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Astrochemistry: overview and challenges

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Abstract. This paper provides a brief overview of the journey of molecules through the Cosmos, from local diffuse interstellar clouds and PDRs to distant galaxies, and from cold dark clouds to hot star-forming cores, protoplanetary disks, planetesimals and exoplanets. Recent developments in each area are sketched and the importance of connecting astronomy with chemistry and other disciplines is emphasized. Fourteen challenges for the field of Astrochemistry in the coming decades are formulated.

Keywords. astrochemistry, molecular data, molecular processes, ISM: molecules, stars: formation, planets: formation, comets, techniques: spectrocopic, galaxies: ISM

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1. Introduction

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 the pioneer of this field, Alexander Dalgarno in 2008. This definition covers not only the chemical aspects of the field, but also recognizes that molecules are excellent diagnostics of the physical conditions and processes in the regions where they reside. Moreover, they actively contribute to the physical state of the gas by being important coolants. From an astronomical perspective, dense molecular clouds are important as the nurseries of new generations of stars and planets, some of which may even harbor life. From the pure chemistry perspective, interstellar space provides a unique environment in which molecular behavior can be studied under extreme conditions. It is this combination that makes Astrochemistry such a fascinating research field, for both astronomers and chemists alike.

More than 200 different molecules have been detected in interstellar space (Fig. 1). The main questions in the field of Astrochemistry therefore include: how, when and where are these molecules produced and excited? What do they tell us about temperatures, densities, gas masses, ionization rates, radiation fields, and dynamics of the clouds? How are they cycled through the various phases of stellar evolution, from birth to death? How far does chemical complexity go? And, most far-reaching, can interstellar molecules become part of new planetary systems and form the building blocks for life elsewhere in the Universe?

The interdisciplinary aspects of this field will be emphasized throughout this overview as a two-way street: Astrochemistry needs basic data on molecular spectroscopy and chemical processes, but it also inspires new chemical physics through studies of different classes of molecules and reactions that are not normally considered on Earth. Astrochemistry is a 'blending of astronomy and chemistry in which each area enriches the other in a mutually stimulating interaction' (Dalgarno 2008). The field is becoming increasingly multidisciplinary: besides chemistry, physics and mathematics, which have traditionally been an integral part of the field, knowledge about biology, geochemistry and informatics becomes important as well.

In the following, a brief overview of recent developments in the large range of topics addressed in this Symposium will be given, together with a challenge for each of these topics. References will be limited to just a few per topic. Recent overviews of astrochemistry with extensive reference lists can be found in Caselli & Ceccarelli (2012); Tielens (2013); van Dishoeck (2014) and the 2013 Chemical Reviews special issue, as well as in the individual papers in this volume.

2. Observational facilities

Progress in Astrochemistry is driven by new observational data. Molecules can be observed through their electronic, vibrational or rotational transitions at optical/UV, infrared and millimeter wavelengths, respectively. Astrochemistry has been fortunate that several of the most powerful new telescopes deployed over the past decade have been particularly well suited to observe interstellar molecules: the *Spitzer Space Telescope* and the *Herschel Space Observatory* at mid- and far-infrared wavelengths, a number of ground-based 8m optical/infrared telescopes equipped with high resolution spectrometers, and various single-dish and interferometers at millimeter wavelengths with increasingly sensitive broad-band detectors, culminating in the Atacama Large Millimeter/submillimeter Array (ALMA). The *Stratospheric Observatory for Infrared Astronomy* (SOFIA) is contributing unique data, and the *James Webb Space Telescope* (JWST), to be launched late 2018, will be the next big jump in mid-infrared capabilities.

On the longer term horizon the situation looks less favorable for Astrochemistry, however. ALMA is expected to be still going strong for decades, and at least one Extremely Large Telescope (ELT) will be equipped with a high resolution infrared spectrometer. However, several new flagship space missions in the 2020s–2035s are dedicated to large area cosmological and galaxy evolution surveys, high energy astrophysics and to the emerging field of gravitational wave astrophysics. Exoplanet atmosphere studies will likely

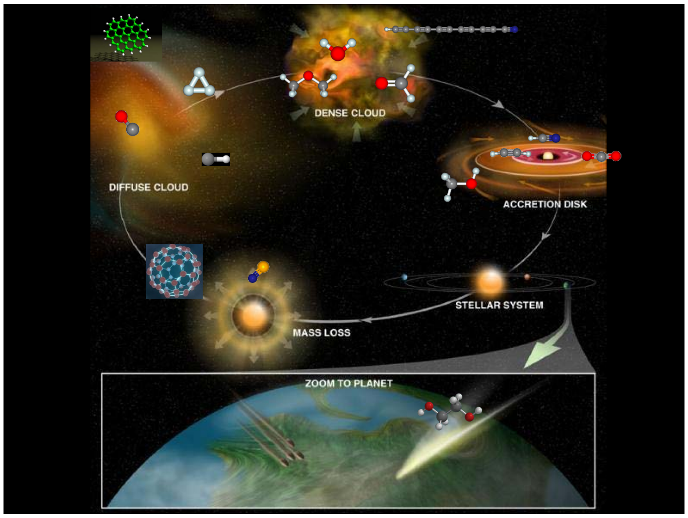

Figure 1. Lifecycle of gas and dust in interstellar space. Some characteristic molecules at each of the star- and planet formation and stellar death stages are indicated. Image by Bill Saxton (NRAO/AUI/NSF) and molecule pictures from *the Astrochymist* (`www.astrochymist.org`; this website also contains a list of detected molecules in space).

be a strong driver for future satellites, but their modest spectral resolution instruments have limited applications in other areas of Astrochemistry.

Challenge 1: *To secure new facilities for Astrochemistry in the 2030–2040 timeframe.*

3. Laboratory astrophysics

The availability of accurate atomic and molecular data is another prerequisite for Astrochemistry. Note that the term 'laboratory astrophysics' implies experiments as well as quantum chemical and molecular dynamics calculations. Over the past decade, several new techniques and new groups have entered the field, ensuring new efforts to address the many chemical-physics questions and the transfer of (often unique) expertise to the younger generation. At the same time, traditional techniques and data gathering remain important as well, even if some of those experiments are not as 'flashy' as using, for example, He-droplets to study ultracold reactions. The key for a fruitful interaction is for astronomers to ask the right questions and have enough chemical physics knowledge of what can, and what cannot, be done in the laboratory. Chemists, in turn, have to sometimes let go of perfectionism, since astronomers are often content at the factor of 2 uncertainty level. Also, astronomers just want a number rather than a deep understanding of the underlying molecular processes. This 'tension' needs to be recognized by both sides, and, importantly, also by the funding agencies. Equally important, astronomers need to properly cite the relevant data used in Astrochemistry to support laboratory scientists.

