

The molecular universe: from observations to laboratory and back

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Abstract. This brief overview stresses the importance of molecular processes in modern astrophysics and provides examples where the availability of new laboratory or theoretical data proved crucial in the analysis. This includes basic data such as spectroscopy and collisional rate coefficients, but also an improved understanding of reactions and photoprocesses in the gaseous and solid state. In spite of many lingering uncertainties, the future of molecular astrophysics is bright with new facilities such as ALMA, JWST and ELTs on the horizon. Together, they will allow increased understanding of the journey of gas and solids from clouds to stars and planets, and back to the interstellar medium.

Keywords. molecular data, molecular processes, astrochemistry, ISM: molecules, techniques: spectroscopic

1. Introduction

Molecules are found in a wide range of astronomical environments, from our Solar system to distant starburst galaxies at the highest redshifts. Thanks to the opening up of the infrared and (sub)millimeter wavelength regime, culminating with *Herschel* and ALMA, more than 180 different species (not counting isotopologs) have now been found throughout the various stages of stellar birth and death. This includes diffuse and dense interstellar clouds, protostars and disks, the envelopes of evolved stars and planetary nebulae, and exo-planetary atmospheres. Molecules and solid-state features are now also routinely detected in the interstellar medium of external galaxies, near and far. Thus, we can now truly speak of a ‘Molecular Universe’ (Tielens 2011).

From a chemical perspective, interstellar space provides a unique laboratory to study basic processes under very different conditions than those normally found in a laboratory on Earth. For astronomers, molecules are unique probes of the many environments where they are found, providing information on density, temperature, dynamics, ionization fractions and magnetic fields. Molecules also play an important role in the cooling of clouds, allowing them to collapse, including the formation of the very first stars and galaxies in the universe. Finally, the molecular composition is sensitive to the history of the material, and ultimately provides critical information on our origins.

This paper briefly summarizes a number of recent observational highlights and provides examples of cases where the availability of new laboratory data proved crucial in the analysis. This includes (i) laboratory spectroscopy; (ii) collisional rate coefficients; (iii) gas-phase chemistry; (iv) photodissociation; (v) solid-state chemistry. There has been no shortage of much more detailed reviews of astrochemistry and the importance of laboratory experiments and theory over the last few years, see Tielens (2013), van Dishoeck (2014), van Dishoeck *et al.* (2013), Herbst (2014), Caselli & Ceccarelli (2012),

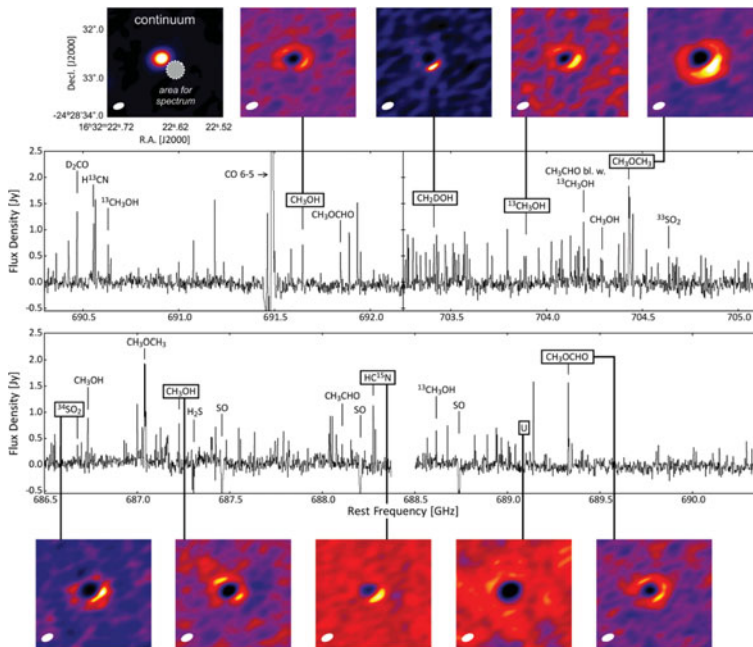


Figure 1. ALMA spectrum at 690 GHz of the low-mass protostar IRAS16293-2422 B taken over a region of $0.3'' \times 0.3''$). Images of the continuum and selected lines are shown as well (Baryshev *et al.* 2015). A significant fraction of these lines have not yet been identified.

Bergin (2013), Savin *et al.* (2012), Herbst & van Dishoeck (2009) and the December 2013 special issue of Chemical Reviews for further information.

2. Gas-phase processes

Spectroscopy. Herschel was particularly well suited to observe light molecules such as hydrides, whose primary transitions occur at far-infrared wavelengths (THz frequencies). New molecules include H_2O^+ which is surprisingly widespread in the diffuse ISM, $\text{HC}1^+$, H_2Cl^+ and $^{36}\text{ArH}^+$ (Gerin *et al.* 2016). These identifications were possible thanks to dedicated laboratory work. In addition, the THz range is well suited to observe high excitation lines of heavy molecules with upper energy levels up to 1000 K. *Herschel* line surveys of well known sources such as Orion-KL and SgrB2(N) beautifully reveal the chemical composition of hot gas but they also show that 5–12% of the channels are unidentified (Crockett *et al.* 2014, Neill *et al.* 2014). Most of the lines are likely to be due to isotopologs and/or vibrationally excited states of known complex organic molecules.

