the first imaging of ‘snow lines’ in disks, i.e., the radius where a molecule changes from being primarily in the gas phase to being frozen out as ice. Because of the vertical structure of disks, a ‘snow surface’ is a more appropriate description. Snow lines are important because they enhance the mass of solids by a factor of a few and thus facilitate planet formation. Also, the coating of grains with water ice enhances the coagulation of grains, the first step in planet formation. Because of their lower binding energies, the snow lines of CO and CO_2 are outside that of H_2O. This selective freeze-out of major ice reservoirs can change the overall elemental [C]/[O] abundance ratio in the gas and thus the composition of the atmospheres of giant planets that are formed there[94]. The CO snowline has been imaged with ALMA through N_2H^+ observations in the nearby TW Hya disk[232]. N_2H^+ is enhanced when its main destroyer, CO, freezes out. Another example is the CO snow line in the HD 163296 disk imaged in CO isotopologs and in the DCO^+ ion, whose abundance peaks when CO freezes out (see § 7.1)[233,234].

In contrast with these simple species, complex molecules have not yet been detected in disks, not even methanol. The most complex molecules found so far are H_2CO, HC_3N and C_3H_2. One option is that the strong UV radiation in disks prevents the build up of more complex species, although methanol should be detectable[235], see Walsh et al. this volume.

Finally, transitional disks which have a hole or gap in their dust distribution are a hot topic since these gaps are likely caused by planets currently forming in the disk (Fig. 8). ALMA images of several transitional disks show remarkably asymmetric dust structures, pointing to traps induced by the young planets in which the mm-sized grains are collected[236–238]. The survival of molecules like CO and the chemistry of other species in dust-free cavities in transitional disks has been modeled by Bruderer[239 240] and is being tested against ALMA observations for the case of H_2CO[241]. Molecules produced in ices may be observable as well when the disk midplane is exposed to the stellar photons at the outer edge of the cavity and molecules can be desorbed[242]. Altogether, these data form a vivid illustration and warning that gas and dust grains do not necessarily follow each other but that they need to be treated separately in the models.

8.2 Exo-planetary atmospheres

The detection and characterization of exo-planets is one of the fastest growing fields in astronomy, see recent reviews[6,243]. A large number of transiting exoplanets has now been detected, most recently with the *Kepler* and *Corot* satellites, and their atmospheres are starting to be studied through high precision measurements when the planet is in front (primary transit) and behind (secondary eclipse) the star. Detection of molecules like CO and H_2O have been claimed and disputed, but both are now firmly identified in a few targets[7,244]. One of the main science goals of future facilities is to study the composition of exo-planetary atmospheres, not only of Jupiter-like planets but down to the (super-)Earth regime. Chemical models of such atmospheres are actively being pursued using techniques from astrochemistry[245,246], coupled with expertise from other fields such as aeronomy.

Liquid water is likely a prerequisite for the emergence of life and much of the water in our oceans on Earth plausibly comes from the impact of asteroids and comets containing ice. The water molecules themselves are mostly formed on the surfaces of grains in the cold interstellar clouds prior to collapse as in § 7.2. Following the water trail from dense cloud cores through collapsing envelopes to planet-forming disks and exoplanets is a major goal of modern astrochemistry and has recently been summarized[230].

9 Concluding remarks

"Is astrochemistry useful"? The answer to this question, asked first by Dalgarno in 1986, is a convincing "yes", with astrochemistry now firmly integrated into astronomy and at the same time stimulating chemical physics. Indeed, the interaction between dust, ice and gas has stimulated the development of solid-state astrochemistry and provided new insights in basic chemistry. Continued close interaction on well-defined questions that can be addressed by the combination of laboratory-observations-models is needed.

There has been a clear shift from pure gas-phase chemistry to a gas-dust-ice chemistry over the past decades, making the topic of this Faraday Discussion very timely. The solid-state routes to water and methanol, two key components of ices, have been firmly established through laboratory experiments and observations, including detection of the intermediates in the network. Gas-grain chemistry now has predictive power and is likely at the basis of many of the complex organic molecules seen in star-forming regions. However, the precise routes are not yet understood, and the presence of the 'cold' complex molecules challenges the convential theory that the grain temperature needs to be elevated above 10 K to drive the reactions. Other puzzles to be solved include why some sources are more line-rich than others, why oxygen- and nitrogen-containing complex molecules are sometimes spatially separated, and why protoplanetary disks are poor in complex molecules.

Because interstellar clouds and protostars are dynamic entities, there is increased activity to couple the full gas-grain chemical models with hydrodynamical models of cloud formation and collapse. Computing power is now available to do so and impressive simulations are being performed. An alternative approach is to couple chemistry with semi-analytical models of protostar and disk formation[247]. Other factors such as the detailed 3D geometry of the source, dust evolution and gas-dust separation now also need to be taken into account. While these avenues clearly need to be pursued, this paper has also advocated the 'back to basics' approach to elucidate the main chemical and physical processes at play.

This review has focused primarily on small molecules and moderate size complex organic molecules built through reactions in and on ices, highlighting the gas-grain interactions. A different route to molecular complexity starts with the much bigger PAH molecules and carbonaceous material, which are known to exist throughout the Universe. Through a series of UV and X-ray photolysis, radical reactions and combustion-type chemistry, these big molecules can also be transformed into smaller species and organic material that can be incorporated in future solar systems[9]. Also, the carriers of the omni-present Diffuse Interstellar Bands, discovered nearly a century ago in diffuse clouds, are still a mystery, see recent reviews Cami and Cox[248]. This alternative chemistry cycle could be an appropriate topic for a future Faraday Discussion.

On the observational side, ALMA is *the* astrochemistry machine of the future and is expected to bring advances in several areas[249]. It can search for new molecules at least a factor of 100 deeper than before, including prebiotic molecules such as glycine. Equally important, it will survey many more sources than just the 'classical' Orion and SgrB2 regions used so far to hunt for new molecules. ALMA has the spatial resolution to image the relevant physical-chemical scales for the first time, such as thin PDR and shock layers, and it can resolve the hot cores and outflow cavities close to protostars. With its high sensitivity and broad frequency range, it can also probe hotter gas and reveal the importance of state-selective processes. Finally, astrochemical studies of high-redshift galaxies are enabled by ALMA, at the level that was used to study galactic clouds 30 years ago.

Besides ALMA, astrochemistry has other exciting new missions on the horizon. The *Rosetta* spacecraft will rendez-vous with the comet 67P/Churyumov-Gerasimenko in summer 2014 and deploy a lander to investigate its surface composition in late 2014. This mission will give a big boost to studies of the connection between solar system and interstellar material. The 6-m *James Webb Space Telescope* (JWST) will be launched in late 2018 and will have near- and mid-infrared spectroscopic instruments to survey ices and gases with unprecedented sensitivity. Finally, the next generation of Extremely Large Telescopes (ELTs) is starting to be built and will provide the ultimate spatial and spectral resolution at optical- and near-infrared wavelengths. Overall, there will be plenty of material for future exciting new 'plots' and 'plays' in astrochemistry.

Acknowledgements

I am indebted to Magnus Persson (Fig. 2,5,6), Sandrine Bottinelli (Fig.3) and Simon Bruderer (Fig. 8) for providing figures. Astrochemistry in Leiden is supported by the Netherlands Organization for Scientific Research (NWO), The Netherlands Research School for Astronomy (NOVA), by a Royal Netherlands Academy of Arts and Sciences (KNAW) professor prize, and by European Union A-ERC grant 291141 CHEMPLAN.

References

1 A. Weiß, C. De Breuck, D. P. Marrone, J. D. Vieira, J. E. Aguirre, K. A. Aird, M. Aravena, M. L. N. Ashby, M. Bayliss, B. A. Benson, M. Béthermin, A. D. Biggs, L. E. Bleem, J. J. Bock, M. Bothwell, C. M. Bradford, M. Brodwin, J. E. Carlstrom, C. L. Chang, S. C. Chapman, T. M. Crawford, A. T. Crites, T. de Haan, M. A. Dobbs, T. P. Downes, C. D. Fassnacht, E. M. George, M. D. Gladders, A. H. Gonzalez, T. R. Greve, N. W. Halverson, Y. D. Hezaveh, F. W. High, G. P. Holder, W. L. Holzapfel, S. Hoover, J. D. Hrubes, K. Husband, R. Keisler, A. T. Lee, E. M. Leitch, M. Lueker, D. Luong-Van, M. Malkan, V. McIntyre, J. J. McMahon, J. Mehl, K. M. Menten, S. S. Meyer, E. J. Murphy, S. Padin, T. Plagge, C. L. Reichardt, A. Rest, M. Rosenman, J. Ruel, J. E. Ruhl, K. K. Schaffer, E. Shirokoff, J. S. Spilker, B. Stalder, Z. Staniszewski, A. A. Stark, K. Story, K. Vanderlinde, N. Welikala and R. Williamson, *Astrophys. J.*, 2013, **767**, 88.

2 A. G. G. M. Tielens, *Annu. Rev. Astron. Astrophys.*, 2008, **46**, 289–337.

3 Y. Gao, C. L. Carilli, P. M. Solomon and P. A. Vanden Bout, *Astrophys. J. Lett.*, 2007, **660**, L93–L96.

4 S. Martín, in *The Molecular Universe*, ed. J. Cernicharo and R. Bachiller, Cambridge University Press, 2011, vol. IAU Symposium 280, pp. 351–360.