Spectroscopy: The most basic information that astronomers need is spectroscopy from UV to millimeter wavelengths. Techniques range from classical absorption set-ups to cavity ringdown spectroscopy, (chirped-pulse) Fourier transform microwave spectroscopy and THz time domain spectroscopy. Transition frequencies and strengths of (sub)mm transitions are summarized in the Jet Propulsion Laboratory catalog (JPL) (Pickett et al. 1998) and the Cologne Database for Molecular Spectroscopy (CDMS) (Endres et al. 2016) †. Databases for vibrational transitions at infrared wavelengths include the HITRAN (Rothman et al. 2009) and the EXOMOL (Tennyson et al. 2016) line lists‡.

Spectroscopy of large samples of PAHs has been mostly carried out with matrix-isolation experiments, although selected PAHs have also been measured in the gas phase (Boersma et al. 2014). Spectroscopic databases of solids include those for ices in Leiden, NASA-Ames, Goddard and Madrid ¶; and the Heidelberg-Jena-St. Petersburg database of optical constants for silicates (Henning 2010). Information on carbonaceous material is more scattered in the literature.

Rate coefficients: Chemical models require rates for thousands of two-body reactions under space conditions. There are only a handful types of reactions, however. In the gas-phase, these are radiative association and associative detachment (formation of bonds); ion-molecule, neutral-neutral and charge-transfer reactions (rearrangement of bonds); and dissociative recombination and photodissociation processes (destruction of bonds).

Gas-phase processes have been summarized by Smith (2011) and Sims, this volume, and many recent developments are described in the 2014 release of the KIDA database (Wakelam et al. 2015). There has been good progress on improving many rate coefficients for ion-molecule and neutral-neutral reactions over a range of temperatures. Radiative association, however, is an example of a process whose rate coefficients continue to have large uncertainties due to their low values and the difficulties of measuring or computing

† `spec.jpl.nasa.gov` and `www.astro.uni-koeln.de/cdms/catalog`
‡ `www.cfa.harvard.edu/hitran` and `www.exomol.com`
¶ `icedb.strw.leidenuniv.nl`

them. Photodissociation and photoionization rates of atoms and molecules exposed to different radiation fields have recently been updated by Heays et al. (2017).

Rate coefficients for collisional excitation of molecules continue to be essential for the quantitative non-LTE excitation analysis of the observed molecular lines. The vast majority of these rates come from theoretical calculations and the field is fortunate to have a steady stream of new results from quantum chemists (Roueff & Lique 2013; Dubernet et al. 2013; Wiesenfeld et al. 2016). With new instrumental developments on the horizon, it may be time for experiments to catch up in this area.

Ice chemistry: The last two decades have seen significant progress in ice astrochemistry studies, with modern surface science techniques at ultra-high vacuum conditions now used to quantitatively study various chemical processes in ices. Summaries of activities across the world are given by Allodi et al. (2013); Linnartz et al. (2015). Molecules such as CH_3OH, H_2O, CO_2 have been demonstrated to form at low temperatures on surfaces through atom addition reactions, validating reaction schemes postulated 30 years earlier (Tielens & Hagen 1982). Binding energies are key to many astrochemical models and more work on astrochemically relevant species and mixtures is needed (Collings et al. 2004; Cuppen et al. 2017).

Many laboratory experiments across the world have been performed using some form of 'processing' that ices are expected to undergo in space: heating, UV irradiation, and exposure to energetic particles and/or electrons (Öberg 2016). All of them produce complex molecules, in some cases even biologically interesting species like amino acids, sugars, and amides, and often in similar amounts. The main differences in outcome may be related to whether or not the strong CO or N_2 bonds can be broken, especially if there is no other source of atomic C or N in the ice mixture. For example, UV radiation longward of 1200 Å does not photodissociate CO or N_2. Otherwise the results seem to mainly depend on the amount of energy deposited in ice, not on which form. In that respect it is useful to recall that UV radiation deposits 10× more energy per molecule in the ice than cosmic rays for typical cosmic ray fluxes in dark clouds (Shen et al. 2004). While products are readily identified, the step-by-step kinetics and mechanisms are still poorly constrained in most of these experiments, so the results cannot be readily incorporated into astrochemical models.

Molecular dynamics techniques can also be extended to solid-state processes, as demonstrated by the detailed study of the photodesorption of water ice and its isotopologs, as well as CO_2 ice formation (Arasa et al. 2015, 2013). Such models provide much insight into the processes occuring in and on the ice.

Challenge 2: To continue to bring chemists, physicists and astronomers together to characterize and quantify molecular processes that are at the heart of Astrochemistry, to have open lines of communication to prioritize needs, and to convince funding agencies to continue supporting this interdisciplinary research.

4. Astrochemical models

Compilations of reaction rate coefficients together with codes that solve the coupled differential equations to compute abundances include the UMIST 2013 database (McElroy et al. 2013), and the KIDA database (Wakelam et al. 2012) †. The latter website includes the Nahoon (formally known as Ohio State) gas-grain chemistry code by Herbst and co-workers. The UCLCHEM code is now also publicly released (Holdship et al. 2017). These databases and codes contain primarily two-body reactions because of the

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

low densities in interstellar space. Three-body reactions become significant at densities above $\sim 10^{13}$ cm^{-3} such as encountered in the inner midplanes of protoplanetary disks and the atmospheres of stars and exoplanets. Here the chemistry may approach that in thermodynamic equilibrium (LTE).

It is important to recognize that astrochemical databases are put together and updated on a 'best effort' basis. Following the good example of atmospheric chemistry, some databases (UMIST, KIDA) have an (estimated) uncertainty associated with each rate coefficient which can then be propagated in the network. Examples of pure gas-phase networks show 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 under dark cloud conditions (Wakelam et al. 2010); for larger molecules, the cumulative effect of many reactions will be even larger. This illustrates the level of agreement one can expect between different models, and between models and observations.

Gas-grain chemistry networks introduce another level of complexity. The overall efficiency 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 standard treatment of the interplay between gas phase and grain surface chemistry is through rate equations (Hasegawa & Herbst 1993; Garrod et al. 2008). This 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.

Chemistry occurs not just at the surface but also deep inside the ice, since UV photons typically penetrate at least 50 monolayers. The atoms and radicals following photodissociation (or some other form of energetic processing) are created with excess energy and are thus initially highly mobile, reacting with neighboring species and overcoming energy barriers. However, they quickly lose this energy on pico-second timescales and become trapped. Alternatively, these radicals become mobile and find each other once the ice temperature increases from $\sim$10 K to 20–40 K. A general concern is how to translate laboratory data to parameters that can be used in grain surface chemistry. Laboratory experiments provide rates as function of H or UV fluence or some other parameter over timescales of hours; astronomical applications involve timescales $> 10^5$ yr (Cuppen et al. 2017).

Which of these gas-phase or gas-grain reactions dominates the formation of a molecule depends on the astrophysical situation. For example, water is primarily formed by ion-molecule reactions in diffuse clouds; by high temperature neutral-neutral reactions in shocks; and by grain-surface chemistry in dense cores (van Dishoeck et al. 2013).

