Interstellar Hydrides

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Abstract
Interstellar hydrides – that is, molecules containing a single heavy element atom with one or more hydrogen atoms – were among the first molecules detected outside the solar system. They lie at the root of interstellar chemistry, being among the first species to form in initially-atomic gas, along with molecular hydrogen and its associated ions. Because the chemical pathways leading to the formation of interstellar hydrides are relatively simple, the analysis of the observed abundances is relatively straightforward and provides key information about the environments where hydrides are found. Recent years have seen rapid progress in our understanding of interstellar hydrides, thanks largely to far-IR and submillimeter observations performed with the Herschel Space Observatory. In this review, we will discuss observations of interstellar hydrides, along with the advanced modeling approaches that have been used to interpret them, and the unique information that has thereby been obtained.
1. INTRODUCTION

1.1. Historical perspective

Although dust and gas clouds were suspected to exist early in the 20th century, the survival of molecules in the harsh ISM was more controversial (e.g. Eddington 1926). Together with CN, the hydrides CH and CH$^+$ were the first gas-phase molecules detected in the 1930’s and 1940’s (e.g. Swings & Rosenfeld 1937; Douglas & Herzberg 1941). The improved spectral resolution of visible light spectrometers allowed the detection of very narrow absorption lines in the spectra obtained towards nearby and bright stars. Their associated wavelengths were well known to molecular spectroscopists and the small line-widths suggested low gas temperatures, much lower than those of the stellar atmospheres producing broad atomic features. Indeed, the observed narrow lines remained stationary in the spectra of spectroscopic binary stars whose photospheric lines showed periodic ve-
Electronic absorption lines in the FUV from sounding rockets and from Copernicus satellite observations have been presented previously by van Dishoeck (1998) and Snow & McCall (2006). These models were also critical in predicting the existence of new hydride molecules in space.

Both atomic and molecular hydrogen were discovered later in the cold neutral medium (CNM), H$_2$ at 1.420 MHz by radio techniques in the 1950's (Ewen & Purcell 1951), and H$_2$O at 22 GHz (Cheung et al. 1969). OH was also the first molecule detected outside the Milky Way (Weliachew 1971). NH and H$_2$O were discovered by the team of Nobel Prize winner C.H. Townes. Most of the subsequent discoveries of new molecules required the development of higher frequency heterodyne receivers in the millimeter and submillimeter domains available from ground-based telescopes (e.g., Falgarone, Phillips & Pearson 2005), and more recently in the far-infrared (FIR), a wavelength region that is only available from stratospheric and space observations (e.g., Gerin et al. 2012 and references therein). These techniques allow the detection of pure rotational transitions at very high spectral resolution (less than 1 km s$^{-1}$); thus fine and hyperfine line splittings can be resolved. In addition, the FIR domain allows the detection of rotationally excited emission lines. This permits high temperature and density environments ($T>100$ K and $n_H>10^4$ cm$^{-3}$), such as those in star forming regions, to be probed. In diffuse and translucent clouds, hydrides such as CH$^+$, CH, HCl, NH, OH, OH$^+$ or SH can be nowadays also studied through their electronic absorption bands in the UV-visible domain at velocity resolutions of a few km s$^{-1}$ (e.g., Federman et al. 1995; Krelowski, Beletsky & Galazutdinov 2010; Zhao et al. 2015). NH in particular, was first detected in the solid phase as ice mantles covering dust grains (see the review by Boogert, Gerakines & Whittet 2015). Their vibrational modes can be detected in the IR domain. The first mantles detected in absorption were water and ammonia ices (Merrill, Russell & Soifer 1976). Table 1 shows a compilation of the detected hydrides and the wavelength range in which they have been observed.

The formation of H$_2$ on grain surfaces rather than in the gas-phase was soon established, and first models suggested that most hydrogen should be molecular at visual extinctions $A_V>1.5$ mag (e.g., Hollenbach, Werner & Salpeter 1971). Other molecules were proposed to form on grains as well (Watson & Salpeter 1972). More complete chemical models of diffuse clouds were developed (Solomon & Klemperer 1972; Black & Dalgarno 1977). The chemistry of molecular cloud interiors (most hydrogen in H$_2$) was also modeled and predicted to be dominated by ion-molecule reactions maintained by cosmic-ray particle ionization (Herbst & Klemperer 1973). These chemical models were the basis of more sophisticated diffuse cloud, dense photodissociation region (PDR), shock and turbulence dissipation models developed later in the 1980’s. Supported by laboratory and theoretical studies, these models were also critical in predicting the existence of new hydride molecules in space. Review articles have been presented previously by van Dishoeck (1998) and Snow & McCall (2006).

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**ISM:** Interstellar Medium

**FUV:** Far ultraviolet, defined as the 91.2 to 200 nm wavelength region, corresponding to photon energies between 6 and 13.6 eV

**FIR:** Far infrared, defined as the 20 to 300 µm wavelength region, corresponding to frequencies between 1 and 15 THz.
### Table 1 Main astrophysical hydrides

| Formula | Name                      | Spectral domain | Ref.                                |
|---------|---------------------------|-----------------|-------------------------------------|
| H₂      | Molecular Hydrogen        | UV-Visible, IR, FIR | Carruthers (1970b)                  |
| H₃⁺     | Protonated molecular hydrogen | IR           | Geballe & Oka (1996)                |
| CH      | Methylidyne               | UV-Visible, IR, FIR | Swings & Rosenfeld (1937)           |
| CH₂     | Methylene                 | IR, (sub)mm     | Hollis, Jewell & Lovas (1995)       |
| CH₃     | Methane                   | IR, (sub)mm     | Feuchtgruber et al. (2000)          |
| CH₄⁺    | Methylidyminium           | UV-Visible, IR, FIR | Lacy et al. (1991)                  |
| CH₅⁺    | Methylidyminium           | IR, (sub)mm     | Douglas & Herzberg (1941)           |
| NH      | Imidogen                  | UV-Visible, (sub)mm | Meyer & Roth (1991)                 |
| NH₂     | Amidogen                  | (sub)mm         | van Dishoeck et al. (1993)          |
| NH₃     | Ammonia                   | (sub)mm, cm     | Cheung et al. (1966)                |
| NH₄⁺    | Ammonium                  | (sub)mm         | Cernicharo et al. (2013)            |
| OH      | Hydroxyl radical          | UV-Visible, FIR, cm | Weintreb et al. (1963)              |
| H₂O     | Water                     | FIR, (sub)mm, cm | Cheung et al. (1969)                |
| OH⁺     | Oxidaniumyl               | UV-Visible, (sub)mm | Wyrowski et al. (2010)              |
| H₂O⁺    | Oxidaniumyl               | UV-Visible, (sub)mm | Ossenkopf et al. (2010)             |
| HF      | Hydrogen fluoride         | FIR, (sub)mm    | Phillips, van Dishoeck & Keene (1992) |
| SH      | Mercapto radical          | UV-visible, FIR | Neufeld et al. (2012)               |
| H₃S     | Hydrogen sulfide          | (sub)mm         | Thaddeus et al. (1972)              |
| SH⁺     | Sulfinium                 | (sub)mm         | Benz et al. (2010); Menten et al. (2011) |
| HCl     | Hydrogen chloride         | UV-visible, (sub)mm | Blake, Keene & Phillips (1983)      |
| HCl⁺    | Chloroniumyl              | FIR             | De Luca et al. (2012)               |
| H₂Cl⁺   | Chloronium                | (sub)mm         | Li et al. (2010a)                   |
| ArH⁺    | Argonium                  | (sub)mm         | Barlow et al. (2013)                |

*Adapted from The Astrochymist (www.astrochymist.org); The corresponding wavelength ranges are: UV-Visible 100 – 1000nm, IR : 1 – 20 µm, FIR 20 – 300 µm; (sub)mm 0.3 – 4 mm; cm 1 - 20 cm; A tentative detection of the isotopologue CH₃D⁺ is reported; The detection of the isotopologue NH₃D⁺ is reported.*

Diffuse interstellar clouds, by Hollenbach & Tielens (1999) on PDRs, and by Bergin & Tafalla (2007) and Caselli & Ceccarelli (2012) for dark clouds.

Recent years have seen rapid progress in our understanding of interstellar hydrides, with new detections and modeling approaches demonstrating their diagnostic power. Thus it seems appropriate to review the current state of observations in different interstellar environments, and the unique astrophysical information that can be obtained. This review is organized as follows. After a general introduction of the thermochemical properties and of the excitation of hydrides, in Section 2 we summarize the main gas-phase and solid-phase processes driving the chemistry of hydrides. We then focus on the appearance of hydride molecules in the diffuse molecular gas (Section 3), in dense and strongly UV-irradiated gas (Section 4), in shocks and turbulent dissipation regions (Section 5), and in cold and dense gas shielded from UV radiation (Section 6). In Section 7 we summarize the diagnostic power of hydrides, and in Section 8 we extend our discussion to external galaxies. We end by giving our conclusions and anticipating some of the exciting prospects for hydride research for the years to come.
### Thermochemistry of interstellar hydrides

Although the interstellar gas is far from thermochemical equilibrium, key features of the chemistry of interstellar hydrides — discussed in detail in Section 2 below — are determined by thermochemistry (Neufeld & Wolfire 2009). Among the elements in the second and third rows of the periodic table, F, O, N, Ne and Ar all have first ionization potentials greater than that of atomic hydrogen (13.60 eV); because hydrogen atoms shield them very effectively from ultraviolet radiation of sufficient energy to ionize them, these elements are predominantly neutral in the CNM. All other elements in the second and third rows of the periodic table — including C, Si, P, S and Cl — have ionization potentials smaller than that of hydrogen; typically, they are predominantly singly-ionized in the cold diffuse ISM. (The exception is Cl, which may exhibit a significant neutral fraction in clouds with a sufficient H\(_2\) fraction: this behavior is a consequence of the rapid reaction of Cl\(^+\) with H\(_2\) to form HCl\(^+\), which subsequently undergoes dissociative recombination to form atomic chlorine).

With the notable exception of hydrogen fluoride, every neutral diatomic hydride has a dissociation energy smaller than that of H\(_2\), as indicated in Figure 1. As a result, hydrogen abstraction reactions of the type X + H\(_2\) → XH + H are all endothermic except in the case where X is fluorine. HF is therefore the only neutral diatomic hydride that can be formed at low temperature through the reaction of an atom with H\(_2\). As for the diatomic hydride cations, HeH\(^+\), OH\(^+\), HF\(^+\), HCl\(^+\), ArH\(^+\) and NeH\(^+\) have dissociation energies larger than that of H\(_2\). They can therefore be produced exothermically via the hydrogen abstraction reaction X\(^+\) + H\(_2\) → XH\(^+\) + H; such reactions are endothermic for all other ions.