5 J. Cami, J. Bernard-Salas, E. Peeters and S. E. Malek, *Science*, 2010, **329**, 1180–.

6 S. Seager and D. Deming, *Annu. Rev. Astron. Astrophys.*, 2010, **48**, 631–672.

7 J. L. Birkby, R. J. de Kok, M. Brogi, E. J. W. de Mooij, H. Schwarz, S. Albrecht and I. A. G. Snellen, *Mon. Not. R. Astron. Soc.*, 2013, **436**, L35–L39.

8 A. Dalgarno, *Annu. Rev. Astron. Astrophys.*, 2008, **46**, 1–20.

9 A. G. G. M. Tielens, *Rev. Mod. Phys.*, 2013, **85**, 1021–1081.

10 E. F. van Dishoeck, E. Herbst and D. A. Neufeld, *Chemical Reviews*, 2013, **113**, 9043–9085.

11 E. Herbst, *Phys. Chem. Chem. Phys.*, 2014, **16**, 3344–3359.

12 P. Caselli and C. Ceccarelli, *Astron. Astrophys. Review*, 2012, **20**, 56.

13 E. A. Bergin, L. I. Cleeves, U. Gorti, K. Zhang, G. A. Blake, J. D. Green, S. M. Andrews, N. J. Evans, II, T. Henning, K. Öberg, K. Pontoppidan, C. Qi, C. Salyk and E. F. van Dishoeck, *Nature*, 2013, **493**, 644–646.

14 E. Herbst and E. F. van Dishoeck, *Annu. Rev. Astron. Astrophys.*, 2009, **47**, 427–480.

15 J. Blum and G. Wurm, *Annu. Rev. Astron. Astrophys.*, 2008, **46**, 21–56.

16 H. J. Habing, *Bull. Astron. Netherlands*, 1968, **19**, 421.

17 B. T. Draine, *Astrophys. J., Suppl. Ser.*, 1978, **36**, 595–619.

18 W. G. Roberge, D. Jones, S. Lepp and A. Dalgarno, *Astrophys. J., Suppl. Ser.*, 1991, **77**, 287–297.

19 S. S. Prasad and S. P. Tarafdar, *Astrophys. J.*, 1983, **267**, 603–609.

20 R. Gredel, S. Lepp, A. Dalgarno and E. Herbst, *Astrophys. J.*, 1989, **347**, 289–293.

21 C. J. Shen, J. M. Greenberg, W. A. Schutte and E. F. van Dishoeck, *Astron. Astrophys.*, 2004, **415**, 203–215.

22 E. F. van Dishoeck, *Annu. Rev. Astron. Astrophys.*, 2004, **42**, 119–167.

23 T. de Graauw, F. P. Helmich, T. G. Phillips, J. Stutzki, E. Caux, N. D. Whyborn, P. Dieleman, P. R. Roelfsema, H. Aarts, R. Assendorp, R. Bachiller, W. Baechtold, A. Barcia, D. A. Beintema, V. Belitsky, A. O. Benz, R. Bieber, A. Boogert, C. Borys, B. Bumble, P. Caïs,

M. Caris, P. Cerulli-Irelli, G. Chattopadhyay, S. Cherednichenko, M. Ciechanowicz, O. Coeur-Joly, C. Comito, A. Cros, A. de Jonge, G. de Lange, B. Delforges, Y. Delorme, T. den Boggende, J. Desbat, C. Diez-González, A. M. di Giorgio, L. Dubbeldam, K. Edwards, M. Eggens, N. Erickson, J. Evers, M. Fich, T. Finn, B. Franke, T. Gaier, C. Gal, J. R. Gao, J. Gallego, S. Gauffre, J. J. Gill, S. Glenz, H. Golstein, H. Goulooze, T. Gunsing, R. Güsten, P. Hartogh, W. A. Hatch, R. Higgins, E. C. Honingh, R. Huisman, B. D. Jackson, H. Jacobs, K. Jacobs, C. Jarchow, H. Javadi, W. Jellema, M. Justen, A. Karpov, C. Kasemann, J. Kawamura, G. Keizer, D. Kester, T. M. Klapwijk, T. Klein, E. Kollberg, J. Kooi, P. Kooiman, B. Kopf, M. Krause, J. Krieg, C. Kramer, B. Kruizenga, T. Kuhn, W. Laauwen, R. Lai, B. Larsson, H. G. Leduc, C. Leinz, R. H. Lin, R. Liseau, G. S. Liu, A. Loose, I. López-Fernandez, S. Lord, W. Luinge, A. Marston, J. Martín-Pintado, A. Maestrini, F. W. Maiwald, C. McCoey, I. Mehdi, A. Megej, M. Melchior, L. Meinsma, H. Merkel, M. Michalska, C. Monstein, D. Moratschke, P. Morris, H. Muller, J. A. Murphy, A. Naber, E. Natale, W. Nowosielski, F. Nuzzolo, M. Olberg, M. Olbrich, R. Orfei, P. Orleanski, V. Ossenkopf, T. Peacock, J. C. Pearson, I. Peron, S. Phillip-May, L. Piazzo, P. Planesas, M. Rataj, L. Ravera, C. Risacher, M. Salez, L. A. Samoska, P. Saraceno, R. Schieder, E. Schlecht, F. Schlöder, F. Schmülling, M. Schultz, K. Schuster, O. Siebertz, H. Smit, R. Szczerba, R. Shipman, E. Steinmetz, J. A. Stern, M. Stokroos, R. Teipen, D. Teyssier, T. Tils, N. Trappe, C. van Baaren, B. van Leeuwen, H. van de Stadt, H. Visser, K. J. Wildeman, C. K. Wafelbakker, J. S. Ward, P. Wesselius, W. Wild, S. Wulff, H. Wunsch, X. Tielens, P. Zaal, H. Zirath, J. Zmuidzinas and F. Zwart, *Astron. Astrophys.*, 2010, **518**, L6.

24 H. Linnartz, N. Wehres, H. van Winckel, G. A. H. Walker, D. A. Bohlender, A. G. G. M. Tielens, T. Motylewski and J. P. Maier, *Astron. Astrophys.*, 2010, **511**, L3.

25 H. M. Pickett, I. R. L. Poynter, E. A. Cohen, M. L. Delitsky, J. C. Pearson and H. S. P. Muller, *J. Quant. Spectrosc. Rad. Transfer*, 1998, **60**, 883–890.

26 H. S. P. Müller, S. Thorwirth, D. A. Roth and G. Winnewisser, *Astron. Astrophys.*, 2001, **370**, L49–L52.

27 H. S. P. Müller, F. Schlöder, J. Stutzki and G. Winnewisser, *J. Mol. Struct.*, 2005, **742**, 215–227.

28 L. S. Rothman, I. E. Gordon, A. Barbe, D. C. Benner, P. E. Bernath, M. Birk, V. Boudon, L. R. Brown, A. Campargue, J. P. Champion, K. Chance, L. H. Coudert, V. Dana, V. M. Devi, S. Fally, J. M. Flaud, R. R. Gamache, A. Goldman, D. Jacquemart, I. Kleiner, N. Lacome, W. J. Lafferty, J. Y. Mandin, S. T. Massie, S. N. Mikhailenko, C. E. Miller, N. Moazzen-Ahmadi, O. V. Naumenko, A. V. Nikitin, J. Orphal, V. I. Perevalov, A. Perrin, A. Predoi-Cross, C. P. Rinsland, M. Rotger, M. Simeckova, M. A. H. Smith, K. Sung, S. A. Tashkun, J. Tennyson, R. A. Toth, A. C. Vandaele and J. Vander Auwera, *J. Quant. Spectrosc. Rad. Transfer*, 2009, **110**, 533–572.

29 C. Boersma, C. W. Bauschlicher, Jr., A. Ricca, A. L. Mattioda, J. Cami, E. Peeters, F. Sánchez de Armas, G. Puerta Saborido, D. M. Hudgins and L. J. Allamandola, *Astrophys. J., Suppl. Ser.*, 2014, **211**, 8.

30 T. Henning, *Annu. Rev. Astron. Astrophys.*, 2010, **48**, 21–46.

31 D. M. Hudgins, S. A. Sandford, L. J. Allamandola and A. G. G. M. Tielens, *Astrophys. J., Suppl. Ser.*, 1993, **86**, 713–870.

32 H. Linnartz, J.-B. Bossa, J. Bouwman, H. M. Cuppen, S. H. Cuylle, E. F. van Dishoeck, E. C. Fayolle, G. Fedoseev, G. W. Fuchs, S. Ioppolo, K. Isokoski, T. Lamberts, K. I. Öberg, C. Romanzin, E. Tenenbaum and J. Zhen, in *The Molecular Universe*, ed. J. Cernicharo and R. Bachiller, Cambridge University Press, 2011, vol. IAU Symposium 280, pp. 390–404.