Challenge 3: To build realistic gas-grain models from microscopic to macroscopic scales, including translation of laboratory ice chemistry experiments into parameters that can be adopted in models.

5. Diffuse and translucent clouds

Astrochemistry started nearly a century ago with optical absorption spectroscopy of atoms and molecules in diffuse clouds along the lines of sight to bright stars. These clouds, and their somewhat denser translucent counterparts, have visual extinctions of a few mag and are in the interesting regime where the transition of most elements from atomic to molecular form takes place (van Dishoeck & Black 1989; Snow & McCall

2006). Because UV photons and cosmic rays can penetrate the clouds to ionize atoms and dissociate molecules, timescales to reach equilibrium are short (few thousand yr) and the chemistry is dominated by ion-molecule reactions. Physical parameters such as density, temperature and UV field are well constrained and even the H_2 column density can be measured directly through UV absorption lines. Thus, these clouds form the best testbed for *precision Astrochemistry*, at the factor of 2 or better level. At the same time, because so many parameters are well determined, they also serve as diagnostics of the physical structure and processes in the interstellar medium (ISM).

Herschel-HIFI data have given a new boost to this field (Gerin et al. 2016). Pure rotational lines of molecules have been seen in absorption throughout the Galaxy along the lines of sight toward distant far-infrared sources. Since most of the population is in the lowest level(s), the conversion from absorption to column density is accurate and straight-forward. H_2 cannot be observed directly at far-infrared wavelengths, but HF has proven to be a reliable tracer of its column density because of its particularly simple chemistry. Small hydrides like H_2O are found to have abundences of 5×10^{-8} with respect to H_2, values that are indeed well explained by low-temperature ion-molecule chemistry.

One of the main *Herschel* surprises has been the discovery of strong OH^+ and H_2O^+ absorption along most galactic lines of sight and even in high-redshift galaxies. Also the first noble gas molecule, $^{36}ArH^+$, has been detected. These species point to an H_2-poor phase of the interstellar medium containing molecules (typically $H/H_2 >10$) that had not been recognized before. As such, the abundances of these molecules form important tests for hydrodynamical simulations of the large scale ISM. They are also excellent diagnostics of the cosmic ray ionization rate in the low density ISM, giving a median value of $\zeta_H = 1.8 \times 10^{-16}$ s^{-1} that agrees well with previous results from H_3^+ data (Indriolo et al. 2015). The origin of this H_2-poor phase is interesting by itself: in contrast with other molecules, timescales for the formation of H_2 itself are very long, up to 10^7 yr. Both analytical and hydrodynamical models for the H/H_2 structure under non steady-state conditions are now being studied (Bialy et al. 2017) †.

On the other hand, there are lingering discrepancies and mysteries even for these simple clouds: the high abundance of CH^+ (and SH^+) requires introduction of additional parameters to capture the effects of turbulent heating at low (column) densities (Godard et al. 2014); the discovery of increasingly complex molecules with abundances similar to those in dark clouds is difficult to explain (Liszt et al. 2005); the need to form grains in the diffuse ISM to solve the dust lifetime problem implies active grain chemistry (Krasnokutski et al. 2014); and the Diffuse Interstellar Bands remain unidentified (except plausibly C_{60}^+, Campbell et al. 2016), pointing to the presence of a reservoir of large carbonaceous molecules. It may well take another century to solve these questions!

Challenge 4: To obtain a full inventory of the chemical constituents of diffuse and translucent clouds, and explain – at the same time – their chemical simplicity and complexity.

6. Photon-Dominated Regions (PDRs)

Photon-Dominated or Photo-Dissociation Regions (PDRs) are clouds exposed to intense FUV radiation (10^3-10^5 times the standard interstellar radiation field, ISRF) controlling their heating and chemistry (Hollenbach & Tielens 1997). The diffuse and translucent clouds discussed above are low density, low FUV PDR examples. Since most of the

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† Non steady-state (or time-dependent) chemistry is often (incorrectly) denoted as non-equilibrium chemistry by hydrodynamical modelers.

molecular gas in galaxies is in the form of PDRs, studies of their structure are highly relevant for understanding spatially unresolved large scale observations. Locally, the layered structure of PDRs, with PAH emission and carbonaceous radicals peaking closer to the UV source than saturated molecules, has been beautifully confirmed by recent observations of the Orion Bar and Horsehead Nebula (Guzmán et al. 2014; Cuadrado et al. 2017). Such studies are also highly relevant for analyzing emission from the surfaces of protoplanetary disks, which are even higher density, higher FUV PDR cases.

X-rays can also affect the chemistry, although the chemical structure of XDRs shows similarities with that of PDRs since X-rays produce UV radiation through the interaction of the secondary electrons with H_2. X-rays, like cosmic rays, can however penetrate much deeper into clouds, heating them over a larger volume (Meijerink et al. 2007). While the individual heating and cooling processes in PDRs and XDRs have been identified decades ago, it is important to realize that the resulting temperature structures differ considerably from model to model (Röllig et al. 2007). This in turn affects the predicted excitation and emission of molecules in those zones such as the high-J H_2 and CO rotational lines (Visser et al. 2012). These uncertainties limit their diagnostic potential and are often not acknowledged by the community.

Large aromatic molecules are readily observed in PDRs, consisting most likely of a mix of neutral and ionized PAHs that emit strongly in mid-infrared bands, although there is still an active discussion on the fraction of aliphatic moieties in the larger carbonaceous species. PAHs constitute about 5–10% of the available carbon, with perhaps trace amounts of nitrogen (Tielens 2008). Fullerenes, C_{60} and C_{70}, have also been identified (Cami et al. 2010), and there is evidence for the conversion of large PAHs to fullerenes when exposed to intense FUV radiation (Berné & Tielens 2012). Large PAHs are stable against FUV radiation (except some stripping of H atoms), but smaller PAHs can be destroyed piecemeal, creating C_2 or C_2H_2 fragments. This, in turn, triggers a top-down chemistry in which small carbonaceous molecules in PDRs may be produced more efficiently from destruction of larger species rather than bottom-up starting from carbon atoms (Zhen et al. 2014). JWST will be particularly powerful in imaging these chemical transition zones in PDRs. Destruction of small carbonaceous grains in the PDR layers of disks by UV and atomic O has also been invoked to explain why Earth is so poor in carbon (Anderson et al. 2017).

Challenge 5: To quantify the importance of top-down versus bottom-up chemistry in the production of carbon-bearing molecules.