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#### Figure 1

Dissociation energies of the neutral diatomic hydrides, in eV, from Neufeld & Wolfire (2009) and based upon the thermochemical data referenced therein.

|       | H\(_2\) | LiH | BeH | BH | CH | NH | OH | HF | NaH | MgH | AlH | SiH | PH | SH | HCl | KH | CaH | GaH | GeH | AsH | SeH | HBr |
|-------|---------|-----|-----|----|----|----|----|----|-----|-----|-----|-----|----|----|-----|----|-----|-----|-----|-----|-----|-----|
| 4.48  | 2.41    | 2.24| 3.44|    | 3.49| 3.22| 4.39| 5.87| 2.04 | 1.99| 2.95| 2.98| 2.87| 3.65| 4.43| 1.87 | 1.77| 2.78| 2.73| 2.66| 3.11| 3.76|

| ScH  | TiH | VH | CrH | MnH | FeH | CoH | NiH | CuH | ZnH |
|------|-----|----|-----|-----|-----|-----|-----|-----|-----|
| 2.09 | 2.08| 1.67| 2.27| 1.27| 1.59| 1.97| 2.57| 2.64| 0.83|

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**CNM:** Cold Neutral Medium. Two neutral phases coexist at pressure equilibrium in the ISM, the warm neutral medium with \(T \sim 10^4\) K and \(n_H \sim 0.3 - 1\) cm\(^{-3}\) and the CNM with \(T \sim 10^2\) K and \(n_H \sim 30 - 100\) cm\(^{-3}\).
XH⁺.

In addition to the ionization potential of each atom, X, and the dissociation energies of the hydrides, XH and XH⁺, another important thermochemical parameter is the proton affinity of X. Because H⁺ is produced efficiently following cosmic-ray ionization of H₂, proton transfer from H⁺ to X can be an important production mechanism for XH⁺ when the proton affinity of X exceeds that of H₂ (422.3 kJ mol⁻¹ or equivalently 4.38 eV). This condition is satisfied for C, O, Si, P, S and Cl – but not for N, F, Ne or Ar – with the result that the first six atoms can react exothermically with H⁺ to form XH⁺. This consideration is most important for O, because it is the only atom among these six to be predominantly neutral in diffuse clouds.

In Figure 2, the thermochemical considerations discussed above are presented in graphical form. For each element, the first ionization potential is given in the second column from the left. The 3rd, 4th, and 5th columns indicate the endothermicity of three key reactions: the reaction of X with H₂ to form XH, the reaction of X⁺ with H₂ to form XH⁺, and the reaction of X with H⁺ to form XH⁺. Here, the endothermicities, ΔE, are presented as temperatures, ΔE/k_B, and given in units of Kelvin. Cells shown in green indicate exothermic reactions, those shown in orange indicate slightly endothermic reactions with ΔE/k_B ≤ 1000 K, and those shown in red indicate endothermic reactions with ΔE/k_B ≥ 1000 K. Particularly for neutral-neutral reactions, the activation energy (i.e. energy barrier) may exceed the endothermicity. For example, the reaction of O with H₂ to form OH and H has an endothermicity, ΔE/k_B ~ 920 K but an activation energy of ΔE_A/k_B ~ 3000 K. Where the reactant (X

| Element | Ionization Potential (eV) | Endothermicity (Kelvin equivalent = ΔE/k_B) for | Driver |
|---------|--------------------------|-----------------------------------------------|--------|
|         | X + H₂ → XH + H          | Exothermic, but primary channel is to H⁺ + X⁺ |        |
|         | X⁺ + H₂ → XH⁺ + H        |                                              |        |
|         | X + H⁺ → XH⁺ + H₂        |                                              |        |
| He      | 24.587                   | No reaction                                  | 29000  |
| C       | 11.260                   | 11000                                        |        |
|         | 4300                      |                                              | Warm gas |
| N       | 14.534                   | 15000                                        |        |
|         | 230                       |                                              | Cosmic rays |
| O       | 13.618                   | 920                                          |        |
|         | Warm gas or cosmic rays   |                                              |        |
| F       | 17.423                   | 10000                                        |        |
| Ne      | 21.564                   | No reaction                                  | 27000  |
| Si      | 8.152                    | 17000                                        |        |
|         | 15000                     |                                              | Warm gas |
| P       | 10.487                   | 19000                                        |        |
|         | 13000                     |                                              | Warm gas |
| S       | 10.360                   | 10000                                        |        |
|         | 10000                     |                                              | Warm gas |
| Cl      | 12.968                   | 515                                          |        |
|         | UV with hν > 12.97 eV     |                                              |        |
| Ar      | 15.760                   | No reaction                                  | 6400   |
|         | 400                       |                                              | Cosmic rays |
or X⁺) is the dominant ionization state of the element in diffuse interstellar gas clouds with a small molecular fraction, the green, orange or red coloring is solid; otherwise, the cell is shaded. The dominant production mechanisms for diatomic interstellar hydrides, and the environments in which they are found, can largely be inferred from the information presented in this matrix. Check marks indicate reactions that have been invoked as significant production routes in astrochemical models in the literature. In some cases, different mechanisms are important in different environments: in the case of oxygen for example, production of OH via the endothermic reaction of O and H₂ becomes rapid in warm (T ≥ 400 K) gas (e.g., Kaufman & Neufeld 1996), while OH⁺ production is effective in cold diffuse gas through reaction of O⁺ with H₂ or (in slightly denser gas with a larger H₂ fraction) of O with H₃⁺ (e.g., Hollenbach et al. 2012).

1.3. Excitation of interstellar hydrides

Several physical processes determine the excitation of interstellar hydrides (e.g., Roueff & Lique 2013 and references therein), including collisional excitation, spontaneous radiative decay, radiative excitation, and formation pumping. At sufficiently high densities, the first of these processes drives the molecular excitation to local thermodynamic equilibrium (LTE), in which the relative level populations are given by Boltzmann factors determined by the gas kinetic temperature. However, the “critical density” needed to achieve LTE is typically larger for the rotational states of hydrides than that for those of non-hydride interstellar molecules, because hydrides have smaller momenta of inertia, larger rotational constants, and much larger spontaneous radiative rates (the latter scaling as the cube of the transition frequency for a given dipole matrix element). At densities below the critical density, the level populations reach a quasi-equilibrium in which the total production and loss rates are equal for every state. In general, the excitation is “sub-thermal,” with the excitation temperatures for most transitions being smaller than the gas kinetic temperature. However, specific transitions can sometimes be supra-thermally-excited, or even inverted, giving rise to maser amplification.

In diffuse molecular clouds, the molecular excitation is often determined primarily by the radiation field; in clouds that are not close to a strong submillimeter radiation source, the cosmic microwave background radiation (CMB) dominates and most rotational transitions have an excitation temperature close to that of the CMB. For molecules such as HF and HCl in which there are no metastable rotational states, this means that most molecules are found in the ground rotational state. For triatomic hydrides such as H₂O, H₂O⁺, and H₂Cl⁺ in which there are two spin symmetries (ortho with total H nuclear spin 1, and para with total H nuclear spin 0), most molecules in diffuse clouds are found in one or other of the lowest rotational states of the two spin symmetries. For symmetric top molecules such as NH₃ and H₂O⁺, in which the rotation is characterized by the quantum numbers J and K, the lowest energy state for any given K is metastable. Thus for NH₃ and H₂O⁺ in diffuse clouds, the population is largely divided amongst those metastable states lying at the bottom of each K-ladder.

While the CMB radiation is ubiquitous, other radiation fields can become important in specific environments: strong mid-IR and FIR radiation is present close to massive protostars, for example, and strong optical and UV radiation is present close to hot stars. Such radiation may affect the rotational populations in the ground vibrational state, as a result of pumping through rotational (FIR), vibrational (mid-IR) and electronic (optical and UV) transitions (Godard & Cernicharo 2013).

In different astrophysical environments, inelastic collisions with H₂, with H and/or with electrons can be important or even dominant in determining the equilibrium populations in the various rovibrational states of an interstellar hydride. Collisions with He can also be important but probably never play a dominant role. In dense, well-shielded molecular clouds, H₂ is the most important collision partner, but in photodissociation regions where the carbon is significantly photoionized, excitation by electrons...
can be important or dominant. While the electron abundance in such regions is only $\sim \text{few} \times 10^{-4}$ relative to $\text{H}_2$, the rate coefficients for electron impact excitation can exceed those for excitation by $\text{H}_2$ or $\text{H}$ by four orders of magnitude, particularly in the case of hydride cations or neutral hydrides with large dipole moments: here, the cross-sections are enhanced by long-range Coulomb interactions (and the mean electron velocities exceed the mean $\text{H}_2$ velocities by the square root of the $\text{H}_2$ to electron mass ratio). In certain environments, and in particular the molecule reformation region behind dissociative shock fronts (see Section 5 below), excitation by atomic hydrogen can also be very important.

There is a considerable and ongoing effort to calculate state-to-state rate coefficients for various hydrides of astrophysical interest, most importantly in recent years for the excitation of water by ortho- and para-$\text{H}_2$ (Daniel, Dubernet & Grosjean 2011 and references therein) and by atomic hydrogen (Daniel et al. 2015). State-of-the-art quantal calculations make use of the so-called close-coupling method and rely upon accurate determinations of the potential energy surface for the system. Such calculations are computationally-expensive, and are often (e.g. in the case of water) limited to a subset of the rovibrational states that have actually been observed in interstellar hydrides. As a result, less computationally-intensive (and less accurate) methods such as quasi-classical trajectory calculations (e.g. Faure et al. 2007) must sometimes be used to interpret astronomical observations, in some cases accompanied by extrapolation methods involving propensity rules (e.g. Faure et al. 2007) or the use of artificial neural networks (Neufeld 2010). The LAMDA (Schöier et al. 2005) and BASECOL (Dubernet et al. 2013) databases have been established to collate collisional rate coefficients and spontaneous radiative decay rates for hydrides and other interstellar molecules in a standard format for use in modeling the excitation.

Formation pumping is a further process that can affect the excitation state of interstellar hydrides. Here, if the lifetime of the molecule is comparable to – or smaller than – the timescale on which the quasi-equilibrium level populations are established, the observed populations may reflect the initial conditions at formation. The most clearly-established case of formation pumping in interstellar hydrides is the excitation of high-lying OH rotational states following the photodissociation of $\text{H}_2\text{O}$ to form OH (Tappe et al. 2008, discussed further in Section 5 below). Formation pumping has also been discussed as an explanation for the observed excitation of $\text{H}_3\text{O}^+$ (e.g. Lis et al. 2014; González-Alfonso et al. 2013), and may be important for other molecular ions as described further in Section 4 below.