33 R. L. Hudson, R. F. Ferrante and M. H. Moore, *Icarus*, 2014, **228**, 276–287.

34 G. M. Munoz Caro, E. Dartois, P. Boduch, H. Rothard, A. Domaracka and A. Jimenez-Escobar, *å*, 2014, in press.

35 V. Mennella, *Astrophys. J.*, 2010, **718**, 867–875.

36 G. M. Muñoz Caro, G. Matrajt, E. Dartois, M. Nuevo, L. D'Hendecourt, D. Deboffle, G. Montagnac, N. Chauvin, C. Boukari and D. Le Du, *Astron. Astrophys.*, 2006, **459**, 147–159.

37 I. W. M. Smith, *Annu. Rev. Astron. Astrophys.*, 2011, **49**, 29–66.

38 D. Chastaing, S. D. Le Picard, I. R. Sims and I. W. M. Smith, *Astron. Astrophys.*, 2001, **365**, 241–247.

39 S. B. Morales, C. J. Bennett, S. D. Le Picard, A. Canosa, I. R. Sims, B. J. Sun, P. H. Chen, A. H. H. Chang, V. V. Kislov, A. M. Mebel, X. Gu, F. Zhang, P. Maksyutenko and R. I. Kaiser, *Astrophys. J.*, 2011, **742**, 26.

40 W. D. Geppert and M. Larsson, *Chemical Reviews*, 2013, **113**, 8872–8905.

41 *MPI-Mainz UV/VIS Spectral Atlas of Gaseous Molecules*, ed. H. Keller-Rudek, G. Moortgat, R. Sander and R. Sörensen, www.uv-vis-spectral-atlas-mainz.org, 2013.

42 M. A. Allodi, R. A. Baragiola, G. A. Baratta, M. A. Barucci, G. A. Blake, P. Boduch, J. R. Brucato, C. Contreras, S. H. Cuylle, D. Fulvio, M. S. Gudipati, S. Ioppolo, Z. Kaňuchová, A. Lignell, H. Linnartz, M. E. Palumbo, U. Raut, H. Rothard, F. Salama, E. V. Savchenko, E. Sciamma-O'Brien and G. Strazzulla, *Space Sci. Rev.*, 2013, **180**, 101–175.

43 M. P. Collings, M. A. Anderson, R. Chen, J. W. Dever, S. Viti, D. A. Williams and M. R. S. McCoustra, *Mon. Not. R. Astron. Soc.*, 2004, **354**, 1133–1140.

44 S. E. Bisschop, H. J. Fraser, K. I. Öberg, E. F. van Dishoeck and S. Schlemmer, *Astron. Astrophys.*, 2006, **449**, 1297–1309.

45 R. Martín-Doménech, G. M. Muñoz Caro, J. Bueno and F. Goesmann, *Astron. Astrophys.*, 2014, **564**, A8.

46 N. Watanabe and A. Kouchi, *Astrophys. J. Lett.*, 2002, **571**, L173–L176.

47 H. Hidaka, N. Watanabe, T. Shiraki, A. Nagaoka and A. Kouchi, *Astrophys. J.*, 2004, **614**, 1124–1131.

48 G. W. Fuchs, H. M. Cuppen, S. Ioppolo, C. Romanzin, S. E. Bisschop, S. Andersson, E. F. van Dishoeck and H. Linnartz, *Astron. Astrophys.*, 2009, **505**, 629–639.

49 S. Ioppolo, H. M. Cuppen, C. Romanzin, E. F. van Dishoeck and H. Linnartz, *Astrophys. J.*, 2008, **686**, 1474–1479.

50 N. Miyauchi, H. Hidaka, T. Chigai, A. Nagaoka, N. Watanabe and A. Kouchi, *Chem. Phys. Lett.*, 2008, **456**, 27–30.

51 F. Dulieu, L. Amiaud, E. Congiu, J. Fillion, E. Matar, A. Momeni, V. Pirronello and J. L. Lemaire, *Astron. Astrophys.*, 2010, **512**, A30.

52 H. M. Cuppen, S. Ioppolo, C. Romanzin and H. Linnartz, *Phys. Chem. Chem. Phys.*, 2010, **12**, 12077–12088.

53 M. Accolla, E. Congiu, G. Manico, F. Dulieu, H. Chaabouni, J. L. Lemaire and V. Pirronello, *Mon. Not. R. Astron. Soc.*, 2013, **429**, 3200–3206.

54 A. G. G. M. Tielens and W. Hagen, *Astron. Astrophys.*, 1982, **114**, 245–260.

55 K. I. Öberg, G. W. Fuchs, Z. Awad, H. J. Fraser, S. Schlemmer, E. F. van Dishoeck and H. Linnartz, *Astrophys. J. Lett.*, 2007, **662**, L23–L26.

56 K. I. Öberg, H. Linnartz, R. Visser and E. F. van Dishoeck, *Astrophys. J.*, 2009, **693**, 1209–1218.

57 E. C. Fayolle, M. Bertin, C. Romanzin, X. Michaut, K. I. Öberg, H. Linnartz and J.-H. Fillion, *Astrophys. J. Lett.*, 2011, **739**, L36.

58 M. Bertin, E. C. Fayolle, C. Romanzin, H. A. M. Poderoso, X. Michaut, L. Philippe, P. Jeseck, K. I. Öberg, H. Linnartz and J.-H. Fillion, *Astrophys. J.*, 2013, **779**, 120.

59 M. H. Moore, R. L. Hudson and P. A. Gerakines, *Spectrochimica Acta*, 2001, **57**, 843–858.

60 J. E. Elsila, J. P. Dworkin, M. P. Bernstein, M. P. Martin and S. A. Sandford, *Astrophys. J.*, 2007, **660**, 911–918.

61 K. I. Öberg, R. T. Garrod, E. F. van Dishoeck and H. Linnartz, *Astron. Astrophys.*, 2009, **504**, 891–913.

62 Y. S. Kim and R. I. Kaiser, *Astrophys. J.*, 2011, **729**, 68.

63 P. A. Gerakines, R. L. Hudson, M. H. Moore and J.-L. Bell, *Icarus*, 2012, **220**, 647–659.

64 F. Islam, G. A. Baratta and M. E. Palumbo, *Astron. Astrophys.*, 2014, **561**, A73.

65 G. D. Cody, E. Heying, C. M. O. Alexander, L. R. Nittler, A. L. D. Kilcoyne, S. A. Sandford and R. M. Stroud, *Proceedings of the National Academy of Science*, 2011, **108**, 19171–19176.

66 F. L. Schöier, F. F. S. van der Tak, E. F. van Dishoeck and J. H. Black, *Astron. Astrophys.*, 2005, **432**, 369–379.

67 F. van der Tak, in *The Molecular Universe*, ed. J. Cernicharo and R. Bachiller, Cambridge University Press, 2011, vol. IAU Symposium 280, pp. 449–460.

68 M.-L. Dubernet, M. H. Alexander, Y. A. Ba, N. Balakrishnan, C. Balança, C. Ceccarelli, J. Cernicharo, F. Daniel, F. Dayou, M. Doronin, F. Dumouchel, A. Faure, N. Feautrier, D. R. Flower, A. Grosjean, P. Halvick, J. Kłos, F. Lique, G. C. McBane, S. Marinakis, N. Moreau, R. Moszynski, D. A. Neufeld, E. Roueff, P. Schilke, A. Spielfiedel, P. C. Stancil, T. Stoecklin, J. Tennyson, B. Yang, A.-M. Vasserot and L. Wiesenfeld, *Astron. Astrophys.*, 2013, **553**, A50.

69 E. F. van Dishoeck, B. Jonkheid and M. C. van Hemert, *Faraday Discussions*, 2006, **133**, 231.

70 M. C. van Hemert and E. F. van Dishoeck, *Chemical Physics*, 2008, **343**, 292–302.

71 W. H. el-Qadi and P. C. Stancil, *Astrophys. J.*, 2013, **779**, 97.

72 Z. Lin, D. Talbi, E. Roueff, E. Herbst, N. Wehres, C. A. Cole, Z. Yang, T. P. Snow and V. M. Bierbaum, *Astrophys. J.*, 2013, **765**, 80.

73 D. E. Woon and E. Herbst, *Astrophys. J.*, 1997, **477**, 204–208.

74 E. Herbst, R. Terzieva and D. Talbi, *Mon. Not. R. Astron. Soc.*, 2000, **311**, 869–876.

75 X. Li, C. Arasa, M. C. van Hemert and E. F. van Dishoeck, *Journal of Physical Chemistry A*, 2013, **117**, 12889–12896.

76 D. E. Woon and E. Herbst, *Astrophys. J., Suppl. Ser.*, 2009, **185**, 273–288.

77 A. Ricca, C. W. Bauschlicher, Jr. and L. J. Allamandola, *Astrophys. J.*, 2013, **776**, 31.

78 S. Andersson, A. Al-Halabi, G.-J. Kroes and E. F. van Dishoeck, *J. Chem. Phys.*, 2006, **124**, 064715.

79 C. Arasa, S. Andersson, H. M. Cuppen, E. F. van Dishoeck and G.-J. Kroes, *J. Chem. Phys.*, 2010, **132**, 184510.

80 J. Koning, G. J. Kroes and C. Arasa, *J. Chem. Phys.*, 2013, **138**, 104701.

81 C. Arasa, M. C. van Hemert, E. F. van Dishoeck and G. J. Kroes, *Journal of Physical Chemistry A*, 2013, **117**, 7064–7074.