7. Evolved stars

The chemistry in circumstellar envelopes combines many important elements of Astrochemistry. From inside to ouside: LTE chemistry in the stellar atmospheres, non-LTE high temperature shock-induced chemistry in the inner envelope, the formation of dust grains as the gas cools, grain surface chemistry, and photodissociation and ion-molecule chemistry at the outer edge (Decin et al. 2010). Because the wind-accelerated material is moving outward, the time-dependent chemistry and dynamics need to be coupled. Circumstellar envelopes are good laboratories to test different types of chemistry, because they tend to be either carbon- (C/O>1) or oxygen-rich (C/O<1). The C/O>1 situation, which results in very bright lines of carbon-chain molecules, occurs under only a few other astrophysical situations, most notably protoplanetary disks (see § 12).

The C/O dichotomy is not completely black-and-white, however. *Herschel* confirmed that H_2O is present in a number of carbon-rich envelopes, as found in earlier SWAS data, but ruled out the interpretation that the water emission orginates in a cold zone

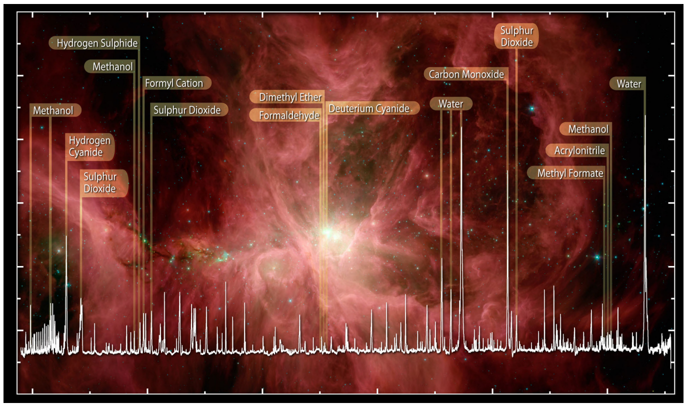

Figure 2. *Herschel*-HIFI spectrum of the Orion KL region around 550 GHz, showing strong emission from water and organic molecules, superposed on a *Spitzer* image (NASA/JPL-Caltech/S.T. Megeath) (Bergin et al. 2010).

of sublimating Kuiper-Belt-like icy planetesimals. More likely, the presence of H_2O under carbon-rich conditions points to a clumpy envelope with photodissociation breaking up CO and liberating oxygen. ALMA now allows these various chemical zones in many different molecules to be imaged, zooming in on the dust formation zone. Together with future high-resolution infrared spectra, these data will form critical tests of the so-far poorly constrained models of dust formation, not only in our own Milky Way but also for sources in nearby galaxies with lower metallicities such as the LMC and SMC. Dust destruction in the (reverse) shocks may also be seen. This will be of fundamental importance for understanding the dust life cycle in the Universe, including the surprising presence of large amounts of dust at high redshifts: does most of our dust come from AGB stars or from supernova remnants?

Almost exactly 30 years prior to this symposium, on Feb. 24 1987, SN 1987A exploded in the Large Magellanic Cloud. I remember watching the supernova shine brightly from a hotel in Puerto Varas where we were vacationing in March 1987 after an observing run at La Silla. It is exciting to see ALMA now detecting the cold dust formation directly in SN 1987A, as well as ^{29}SiO in the ejecta (Matsuura et al. 2017). SiO was actually first observed by its strong infrared emission a year after the explosion and chemically modeled at that time by Liu & Dalgarno (1994).

Challenge 6: To nail down the dust formation and destruction processes and their efficiencies in the envelopes of evolved low- and high-mass stars, for different metallicities.

8. Extragalactic astrochemistry

Astrochemistry and cosmology go hand-in-hand: the first stars in the Universe could not have formed without at least some H_2 and HD being present as coolants to allow cloud collapse (Galli & Palla 2013). This ‘dawn of chemistry’ (term coined by Dalgarno & Lepp 1987) at redshifts z more than 1000 involves primarily H, D and He and has been well studied. It also highlights the importance of accurate rate coefficients for critical reactions (at the better than 50% level) (Kreckel et al. 2010). Early Universe chemistry remains outside the realm of direct observational tests, however.

Chemistry in high-redshift galaxies out to $z \approx 10$ can be observed by different techniques. Quasar absorption line observations at optical and millimeter wavelengths probe mostly low-density gas in intervening galaxies, and reveal H_2 and a suite of molecules including OH^+, H_2O^+ and ArH^+ (Muller et al. 2016) that have been seen in diffuse galactic clouds (§5). Thus, *Herschel* flew just in time: without those data, astrochemists would not have been able to make sense of these extragalactic detections.

Far-infrared and millimeter emission line data probing the denser ISM show a wide variety of molecules including more complex species (González-Alfonso et al. 2012; Costagliola et al. 2015). Indeed, some of the ALMA spectra of nearby star-forming galaxies are as rich as those of Orion were 30 years ago with the poorer sensitivity and spatial resolution available at that time.

Most studies of extragalactic molecular clouds have been carried out at kpc scales. ALMA now allows surveys down to scales of $\lesssim$ 20 pc, and exceptionally probing down to 2 pc in nearby galaxies (Schruba et al. 2017). Lensed systems provide an opportunity to image high-z galaxies on sub-kpc scales (ALMA Partnership et al. 2015). There is a large range in 'metallicities' in these galaxies, with carbon and oxygen underabundant by factors of 5 to >10 compared with solar abundances. In contrast, most galactic astrochemistry studies have been done at <0.1–1 pc scales in clouds with close to solar metallicities. Thus, there is a huge gap between galactic and extragalactic molecular cloud studies that needs to be bridged (Kennicutt & Evans 2012); so far, this has not yet been done even for CO, let alone for other molecules. It is somewhat embarrassing that after nearly 50 years of millimeter observations, the observed distributions and abundance ratios in galaxies are such a puzzle. Cloud-scale surveys in the Milky Way and nearby galaxies on 1–20 pc scales in key tracers of different physical structures (e.g., cold gas: N_2H^+; warmer gas: SO, CH_3OH; dense gas: HCN, HCO^+) will therefore become increasingly important to place the extragalactic data in context (Pety et al. 2017; Watanabe et al. 2017).

Challenge 7: To bridge the gap between subpc galactic and kpc extragalactic astrochemical studies as functions of metallicity out to the highest redshifts, and to use molecular observations of calibrated tracers to unveil a new understanding of star formation in the early Universe.

9. Dense prestellar cores and cold protostellar envelopes

Dense cold clouds prior to star formation, with typical temperatures of 10 K and densities of $10^4 - 10^5$ cm^{-3}, exhibit a variety of chemical characteristics, including long carbon chain molecules, ice formation and heavy deuterium fractionation (Bergin & Tafalla 2007). Most of these chemical signatures are transferred to the protostellar stage where they are observed in the outer parts of the collapsing envelope (Fig. 1).

Ice formation. Infrared observations of ice features toward reddened background stars show that formation of water ice starts in the translucent cloud phase at A_V of a few mag, when densities are of order 10^3 cm^{-3} and dust temperatures $\lesssim$ 15 K (Boogert et al. 2015). The formation of water ice is now well characterized in the laboratory and models, and tested against observations of cold water gas and intermediate products such as HO_2 and H_2O_2 (see review by van Dishoeck et al. 2013). CH_4, NH_3 and some CO_2 ice are also made in this early phase, with the amount of ice rapidly increasing as the cores become more concentrated. All of these molecules are made on the grain surfaces, from reactions of atomic O, C and N with atomic hydrogen; they are not accreted from the gas.