2. CHEMISTRY

2.1. Gas phase processes

As anticipated in Section 1.2, hydrides are mostly formed in the gas through series of hydrogen abstraction reactions combined with dissociative recombination. The chemistry of carbon, oxygen and nitrogen hydrides is illustrated in Figure 3. This relative simplicity hides subtleties introduced by i) the presence of highly endothermic reactions on important pathways (e.g. the initiation reaction of the carbon chemistry between ionized carbon and molecular hydrogen has an endothermicity of 0.37 eV or 4300 K), and ii) the dependence of the reaction rates and products on the molecular hydrogen spin symmetry state, or more generally on the initial rovibrational state (for molecules) or the fine structure level (for atoms) of the reactants (e.g. Faure et al. 2013; Li et al. 2013). Fortunately, many of the key reactions for hydride synthesis have been studied through theoretical calculations and laboratory measurements because of their fundamental interest for molecular physics. For example, the neutral-neutral reaction between F and $\text{H}_2$ forming HF and H is one of the benchmark systems for the tunneling effect. Combining measurements down to 11 K and new theoretical calculations, Tizniti et al. (2014) have provided an accurate determination of this important reaction rate.

The hydrogen abstraction reactions initiating the oxygen, nitrogen, chlorine and argon chemistry
HNC

UV driven chemistry

Figure 3

Illustration of the chemical network initiating the carbon, oxygen and nitrogen chemistry in diffuse cloud conditions \(n_H = 50 \text{ cm}^{-3}, A_V = 0.4 \text{ mag}, T = 1\). The black arrows show the reactions with H, H\(^+\), H\(_2\), H\(_3^+\), C\(^+\) and N, with values of the endothermicity for the reaction between N\(^2\) and H\(_2\), and for the charge exchange reaction between O and H\(^+\). Note that CH\(_2^+\) is formed in the slow radiative association reaction between C\(^+\) and H\(_2\). The dashed blue arrows indicate the reactions induced by far ultra violet (FUV) photons or cosmic rays. Dissociative recombination reactions with electrons are shown with green dotted arrows. Purple arrows show the neutralization reactions on dust grains and PAHs. Adapted from Godard, Falgarone & Pineau des Forêts (2014).

are exothermic or moderately endothermic (for N). Because dissociative recombination reactions are fast, photodissociation is usually not a dominant destruction process for the hydride ions, while it affects neutral hydrides. The hydride chemistry is sensitive to the strength and spectrum of the incident X-ray and UV radiation field, and to the ionization rate due to cosmic rays, the two main sources of ionized species. The exact energy distribution of the UV field is particularly important for the chlorine chemistry since the ionization potential of atomic chlorine, 12.968 eV, is very close to the Lyman edge (13.6 eV). Polycyclic Aromatic Hydrocarbons (PAHs) play a role in the chemistry because cations (e.g. H\(^+\), C\(^+\), N\(^+\)) get neutralized when encountering a neutral or negatively charged PAH. Hence PAHs reduce the efficiency of molecule formation. This is especially important for the oxygen chemistry in which the initiating charge exchange reaction between H\(^+\) and O competes with neutralization on PAHs.

Given the relatively large reaction rates, the chemical time scales for gas phase hydride production are short, typically less than a few 100 yr provided molecular hydrogen has reached its equilibrium abundance. The formation of molecular hydrogen itself, which occurs on grain surfaces, is significantly slower, with typical time scales of 10 Myr for diffuse gas densities. Numerical simulations of the diffuse ISM, using either hydrodynamical or magnetohydrodynamic (MHD) codes, have shown however that the equilibrium molecular hydrogen fraction can be reached faster in a dynamical medium because the compressions induce transient density enhancements where H\(_2\) forms more rapidly than in an uniform medium (Glover & Mac Low [2007]). The time scale for conversion between the H\(_2\) spin symmetry states strongly depends whether only gas phase processes contribute, or whether H\(_2\) is

Cosmic Rays (CR): Cosmic Rays are energetic particles (electrons, protons, and heavier nuclei), accelerated at energies between 0.1 and 10\(^{8}\) GeV in fast shocks.

PAHs: Polycyclic Aromatic Hydrocarbons are carbon and hydrogen molecules composed of multiple benzenic cycles with hydrogen atoms at the boundaries.
Variation of the gas phase abundances of various species relative to the total hydrogen content as a function of depth $A_V$ for a cloud with constant pressure $P/k_B = 4 \times 10^7$ K cm$^{-3}$, irradiated by the average interstellar radiation field ($x = 1$) from the left side, and a cosmic ray ionization rate $Q_0 = 2 \times 10^{-16}$ s$^{-1}$, computed with the Meudon PDR code (Le Bourlot et al. 2012). The left panel displays the hydrogen (H, H$_2$), carbon (C$^+$, C, CO), nitrogen (N, N$_2$ not shown) reservoirs together with the electron abundance and the kinetic temperature (right vertical scale). The gas density ranges from about 40 cm$^{-3}$ at $A_V \sim 0.01$ mag up to ~150 cm$^{-3}$ at $A_V > 1$ mag. The right panel shows the main carbon and nitrogen hydride abundances as a function of extinction.

Fig. 4 illustrates the behavior of carbon and nitrogen hydrides for a constant pressure cloud with $P/k_B = 4 \times 10^7$ K cm$^{-3}$ using a pure gas-phase chemical network (except for H$_2$). The behavior of oxygen hydrides is illustrated in the left panel of Fig. 5 (Section 4) which displays a model with a similar value of the control parameter $\chi/n_H$ where $\chi$ represents the enhancement factor of the incident FUV radiation field over the mean interstellar radiation field in the solar neighborhood. It is interesting to note that CH and CH$_2$ show a very similar behavior with a first rise of their relative abundances nearly coinciding with the H/H$_2$ transition at $A_V \sim 0.1$ for this particular model. The appearance of nitrogen hydrides (NH, NH$_2$ and NH$_3$) takes place further inside the cloud at $A_V \sim 1$, and coincides with the CO formation zone. The NH$^+$ abundance remains low, in agreement with Herschel observations (Persson et al. 2012). The series of molecular ions O$^+$, H$_2$O$^+$ and H$_3$O$^+$ behaves somewhat differently from the carbon and nitrogen hydrides: each ion is predicted to probe a different zone of molecular hydrogen content, with $f_{\text{frac}} = 2n(H_2)/[2n(H_2) + n(H)]$, the molecular fraction, increasing from OH$^+$ to H$_2$O$^+$. As will be discussed further in Section 7 below, this property is fully consistent with observations and can be used to derive the fraction of molecular hydrogen in the region of maximum OH$^+$ abundance.
2.2. Solid phase processes

Molecular hydrogen is not the only molecule formed in the solid phase. Recent studies have shown, that even under diffuse ISM conditions, the formation of molecules on grain surfaces can be efficient (see e.g. Sonnentrucker et al. 2015 for H₂O). Hydrides are particularly susceptible to being formed on grain surfaces because of the ubiquitous presence of hydrogen. Laboratory experiments using beams of hydrogen and oxygen atoms hitting a cold surface have clearly demonstrated that water ice forms in this process. A fraction of the newly formed molecules does not stay on the cold surface but is immediately released in the gas phase (Dulieu et al. 2013), a process called chemical desorption. The fractions of trapped versus ejected molecules depend on the nature of the surface, the ice coverage, and the exact reaction mechanism. In a similar manner as water ice, the hydrogenation of carbon and nitrogen atoms produces methane and ammonia. Laboratory experiments are now able to probe these processes including exchanges between H and D atoms and the production of deuterated species (Fedoseev, Ioppolo & Limarzi 2015).

Once formed on the cold grain surfaces, four mechanisms may release molecules to the gas phase: i) thermal sublimation when the grains reach temperatures larger than the ice sublimation threshold, ii) photo-desorption when FUV photons are absorbed by the grain surface and kick some molecules out of the ice, iii) cosmic ray induced desorption when an energetic particle interacts with a grain mantle, and iv) chemical desorption during the formation process. Laboratory experiments have been performed to study these mechanisms and understand in which conditions they operate. Theoretical and laboratory studies of ice photodesorption have concluded that this process is complex. FUV photons can dissociate a frozen water molecule producing two fragments (H and OH) that have excess energy. These fragments can either recombine as a gas phase water molecule, or the excited H can kick out another frozen water molecule. The outcome depends on many parameters, first of all where the FUV photon is absorbed, since only the upper ice layers participate to the desorption. The presence of other isotopologues, of other molecules like CO, which does not dissociate upon the absorption of a FUV photon, will also affect the desorption yield. Overall the photodesorption yields range between 10⁻⁴ and 10⁻² molecules/photon (Arasa et al. 2015). With such numbers, most of the species are predicted to be frozen in dense core conditions, with a minor fraction remaining in the gas phase. As illustrated in Fig. 8, water vapor reaches its peak abundance for extinctions of a few magnitudes. Chemical models also include a temporal dimension because the dynamical time scales, which scale with the free fall time \( t_{ff} = \sqrt{3\pi/32G\rho} \sim 10^5 \sqrt{5 \times 10^6 \text{cm}^{-3}/m(H_2)} \) yr, are similar to the chemical time scales. For instance, the freeze-out time scale in the absence of desorption is \( t_{freeze} \sim 10^6 \left(10^4 \text{cm}^{-3}/m(H_2)\right) \) yr.

While the respective abundances of H₂O, CH₄ and NH₃ are fairly well documented in interstellar ices, little is known about the presence of hydrides composed of the heavier elements F, S or Cl in ices. The somewhat lower elemental abundances precludes a direct identification given the limited sensitivity of infrared spectroscopy of solid features, 1% of the water ice content. Solid phase and gas phase processes are coupled, as shown for instance by the production of H₂ and methane during the FUV irradiation of hydrogenated amorphous carbons (Alata et al. 2014). Although laboratory experiments have led to steady progress in the understanding of the solid phase chemistry, the state of the art is still far from that of the chemistry in gas phase, even for simple hydrides. The relative contributions of solid phase and gas phase routes to the formation of nitrogen hydrides deserves specific attention. While the reaction between N⁺ and H₂ initiates the nitrogen chemistry in UV-illuminated regions, NH is mostly formed as a minor channel in the dissociative recombination of N₂H⁺ in shielded regions. As discussed by Wagenblast et al. (1993), the gas-phase production route for nitrogen hydrides is not efficient enough to explain the observed abundance in diffuse clouds, especially if the cosmic ray ionization rate is low. An alternative formation mechanism for nitrogen hydrides involves the hydrogenation of nitrogen atoms on grain surfaces to form ammonia, and its release into the gas phase for
further processing. Given the wealth of data now available, the relative contributions of solid phase and gas phase routes in the nitrogen chemistry should be assessed, especially for diffuse conditions. More generally, more quantitative evaluations of the reactivity of atoms and molecules (including diffusion) and of the efficiency of the various desorption processes is needed to improve astrophysical models.