82 M. Asplund, N. Grevesse, A. J. Sauval and P. Scott, *Annu. Rev. Astron. Astrophys.*, 2009, **47**, 481–522.

83 N. Przybilla, M.-F. Nieva and K. Butler, *Astrophys. J. Lett.*, 2008, **688**, L103–L106.

84 B. T. Draine, *Annu. Rev. Astron. Astrophys.*, 2003, **41**, 241–289.

85 B. T. Draine, *Physics of the Interstellar and Intergalactic Medium*, Princeton University Press, 2011.

86 A. G. G. M. Tielens, *The Physics and Chemistry of the Interstellar Medium*, Cambridge University Press, Cambridge, 2005.

87 I. Oliveira, J. Olofsson, K. M. Pontoppidan, E. F. van Dishoeck, J.-C. Augereau and B. Merín, *Astrophys. J.*, 2011, **734**, 51.

88 L. Testi, T. Birnstiel, L. Ricci, S. Andrews, J. Blum, J. Carpenter, C. Dominik, A. Isella, A. Natta, J. Williams and D. Wilner, in *Protostars & Planets VI*, ed. Beuther, H., Klessen, R., Dullemond, K., Henning, Th., Univ. Arizona Press: Tucson, 2014, p. in press.

89 A. P. Jones, L. Fanciullo, M. Köhler, L. Verstraete, V. Guillet, M. Bocchio and N. Ysard, *Astron. Astrophys.*, 2013, **558**, A62.

90 A. C. A. Boogert, K. M. Pontoppidan, F. Lahuis, J. K. Jørgensen, J. Augereau, G. A. Blake, T. Y. Brooke, J. Brown, C. P. Dullemond, N. J. Evans, II, V. Geers, M. R. Hogerheijde, J. Kessler-Silacci, C. Knez, P. Morris, A. Noriega-Crespo, F. L. Schöier, E. F. van Dishoeck, L. E. Allen, P. M. Harvey, D. W. Koerner, L. G. Mundy, P. C. Myers, D. L. Padgett, A. I. Sargent and K. R. Stapelfeldt, *Astrophys. J., Suppl. Ser.*, 2004, **154**, 359–362.

91 A. C. A. Boogert, K. M. Pontoppidan, C. Knez, F. Lahuis, J. Kessler-Silacci, E. F. van Dishoeck, G. A. Blake, J. Augereau, S. E. Bisschop, S. Bottinelli, T. Y. Brooke, J. Brown, A. Crapsi, N. J. Evans, II, H. J. Fraser, V. Geers, T. L. Huard, J. K. Jørgensen, K. I. Öberg, L. E. Allen, P. M. Harvey, D. W. Koerner, L. G. Mundy, D. L. Padgett, A. I. Sargent and K. R. Stapelfeldt, *Astrophys. J.*, 2008, **678**, 985–1004.

92 J. H. Novozamsky, W. A. Schutte and J. V. Keane, *Astron. Astrophys.*, 2001, **379**, 588–591.

93 F. A. van Broekhuizen, K. M. Pontoppidan, H. J. Fraser and E. F. van Dishoeck, *Astron. Astrophys.*, 2005, **441**, 249–260.

94 K. I. Öberg, A. C. A. Boogert, K. M. Pontoppidan, S. van den Broek, E. F. van Dishoeck, S. Bottinelli, G. A. Blake and N. J. Evans, II, *Astrophys. J.*, 2011, **740**, 109.

95 A. G. G. M. Tielens, A. T. Tokunaga, T. R. Geballe and F. Baas, *Astrophys. J.*, 1991, **381**, 181–199.

96 K. M. Pontoppidan, H. J. Fraser, E. Dartois, W. Thi, E. F. van Dishoeck, A. C. A. Boogert, L. d'Hendecourt, A. G. G. M. Tielens and S. E. Bisschop, *Astron. Astrophys.*, 2003, **408**, 981–1007.

97 D. C. B. Whittet, C. A. Poteet, J. E. Chiar, L. Pagani, V. M. Bajaj, D. Horne, S. S. Shenoy and A. J. Adamson, *Astrophys. J.*, 2013, **774**, 102.

98 P. Caselli, C. M. Walmsley, M. Tafalla, L. Dore and P. C. Myers, *Astrophys. J. Lett.*, 1999, **523**, L165–L169.

99 K. M. Pontoppidan, *Astron. Astrophys.*, 2006, **453**, L47–L50.

100 E. A. Bergin, J. Alves, T. Huard and C. J. Lada, *Astrophys. J. Lett.*, 2002, **570**, L101–L104.

101 K. I. Öberg, S. Bottinelli, J. K. Jørgensen and E. F. van Dishoeck, *Astrophys. J.*, 2010, **716**,

825–834.

102 A. Remijan, L. E. Snyder, D. N. Friedel, S.-Y. Liu and R. Y. Shah, *Astrophys. J.*, 2003, **590**, 314–332.

103 D. Quan, E. Herbst, Y. Osamura and E. Roueff, *Astrophys. J.*, 2010, **725**, 2101–2109.

104 V. Ossenkopf, H. S. P. Müller, D. C. Lis, P. Schilke, T. A. Bell, S. Bruderer, E. Bergin, C. Ceccarelli, C. Comito, J. Stutzki, A. Bacman, A. Baudry, A. O. Benz, M. Benedettini, O. Berne, G. Blake, A. Boogert, S. Bottinelli, F. Boulanger, S. Cabrit, P. Caselli, E. Caux, J. Cernicharo, C. Codella, A. Coutens, N. Crimier, N. R. Crockett, F. Daniel, K. Demyk, P. Dieleman, C. Dominik, M. L. Dubernet, M. Emprechtinger, P. Encrenaz, E. Falgarone, K. France, A. Fuente, M. Gerin, T. F. Giesen, A. M. di Giorgio, J. R. Goicoechea, P. F. Goldsmith, R. Güsten, A. Harris, F. Helmich, E. Herbst, P. Hily-Blant, K. Jacobs, T. Jacq, C. Joblin, D. Johnstone, C. Kahane, M. Kama, T. Klein, A. Klotz, C. Kramer, W. Langer, B. Lefloch, C. Leinz, A. Lorenzani, S. D. Lord, S. Maret, P. G. Martin, J. Martin-Pintado, C. McCoey, M. Melchior, G. J. Melnick, K. M. Menten, B. Mookerjea, P. Morris, J. A. Murphy, D. A. Neufeld, B. Nisini, S. Pacheco, L. Pagani, B. Parise, J. C. Pearson, M. Pérault, T. G. Phillips, R. Plume, S. Quin, R. Rizzo, M. Röllig, M. Salez, P. Saraceno, S. Schlemmer, R. Simon, K. Schuster, F. F. S. van der Tak, A. G. G. M. Tielens, D. Teyssier, N. Trappe, C. Vastel, S. Viti, V. Wakelam, A. Walters, S. Wang, N. Whyborn, M. van der Wiel, H. W. Yorke, S. Yu and J. Zmuidzinas, *Astron. Astrophys.*, 2010, **518**, L111.

105 A. O. Benz, S. Bruderer, E. F. van Dishoeck, P. Stäuber, S. F. Wampfler, M. Melchior, C. Dedes, F. Wyrowski, S. D. Doty, F. van der Tak, W. Bächtold, A. Csillaghy, A. Megej, C. Monstein, M. Soldati, R. Bachiller, A. Baudry, M. Benedettini, E. Bergin, P. Bjerkeli, G. A. Blake, S. Bontemps, J. Braine, P. Caselli, J. Cernicharo, C. Codella, F. Daniel, A. M. di Giorgio, P. Dieleman, C. Dominik, P. Encrenaz, M. Fich, A. Fuente, T. Giannini, J. R. Goicoechea, T. de Graauw, F. Helmich, G. J. Herczeg, F. Herpin, M. R. Hogerheijde, T. Jacq, W. Jellema, D. Johnstone, J. K. Jørgensen, L. E. Kristensen, B. Larsson, D. Lis, R. Liseau, M. Marseille, C. McCoey, G. Melnick, D. Neufeld, B. Nisini, M. Olberg, V. Ossenkopf, B. Parise, J. C. Pearson, R. Plume, C. Risacher, J. Santiago-García, P. Saraceno, R. Schieder, R. Shipman, J. Stutzki, M. Tafalla, A. G. G. M. Tielens, T. A. van Kempen, R. Visser and U. A. Yıldız, *Astron. Astrophys.*, 2010, **521**, L35.

106 M. De Luca, H. Gupta, D. Neufeld, M. Gerin, D. Teyssier, B. J. Drouin, J. C. Pearson, D. C. Lis, R. Monje, T. G. Phillips, J. R. Goicoechea, B. Godard, E. Falgarone, A. Coutens and T. A. Bell, *Astrophys. J. Lett.*, 2012, **751**, L37.