At densities around 10^5 cm^{-3}, the timescales for freeze-out become shorter than the lifetime of the core, and CO – the dominant form of volatile carbon at these high densities – rapidly depletes from the gas onto the grains. This 'catastrophic' freeze-out of CO results in a separate 'water-poor' or 'apolar' ice phase, which has been observed directly in CO ice profiles. The CO-rich ice can subsequently react with atomic H to form H_2CO and CH_3OH, a process that has been demonstrated to be effective at low temperatures in the laboratory (Hidaka et al. 2009; Fuchs et al. 2009). Various other routes can transform CO to CO_2 and more complex organic ices.

One of the main observational surprises has been the recent detection of various complex organic molecules in cold cores (Bacmann et al. 2012; Öberg et al. 2010). The issue is not their production, since several laboratory experiments have now demonstrated that they can be formed at low temperatures without the need for heating. The main puzzle is their return to the gas phase at dust temperatures well below that for thermal desorption. Non-thermal processes such as photodesorption, cosmic-ray induced spot heating and reactive desorption have been proposed, and are being studied theoretically and in the laboratory, but they remain difficult to quantify and may lead to desorption of only fragments (Ivlev et al. 2015; Minissale et al. 2016; Bertin et al. 2016). Chemical models often still use a 'fudge factor' to prevent molecules from being fully frozen out: in older models this used to be a sticking probability of 90–99% rather than 100%. In modern models including detailed grain surface chemistry, a reactive desorption probability of ∼1% is often introduced to explain observations (Garrod et al. 2007).

Challenge 8: To identify and quantify the mechanisms by which molecules, including the more complex ones, are desorbed (intact) from the grain surface in cold clouds.

Carbon-chain molecules. A number of cold cores (but not all) show relatively strong lines of carbon-chain molecules such as HC_3N, HC_5N, C_4H and CCS, with TMC-1CP still the iconic example (Kaifu et al. 2004). Other cores are more abundant in species like NH_3. One interpretation is that cores rich in carbon chains have only recently contracted from the diffuse cloud phase and are thus still rich in atomic carbon, which can be inserted into small molecules to make longer chains (Suzuki et al. 1992). Another explanation is their environment: if these cores are embedded in filaments or fibers from which they are still accreting fresh atomic carbon-rich material, they could build carbon chains through the same process. In the evolutionary explanation, the statistics on cores with or without carbon-chain molecules could be used to infer timescales for this phase.

Cold carbon-chain chemistry should not be confused with the warm carbon-chain molecule chemistry (WCCC) associated with some low-mass protostars at a later stage of evolution (Sakai & Yamamoto 2013). Here one explanation is sublimation of CH_4 ice at moderate dust temperatures, triggering a gas-phase chemistry that also leads to carbon-chain molecules. Alternatively, UV-irradiated outflow cavity walls can be rich in carbon-bearing molecules such as c-C_3H_2 (Murillo et al., subm.).

Deuterium fractionation. Cold clouds have high abundances of deuterated molecules such as DCO^+, DCN and HDCO, with ratios to their undeuterated counterparts at least three orders of magnitude higher than the overall [D]/[H] ratio of $\sim 2 \times 10^{-5}$. Even doubly- and triply-deuterated molecules such as D_2CO and ND_3 have been detected (Ceccarelli et al. 2014). This huge fractionation can be explained by two effects. First, the lower zero-point vibrational energy of deuterated molecules 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 liberates 230 K. Correct calculation of the H_2D^+ abundance requires explicit treatment of the nuclear spin states (ortho and para) of all the species involved in the reactions (Sipilä et al. 2010). At slightly elevated temperatures, the CH_2D^+ ion, formed by reaction of $CH_3^+ + HD$, becomes more effective in controlling the DCN/HCN ratio.

The second boost in deuterium fractionation occurs in the densest coldest phase when CO, the main destroyer of both H_3^+ and H_2D^+, freezes out (Roberts et al. 2003). The increased atomic D/H ratio in the gas also leads to enhanced deuteration of grain surface species like H_2CO, NH_3 and CH_3OH (Tielens 1983; Furuya et al. 2016). Thus, the amount of deuteration in principle provides information on the formation history. Similarly, analysis of the size of the freeze-out zones of pre- and protostellar cores can be used to infer a lifetime of this heavy freeze-out phase of about 10^5 yr (Jørgensen et al. 2005).

Challenge 9: To use chemical signatures to constrain physical structure, evolutionary stage and the amount of time spent in certain cloud phases.

10. Shocks, jets and outflows

Shocks with velocities of tens to hundreds of km s^{-1} are common in the ISM, triggered by a variety of physical phenomena such as supernova explosions, cloud-cloud collisions as well as jets and winds from young stars which sweep up surrounding material in outflows. In the thin shocked layer, gas temperatures increase to a few thousand K, thus triggering chemical reactions with energy barriers that cannot proceed in cold gas. Well-known examples are the $O + H_2$ and $OH + H_2$ reactions leading to the formation of water, each of which has an energy barrier of about 2000 K. The ubiquitous strong and broad water line profiles revealed by *Herschel*-HIFI in star-forming regions are a testimony to this high-temperature chemistry (Kristensen et al. 2012; San José-García et al. 2016).

Shocks can also sputter ice mantles, further enhancing H_2O and other ice mantle molecules like CH_3OH into the gas, and at high velocity even the grain cores themselves (Bachiller & Tafalla 1999). Thus, they can reveal ice mantle material in dark clouds far away from the driving source (Arce et al. 2008; Lefloch et al. 2017). The release of Si and S leads to strong emission from molecules like SiO, SO and SO_2 associated with jets. Kinematical signatures in the H_2O line profiles demonstrate the presence of multiple types of shocks that have not yet been spatially resolved. The observed low H_2O abundance, high OH/H_2O ratio and the presence of hydrides like CH^+ point to the importance of UV irradiation of the (pre-)shocked gas and outflow cavity walls in the chemistry (Karska et al. 2014). All of these processes are now being imaged at high angular resolution by ALMA, especially close to the base of the outflows where they originate and first impact the surrounding envelope.

Challenge 10: To characterize the chemical and physical structure of outflows, especially near the launching point of the jets and (disk) winds that drive them.