3. HYDRIDES IN DIFFUSE GAS

3.1. Overview

With the exception of CH₄, CH⁺³ and NH⁺², all the hydride molecules listed in Table 1 are known to be present in diffuse molecular clouds. Observations of hydrides in diffuse clouds have targeted transitions over a wide range of wavelengths, from a 122 nm electronic transition (of OH) to a set of 18 cm lambda-doubling transitions (also of OH). Typically, molecules in diffuse clouds have been observed in absorption toward background sources of continuum radiation; these include hot stars (at ultraviolet wavelengths), warm dust in regions of active star formation (at FIR and submillimeter wavelengths), and HII regions (at centimeter wavelengths). With the exception of those targeting centimeter-wavelength lambda-doubling transitions, absorption-line observations yield relatively robust and model-independent estimates of molecular column densities. This advantage results from the fact – discussed previously in Section 1.3 – that under typical conditions in diffuse clouds, most hydride molecules are found primarily in the ground state (or, for triatomic hydrides, in the lowest energy states of the ortho- and para-symmetry states); thus, stimulated emission is typically negligible, and the scaling between absorption line optical depth and molecular column density is only weakly dependent upon the physical conditions. In the remainder of this section, the observational data on hydride molecules in diffuse clouds will be reviewed. In Section 7 below, we will discuss how the measured abundances of interstellar hydrides can be used as quantitative probes of the environment in which they are found.

3.2. Optical/UV and centimeter-wavelength observations of interstellar hydrides

In diffuse molecular clouds, several hydride molecules show observable absorption at optical and ultraviolet wavelengths through their electronic transitions. These include three molecules – CH, CH⁺, and NH – that were first detected (see Table 1) in this spectral region; two molecules – OH⁺ (Krełowski, Beletsky & Galazutdinov 2010) and SH (Zhao et al. 2015) – with optical/UV transitions that were detected shortly after their initial discovery at submillimeter wavelengths; as well as OH, detected both at vacuum UV (e.g. Snow 1976) and near-UV wavelengths (e.g. Porras et al. 2014). In this spectral region, spectral resolving powers \( R = \lambda/\Delta \lambda \) in excess of ~ 10⁵ can be achieved with echelle spectrometers. Although not as high as those achievable at submillimeter wavelengths using heterodyne receivers, these spectral resolving powers yield valuable kinematic information about the absorbing molecules. For example, a recent analysis of near-UV spectra showing OH⁺, OH, CH, CH⁺, and CN absorption (Porras et al. 2014) has revealed a kinematic association between OH⁺, CH⁺, and neutral atoms on the one hand; and CN and OH on the other hand. CH is associated with both families, but with the largest CH column densities usually occurring in gas with a high molecular fraction. Because of the effects of dust extinction, optical/UV observations of absorption by molecules in the Galactic disk are limited to relatively nearby material, in contrast to the case of the submillimeter observations described in Section 3.3 below. At centimeter-wavelengths, two hydride molecules – OH (e.g. Allen, Hogg & Engelke 2015 and references therein) and CH (e.g. Chastain, Cotten & Magnani 2010) – have been widely observed in diffuse interstellar gas clouds, by means of their lambda-doubling transitions at 18 cm and 9 cm respectively. Such transitions, which are typically observed in emission,
have provided a valuable tracer of molecular hydrogen, as discussed in Section 7 below.

### 3.3. FIR and submillimeter observations of absorption by interstellar hydrides

Over the past five years, *Herschel* and SOFIA have provided unique opportunities to observe submillimeter absorption by many interstellar hydrides in diffuse clouds along the sight-lines to bright submillimeter continuum sources. Heterodyne spectrometers available on both these observatories – the HIFI instrument on *Herschel* and the GREAT instrument on SOFIA – have provided extremely high (sub-km/s) spectral resolution that is unmatched by other spectrometric techniques operating at submillimeter, infrared or visible wavelengths. *Herschel* observations have led to the discovery of interstellar SH⁺, HCl⁺, H₂Cl⁺, H₂O⁺ and ArH⁺, and the first extensive observations of HF and

### Table 2  Typical hydride abundances in diffuse clouds

| Molecule | Average abundance relative to H or H₂ | Average abundance (fraction of gas phase elemental) | Method | Reference for hydride column densities |
|----------|--------------------------------------|-----------------------------------------------|--------|--------------------------------------|
| CH       | 3.5 × 10⁻⁸                          | 1.3 × 10⁻⁸                                    | V⁺, UV⁺, M⁺ | Sheffer et al. (2008) |
| CH₅⁺     | 1.6 × 10⁻⁸                          | 6 × 10⁻⁵                                     | S, CH, M  | Polehampton et al. (2005) |
| CH⁺⁺     | 6 × 10⁻⁹                           | 4 × 10⁻⁵                                     | V, Re, M  | Grede et al. (1997); Cran, Lambert & Sheffer (1995) |
| CH⁺⁺⁺    | < 2 × 10⁻⁹                         | < 1.4 × 10⁻⁵                                  | Re, V    | Indriolo et al. (2010) |
| NH       | 8 × 10⁻⁹                           | 6 × 10⁻⁵                                     | S, CH, 1  | Persson et al. (2010) |
| NH₂      | 4 × 10⁻⁹                           | 3 × 10⁻⁵                                     | S, CH, 1  | Persson et al. (2010) |
| NH₃      | 4 × 10⁻⁹                           | 3 × 10⁻⁵                                     | S, CH, 1  | Persson et al. (2010) |
| NH⁺⁺     | < 4 × 10⁻¹⁰                        | < 6 × 10⁻⁶                                   | S, HI, 1  | Persson et al. (2010) |
| OH       | 1 × 10⁻⁷                           | 1.6 × 10⁻⁷                                   | V, S, CH, M | Wiesemeyer et al. (2015); Lucas & Liszt (1996) |
| H₂O      | 2.4 × 10⁻⁸                          | 4 × 10⁻⁵                                     | S, CH, M  | Flagey et al. (2013) |
| OH⁺⁺     | 1.2 × 10⁻⁸                          | 4 × 10⁻⁵                                     | S, HI, M⁺ | Indriolo et al. (2015) |
| H₂O⁺⁺    | 2 × 10⁻⁹                           | 6.5 × 10⁻⁶                                   | S, HI, M⁺ | Indriolo et al. (2015) |
| H₂O⁺⁺⁺   | 2.5 × 10⁻⁹                         | 4 × 10⁻⁶                                     | S, CH, 1  | Lis et al. (2014) |
| H⁺⁺⁺     | 1.4 × 10⁻⁸                          | 0.4                                           | S, CH, M  | Sonnentrucker et al. (2010) |
| SH       | 1.1 × 10⁻⁸                          | 4 × 10⁻⁵                                     | S, CH, M  | Neufeld et al. (2015a) |
| H₂S      | 5 × 10⁻⁹                           | 1.8 × 10⁻⁴                                   | S, CH, M  | Neufeld et al. (2015a) |
| SH⁺⁺     | 1.1 × 10⁻⁸                          | 8 × 10⁻⁴                                     | S, HI, M  | Godard et al. (2013) |
| HCl⁺     | 1.5 × 10⁻⁹                         | 0.004                                         | S, CH, 1  | Monje et al. (2013) |
| HCl⁺⁺    | 8 × 10⁻⁹                           | 0.04                                          | S, CH, M  | De Luca et al. (2012) |
| H₂Cl⁺    | 3 × 10⁻⁹                           | 0.02                                          | S, CH, M  | Neufeld et al. (2015a) |
| ArH⁺⁺⁺   | 3 × 10⁻¹⁰                          | 1 × 10⁻⁵                                     | S, HI, M⁺ | Schilke et al. (2019) |

*Assumes the following gas-phase elemental abundances relative to hydrogen in the diffuse ISM: carbon = 1.4 × 10⁻⁴; oxygen = 3.1 × 10⁻⁴; nitrogen = 6.8 × 10⁻⁵; fluorine = 1.8 × 10⁻⁵; sulphur = 1.8 × 10⁻⁷; chlorine = 3.2 × 10⁻⁶.

*Method for determination of hydride column density: V = visible or infrared observations of nearby stars; S = submillimeter, FIR (CH₃) or millimeter (H₂S) wavelength observations. Abundances determined from visible observations refer to the solar neighborhood while abundances determined from (sub)millimeter and FIR observations also probe the Galactic plane halfway between the Galactic center and the solar circle.

*Method for determination of H₂ or atomic hydrogen column density: UV = UV observations of H₂ Lyman and Werner bands; Re = reddening of background star; CH = submillimeter observations of CH; for an assumed N(CH)/(N(H₂)) ratio of 3.5 × 10⁻⁴; HI = HI 21 cm absorption line observations.

*Sample size: M = average (median) over multiple sources; L = average (mean) over line-of-sight to W31C.

*Median value excludes clouds in the Galactic Center, where the abundances are typically an order-of-magnitude higher.

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**Herschel:** The *Herschel* Space Observatory, a FIR and submillimeter satellite observatory (55 - 672μm) with a 3.5 m primary mirror, operated by ESA between 2009 and 2013, and with important participation from NASA.
Absorption spectra observed toward W31C. Left panel from top to bottom: spectra of H$_2$S $^{10}_{01}$ at 168.8 GHz (based on data published by Neufeld et al. (2015a)); CH$_2$π$_{3/2}^{3/2} - J = 3/2 - 1/2$ at 532.7/536.8 GHz (Gerin et al. 2010a); SH $^{10}_{3/2} - 3/2$ at 1381 GHz Neufeld et al. (2015a); HF $^{10}_{1} - 0$ at 1232 GHz; H$_2$O $^{11}_{00} - 00$ at 1113 GHz (Neufeld et al. 2010); NH $^{21}_{1} - 10$ at 974.5 GHz; NH$_3$ $^{21}_{1} - 11$ at 1215.2 GHz (Persson et al. 2010). Right panel from top to bottom: H$_i$ 21 cm (Winkel et al. in preparation); $^{13}$CH$_+^{1} - 0$ at 835.1 GHz; $^{13}$CH$^+$ $^{1} - 0$ at 830.2 GHz (Gard et al. 2012); ArH$^+$ $^{1} - 0$ at 617.5 GHz (Schilke et al. 2014); OH$^+$ $^{3}P_{3/2} - 3/2$ at 971.8 GHz; H$_2$O$^{+}$ $^{1}_{00} - 00$ at 1115 GHz (Gerin et al. 2010b); H$_2$Cl$^+$ $^{11}_{00} - 00$ at 485.4 GHz (Neufeld et al. 2012). For species with a partially-resolved hyperfine splitting (CH, SH, NH, OH$^+^{+}$, H$_2$O$^{+}$), black histograms show the observations and color histograms show the hyperfine-deconvolved spectra. For clarity, the spectra are separated by vertical offsets. The ArH$^+$ spectrum is expanded by a factor 4 (in addition to being translated) so that the relatively weak absorption is clearer.