107 D. C. Lis, J. C. Pearson, D. A. Neufeld, P. Schilke, H. S. P. Müller, H. Gupta, T. A. Bell, C. Comito, T. G. Phillips, E. A. Bergin, C. Ceccarelli, P. F. Goldsmith, G. A. Blake, A. Bacmann, A. Baudry, M. Benedettini, A. Benz, J. Black, A. Boogert, S. Bottinelli, S. Cabrit, P. Caselli, A. Castets, E. Caux, J. Cernicharo, C. Codella, A. Coutens, N. Crimier, N. R. Crockett, F. Daniel, K. Demyk, C. Dominic, M.-L. Dubernet, M. Emprechtinger, P. Encrenaz, E. Falgarone, A. Fuente, M. Gerin, T. F. Giesen, J. R. Goicoechea, F. Helmich, P. Hennebelle, T. Henning, E. Herbst, P. Hily-Blant, Å. Hjalmarson, D. Hollenbach, T. Jack, C. Joblin, D. Johnstone, C. Kahane, M. Kama, M. Kaufman, A. Klotz, W. D. Langer, B. Larsson, J. Le Bourlot, B. Lefloch, F. Le Petit, D. Li, R. Liseau, S. D. Lord, A. Lorenzani, S. Maret, P. G. Martin, G. J. Melnick, K. M. Menten, P. Morris, J. A. Murphy, Z. Nagy, B. Nisini, V. Ossenkopf, S. Pacheco, L. Pagani, B. Parise, M. Pérault, R. Plume, S.-L. Qin, E. Roueff, M. Salez, A. Sandqvist, P. Saraceno, S. Schlemmer, K. Schuster, R. Snell, J. Stutzki, A. Tielens, N. Trappe, F. F. S. van der Tak, M. H. D. van der Wiel, E. van Dishoeck, C. Vastel, S. Viti, V. Wakelam, A. Walters, S. Wang, F. Wyrowski, H. W. Yorke, S. Yu, J. Zmuidzinas, Y. Delorme, J.-P. Desbat, R. Güsten, J.-M. Krieg and B. Delforge, *Astron. Astrophys.*, 2010, **521**, L9.

108 K. M. Menten, F. Wyrowski, A. Belloche, R. Güsten, L. Dedes and H. S. P. Müller, *Astron. Astrophys.*, 2011, **525**, A77.

109 D. A. Neufeld, E. Falgarone, M. Gerin, B. Godard, E. Herbst, G. Pineau des Forêts, A. I. Vasyunin, R. Güsten, H. Wiesemeyer and O. Ricken, *Astron. Astrophys.*, 2012, **542**, L6.

110 M. J. Barlow, B. M. Swinyard, P. J. Owen, J. Cernicharo, H. L. Gomez, R. J. Ivison, O. Krause, T. L. Lim, M. Matsuura, S. Miller, G. Olofsson and E. T. Polehampton, *Science*, 2013, **342**, 1343–1345.

111 P. Schilke, D. A. Neufeld, H. S. P. Müller, C. Comito, E. A. Bergin, D. C. Lis, M. Gerin, J. H. Black, M. Wolfire, N. Indriolo, J. C. Pearson, K. M. Menten, B. Winkel, Á. Sánchez-Monge, T. Möller, B. Godard and E. Falgarone, *Astron. Astrophys.*, 2014, **566**, A29.

112 M. J. F. Rosenberg, O. Berné and C. Boersma, *å*, 2014, in press.

113 D. Gerlich, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 2199–2208.

114 E. F. van Dishoeck, in *Rate Coefficients in Astrochemistry*, ed. T. J. Millar and D. A. Williams, Kluwer, Dordrecht, 1988, vol. 146, pp. 49–72.

115 E. F. van Dishoeck and R. Visser, in *Modern Concepts in Laboratory Astrochemistry*, ed. H. Schlemmer, S. Mutschke and T. Giesen, Wiley, 2014, p. in press.

116 H. Abgrall, E. Roueff and I. Drira, *Astron. Astrophys., Suppl. Ser.*, 2000, **141**, 297–300.

117 R. Visser, E. F. van Dishoeck, S. D. Doty and C. P. Dullemond, *Astron. Astrophys.*, 2009, **495**, 881–897.

118 X. Li, A. N. Heays, R. Visser, W. Ubachs, B. R. Lewis, S. T. Gibson and E. F. van Dishoeck, *Astron. Astrophys.*, 2013, **555**, A14.

119 A. N. Heays, R. Visser, R. Gredel, W. Ubachs, B. R. Lewis, S. T. Gibson and E. F. van Dishoeck, *Astron. Astrophys.*, 2014, **562**, A61.

120 E. F. van Dishoeck and J. H. Black, *Astrophys. J.*, 1988, **334**, 771–802.

121 B. J. McCall, A. J. Huneycutt, R. J. Saykally, T. R. Geballe, N. Djuric, G. H. Dunn, J. Semaniak, O. Novotny, A. Al-Khalili, A. Ehlerding, F. Hellberg, S. Kalhori, A. Neau, R. Thomas, F. Österdahl and M. Larsson, *Nature*, 2003, **422**, 500–502.

122 H. Buhr, J. Stuetzel, M. B. Mendes, O. Novotny, D. Schwalm, M. H. Berg, D. Bing, M. Grieser, O. Heber, C. Krantz, S. Menk, S. Novotny, D. A. Orlov, A. Petrignani, M. L. Rappaport, R. Repnow, D. Zajfman and A. Wolf, *Phys. Rvw. Lett.*, 2010, **105**, 103202.

123 W. D. Geppert, M. Hamberg, R. D. Thomas, F. Österdahl, F. Hellberg, V. Zhaunerchyk, A. Ehlerding, T. J. Millar, H. Roberts, J. Semaniak, M. A. Ugglas, A. Källberg, A. Simonsson, M. Kaminska and M. Larsson, *Faraday Discussions*, 2006, **133**, 177.

124 E. Herbst and W. Klemperer, *Astrophys. J.*, 1973, **185**, 505–534.

125 R. Atkinson, D. Baulch, R. Cox, J. Crowley, R. Hampson and R. Hynes, *Atmos. Chem. Phys.*, 2004, **4**, 1461.

126 D. McElroy, C. Walsh, A. J. Markwick, M. A. Cordiner, K. Smith and T. J. Millar, *Astron. Astrophys.*, 2013, **550**, A36.

127 V. Wakelam, E. Herbst, J.-C. Loison, I. W. M. Smith, V. Chandrasekaran, B. Pavone, N. G. Adams, M.-C. Bacchus-Montabonel, A. Bergeat, K. Béroff, V. M. Bierbaum, M. Chabot, A. Dalgarno, E. F. van Dishoeck, A. Faure, W. D. Geppert, D. Gerlich, D. Galli, E. Hébrard, F. Hersant, K. M. Hickson, P. Honvault, S. J. Klippenstein, S. Le Picard, G. Nyman, P. Pernot, S. Schlemmer, F. Selsis, I. R. Sims, D. Talbi, J. Tennyson, J. Troe, R. Wester and L. Wiesenfeld, *Astrophys. J., Suppl. Ser.*, 2012, **199**, 21.

128 Y. Aikawa and E. Herbst, *Astron. Astrophys.*, 2001, **371**, 1107–1117.

129 H. M. Cuppen and E. Herbst, *Astrophys. J.*, 2007, **668**, 294–309.

130 A. G. G. M. Tielens and S. B. Charnley, *Origins of Life and Evolution of the Biosphere*, 1997, **27**, 23–51.

131 R. T. Garrod and E. Herbst, *Astron. Astrophys.*, 2006, **457**, 927–936.

132 R. T. Garrod, *Astron. Astrophys.*, 2008, **491**, 239–251.

133 H. M. Cuppen, E. F. van Dishoeck, E. Herbst and A. G. G. M. Tielens, *Astron. Astrophys.*, 2009, **508**, 275–287.

134 H. M. Cuppen, L. J. Karssemeijer and T. Lamberts, *Chemical Reviews*, 2013, **113**, 8840–8871.

135 T. I. Hasegawa and E. Herbst, *Mon. Not. R. Astron. Soc.*, 1993, **263**, 589.

136 A. Al-Halabi and E. F. van Dishoeck, *Mon. Not. R. Astron. Soc.*, 2007, **382**, 1648–1656.

137 E. Matar, H. Bergeron, F. Dulieu, H. Chaabouni, M. Accolla and J. L. Lemaire, *The Journal of Chemical Physics*, 2010, **133**, –.

138 J. C. Brown, H. E. Potts, L. J. Porter and G. Le Chat, *Astron. Astrophys.*, 2011, **535**, A71.

139 A. Leger, M. Jura and A. Omont, *Astron. Astrophys.*, 1985, **144**, 147–160.

140 R. T. Garrod, V. Wakelam and E. Herbst, *Astron. Astrophys.*, 2007, **467**, 1103–1115.

141 F. Dulieu, E. Congiu, J. Noble, S. Baouche, H. Chaabouni, A. Moudens, M. Minissale and S. Cazaux, *Nature Sci. Rep.*, 2013, **3**, 1338.

142 L. B. D'Hendecourt, L. J. Allamandola, F. Baas and J. M. Greenberg, *Astron. Astrophys.*, 1982, **109**, L12–L14.

143 R. C. Bohlin, B. D. Savage and J. F. Drake, *Astrophys. J.*, 1978, **224**, 132–142.

144 B. L. Rachford, T. P. Snow, J. D. Destree, T. L. Ross, R. Ferlet, S. D. Friedman, C. Gry, E. B. Jenkins, D. C. Morton, B. D. Savage, J. M. Shull, P. Sonnentrucker, J. Tumlinson, A. Vidal-Madjar, D. E. Welty and D. G. York, *Astrophys. J., Suppl. Ser.*, 2009, **180**, 125–137.