11. Warm protostellar envelopes, hot cores

The gas and dust close to a protostar are heated by its luminosity, with temperatures increasing from 10 K in the outer envelope to a few hundred K in the innermost region. This can result in numerous chemical changes (Herbst & van Dishoeck 2009): radicals become mobile in and on icy surfaces and recombine to form even more complex molecules (so-called first generation complex molecules) and increased UV and X-rays trigger further chemistry in the ice and gas. When dust temperatures become high enough for ices to sublimate, molecules do so presumably in a sequence according to their binding energies. Once dust temperatures of $\sim$100 K are reached, even the strongly-bound water and methanol ice sublimate, together with any minor molecules trapped in them, resulting in particularly rich gas-phase millimeter spectra (Fig. 2). This inner 100 K zone is called the 'hot core'. Here high-temperature gas-phase reactions between sublimated molecules can result in 'second generation' complex organic molecules (Charnley et al. 1992).

Observationally, most chemical surveys of star-forming regions have still been performed with single-dish millimeter telescopes equipped with broadband receivers. Over the past decade, pioneering high-frequency surveys have been carried out with *Herschel* of well-known sources such as Orion (Crockett et al. 2015). With ALMA, a new era has started, since ALMA can image each line *and* spatially resolve the hot core region. Also, ALMA has increased sensitivity to complex molecules by 1–2 orders of magnitude, and it can study solar-mass protostars on solar-system scales, not just the most luminous high-mass sources. A 'sweet' example is the ALMA-PILS survey of the low-mass protobinary IRAS16293-2422, where an increasing number of complex molecules is found that had previously only been seen in SgrB2 and Orion (Jørgensen et al. 2016). This includes prebiotic molecules like glycolaldehyde and ethelyne glycol, and most recently methyl isocyanate – a precursor to peptides (Martín-Doménech et al. 2017; Ligterink et al. 2017). In SgrB2, the quest for the 'molecular bricks of life' has now succeeded in the detection of the first chiral molecule, propylene oxide (McGuire et al. 2016), and branched cyanides such as iso-propylcyanide and N-methyl formamide (Belloche et al. 2017).

Detection of even more complex molecules is becoming hard, however, even with ALMA, because of the confusion limit. Whether lower frequency searches with the future SKA or ngVLA provide indeed the advantages that are claimed still needs to be demonstrated. Also, the current focus is still on the hunt for individual species in a few sources; the field should soon move to larger samples with ALMA and address the deeper underlying questions as to when, where and how certain classes of complex molecules are produced.

Both single-dish and interferometric surveys show that not all protostars have line-rich spectra, even though there is evidence for warm dense dust in their immediate surroundings (e.g., from SED fitting) (Fayolle et al. 2015). Thus, strictly speaking, not all 'hot cores' have a 'hot core chemistry'. Both evolutionary effects and geometry, such as the presence of a large cold disk on similar scales as the hot core, as well as beam dilution (for single-dish data) have been suggested as explanations. Dynamics may also play a role, especially if infall is fast and molecules spend only a short time in the hot core region and/or are exposed to excess UV *en route* from cloud to disk (Drozdovskaya et al. 2016). Since the time scales of many of the relevant chemical and dynamical processes in star formation are similar, there may be subtle effects at play that can lead to large differences. Coupling chemistry with full (magneto) hydrodynamical models of star formation is still computationally challenging and allows investigation of only a limited number of cases (Hincelin et al. 2016).

While complex molecules are traditionally associated only with protostellar hot cores, they are actually now found at all stages of star formation: in cold cores (§ 9), shocks (§ 10), near PDRs (§ 6) and in protoplanetary disks (§ 12). This points to the increasing importance of forming these molecules under cold conditions as zero-generation ices without the need for 'energetic' or UV processing, rather than as first- or second generation species. Cold gas-phase chemistry involving fragments coming off the ice may play a role in cold clouds and high temperature gas-phase chemistry could still be important for selected complex species in hot cores (Taquet et al. 2016). The chemical specificity, i.e., the fact that some complex molecules like $HCOOCH_3$ and CH_3OCH_3 are more abundant than others, must hold clues on the relative importance of the various reaction pathways (Tielens 2013).

Challenge 11: To identify the main formation routes of complex molecules in dense clouds, to push detections to even higher levels of complexity including prebiotic species like amino acids, and to assess how dynamics and geometry during star formation can affect their abundances.

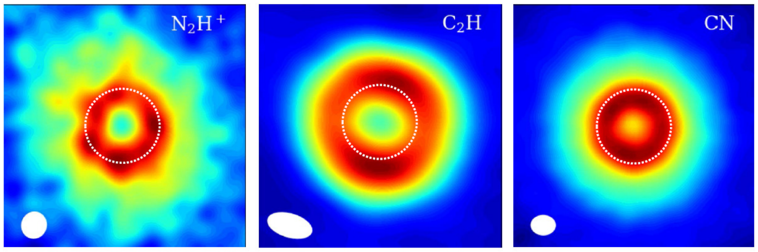

Figure 3. Molecular rings observed with ALMA in the TW Hya protoplanetary disk, showing different locations for each species. The white dotted circle indicates the location of the N_2H^+ ring; C_2H peaks outside and CN inside this ring (Figure by P. Cazzoletti, using data from Qi et al. 2013; Bergin et al. 2016; Teague et al. 2017; each image is $6'' \times 6''$, $1''$=54 AU).

12. Protoplanetary disks

Protoplanetary disks have become one of the centerpieces of Astrochemistry, providing the initial chemical conditions for planet formation. They remain difficult to study both observationally and theoretically, however. Observationally, signals are very weak since they are small (typically less than $1''$ on the sky) and their mass is only 1% of that of the collapsing cloud. Theoretically, they are a challenge since they cover a huge range of densities and temperatures in at least two dimensions, from >1000 K in the inner disk and upper layers, to $\leqslant$10 K in the outer midplane, and from densities of $> 10^{13}$ cm^{-3} in the inner midplane down to 10^5 cm^{-3} in the upper outer layers. Impinging UV radiation fields from the central star can be as high as 10^5 times the ISRF in the surface layers at 10 AU, setting up a PDR-like structure in the vertical direction. Thus, different types of chemistry are important in different parts of the disks. Moreover, gas and dust are largely decoupled (except for the smallest grains): dust grains grow to pebble size (few cm), settle to the midplane and drift in radially (Fig. 4). If they encounter a pressure bump, dust traps can form where particles can grow to even larger, planetesimal sizes. Gas/dust ratios can therefore differ significantly from 100.

The decreasing temperature in the radial direction sets up a range of snowlines, i.e., radii where molecules freeze-out onto the grains, defined as the half-gas, half-ice point. Because of the vertical temperature gradient, the 2D snow surfaces are actually curved, but usually only midplane snowline radii are cited. Snowlines are thought to play a significant role in planet formation, since ice coating of grains enhances the solid mass and promotes coagulation of grains to larger particles, effects which are particularly prominent just outside the snowline. They also control the composition of the icy planetesimals and gas from which exoplanetary atmospheres are built (§13, 14).