Figure 5

Absorption spectra observed toward W31C. Left panel from top to bottom: spectra of H$_2$S $^{10}_{01} - 00$ at 168.8 GHz (based on data published by Neufeld et al. (2015a)); CH$_2$π$_{3/2}^{3/2} - J = 3/2 - 1/2$ at 532.7/536.8 GHz (Gerin et al. 2010a); SH $^{10}_{3/2} - 3/2$ at 1381 GHz Neufeld et al. (2015a); HF $^{10}_{1} - 0$ at 1232 GHz; H$_2$O $^{11}_{00} - 00$ at 1113 GHz (Neufeld et al. 2010); NH $^{21}_{1} - 10$ at 974.5 GHz; NH$_3$ $^{21}_{1} - 11$ at 1215.2 GHz (Persson et al. 2010). Right panel from top to bottom: H$_i$ 21 cm (Winkel et al. in preparation); $^{13}$CH$_+^{1} - 0$ at 835.1 GHz; $^{13}$CH$^+$ $^{1} - 0$ at 830.2 GHz (Gard et al. 2012); ArH$^+$ $^{1} - 0$ at 617.5 GHz (Schilke et al. 2014); OH$^+$ $^{3}P_{3/2} - 3/2$ at 971.8 GHz; H$_2$O$^{+}$ $^{1}_{00} - 00$ at 1115 GHz (Gerin et al. 2010b); H$_2$Cl$^+$ $^{11}_{00} - 00$ at 485.4 GHz (Neufeld et al. 2012). For species with a partially-resolved hyperfine splitting (CH, SH, NH, OH$^+^{+}$, H$_2$O$^{+}$), black histograms show the observations and color histograms show the hyperfine-deconvolved spectra. For clarity, the spectra are separated by vertical offsets. The ArH$^+$ spectrum is expanded by a factor 4 (in addition to being translated) so that the relatively weak absorption is clearer.

**SOFIA**: The Stratospheric Observatory For Infrared Astronomy is an airborne 2.7 m telescope, covering the wavelength range 1 - 655 $\mu$m, operated by NASA and the German Aerospace Center (DLR).

OH$^+$; SOFIA observations have enabled the first detection of interstellar SH, and the first heterodyne observations of the 2.5 THz ground state rotational line of OH.

Submillimeter absorption-line studies with Herschel and SOFIA have typically made use of strong continuum sources in the Galactic plane, at distances up to $\sim$ 11 kpc from the Sun and with sightlines that can intersect multiple diffuse clouds in foreground spiral arms. Thanks to the differential rotation of the Galaxy, different diffuse clouds along a single sightline give rise to separate velocity components in the observed absorption spectra. Herschel observations have been performed towards $\sim$ 20 such continuum sources, revealing $\sim$ 100 distinct components in which molecular column densities can be determined.

Figure 5 shows the spectra of a dozen hydride molecules observed along the sightline to W31C, a region of high-mass star formation located 4.95 kpc from the Sun, along with the H$_i$ 21 cm absorption line. All the spectra shown in Figure 5 show clear evidence for absorption by foreground material in
diffuse clouds along the sight-line. For some molecules (e.g. SH and H$_2$S), the observed absorption is concentrated into five or six narrow features with linewidths $\sim 1 - 3$ km s$^{-1}$; other molecules – including most of the molecular ions – show a more extended distribution in velocity space and are less strongly concentrated into narrow absorption components. Neufeld et al. (2015b) have presented a more quantitative examination of the similarities and differences between these absorption spectra with the use of Principal Component Analysis (PCA). Here, each optical depth spectrum (i.e. plot of optical depth against velocity) is represented as a linear combination of a set of orthogonal (i.e. uncorrelated) eigenfunctions, $S_j$, the latter chosen such that the first eigenfunction contains as much of the variation as possible, the second eigenfunction containing as much of the remaining variation as possible, and so forth. Typically, the spectrum of any species, $i$, may be represented by a linear combination of the first two or three eigenfunctions, $C_i S_1 + C_i S_2 (\pm C_i S_3)$, which provides an excellent fit to the observed optical depth spectra, and the coefficients within that linear combination – $C_i$ – can be used to describe the distribution of each absorbing species. Figure 6 shows the first three coefficients obtained from a joint analysis of ten species along the W31C sightlines. Here, diamonds indicate the coefficients obtained for each species in the $C_{i1}$-$C_{i2}$ (left panel) and $C_{i2}$-$C_{i3}$ (right) planes, and solid lines connect the origin to each diamond. In the limit where the first two principal components account for most of the variation in the spectra, the diamonds in the left panel lie on the unit circle, as explained by Neufeld et al. (2015b); moreover, the angle between the lines corresponding to any pair of species in that limit is equal to the arccosine of their correlation coefficient. The PCA results confirm that most of the molecular ions show a common distribution, which is similar to that of atomic hydrogen, while most neutral species - particularly NH$_3$ and H$_2$S - tend to follow a distribution that is uncorrelated with H$_i$. The ArH$^+$ molecular ion appears largely uncorrelated both with the other molecular ions and with the neutral molecules.

In Table 2, we summarize the typical hydride abundances derived for the diffuse ISM. In the case of molecular ions (with the exception of H$_2$O$^+$), these are shown relative to atomic hydrogen, whereas for neutral molecules, they are shown relative to H$_2$. In both cases, the corresponding abundances are also given relative to the gas-phase abundance of the relevant heavy element. The values shown in Table 2 indicate that most hydride molecules in diffuse gas are only minor reservoirs of the heavy element they contain, with most heavy elements remaining overwhelmingly in atomic or singly-ionized form. The notable exception is HF, which, in diffuse regions with a large molecular hydrogen fraction,
can account for most of the gas-phase fluorne. Chlorine is another element with a fairly strong ten-
dency toward hydride formation; in clouds with a modest H$_2$ fraction, H$_2$Cl$^+$ can account for several
percent of the gas-phase chlorine abundance. These behaviors are thought to reflect the thermoche-
matic considerations summarized in Figure 2 fluorine and chlorine are the only elements that can react
exothermically with H$_2$ when in their dominant stage of ionization (i.e. F and Cl$^+$) in diffuse clouds.

4. HYDRIDES IN DENSE, STRONGLY UV-IRRADIATED GAS

While many aspects of diffuse molecular clouds can be understood in the framework of low $A_V$, low
FUV field PDR models (for a review see Hollenbach & Tielens 1999), in this section we focus on the
presence of hydrides in more strongly UV-irradiated ($q > 10^3$ times the average interstellar radiation
field), and denser gas ($n_H > 10^6$ cm$^{-3}$). These are conditions typical of the surface of dense molecular
clouds illuminated by nearby massive stars, and also of the outer layers of irradiated protoplanetary
disks (e.g. proplyds). Such “dense PDRs” are regulated by the presence of stellar FUV photons
up to several magnitudes of extinction (high $A_V$). UV photons with energies higher than 13.6 eV
ionize hydrogen atoms but they are absorbed in the adjacent H II regions. FUV photons, however, do
dissociate molecules and ionize molecules and atoms with ionization potentials below 13.6 eV (C, S,
Si, Na, Fe, etc.). Therefore, like diffuse clouds, dense PDRs are predominantly neutral, with maximum
ionization fractions of $n_e/n_H > 10^{-4}$, roughly the gas-phase carbon abundance. The chemistry of dense
PDRs is driven by photo-reactions (Sternberg & Dalgarno 1995) and is also characterized by the warm
temperatures attained by the gas ($T > 100-1000$ K) and by the presence of large fractions of (FUV-
pumped) vibrationally excited molecular hydrogen, H$_2$ (e.g. Black & van Dishoeck 1987).

Despite the large FUV radiation fields, H$_2$ molecules form on the surfaces of relatively warm dust
grains ($T_{dust} > 50$ K for $q > 10^3$, e.g. Cazaux & Tielens 2004 Bron, Le Bourlot & Le Petit 2014 and
references therein). As the H$_2$ abundance increases from the PDR edge to the cloud interior, reactions
of H$_2$ with neutral and singly ionized atoms initiate the chemistry and lead to the formation of hydrides.
Owing to the higher gas and electron densities compared to diffuse clouds, the excitation temperatures rise
above the background temperature and rotational line emission is observed. Recent detections in
dense PDRs include NH$_3$, CH$_+$, SH$^+$, OH$^+$, H$_2$O, OH, HF, CH and H$_2$Cl$^+$ (e.g. Barla & Wilson 2003
Habart et al. 2010 Goicoechea et al. 2011 Nagy et al. 2013 van der Tak et al. 2012 2013 Neufeld et al. 2012).