145 V. Wakelam, E. Herbst, J. Le Bourlot, F. Hersant, F. Selsis and S. Guilloteau, *Astron. Astrophys.*, 2010, **517**, A21.

146 E. F. van Dishoeck, in *The Molecular Astrophysics of Stars and Galaxies*, Clarendon Press, Oxford, 1998, 1998, vol. 4, p. 53.

147 D. Hollenbach, M. J. Kaufman, D. Neufeld, M. Wolfire and J. R. Goicoechea, *Astrophys. J.*, 2012, **754**, 105.

148 N. Flagey, P. F. Goldsmith, D. C. Lis, M. Gerin, D. Neufeld, P. Sonnentrucker, M. De Luca, B. Godard, J. R. Goicoechea, R. Monje and T. G. Phillips, *Astrophys. J.*, 2013, **762**, 11.

149 R. Terzieva and E. Herbst, *Astrophys. J.*, 1998, **501**, 207–220.

150 M. Tafalla, P. C. Myers, P. Caselli, C. M. Walmsley and C. Comito, *Astrophys. J.*, 2002, **569**, 815–835.

151 E. Keto and P. Caselli, *Mon. Not. R. Astron. Soc.*, 2010, **402**, 1625–1634.

152 M. Padovani, C. M. Walmsley, M. Tafalla, P. Hily-Blant and G. Pineau Des Forêts, *Astron. Astrophys.*, 2011, **534**, A77.

153 P. Caselli, E. Keto, E. A. Bergin, M. Tafalla, Y. Aikawa, T. Douglas, L. Pagani, U. A. Yíldíz, F. F. S. van der Tak, C. M. Walmsley, C. Codella, B. Nisini, L. E. Kristensen and E. F. van Dishoeck, *Astrophys. J. Lett.*, 2012, **759**, L37.

154 J. C. Mottram, E. F. van Dishoeck, M. Schmalzl, L. E. Kristensen, R. Visser, M. R. Hogerheijde and S. Bruderer, *Astron. Astrophys.*, 2013, **558**, A126.

155 E. Keto, J. Rawlings and P. Caselli, *Mon. Not. R. Astron. Soc.*, 2014, **440**, 2616–2624.

156 M. Schmalzl and et al., *Astron. Astrophys.*, 2014, submitted.

157 S. D. Doty, F. L. Schöier and E. F. van Dishoeck, *Astron. Astrophys.*, 2004, **418**, 1021–1034.

158 M. Gerin, M. de Luca, J. Black, J. R. Goicoechea, E. Herbst, D. A. Neufeld, E. Falgarone, B. Godard, J. C. Pearson, D. C. Lis, T. G. Phillips, T. A. Bell, P. Sonnentrucker, F. Boulanger, J. Cernicharo, A. Coutens, E. Dartois, P. Encrenaz, T. Giesen, P. F. Goldsmith, H. Gupta, C. Gry, P. Hennebelle, P. Hily-Blant, C. Joblin, M. Kazmierczak, R. Kolos, J. Krelowski, J. Martin-Pintado, R. Monje, B. Mookerjea, M. Perault, C. Persson, R. Plume, P. B. Rimmer, M. Salez, M. Schmidt, J. Stutzki, D. Teyssier, C. Vastel, S. Yu, A. Contursi, K. Menten, T. Geballe, S. Schlemmer, R. Shipman, A. G. G. M. Tielens, S. Philipp-May, A. Cros, J. Zmuidzinas, L. A. Samoska, K. Klein and A. Lorenzani, *Astron. Astrophys.*, 2010, **518**, L110.

159 M. R. Schmidt, J. Krełowski, G. A. Galazutdinov, D. Zhao, M. A. Haddad, W. Ubachs and H. Linnartz, *Mon. Not. R. Astron. Soc.*, 2014, in press.

160 R. Gredel, E. F. van Dishoeck and J. H. Black, *Astron. Astrophys.*, 1993, **269**, 477–495.

161 D. A. Neufeld, P. Sonnentrucker, T. G. Phillips, D. C. Lis, M. de Luca, J. R. Goicoechea, J. H. Black, M. Gerin, T. Bell, F. Boulanger, J. Cernicharo, A. Coutens, E. Dartois, M. Kazmierczak, P. Encrenaz, E. Falgarone, T. R. Geballe, T. Giesen, B. Godard, P. F. Goldsmith, C. Gry, H. Gupta, P. Hennebelle, E. Herbst, P. Hily-Blant, C. Joblin, R. Kołos, J. Krełowski, J. Martín-Pintado, K. M. Menten, R. Monje, B. Mookerjea, J. Pearson, M. Perault, C. Persson, R. Plume, M. Salez, S. Schlemmer, M. Schmidt, J. Stutzki, D. Teyssier, C. Vastel, S. Yu, P. Cais, E. Caux, R. Liseau, P. Morris and P. Planesas, *Astron. Astrophys.*, 2010, **518**, L108.

162 P. Sonnentrucker, D. A. Neufeld, T. G. Phillips, M. Gerin, D. C. Lis, M. de Luca, J. R. Goicoechea, J. H. Black, T. A. Bell, F. Boulanger, J. Cernicharo, A. Coutens, E. Dartois, M. Kaźmierczak, P. Encrenaz, E. Falgarone, T. R. Geballe, T. Giesen, B. Godard, P. F. Goldsmith, C. Gry, H. Gupta, P. Hennebelle, E. Herbst, P. Hily-Blant, C. Joblin, R. Kołos, J. Krełowski, J. Martín-Pintado, K. M. Menten, R. Monje, B. Mookerjea, J. Pearson, M. Perault, C. M. Persson, R. Plume, M. Salez, S. Schlemmer, M. Schmidt, J. Stutzki, D. Teyssier, C. Vastel, S. Yu, E. Caux, R. Güsten, W. A. Hatch, T. Klein, I. Mehdi, P. Morris and J. S. Ward, *Astron. Astrophys.*, 2010, **521**, L12.

163 T. P. Snow and B. J. McCall, *Annu. Rev. Astron. Astrophys.*, 2006, **44**, 367–414.

164 P. P. van der Werf, K. G. Isaak, R. Meijerink, M. Spaans, A. Rykala, T. Fulton, A. F. Loenen, F. Walter, A. Weiß, L. Armus, J. Fischer, F. P. Israel, A. I. Harris, S. Veilleux, C. Henkel, G. Savini, S. Lord, H. A. Smith, E. González-Alfonso, D. Naylor, S. Aalto, V. Charmandaris, K. M. Dasyra, A. Evans, Y. Gao, T. R. Greve, R. Güsten, C. Kramer, J. Martín-Pintado, J. Mazzarella, P. P. Papadopoulos, D. B. Sanders, L. Spinoglio, G. Stacey, C. Vlahakis, M. C. Wiedner and E. M. Xilouris, *Astron. Astrophys.*, 2010, **518**, L42.

165 A. E. Douglas and G. Herzberg, *Astrophys. J.*, 1941, **94**, 381.

166 B. Godard, E. Falgarone and G. Pineau Des Forêts, *Astron. Astrophys.*, 2009, **495**, 847–867.

167 E. Falgarone, B. Godard, J. Cernicharo, M. de Luca, M. Gerin, T. G. Phillips, J. H. Black,

D. C. Lis, T. A. Bell, F. Boulanger, A. Coutens, E. Dartois, P. Encrenaz, T. Giesen, J. R. Goicoechea, P. F. Goldsmith, H. Gupta, C. Gry, P. Hennebelle, E. Herbst, P. Hily-Blant, C. Joblin, M. Kaźmierczak, R. Kołos, J. Krełowski, J. Martin-Pintado, R. Monje, B. Mookerjea, D. A. Neufeld, M. Perault, J. C. Pearson, C. Persson, R. Plume, M. Salez, M. Schmidt, P. Sonnentrucker, J. Stutzki, D. Teyssier, C. Vastel, S. Yu, K. Menten, T. R. Geballe, S. Schlemmer, R. Shipman, A. G. G. M. Tielens, S. Philipp, A. Cros, J. Zmuidzinas, L. A. Samoska, K. Klein, A. Lorenzani, R. Szczerba, I. Péron, P. Cais, P. Gaufre, A. Cros, L. Ravera, P. Morris, S. Lord and P. Planesas, *Astron. Astrophys.*, 2010, **521**, L15.

168 B. Godard, E. Falgarone, M. Gerin, D. C. Lis, M. De Luca, J. H. Black, J. R. Goicoechea, J. Cernicharo, D. A. Neufeld, K. M. Menten and M. Emprechtinger, *Astron. Astrophys.*, 2012, **540**, A87.

169 A. Sternberg and A. Dalgarno, *Astrophys. J., Suppl. Ser.*, 1995, **99**, 565.

170 A. G. G. M. Tielens, M. M. Meixner, P. P. van der Werf, J. Bregman, J. A. Tauber, J. Stutzki and D. Rank, *Science*, 1993, **262**, 86–89.

171 M. R. Hogerheijde, D. J. Jansen and E. F. van Dishoeck, *Astron. Astrophys.*, 1995, **294**, 792–810.

172 M. H. D. van der Wiel, F. F. S. van der Tak, V. Ossenkopf, M. Spaans, H. Roberts, G. A. Fuller and R. Plume, *Astron. Astrophys.*, 2009, **498**, 161–165.