Pre-ALMA observations of disks at millimeter and far-infrared wavelengths detected mostly simple molecules originating from the intermediate height warm layers (see Bergin et al. 2007; Henning & Semenov 2013, for reviews), and confirmed the gas-dust temperature decoupling predicted by disk models (Bruderer et al. 2012). ALMA is now starting to probe deeper into the disk and spatially resolve the emission, revealing rings of molecular emission that could be associated with snowlines. The most obvious example is N_2H^+, tracing the CO snowline because its abundance is enhanced when CO is frozen out (Fig. 3). However, many other molecular rings are observed at different locations, with each of them having different explanations: CO snowlines (N_2H^+, DCO^+), CO photodesorption (DCO^+), chemistry (DCN, DCO^+ inner ring), UV (CN), C/O ratios (C_2H, C_3H_3), gas gaps or cavities (CO isotopologues, CS). Only two complex molecules, CH_3CN and CH_3OH, have been detected so far, and only barely. Even the brightest disks do not show rich line forests such as found for hot cores. Deep observations of these and other species in a much larger sample of disks are needed to understand what the different molecular images are telling us about the gaseous physical and chemical structure of disks and its relation to that of the dust. Whether time allocation committees can be convinced to give large amounts of time to this topic is a challenge in itself.

The important water snowline is generally out of reach because it typically occurs at a few AU for T Tauri stars, too small for ALMA to image. Systems undergoing luminosity outbursts such as V883 Ori (Cieza et al. 2016) or young disks with enhanced accretion luminosity (Harsono et al. 2015), for which the water snowlines have moved out to tens of AU, may offer the best opportunity for direct imaging. More generally, determining the chemical composition and structure of young embedded disks may be highly relevant for comparison with comets, if planetesimal formation indeed starts early (§ 13).

The warm gas in the upper layers of the inner disk ($<$10 AU) emits strongly at mid-infrared wavelengths. Indeed, a dense forest of lines due to simple molecules has been detected by *Spitzer* and ground-based infrared telescopes, providing a glimpse of the chemistry in that region (Pontoppidan et al. 2014). Here the high temperatures can completely 'reset' the chemistry. A big advantage of mid-IR spectroscopy is that key abundant molecules without a dipole moment such as CO_2 and C_2H_2 can be observed, together with H_2O, OH and HCN, allowing tests of high temperature chemistry. The degree to which these data can probe the disk midplane chemistry and ice sublimation, relevant for planet formation models, is still unclear however, since the mid-infrared dust and line emission is highly optically thick. JWST will be poised to provide much deeper searches for CH_4, NH_3 and minor species, detect isotopologs to constrain line optical depth, and follow the inner disk chemistry (at least in the surface layers) from the youngest embedded disks to the debris disk stage, and across the stellar type range.

Challenge 12: To make a chemical inventory of disks (from inner to outer, surface to midplane, and young to old) and relate observed molecular structures to underlying gas and dust structures.

13. Planet building blocks: comets, planetesimals

ALMA and high contrast infrared imaging of disks are providing striking pictures of the first steps of planet formation: rings, gaps, cavities, asymmetric structures, and / or spiral arms. Just as for the molecular rings there are many possible interpretations of these structures (§ 12), but they do indicate that growth of dust grains to pebbles and planetesimals is taking place, starting even in the embedded phase.

How does this affect the chemistry? First hints came from the very deep *Herschel*-HIFI integrations of H_2O lines in disks, which revealed surprisingly weak features (Hogerheijde et al. 2011; Du et al. 2017). The favorite interpretation is that most water is locked up in large icy bodies in the midplane and no longer participates in the chemistry at intermediate disk layers where the gaseous lines can be observed. The second clue comes from weak CO isotopologue lines in most disks (Favre et al. 2013; Ansdell et al. 2016). These lines are reduced in strength not just due to the well understood processes of freeze-out and isotope selective photodissociation (Miotello et al. 2017), but also by chemistry transforming CO into CH_3OH, CO_2 or hydrocarbons (Yu et al. 2017). Alternatively, the rapid planetesimal growth invoked for H_2O also locks up significant amounts of CO and volatile carbon in various forms.

Thus, the overall picture of the outer disk is that much of the volatile oxygen and carbon is locked up in ices in large bodies. Since the dominant H_2O and CO_2 ices have

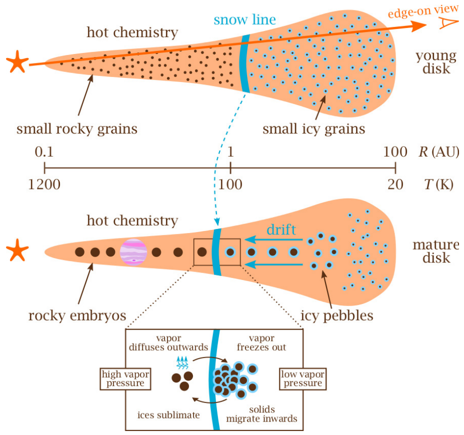

Figure 4. Sketch of the importance of grain growth, radial drift of icy pebbles and snowlines in disk chemistry and in building planets and their atmospheres (Figure by R. Visser, after Sato et al. 2016).

more oxygen than carbon, the ice is oxygen rich, with an overall C/O ratio that is lower than the interstellar or solar abundance (Öberg et al. 2011). In contrast, the gas is carbon rich even though it is overall depleted in carbon and oxygen. Once C/O>1, the same situation occurs as for carbon-rich AGB stars: the gas has high abundances of small hydrocarbon molecules. This can indeed explain the strong observed C_2H and c-C_3H_2 emission in some disks (Bergin et al. 2016) (Fig. 3), although midplane chemistry tends to evolve toward gaseous C/O significantly less than 1 (Eistrup et al. 2017). JWST will be able to observationally constrain the ice composition in planet-forming zones, but only for a handful of near edge-on disks and then only in the intermediate layers.

So how do we determine the disk chemical composition just prior to planet formation? Much of the chemistry of planet formation is unfortunately hidden from our view, including the bulk C- and O-containing species. One option is to observe warmer, younger disks where less of the material is frozen out and fewer planetesimals have formed. The forming disks around Class 0 sources, like those for IRAS16293-2422, may well provide the most detailed information of chemistry on solar-system scales, even if the material has not yet settled into a Keplerian structure. That chemistry, in turn, may have been set already to a large degree in the dense cold core just prior to and during collapse, arguing for an 'inheritance' rather than a 'reset' scenario, at least in the outer disk.

Alternatively, comets and other icy bodies in our own solar system provide clues to the chemistry in our natal solar nebula disk, if they are largely unchanged since their formation 4.5 billion years ago. Comparisons between cometary and interstellar abundances have shown some tantalizing similarities (Mumma & Charnley 2011), but there is a large scatter on both axes. The *Rosetta* mission provides an unprecedented view of the chemical composition of one comet, 67P/C-G (Altwegg, this volume), which can be compared with that inferred for protostars such as IRAS16293-2422. However, this is just one comet and one protostar; ultimately, one would like at least 10 Rosetta-type missions to comets originating in different parts of our solar system! More bright comets like Hale-Bopp that can be probed with ALMA and infrared instruments, including determining their D/H ratio in water, will provide further insight into their origin.