4.1. The role of vibrationally excited H$_2$ in the chemistry

The absorption of FUV photons in the Lyman ($B^1\Sigma_u^- - X^1\Sigma_g^+$) and Werner ($C^1\Pi_u - X^1\Sigma_g^+$) bands pro-
duces molecular hydrogen in excited electronic states. 10% of absorptions are followed by emission
into the unbound continuum, leading to dissociation of the molecule. 90% of the absorptions, how-
ever, are followed by rapid radiative decay to the ground electronic state $X$. See an early historical
review by Field, Somerville & Dressler (1966) and later quantitative developments by e.g. Black &
Dalgarno (1976 and references therein). PDRs thus naturally produce large fractional abundances,
$f = n(H_2 v \geq 1)/n(H_2 v = 0)$, of vibrationally excited molecular hydrogen, H$_2^*$. In low density PDRs
($\leq 10^4$ cm$^{-3}$) H$_2$ is excited by FUV absorption followed by radiative fluorescent emission. The main
gas heating mechanism is the photoelectric effect on PAHs and grain surfaces. For higher gas densities,
collisional de-excitation through inelastic H-H and H$_2$-H collisions start to be important, and
collisional de-excitation of FUV-pumped H$_2$ can dominate the gas heating. In addition, pure rotational
lines of HD (Wright et al. 1999) and H$_2$ (Allers et al. 2005) can be detected. Their low critical
densities make them good diagnostics of the warm gas temperature.
Figure 7

(Left): PDR model adapted to the physical conditions in the Orion Bar: \( n_H = 10^8 \text{ cm}^{-3} \) and \( T = 3 \times 10^4 \). Abundances relative to \( n_H \) are shown for \( \text{H}_2 \), \( \text{H}_2(\nu \geq 1) = \text{H}_2^* \), \( \text{C}^+ \), and \( \text{CH}^+ \) as a function of depth \( A_V \) into the cloud. Also shown is \( f^* = n(\text{H}_2 \nu \geq 1)/n(\text{H}_2 \nu = 0) \), the fraction of vibrationally excited \( \text{H}_2 \) with respect to the ground vibrational state, and the gas temperature \( T \). For the \( \text{CH}^+ \) abundance profile, the dashed line is for a specific model that only considers reactions of \( \text{C}^+ \) with \( \text{H}_2 \) in the ground vibrationally state (\( \nu = 0 \)). The continuous curve shows the \( \text{CH}^+ \) abundance including also state-to-state reactions of \( \text{C}^+ \) with \( \text{H}_2^* \) (adapted from Agúndez et al. 2010). (Right): Velocity-resolved observations of the Orion Bar with Herschel/HIFI. \( \text{CH}^+ \ J=1-0 \) and \( 2-1 \) lines are broader than those of \( [\text{C}^\text{ii}] \) and CO \( J=16-15 \). This may be the signature of formation pumping as explained at the end of Sect. 4.3 (from Nagy et al. 2013).

The \( \text{H}_2 \nu = 1 \) levels have energies \( > 0.5 \text{ eV} \) (\( \sim 5800 \text{ K} \)) above the ground state \( \nu = 0 \) and this energy can be used to overcome the endothermicity (or energy barrier) of chemical reactions involved in the formation of some hydrides, thus enhancing their production rate in PDRs. A very favorable case is \( \text{CH}^+ \). As previously noted, the \( \text{C}^+ + \text{H}_2 \rightarrow \text{CH}^+ + \text{H} \) reaction is endothermic by \( \sim 4300 \text{ K} \) (see Figure 2), temperatures (\( T > 1000 \text{ K} \)) are required to produce significant amounts of \( \text{CH}^+ \) when \( \text{H}_2 \) is in the \( \nu = 0 \) state. Laboratory experiments (Hierl, Morris & Viggiano 1997) and quantum calculations (e.g. Zanchet et al. 2013b), however, show that the reaction becomes exothermic when \( \text{H}_2^* \) and not \( \text{H}_2(\nu = 0) \), is the reactant. The reaction rate \( k^* \) then reaches the Langlevin limiting case, and becomes almost independent of the temperature. In practice, enhanced \( \text{XH}^+ \) (or \( \text{XH} \)) hydride abundances will be produced through reactions \( \text{X}^+ + \text{H}_2^* \rightarrow \text{XH}^+ + \text{H} \) (or \( \text{X} + \text{H}_2^* \rightarrow \text{XH} + \text{H} \)) if the product \( f^* \Delta k(T) \) is larger than 1. Here, \( \Delta k(T) = k^*(T)/k^0(T) \) is the reaction rate ratio when \( \text{H}_2^* \) and \( \text{H}_2(\nu = 0) \) are the reactants respectively (see Agúndez et al. 2010). In addition, \( k^*(T) \), the specific reaction rate with \( \text{H}_2^* \), has to be large enough compared to other reactions removing the atom \( \text{X}^+ \) (or \( \text{X} \)), for example, \( \text{X}^+ \) neutralization reactions with PAHs and small grains.

Rotationally excited \( \text{CH}^+ \) emission lines were first detected toward planetary nebula NGC 7027 (Cernicharo et al. 1997). These lines arise from the warm and dense PDR surrounding the ionized nebula that is irradiated by the strong UV field from the hot central star (\( T_{\text{eff}} \approx 200,000 \text{ K} \)). The same pure rotation emission lines have been detected in the Orion Bar (Nagy et al. 2013) see Figure 7 (right) and in the irradiated surface of the protoplanetary disk around Herbig Be star HD 100546 (Thi et al. 2011). As there is no reaction pathway that can efficiently produce \( \text{CH}^+ \) in FUV-shielded cold gas, \( \text{CH}^+ \) is expected to peak near the PDR edge where \( \text{C}^+ \) and \( \text{H}_2^* \) are abundant (see Figure 7 left). A similar argument applies to \( \text{SH}^+ \), with the difference that the \( \text{S}^+ + \text{H}_2 \rightarrow \text{SH}^+ + \text{H} \) reaction is even more endothermic (\( \sim 10,000 \text{ K} \)) and only becomes exothermic when \( \text{H}_2 \) is in the \( \nu = 2 \) or higher vibrational states (Zanchet et al. 2013a). Line emission from both ions has been observed in the Orion Bar with
ALMA: The Atacama Large Millimeter/submillimeter Array is an ensemble of 66 (sub)millimeter telescopes operating between 80 and 900 GHz.

Herschel (Nagy et al. 2013), but $^{13}$CH$^+$ and SH$^+$ can be detected from ground-based telescopes such as ALMA. Note that rotationally excited CH$^+$ has also been recently observed in visible absorption (Oka et al. 2013) toward lower density PDR environments close to hot massive stars, where vibrationally excited H$_2$ is also observed in FUV absorption (Rachford, Snow & Ross 2014).

The role of FUV-pumped H$_2$ in the chemistry may also be important at the scales of entire molecular cloud complexes. In template star-forming regions like Orion, >98% of the large-scale near-IR H$_2$ emission is thought to arise from FUV-excited fluorescent emission in PDR gas (Luhman et al. 1994). This widespread H$_2$ emission traces the extended molecular gas that is illuminated by the strong FUV radiation field from massive stars in the Trapezium cluster. Its presence likely explains the large-scale CH$^+$ $J$=1-0 emission detected in Orion molecular cloud (J.R. Goicoechea priv.comm.). The high abundances of H$_2$ in local massive star-forming regions may have consequences for the interpretation of hydride spectra in the extragalactic context, as many actively star-forming galaxies are dominated by PDR emission. In diffuse molecular gas (much lower density and FUV fluxes), the H$_2$ abundance and $f^+$ fractions are significantly lower. Indeed, the large CH$^+$ and SH$^+$ column densities inferred from line absorption observations of diffuse clouds cannot be explained by standard PDR models adapted to the $n_H$=100 cm$^{-3}$ and $\chi$=1 conditions prevailing in these clouds (e.g. Godard et al. 2012 and references to older models therein).

4.2. Oxygen hydrides

Relatively low water vapor abundances are expected in dense PDRs. H$_2$O has a high adsorption energy and thus it freezes at $T_{\text{dust}}$<100 K in dense cloud conditions (as compared to ~20 K for CO). Photodesorption of water ice mantles takes place in PDRs but H$_2$O molecules are readily photodissociated by the intense FUV radiation field (Hollenbach et al. 2009). This process results predominantly in OH + H (e.g. van Dishoeck, Herbst & Neufeld 2013 hereafter vD13). Low excitation H$_2$O rotational lines have been observed toward high FUV flux PDRs such as the Orion Bar (Habart et al. 2010; Choi et al. 2014) and Mon R2 (Pilleri et al. 2012). The inferred gas-phase H$_2$O abundances are below a few 10$^{-7}$. Rotationally excited OH emission lines have been also detected in the Orion Bar. They are consistent with a OH/H$_2$O>1 column density ratio (Goicoechea et al. 2011), similar to the diffuse cloud values, whereas OH/H$_2$O<1 ratios are typically observed toward warm shocked gas (see next Section). Regarding OH formation, the dominant route near the edge of a strongly UV-irradiated PDR is the endothermic reaction O + H$_2$ $\rightarrow$ OH + H (see the first OH abundance peak in Figure 5 right). However, the reaction remains slow when the H$_2$ is vibrationally excited (Sultanov & Balakrishnan 2005). Consequently, the OH formation rate is likely more sensitive to the gas temperature than to the H$_2$ abundance. For lower FUV fields and temperatures, OH forms from H$_2$O$^+$ electron recombination and from grain surface reactions (e.g. Hollenbach et al. 2009, 2012).

In the Milky Way, OH$^+$ rotational line emission has been detected toward high electron density environments: the Orion Bar (van der Tak et al. 2013), planetary nebulae hosting hot central stars with $T_{\text{e}}$>100,000 K (Aleman et al. 2014), and toward the Supernova remnant in the Crab Nebula (Barlow et al. 2013). The non-detection of H$_2$O$^+$ and H$_2$O$^+$ emission in these environments indicates that OH$^+$ lines arise in gas layers where most hydrogen is in atomic form, and OH$^+$ is predominantly formed by the O$^+$ + H$_2$ $\rightarrow$ OH$^+$ + H exothermic reaction. Figure 5 left shows predictions of a steady-state PDR model for a $n_H$=10$^6$ cm$^{-3}$ cloud illuminated by a FUV field that is 100 times the mean ISRF. These conditions are representative of a molecular cloud close to massive O and B stars. The model includes reactions with PAHs and freeze-out of gas-phase species (important at $A_V$>4). It shows that OH$^+$ peaks closer to the PDR edge than other oxygen hydrides. Figure 5 right shows the results for a higher density, $n_H$=10$^9$ cm$^{-3}$, and higher FUV irradiation model, $\chi$=10$^3$. These conditions are more typical of
Figure 8
Predicted gas-phase abundances of several hydrides with respect to H nuclei as a function of depth \( A_V \) into the cloud for PDRs with \( n_H = 10^4 \) cm\(^{-3}\), \( \chi = 100 \), and \( \zeta_{CR} = 2 \times 10^{-16} \) s\(^{-1}\) (left), and with \( n_H = 10^6 \) cm\(^{-3}\) and \( \chi = 10^3 \) (right). From Hollenbach et al. (2012).

the compressed PDR layers at the boundary of a H\( \text{II} \) region surrounding a massive star or the surface layers of protoplanetary disks. In this model, H\(_2\) collisional de-excitation dominates the gas heating and the gas attains higher temperatures (\( T \approx 1000 \) K at \( A_V = 1 \)). This triggers a fast warm gas-phase in which many endothermic reactions can proceed rapidly. The dense PDRs located at the walls of outflow cavities irradiated by a high mass young stellar object have been modeled by Bruderer et al. (2010), who predicted high abundances of CH\(^+\), OH\(^+\) and NH\(^+\) within such regions.