173 J. Pety, D. Teyssier, D. Fossé, M. Gerin, E. Roueff, A. Abergel, E. Habart and J. Cernicharo, *Astron. Astrophys.*, 2005, **435**, 885–899.

174 M. Gerin, J. R. Goicoechea, J. Pety and P. Hily-Blant, *Astron. Astrophys.*, 2009, **494**, 977–985.

175 M. Agúndez, J. Cernicharo and J. R. Goicoechea, *Astron. Astrophys.*, 2008, **483**, 831–837.

176 W.-F. Thi, F. Ménard, G. Meeus, C. Martin-Zaïdi, P. Woitke, E. Tatulli, M. Benisty, I. Kamp, I. Pascucci, C. Pinte, C. A. Grady, S. Brittain, G. J. White, C. D. Howard, G. Sandell and C. Eiroa, *Astron. Astrophys.*, 2011, **530**, L2.

177 B. Godard and J. Cernicharo, *Astron. Astrophys.*, 2013, **550**, A8.

178 J. H. Black, *Faraday Discussions*, 1998, **109**, 257.

179 P. Stäuber and S. Bruderer, *Astron. Astrophys.*, 2009, **505**, 195–203.

180 D. C. Lis, P. Schilke, E. A. Bergin, M. Gerin, J. H. Black, C. Comito, M. De Luca, B. Godard, R. Higgins, F. Le Petit, J. C. Pearson, E. W. Pellegrini, T. G. Phillips and S. Yu, *Astrophys. J.*, 2014, **785**, 135.

181 F. F. S. van der Tak, V. Ossenkopf, Z. Nagy, A. Faure, M. Röllig and E. A. Bergin, *Astron. Astrophys.*, 2012, **537**, L10.

182 A. Wootten, in *Astrochemistry*, ed. M. S. Vardya and S. P. Tarafdar, Kluwer, Dordrecht, 1987, vol. IAU Symposium 120, pp. 311–318.

183 C. Ceccarelli, P. Caselli, D. Bockelée-Morvan, O. Mousis, F. Pizzarello, F. Robert and D. Semenov, in *Protostars & Planets VI*, ed. Beuther, H., Klessen, R., Dullemond, K., Henning, Th., Univ. Arizona Press: Tucson, 2014, p. in press.

184 R. Stark, F. F. S. van der Tak and E. F. van Dishoeck, *Astrophys. J. Lett.*, 1999, **521**, L67–L70.

185 P. Caselli, F. F. S. van der Tak, C. Ceccarelli and A. Bacmann, *Astron. Astrophys.*, 2003, **403**, L37–L41.

186 C. Vastel, T. G. Phillips and H. Yoshida, *Astrophys. J. Lett.*, 2004, **606**, L127–L130.

187 B. Parise, A. Belloche, F. Du, R. Güsten and K. M. Menten, *Astron. Astrophys.*, 2011, **526**, A31.

188 L. Pagani, M. Salez and P. G. Wannier, *Astron. Astrophys.*, 1992, **258**, 479–488.

189 L. Pagani, P. Lesaffre, M. Jorfi, P. Honvault, T. González-Lezana and A. Faure, *Astron. Astrophys.*, 2013, **551**, A38.

190 C. M. Walmsley, D. R. Flower and G. Pineau des Forêts, *Astron. Astrophys.*, 2004, **418**, 1035–1043.

191 O. Sipilä, E. Hugo, J. Harju, O. Asvany, M. Juvela and S. Schlemmer, *Astron. Astrophys.*, 2010, **509**, A98.

192 H. Roberts, E. Herbst and T. J. Millar, *Astrophys. J. Lett.*, 2003, **591**, L41–L44.

193 B. Parise, S. Leurini, P. Schilke, E. Roueff, S. Thorwirth and D. C. Lis, *Astron. Astrophys.*, 2009, **508**, 737–749.

194 K. I. Öberg, C. Qi, D. J. Wilner and M. R. Hogerheijde, *Astrophys. J.*, 2012, **749**, 162.

195 E. A. Bergin and M. Tafalla, *Annu. Rev. Astron. Astrophys.*, 2007, **45**, 339–396.

196 Y. Oba, N. Watanabe, T. Hama, K. Kuwahata, H. Hidaka and A. Kouchi, *Astrophys. J.*, 2012, **749**, 67.

197 H. Chaabouni, M. Minissale, G. Manic, E. Congiu, J. A. Noble, S. Baouche, M. Accolla, J. L.

Lemaire, V. Pirronello and F. Dulieu, *The Journal of Chemical Physics*, 2012, **137**, –.
198 P. Bergman, B. Parise, R. Liseau, B. Larsson, H. Olofsson, K. M. Menten and R. Güsten, *Astron. Astrophys.*, 2011, **531**, L8.
199 B. Parise, P. Bergman and F. Du, *Astron. Astrophys.*, 2012, **541**, L11.
200 F. Du and B. Parise, *Astron. Astrophys.*, 2011, **530**, A131.
201 B. Larsson, R. Liseau, L. Pagani, P. Bergman, P. Bernath, N. Biver, J. H. Black, R. S. Booth, V. Buat, J. Crovisier, C. L. Curry, M. Dahlgren, P. J. Encrenaz, E. Falgarone, P. A. Feldman, M. Fich, H. G. Florén, M. Fredrixon, U. Frisk, G. F. Gahm, M. Gerin, M. Hagström, J. Harju, T. Hasegawa, Å. Hjalmarson, L. E. B. Johansson, K. Justtanont, A. Klotz, E. Kyrölä, S. Kwok, A. Lecacheux, T. Liljeström, E. J. Llewellyn, S. Lundin, G. Mégie, G. F. Mitchell, D. Murtagh, L. H. Nordh, L.-Å. Nyman, M. Olberg, A. O. H. Olofsson, G. Olofsson, H. Olofsson, G. Persson, R. Plume, H. Rickman, I. Ristorcelli, G. Rydbeck, A. A. Sandqvist, F. V. Schéele, G. Serra, S. Torchinsky, N. F. Tothill, K. Volk, T. Wiklind, C. D. Wilson, A. Winnberg and G. Witt, *Astron. Astrophys.*, 2007, **466**, 999–1003.
202 R. Liseau, P. F. Goldsmith, B. Larsson, L. Pagani, P. Bergman, J. Le Bourlot, T. A. Bell, A. O. Benz, E. A. Bergin, P. Bjerkeli, J. H. Black, S. Bruderer, P. Caselli, E. Caux, J.-H. Chen, M. de Luca, P. Encrenaz, E. Falgarone, M. Gerin, J. R. Goicoechea, Å. Hjalmarson, D. J. Hollenbach, K. Justtanont, M. J. Kaufman, F. Le Petit, D. Li, D. C. Lis, G. J. Melnick, Z. Nagy, A. O. H. Olofsson, G. Olofsson, E. Roueff, A. Sandqvist, R. L. Snell, F. F. S. van der Tak, E. F. van Dishoeck, C. Vastel, S. Viti and U. A. Yıldız, *Astron. Astrophys.*, 2012, **541**, A73.
203 E. A. Bergin, M. R. Hogerheijde, C. Brinch, J. Fogel, U. A. Yıldız, L. E. Kristensen, E. F. van Dishoeck, T. A. Bell, G. A. Blake, J. Cernicharo, C. Dominik, D. Lis, G. Melnick, D. Neufeld, O. Panić, J. C. Pearson, R. Bachiller, A. Baudry, M. Benedettini, A. O. Benz, P. Bjerkeli, S. Bontemps, J. Braine, S. Bruderer, P. Caselli, C. Codella, F. Daniel, A. M. di Giorgio, S. D. Doty, P. Encrenaz, M. Fich, A. Fuente, T. Giannini, J. R. Goicoechea, T. de Graauw, F. Helmich, G. J. Herczeg, F. Herpin, T. Jacq, D. Johnstone, J. K. Jørgensen, B. Larsson, R. Liseau, M. Marseille, C. Mc Coey, B. Nisini, M. Olberg, B. Parise, R. Plume, C. Risacher, J. Santiago-García, P. Saraceno, R. Shipman, M. Tafalla, T. A. van Kempen, R. Visser, S. F. Wampfler, F. Wyrowski, F. van der Tak, W. Jellema, A. G. G. M. Tielens, P. Hartogh, J. Stützki and R. Szczerba, *Astron. Astrophys.*, 2010, **521**, L33.
204 U. A. Yıldız, K. Acharyya, P. F. Goldsmith, E. F. van Dishoeck, G. Melnick, R. Snell, R. Liseau, J.-H. Chen, L. Pagani, E. Bergin, P. Caselli, E. Herbst, L. E. Kristensen, R. Visser, D. C. Lis and M. Gerin, *Astron. Astrophys.*, 2013, **558**, A58.
205 D. Jing, J. He, J. R. Brucato, G. Vidali, L. Tozzetti and A. De Sio, *Astrophys. J.*, 2012, **756**, 98.
206 J. K. Jørgensen, C. Favre, S. E. Bisschop, T. L. Bourke, E. F. van Dishoeck and M. Schmalzl, *Astrophys. J. Lett.*, 2012, **757**, L4.
207 S. B. Charnley, A. G. G. M. Tielens and T. J. Millar, *Astrophys. J. Lett.*, 1992, **399**, L71–L74.
208 H. G. Arce, J. Santiago-García, J. K. Jørgensen, M. Tafalla and R. Bachiller, *Astrophys. J. Lett.*, 2008, **681**, L21–L24.
209 K. I. Öberg, N. van der Marel, L. E. Kristensen and E. F. van Dishoeck, *Astrophys. J.*, 2011, **740**, 14.
210 A. Bacmann, V. Taquet, A. Faure, C. Kahane and C. Ceccarelli, *Astron. Astrophys.*, 2012, **541**, L12.
211 S. E. Bisschop, J. K. Jørgensen, E. F. van Dishoeck and E. B. M. de Wachter, *Astron. Astrophys.*, 2007, **465**, 913–929.
212 K. I. Öberg, M. D. Boamah, E. C. Fayolle, R. T. Garrod, C. J. Cyganowski and F. van der Tak, *Astrophys. J.*, 2013, **771**, 95.
213 A. I. Vasyunin and E. Herbst, *Astrophys. J.*, 2013, **769**, 34.
214 Y. Aikawa, G. J. van Zadelhoff, E. F. van Dishoeck and E. Herbst, *Astron. Astrophys.*, 2002, **386**, 622–632.
215 E. A. Bergin, in *XVII Special Courses at the National Observatory of Rio de Janeiro*, AIP Conference Proceedings, 2014, p. in press.
216 T. Henning and D. Semenov, *Chemical Reviews*, 2013, **113**, 9016–9042.
217 K. M. Pontoppidan, C. Salyk, E. A. Bergin, S. Brittain, B. Marty, O. Mousis and K. L. Oberg, in *Protostars & Planets VI*, ed. Beuther, H., Klessen, R., Dullemond, K., Henning, Th., Univ. Arizona Press: Tucson, 2014, p. in press.
218 A. Dutrey, D. Semenov, E. Chapillon, U. Gorti, S. Guilloteau, F. Hersant, M. Hogerheijde, M. Hughes, G. Meeus, H. Nomura, V. Piétu, C. Qi and V. Wakelam, in *Protostars & Planets VI*,