Challenge 13: To determine the (bulk) chemical composition and origin of planet-forming material (inheritance or reset) and relate that to what is found for icy bodies in our own Solar System.

14. Exoplanetary atmospheres

The chemical composition and origin of exoplanet atmospheres, from Super-Earths to mini-Neptunes and Jovian planets, is clearly the next frontier for Astrochemistry. So far, only CO and H_2O have been robustly detected, with hints of CH_4, NH_3 and/or HCN (Madhusudhan et al. 2016). Clouds and hazes often obscure optical and near-infrared features, especially for the lower mass planets. Even when features are detected, inferring accurate absolute abundances is a challenge, although relative abundances are more reliable. For those planets with clear features, a C/O ratio < 1 has generally been inferred, with so far only one potentially carbon-rich planet.

Exoplanet chemistry models are being developed by various groups, and vary in sophistication from pure LTE chemistry to the inclusion of kinetic chemistry, especially photochemistry in the upper parts of the atmosphere (Venot et al. 2015). Titan is a good example of a body in our own solar system to test nitrogen-rich photochemistry †, at the same time also highlighting its complexity.

One of the ultimate goals is to link the planetary atmosphere composition with its formation history in the natal protoplanetary disk. On the one hand, the changing C/O ratio with disk radius could provide such a probe of the formation location. However, the route from disk gas+dust to a mature planet is long and involves many steps, each of them with significant uncertainties (Mordasini et al. 2016). For example, are the heavy elements (i.e., other than H and He) in a giant planet atmosphere accreted mostly from the gas or delivered by icy pebbles? How does the migration history affect the outcome? Moreover, the disk structure and chemistry is not static but evolving, modifying the C/O 'step function', as does the growth and drift of particles (Piso et al. 2015; Eistrup et al. 2017). Thomas Henning, at the Kavli Exo-atmospheres meeting July 2017, lists at least 11 challenges for the field to overcome, most notably our poor understanding of mass and angular momentum transport in disks (see also Hartmann et al. 2017). It is also clear that individual molecule abundances will be fully reset in giant planet atmosphere, preserving only the overall C/O, C/N, O/H etc. abundance ratios. And even those could be affected if part of the atmosphere material is cycled to the planetary core. Thus, as exciting as this topic is, there are some sobering notes.

The atmospheres of rocky terrestrial planets may have an even more complicated history. Well outside the water snowline, the planets are built up largely from planetesimals that are roughly half rock and half ice. When these planets move inward, water becomes liquid, resulting in ocean planets or water worlds. Inside the snowline, the planets are usually thought to be very dry. Computing the atmospheric composition of terrestrial exoplanets is significantly more complex than that of giant exoplanets and requires consideration of many additional processes, including even plate tectonics (Kaltenegger 2017). Because they are very hot initially, they lose most of their original volatiles through outgassing and atmospheric erosion. A secondary atmosphere can however be formed through impacts of (icy) planetesimals in the *late* stages of their formation, including comets such as 67P/C-G which can deliver water and organics to the young planet. The survival of these organics depends on planetesimal size and impact speed, and whether the volatile material can perhaps be shielded by a protective layer on the parent body. If they do, then there would indeed be a direct link between interstellar molecules and the building blocks for life on new planets.

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† Photochemistry in the chemical sense, i.e., the fragments resulting from photodissociation are produced in excited states that react immediately to products before relaxing to the ground state. Within Astrochemistry, the term photochemistry should not be used for gas phase photodissociation.

Finding signs of life on an alien habitable planet is an ultimate goal of exoplanet science, and of astronomy as a whole, and is the driver for the biggest future telescopes and space missions. Biomarker molecules have been identified whose detection could indicate the presence of life on other planets. Key molecules are O_2, O_3, CH_4, N_2O and CH_3Cl. However it is also clear that a single molecule such as O_3 is not sufficient but that a combination of features, including at least one oxidizing and reducing species, is needed (Kaltenegger 2017; Catling et al. 2017).

In this context, it is interesting that several biomarker molecules, most notably O_2 (Bieler et al. 2015) and CH_3Cl (a molecule produced on Earth primarily by biological and industrial processes) (Fayolle et al. 2017), have recently been detected in comet 67P/C-G. For O_2, the abundance of 4% with respect to water makes it the fourth most abundant ice species. If comets are representative of the icy planetesimals from which terrestrial planet atmospheres are built, one should be careful of such 'false positives' that can have an abiotic origin.

Challenge 14: To determine exoplanetary atmosphere compositions and to characterize the chemical changes along the many steps to planet formation, necessary to relate exoplanetary atmosphere compositions to their birth sites in disks.

15. Conclusions

Looking out over the beautiful Llanquihue lake at the snowline on the Osorno volcano, the quote attributed to Rabindranath Tagore becomes very appropriate: *'You can't cross the sea merely by standing and staring at the water'*. The field of Astrochemistry is vibrant and poised to address major topics in astronomy. It forms the scientific basis for one of mankind's biggest questions: 'are we alone?'. To deliver on this promise, however, Astrochemistry has to tackle the questions and challenges outlined above, do the hard (not always glorious) work and provide the hard numbers. The field also has to build the right ships (i.e., new telescopes, new laboratory experiments, new modeling tools), get the right crew (i.e., excellent young people with diverse backgrounds), and make the right connections (i.e., with neighboring fields) to be able to steer the ship in the right direction and cross the water. This will take time but having this long term vision ensures that there will be exciting developments in the coming decades, leading up to Astrochemistry XV!

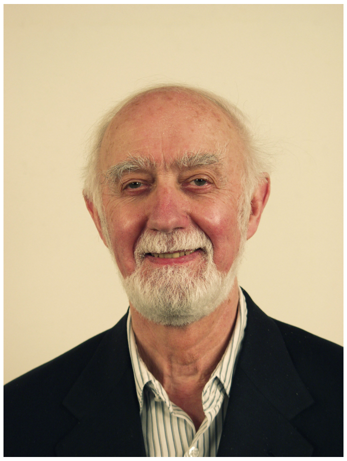

Figure 5. Alexander Dalgarno in 2003.

Acknowledgments. This overview is dedicated to Alexander Dalgarno (1928–2015), who initiated the IAU working group on Astrochemistry and organized the first two symposia in this series. His pioneering work to bring molecular physics into astronomy inspired many young scientists (including this author) to enter our field. The broad scope of these meetings reflect the spirit of his work, having contributed to all aspects of Astrochemistry, and bringing people from across the world together.

The responses from IAU S332 participants to my question on the future of Astrochemistry, as well as comments on this draft by E. Bergin, G. Blake, E. Herbst, T. Millar, C. Walsh and members of my group, are much appreciated. The writing of this review was supported by EU A-ERC grant 291141 CHEMPLAN.

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