4.3. Formation pumping and the excitation of reactive hydride ions
Reactive collisions (collisions that lead to a chemical reaction) influence the excitation of molecules when the time-scale of the chemical reaction becomes comparable, or shorter, than that of nonreactive collisions. This makes the lifetime of the molecule so short that it does not get "thermalized" by collisions with non reactive species, or by radiative absorptions of the background radiation field. This is referred to as "formation pumping"; the molecule retains an excited state due to its formation, and a proper treatment of the molecule excitation requires including chemical formation and destruction rates in the statistical equilibrium calculation determining the level populations (e.g. Black 1998). Reactive ions such as CH\(^+\) or OH\(^+\) are a special kind because they can be destroyed on nearly every collision with the most abundant species: H\(_2\), H and e\(^-\) (OH\(^+\) in particular does not react with H). Detailed CH\(^+\) excitation models show that formation pumping dominates the population of CH\(^+\) rotationally excited levels in PDRs such as the Orion Bar (Godard & Cernicharo 2013). In addition, the effects of molecule destruction and molecule formation in excited levels needs to be taken into account in chemical networks. It is becoming common to refer to "state-to-state" chemistry when the specific state-dependent reaction rates are included in models.

Reactions of C\(^+\) with H\(_2\)(\(v=0, J>7\)) or with H\(_2\)(\(v\geq1\)) are exothermic and drive the CH\(^+\) production in PDRs such as the Orion Bar (see Section 4.1). Therefore, CH\(^+\) formation results in an excess of
energy equivalent to several thousand K. This energy may be redistributed into translational motion of
the newly formed CH$^+$ molecules (Black 1998). CH$^+$ reacts so quickly with H, H$_2$ and electrons that
its translational motions may never thermalize to the gas kinetic temperature. The broader CH$^+$ \textit{J}=1-0
emission line widths observed toward the Orion Bar (\sim 5.5 \text{ km s}^{-1}, corresponding to a temperature of
several thousand K) compared to those of other molecular lines (usually \sim 2-3 \text{ km s}^{-1}, see Figure 7
right) has been interpreted as the signature of CH$^+$ formation pumping and of non-thermal velocity
distributions (Nagy et al. 2013). Formation pumping also influences OH$^+$ excitation (Gómez-Carrasco
et al. 2014) and may also explain the broad OH$^+$ emission lines (van der Tak et al. 2013).

5. HYDRIDES IN SHOCKS AND TURBULENT DISSIPATION REGIONS

5.1. Shocks

Several astrophysical phenomena – including protostellar outflows and supernovae – give rise to supersonic motions in the interstellar medium, and these motions can drive shock waves that heat and compress the gas. Such shock waves modify both the chemistry of – and the emission from – interstellar hydrides, greatly enhancing the abundances of certain species, populating high-lying rotational states, and triggering strong maser amplification in specific transitions of OH and H$_2$O.

The chemical effects of shock waves include the sputtering of dust grains, which releases grain materials into the gas-phase, and the enhancement of gas-phase endothermic reactions that are negligibly slow at the typical temperatures ($T \lesssim 80$ K) of cold interstellar gas clouds but can become rapid behind shock waves. In dense molecular clouds, where dust grains are coated with icy grain mantles, the sputtering of grain mantles has a profound effect upon the water vapor abundances behind shocks. The sputtering process has been the subject of several theoretical studies (Draine, Roberge & Dalgarno 1983; Jiménez-Serra et al. 2008; Gusdorf et al. 2008), which suggest that grain mantles are completely removed in shocks propagating at velocities, $v_s$, larger than $\sim 20$ – 25 km s$^{-1}$, resulting in the release of water and other volatile grain mantle materials into the gas-phase. Observationally, the interstellar water vapor abundance measured by satellite observatories such as the Submillimeter Wave Astronomy Satellite (SWAS), Odin and Herschel is known to vary by more than three orders of magnitude (see vD13 and references therein), with the largest abundances observed in warm shocked regions associated with protostellar outflows and supernova remnants. Here, the water vapor abundance can reach several $\times 10^{-4}$ relative to hydrogen nuclei, an abundance comparable to that of carbon monoxide. However, many determinations of the water vapor abundances in shocked regions (vD13, their Table 4) are considerably smaller and lie below the predictions for shocks capable of sputtering icy grain mantles. This discrepancy may reflect the fact that many abundance determinations are averages over a mixture of shocks of varying velocity, some of which are too slow to sputter mantles, or due to UV irradiation of the shocked gas lowering the H$_2$O abundance and enhancing OH (Karska et al. 2014; Goicoechea et al. 2015). In a recent study (Neufeld et al. 2014) of the far-IR line emission detected by Herschel and Spitzer from shocked gas in NGC 2071, W28, and 3C391, the relative line intensities for multiple transitions of H$_2$O, CO and H$_2$ were found to be in acceptable agreement with standard theoretical models for nondissociative shocks that predict the complete vaporization of grain mantles in shocks of velocity $\sim 25$ km s$^{-1}$, behind which the characteristic gas temperature is $\sim 1300$ K and the H$_2$O/CO ratio is 1.2.

The second chemical effect of shock waves is to selectively increase the abundances of molecules that can be produced rapidly by endothermic reactions that are slow at the temperatures of cold quiescent gas clouds. Behind shock waves, elevated gas temperatures $\sim \text{few} \times 10^3$ to $\sim \text{few} \times 10^4$ K can be sufficient to overcome the barriers for several of the endothermic H-atom abstraction reactions listed in Fig. 2, greatly increasing the predicted abundances of CH$^+$, SH$^+$, CH, SH, OH and H$_2$O.
tion to the effects of the elevated temperatures behind interstellar shock waves, velocity drifts between the ions (which are coupled to the magnetic field) and the neutral species (which are not) can lead to an additional enhancement in the rates of ion-neutral reactions. Magnetohydrodynamic shock waves propagating at $\sim 10$ km s$^{-1}$, in which such velocity drifts are present, have been invoked (e.g. Draine & Katz 1986; Pineau des Forêts, Roueff & Flower 1986; Pineau des Forêts et al. 1986) to explain large discrepancies between the observed abundances of CH$^+$, SH$^+$, and SH in diffuse molecular clouds and the predictions of standard photochemical models for cold ($T \leq 80$ K) diffuse gas.

In addition to their chemical effects, shock waves propagating in dense molecular gas also populate high-lying rotational states of hydrides that lead to a distinctive emission spectrum dominated by high-lying, collisional-pumped rotational transitions of H$_2$, CO, H$_2$O, and OH (Chernoff, McKee & Hollenbach 1982; Draine & McKee 1993). Figure 9 shows a comparison of the FIR spectra of three environments: a molecular outflow and associated shocked gas, the Galactic Center combining dense gas and foreground absorption by diffuse gas, and a highly UV-irradiated diffuse PDR. While the shocked region shows intense OH and H$_2$O emission lines, the dense and warm environment of the Galactic Center region has a more diverse spectrum with other hydrides like NH$_3$, H$_3$O$^+$ and H$_2$O$^+$ showing up, indicating the presence of UV and CR irradiated molecular gas. The PDR spectrum is dominated by strong [Cn] and [O$_3$] emission, with faint lines from H$_2$O and rotationally excited CH$^+$.

In the case of OH, mid-IR transitions with upper state energies, $E_u/k_B$ of several $10^4$ K can also be excited following the photodissociation of H$_2$O by shock-generated UV radiation; this phenomenon,
observed by Spitzer toward HH 211 and illustrated in Figure 10 (Tappe et al. 2008), occurs because the photodissociation of H$_2$O following absorption of Lyman alpha radiation leaves OH in states of rotational quantum number 30 - 50.

Along with the normal (non-inverted) OH and H$_2$O line radiation emitted by warm shocked regions, strong maser action is observed in several transitions: these include the 22 GHz 6$_{16}$ - 5$_{23}$ transition of H$_2$O, frequently observed from outflow-driven shock waves along with several submillimeter water maser transitions (e.g. Neufeld et al. 2013, and references therein), and the 1720 MHz transition of OH, a signpost of supernova-driven shock waves (e.g. Frail & Mitchell 1998). Maser lines are typically characterized by small spots of emission, often unresolved even in long-baseline interferometric observations, narrow line width, and variability on timescales of months or less. Emission in the 22 GHz water maser transition, in particular, can achieve extraordinarily high brightness temperatures that may exceed 10$^{14}$ K. Theoretical models for water maser emissions invoke either fast, dissociative jump (“J”-type) shocks (Elitzur, Hollenbach & McKee 1989; Hollenbach, Elitzur & McKee 2013), or slower non-dissociative “C-type” shocks in which the fluid velocities vary continuously (Kaufman & Neufeld 1996). Where multiple water maser transitions are observed, maser line ratios can provide constraints on the gas temperature in the masing region and the nature of the shocks that are present. Paradoxically, non-dissociative shocks can produce hotter molecular material than faster dissociative shocks, where molecules are quickly destroyed behind the shock front and are reformed only after the gas has cooled to ~ 500 K. In some maser sources, gas temperatures of at least ~ 900 K are implied by the observed water maser line ratios, indicating the presence of non-dissociative shocks (Melnick et al. 1993). Where supernova-driven shock waves encounter molecular clouds, widespread 1720 MHz OH maser emission is observed; here, the enhanced column densities of OH needed to explain the observed maser emission are believed to result from the effects of X-rays and/or cosmic rays in dissociating H$_2$O to form OH (Wardle & Yusef-Zadeh 2002).
5.2. Turbulent dissipation regions

Turbulent dissipation regions (TDR; Godard, Falgarone & Pineau Des Forêts 2009; Godard et al. 2012; Godard, Falgarone & Pineau des Forêts 2014) represent an alternative but related scenario in which endothermic reaction rates can be enhanced as a result of locally-elevated gas temperatures and ion-neutral drift. In this scenario, molecules are produced in turbulent dissipation regions, represented as vortices in which the ion-neutral drift is induced by the ambient magnetic field. Model parameters include the physical conditions in the ambient medium ($n$, $\chi$, $A_V$, $\zeta$) along with four adjustable variables describing the turbulence dissipation rate, the ion-neutral drift, the vortex magnitude and lifetime. Given reasonable assumptions about the parameters that describe the turbulence, TDR models have been successful in accounting for the observed abundances of CH$^+$, SH$^+$ and SH in diffuse molecular clouds. Figure 11, a ternary diagram from the recent study of Godard, Falgarone & Pineau des Forêts (2014), shows – for five diatomic molecules – the relative fractions of the total column density in three separate components: (1) ambient material currently unaffected by turbulent dissipation; (2) material within the vortices that are the assumed sites of turbulent dissipation in this model (“vortex”); (3) material that has passed through a dissipative vortex and is currently relaxing to the ambient chemistry (“relaxation”). This model indicates that the, CH$^+$ and SH$^+$ column densities are dominated by material in dissipative vortices (component 2); the HF column density, by contrast, originates primarily in the ambient gas (component 1). The behavior of CH depends on the density, with the dominant component switching from vortex (component 2) to the ambient gas (component 1). The different behaviors predicted for these four hydrides reflect the fact that the production of CH, CH$^+$ and SH$^+$ is endothermic, while that of HF is exothermic. While the extensive chemical calculations leading to the results shown in Fig. 11 are based upon a simple characterization of interstellar turbulence with several adjustable parameters, a complementary approach makes use of more sophisticated numerical simulations of turbulence (Myers, McKee & Li 2015). To date, studies adopting the latter approach have included a more limited chemistry focused on the CH$^+$ problem.