Line surveys with ALMA are only just starting and are more suited to detect new complex molecules because of the higher angular resolution and sensitivity, combined with the fact that the strongest lines of large molecules occur at lower frequencies (Fig. 1). One early highlight is the detection of *i*-propyl cyanide toward SgrB2(N), the first branched molecule (Belloche *et al.* 2014). Such side chains are characteristics of amino acids, which have not yet been detected in interstellar space. This detection was made toward a position in SgrB2(N) with particularly narrow lines, minimizing line confusion. Similarly, the low-mass source IRAS 16293-2422B has very narrow lines which allows identification of prebiotic molecules toward solar-mass protostars for the first time (Jørgensen *et al.* 2012, Baryshev *et al.* 2015, Fig. 1). The ALMA spectrum of the carbon-rich AGB star

IRC+10216 shows many U-lines, in contrast with the *Herschel* spectrum (Cernicharo *et al.* 2013). All these surveys point to the continued need for laboratory spectroscopy at (sub)millimeter wavelengths, both of known molecules and of new increasingly more complex organic molecules.

At optical and near-IR wavelengths there has been great progress in measuring the spectra of long carbon chains and aromatic molecules that could give rise to the diffuse interstellar bands (Steglich *et al.* 2010, 2013, Contreras *et al.* 2013, Zhao *et al.* 2014) (see also Cox & Cami 2014). Silicon-containing chains have been a recent focus (Steglich *et al.* 2015), triggered by the detection of SiCSi (Cernicharo *et al.* 2015). The gas phase spectrum of C_{60}^+ has finally been measured and shown to be indeed responsible for two DIB features at near-IR wavelengths (Campbell *et al.* 2015), as proposed originally by Foing & Ehrenfreund (1997).

Collisional rate coefficients. Much progress has been made in this area thanks to coordinated efforts between various groups. State-to-state collisional rate coefficients with H_2 for pure rotational transitions have been computed in the last decade for H_2O , H_2CO , HCN, HNC, CN, CS, SO, SO_2 , HF, HCl, OH^+ , NH_2D , CH_3CN , and CH_3OH , among others. For ions and molecules with large dipole moments such as HF, CH^+ and ArH^+ , collisions with electrons are also important (Hamilton *et al.* 2016). Another new development is the calculation of rate coefficients for vibration-rotation transitions seen at infrared wavelengths (Pontoppidan *et al.* 2010, Brown *et al.* 2013). New data have been provided for H_2O and CO with H_2 and H (Faure *et al.* 2008, Song *et al.* 2015). These calculations of the potential energy surfaces and subsequent dynamics are very computationally and labor intensive, sometimes taking a decade of dedicated work. The data can be accessed through the BASECOL database (Dubernet *et al.* 2013) and the LAMDA database (Schöier *et al.* 2005, van der Tak 2011).

Chemical reactions. The main databases for gas-phase chemical reactions, UMIST (McElroy *et al.* 2013) and KIDA (Wakelam *et al.* 2015), continue to be updated with new results from the chemical physics literature. Particular attention has been paid to neutral-neutral reactions with C and N atoms leading to carbon chain molecules (Daranlot *et al.* 2012, Loison *et al.* 2014). There are also new merged beam experiments on atom-molecular ion reactions at a range of temperatures (O'Connor *et al.* 2015).

Photodissociation. An update of the wavelength dependence of the photodissociation and photoionization cross sections for many astrophysically important molecules has been made (Heays *et al.*, submitted), making use of databases such as the MPI-Mainz UV/VIS spectral atlas of gaseous molecules. Rates are provided both for the interstellar radiation field and for the cosmic ray induced field (important inside dark cores and disks). Photodissociation rates by the solar radiation field (important for comets) have been updated by Huebner & Mukherjee (2015). The photodissociation of CO and its isotopologs has been further studied and self- and mutual shielding factors quantified (Visser *et al.* 2009, and refs cited). The photodissociation of N_2 and $^{14}N^{15}N$ are finally well understood thanks to decades of experimental and theoretical work (Heays *et al.* 2014, and refs cited). Figure 2 illustrates the diversity in cross sections and their wavelength dependence for various interstellar molecules. Taking this wavelength dependence into account is particularly important for the chemistry in protoplanetary disks around different types of stars.