ed. Beuther, H., Klessen, R., Dullemond, K., Henning, Th., Univ. Arizona Press: Tucson, 2014, p. in press.

219 F. Lahuis, E. F. van Dishoeck, A. C. A. Boogert, K. M. Pontoppidan, G. A. Blake, C. P. Dullemond, N. J. Evans, II, M. R. Hogerheijde, J. K. Jørgensen, J. E. Kessler-Silacci and C. Knez, *Astrophys. J. Lett.*, 2006, **636**, L145–L148.

220 J. S. Carr and J. R. Najita, *Science*, 2008, **319**, 1504.

221 C. Salyk, K. M. Pontoppidan, G. A. Blake, F. Lahuis, E. F. van Dishoeck and N. J. Evans, II, *Astrophys. J. Lett.*, 2008, **676**, L49–L52.

222 I. Pascucci, D. Apai, K. Luhman, T. Henning, J. Bouwman, M. R. Meyer, F. Lahuis and A. Natta, *Astrophys. J.*, 2009, **696**, 143–159.

223 C. Salyk, K. M. Pontoppidan, G. A. Blake, J. R. Najita and J. S. Carr, *Astrophys. J.*, 2011, **731**, 130.

224 K. M. Pontoppidan, C. Salyk, G. A. Blake, R. Meijerink, J. S. Carr and J. Najita, *Astrophys. J.*, 2010, **720**, 887–903.

225 J. R. Najita, J. S. Carr, K. M. Pontoppidan, C. Salyk, E. F. van Dishoeck and G. A. Blake, *Astrophys. J.*, 2013, **766**, 134.

226 E. L. Gibb and D. Horne, *Astrophys. J. Lett.*, 2013, **776**, L28.

227 A. M. Mandell, J. Bast, E. F. van Dishoeck, G. A. Blake, C. Salyk, M. J. Mumma and G. Villanueva, *Astrophys. J.*, 2012, **747**, 92.

228 E. F. van Dishoeck, *Proc. Natl. Acad. Sci., U.S.A.*, 2006, **103**, 12249–12256.

229 D. Fedele, S. Bruderer, E. F. van Dishoeck, J. Carr, G. J. Herczeg, C. Salyk, N. J. Evans, J. Bouwman, G. Meeus, T. Henning, J. Green, J. R. Najita and M. Güdel, *Astron. Astrophys.*, 2013, **559**, A77.

230 E. F. van Dishoeck, E. A. Bergin, D. C. Lis and J. I. Lunine, in *Protostars & Planets VI*, ed. Beuther, H., Klessen, R., Dullemond, K., Henning, Th., Univ. Arizona Press: Tucson, 2014, p. in press.

231 M. R. Hogerheijde, E. A. Bergin, C. Brinch, L. I. Cleeves, J. K. J. Fogel, G. A. Blake, C. Dominik, D. C. Lis, G. Melnick, D. Neufeld, O. Panić, J. C. Pearson, L. Kristensen, U. A. Yıldız and E. F. van Dishoeck, *Science*, 2011, **334**, 338.

232 C. Qi, K. I. Öberg, D. J. Wilner, P. D'Alessio, E. Bergin, S. M. Andrews, G. A. Blake, M. R. Hogerheijde and E. F. van Dishoeck, *Science*, 2013, **341**, 630–632.

233 G. S. Mathews, P. D. Klaassen, A. Juhász, D. Harsono, E. Chapillon, E. F. van Dishoeck, D. Espada, I. de Gregorio-Monsalvo, A. Hales, M. R. Hogerheijde, J. C. Mottram, M. G. Rawlings, S. Takahashi and L. Testi, *Astron. Astrophys.*, 2013, **557**, A132.

234 C. Qi, P. D'Alessio, K. I. Öberg, D. J. Wilner, A. M. Hughes, S. M. Andrews and S. Ayala, *Astrophys. J.*, 2011, **740**, 84.

235 C. Walsh, T. J. Millar, H. Nomura, E. Herbst, S. Widicus Weaver, Y. Aikawa, J. C. Laas and A. I. Vasyunin, *Astron. Astrophys.*, 2014, **563**, A33.

236 N. van der Marel, E. F. van Dishoeck, S. Bruderer, T. Birnstiel, P. Pinilla, C. P. Dullemond, T. A. van Kempen, M. Schmalzl, J. M. Brown, G. J. Herczeg, G. S. Mathews and V. Geers, *Science*, 2013, **340**, 1199–1202.

237 S. Casassus, G. van der Plas, S. P. M, W. R. F. Dent, E. Fomalont, J. Hagelberg, A. Hales, A. Jordán, D. Mawet, F. Ménard, A. Wootten, D. Wilner, A. M. Hughes, M. R. Schreiber, J. H. Girard, B. Ercolano, H. Canovas, P. E. Román and V. Salinas, *Nature*, 2013, **493**, 191–194.

238 L. M. Pérez, A. Isella, J. M. Carpenter and C. J. Chandler, *Astrophys. J. Lett.*, 2014, **783**, L13.

239 S. Bruderer, *Astron. Astrophys.*, 2013, **559**, A46.

240 S. Bruderer, N. van der Marel, E. F. van Dishoeck and T. A. van Kempen, *Astron. Astrophys.*, 2014, **562**, A26.

241 N. van der Marel, E. F. van Dishoeck, S. Bruderer and T. A. van Kempen, *Astron. Astrophys.*, 2014, **563**, A113.

242 L. I. Cleeves, E. A. Bergin, T. J. Bethell, N. Calvet, J. K. J. Fogel, J. Sauter and S. Wolf, *Astrophys. J. Lett.*, 2011, **743**, L2.

243 N. Madhusudhan, H. Knutson, J. Fortney and T. Barman, in *Protostars & Planets VI*, ed. Beuther, H., Klessen, R., Dullemond, K., Henning, Th., Univ. Arizona Press: Tucson, 2014, p. in press.

244 D. Deming, A. Wilkins, P. McCullough, A. Burrows, J. J. Fortney, E. Agol, I. Dobbs-Dixon, N. Madhusudhan, N. Crouzet, J.-M. Desert, R. L. Gilliland, K. Haynes, H. A. Knutson, M. Line, Z. Magic, A. M. Mandell, S. Ranjan, D. Charbonneau, M. Clampin, S. Seager and A. P. Show-

man, *Astrophys. J.*, 2013, **774**, 95.

245 C. Helling, P. Woitke, P. B. Rimmer, I. Kamp, W.-F. Thi and R. Meijerink, *Life*, 2014, **4**, 142–173.

246 M. Agúndez, V. Parmentier, O. Venot, F. Hersant and F. Selsis, *Astron. Astrophys.*, 2014, **564**, A73.

247 R. Visser, S. D. Doty and E. F. van Dishoeck, *Astron. Astrophys.*, 2011, **534**, A132.

248 *The Diffuse Interstellar Bands*, ed. J. Cami and N. L. J. Cox, Cambridge University Press, 2014, vol. 297.

249 E. Herbst and T. Millar, in *Low Temperatures and Cold Molecules*, ed. I.W.M. Smith, Imperial College: London, 2008, p. 1.