The photostability of PAHs is much larger than that of small molecules (see review by van Dishoeck & Visser 2015) but is important in protoplanetary disks where UV fields

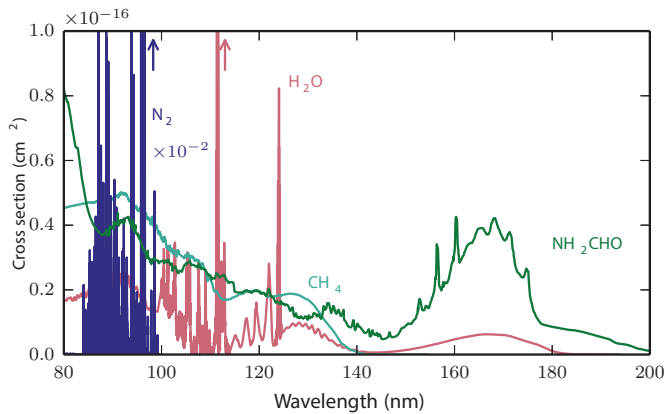


Figure 2. Examples of photodissociation cross sections of interstellar molecules. Note that some cross sections are highly structured (e.g., N_2) whereas others have broad absorption features over a large range of wavelengths. Figure by Alan Heays.

can be enhanced by six orders of magnitude compared with the standard interstellar radiation field. There are new experiments to measure and quantify the loss of hydrogen and C_2 fragments by photodestruction in the laboratory (Zhen *et al.* 2015).

3. Ice processes

Freeze out and desorption. At low grain temperatures of ~ 10 K, the probability for molecules to freeze out on dust grains is unity on every collision. The main question is how to get molecules off the grains at temperatures well below their thermal desorption rates. One option is photodesorption, a process that has been studied both in the laboratory (Öberg *et al.* 2009a, Fayolle *et al.* 2011, Fillion *et al.* 2014) and through molecular dynamics modeling (Andersson & van Dishoeck 2015, Arasa *et al.* 2015). It is important to note that the processes of photodesorption and photodissociation in the ice are linked for most molecules (exceptions are CO and N_2 below 11 eV), but that this is usually not treated correctly in astrochemical models. As for gas-phase processes, the dissociation and/or desorption efficiencies also have a strong wavelength dependence.

The process of chemical desorption, in which part of the energy liberated by formation of the chemical bond is used to desorb the molecule, is potentially important for explaining the observed gas-phase abundances in cold clouds. New experiments to quantify this process have just been reported (Minissale *et al.* 2015). Alternative ways to get molecules back into the gas include impulsive spot heating by cosmic rays (Ivlev *et al.* 2015).

Formation of complex organic molecules. Much (but not all) of the chemical complexity in star-forming regions is thought to be due to reactions occurring on top of, and within, ices that coat interstellar dust grains. One of the recent observational surprises is the fact that complex organic molecules such as HCOOCH_3 are detected not just in hot cores surrounding protostars (Herbst & van Dishoeck 2009) but also on larger scales in the low temperature parts of envelopes (Öberg *et al.* 2010) and even in the coldest pre-stellar cores (Bacmann *et al.* 2012, Vastel *et al.* 2014). Ultra-high vacuum solid-state laboratory experiments have demonstrated that the formation of complex molecules can indeed occur at temperatures as low as 10 K without any energy input (Hidaka *et al.* 2004, Fuchs *et al.* 2009, Fedoseev *et al.* 2015, Fresneau *et al.* 2015, Chuang *et al.* 2016). UV irradiation of ices breaks bonds, produces radicals which become mobile upon heating

and this leads to further complexity, with experiments on mixed ices dating back to the 1980s (d'Hendecourt *et al.* 1986, Öberg *et al.* 2009b).

The challenge for the next decade is to translate these experiments into binding energies and reaction barriers that can be used in gas-grain models. The overall efficiency of surface reactions depends on the probability that species stick to the grains, their mobility on the surface, and the probability that molecule formation occurs. Diffusion of at least one of the two reactants is thought to control the rate of the reaction. This requires a prescription to hop from site to site, in which the crucial parameter is the energy barrier E_{hop} . Usually $E_{\text{hop}} = c^{\text{st}} \times E_{\text{bind}}$ is assumed with c^{st} varying between 0.3 and 0.7. For rough surfaces, the hopping barriers may actually vary from site to site. 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. Recent Monte Carlo simulations have found values of 0.31 and 0.39 for CO and CO₂ on water ice, respectively (Karssemeijer & Cuppen 2014).

4. Outlook

In summary, there is steady progress in spectroscopy and in pinning down the key processes that determine the excitation, formation and evolution of molecules in the Universe. Compared with atomic data studies, molecular physics lags behind by several decades and needs to address a wider variety of species and processes. Concerted efforts within and between various countries, such as being discussed by the US AAS Laboratory Astrophysics Division, the ACS Astrochemistry Division and the European task force on Laboratory Astrophysics, are key to make the next step forward. With ALMA still going strong for the next 25+ years, JWST being launched late 2018, and Extremely Large Telescopes becoming operational in the mid-2020s, there is a growing need for accurate molecular data. The IAU, and in particular Commission B5 on Laboratory Astrophysics and Commission H2 on Astrochemistry, can play a role in bringing astronomers, chemists and molecular physicists together to make all these experiments and calculations happen!

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