In both shocks and TDRs, the dynamical timescales can be short compared to the time needed to
establish a chemical equilibrium in which the rates of molecular formation and destruction are equal; a time-dependent treatment of the chemical rate equations is therefore needed. Simple shock models are sometimes described as ”steady-state” models if the physical and chemical conditions are non-varying in a particular inertial frame, but the meaning here is different from ”chemical quasi-equilibrium” in which the net rates of formation and destruction are nearly equal for each species. We note also in this context that even ”chemical quasi-equilibrium”, which is often a good approximation where shocks and TDRs are absent, is quite different from thermochemical equilibrium (TE), in which the rate of every chemical process equals that of its reverse process and the molecular abundances are determined solely by thermodynamics. The condition of TE never applies in the ISM, because of the presence of cosmic-rays and – in diffuse and translucent interstellar clouds – of UV radiation that would be entirely absent in thermal equilibrium at the gas kinetic temperature.

6. HYDRIDES IN DENSE AND SHIELDED GAS

Many neutral hydrides stay abundant in shielded regions, even in dense prestellar and protostellar cores. At the low gas and dust temperatures of these regions ($\sim$ 10 K), molecules freeze on dust grains, building an ice layer. Ice mantles also grow thanks to the condensation of atoms, which, by hydrogenation, contribute to the formation of saturated hydrides: H$_2$O for oxygen, CH$_4$ for carbon and NH$_3$ for nitrogen. Figure 12 shows a representative IR spectrum of a massive star forming region with prominent absorption features tracing the composition of the ice mantle. Water ice is the dominant species, with NH$_3$ and CH$_4$ reaching a few percent of the water ice (Boogert, Gerakines & Whittet 2015).

The low temperatures ($T \sim$ 10 K) and absence of FUV radiation represent a favorable environment
for fractionation, the chemical process leading to a higher fraction of an isotope in a given molecule (an isotopologue) than the ratio of the elemental abundances. The most efficient process is deuterium fractionation, in which one or several hydrogen atoms are substituted by deuterium atoms. As reviewed by Caselli & Ceccarelli (2012), deuterium fractionation can be very efficient in cold regions, with several molecules reaching abundance ratios [XH]/[XD] exceeding one percent, while the elemental D/H ratio is about 2 × 10^{-5}. Fractionation may also involve other isotopes like ^13C, ^18O, ^17O or ^15N. Fractionation in D or ^15N are studied to relate ISM processes with the formation of the first solids in the solar system, since primitive material shows localized D and ^15N enhancements (Aléon 2010).

In the dense gas around protostars (n(H_2) > 10^4 cm^{-3}), the dust temperature increases up to the ice sublimation threshold (T = 100 K for water ice). The gas phase abundances of neutral hydrides significantly increase in these hot cores (for massive stars) and hot corinos (for low mass stars). These objects exhibit a rich spectrum, including numerous hydride emission lines at (sub)millimeter wavelengths (e.g. Figure 8), and absorption lines in the infrared, revealing a high abundance of water vapor (Boonman et al. 2003), methane and CH_3 (e.g. Knez et al. 2009) in the hot gas within a few hundred AU of the protostar. Highly excited NH_3 inversion lines at cm wavelengths also trace the same region (Goddi, Zhang & Moscadelli 2015). Such spectra provide key information about the temperature and velocity field in the vicinity of the protostars.

Hydrides, and especially water and OH, are interesting probes of protoplanetary disks, since different lines can be used to probe different regions: ground state lines trace the cold outer regions of the disk, while excited lines trace the illuminated surface closer to the central protostar. Following the first detections of water vapor in the inner region (within a few AU) (e.g. Salyk et al. 2008; Carr & Najita 2008), Herschel/PACS spectroscopy in the FIR has confirmed the presence of OH and H_2O in protoplanetary disks around both T Tauri and Herbig AeBe stars, the latter having a higher OH/H_2O abundance ratio than the former (Fedele et al. 2013). Both ortho and para H_2O ground state lines have been detected by Herschel/HIFI towards TW-Hya (Hogerheijde et al. 2011). Most of the water is frozen as ice in the disk mid-plane, and water vapor represents a very minor fraction of the water reservoir. Because of the high line opacity, the interpretation of the detected signals requires a good understanding of the disk geometry and sophisticated radiative transfer calculations. Other Herschel detections include CH^+ tracing the UV-irradiated disk surface, and o-NH_3 associated with cool layers (Thi et al. 2011).

### 6.1. Water and oxygen hydrides

In dense gas, water is the main oxygen hydride, together with hydroxyl radical OH, and their deuterated counterparts HDO, D_2O, OD, while the main ion is H_3O^+. While water ice is ubiquitous in molecular clouds, with a detection threshold of about 3 magnitudes of visual extinction (Whittet et al. 2013), the detection of water vapor in cold cores is very challenging because of the need of a spaceborne system combining high sensitivity and high spectral resolution. Thanks to Herschel/HIFI, water vapor was detected towards the L1544 prestellar core (Caselli et al. 2012). The line profile shows an inverse P-Cygni profile, with a blue-shifted emission peak and a red-shifted absorption tracing the slow gravitational collapse of this core. Although the water abundance relative to H_2 is very small, ∼ 10^{-9}, the mere presence of water vapor in such a cold (T = 7 K) and dense (n(H_2) > 10^9 cm^{-3}) environment indicates that the desorption induced by the secondary FUV photons (τ = 10^{-4}, Prasad & Tarafdar 1983) produced during the interaction of cosmic rays with molecular hydrogen is efficient. This observation is consistent with predictions from chemical models such as those shown in Figure 8 where water vapor is present at a cloud depth of a few magnitudes of extinction (Hollenbach et al. 2012). In dense and cold gas, water is cycled between the gas and solid phase through H_2O^+. Hence

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**JWST:** The James Webb Space Telescope, a 6.5 m telescope, operating between 0.6 and 28 µm, will be launched in late 2018.
the water OPR is expected to deviate from thermal equilibrium in a similar way as for NH$_3$ (Sipila, Caselli & Harju 2015). Observations of H$_3$O$^+$ or of its deuterated counterparts H$_2$DO$^+$, HD$_2$O$^+$ and D$_2$O$^+$ could provide further constraints on the cosmic ray ionization rate. While no detection towards cold cores has been achieved so far, several H$_3$O$^+$ lines show up in emission towards massive star forming regions tracing the presence of energetic radiation and/or cosmic rays produced by the embedded protostar (Benz et al. 2013).

Although most rotational water lines are not observable from the ground, because of the presence of water vapor in the Earth atmosphere, the transmission is good for rotational lines of heavy water. Both HDO (Beckman et al. 1982) and D$_2$O (Butner et al. 2007) are present with a moderate level of fractionation. The number of measurements of HDO/H$_2$O and D$_2$O/HDO abundance ratios in the same source is small. In Orion-KL, the prototypical hot-core, HDO/H$_2$O $\sim 3 \times 10^{-3}$, a factor of two larger than D$_2$O/HDO (Neill et al. 2013). Most species show a D/H ratio in the range $2 - 8 \times 10^{-3}$ in this source. As reviewed by Caselli & Ceccarelli (2012), the deuterium fractionation of water vapor is a complex phenomenon, because it is controlled by both solid-phase and gas-phase processes and is likely time-dependent given the similarity of the chemical time scales with the free fall time of dense cores. The OD radical has been detected with the SOFIA airborne observatory in the cold envelope surrounding the low mass protostar IRAS16293-2422 (Parise et al. 2012). The large OD/HDO abundance ratio (OD/HDO $= 20 - 90$) remains to be fully explained. The dissociative recombination of H$_2$DO$^+$ may contribute to the OD enhancement, but a quantitative assessment awaits a measurement of the branching ratios toward HDO and OD. Because of their large critical densities and upper energy levels, the sole HDO transitions detectable in cold cores are the two ground state transitions at 465 GHz (1$_{01} - 0_{00}$) and 894 GHz (1$_{11} - 0_{00}$). In hot cores and hot corinos the conditions are favorable for collisional excitation of many HDO levels, leading to a richer spectrum. For a collapsing core around a massive protostar, the HDO ground state transitions are particularly sensitive to the velocity field in the collapsing envelope while the excited lines probe the hot inner region (e.g. Coutens et al. 2014). Like H$_2$O, D$_2$O has two spin symmetry states, with $\text{p-D}_2\text{O}$ being the more stable species. $\text{o-D}_2\text{O}$ has its lowest rotational state at an energy 17 K above that of $\text{p-D}_2\text{O}$, and ortho-states have a spin degeneracy twice that of para-states. From Herschel observations of both $\text{p-D}_2\text{O}$ and $\text{o-D}_2\text{O}$, Vastel et al. (2010) concluded that the OPR is consistent with the statistical value of 2.

6.2. Methane and carbon hydrides

As it is for oxygen hydrides, the competition between condensation and desorption is also important for carbon hydrides in dense and FUV-shielded gas. There are, however, two important differences with oxygen: i) the carbon reservoir is CO and not methane, ii) carbon hydride radicals (CH, CH$_2$, CH$_3$) and ions (CH$^+$) initiate the organic chemistry and therefore play a pivotal role in the formation of a large fraction of the molecules present in the ISM. Another interesting property of the methylidyne radical, CH, is the linear scaling of its column density, deduced from the intensity of its A-doubling transitions at 3.3 GHz, with that of H$_2$ up to $A_V \sim 3$ mag (Mattila 1986; Chastain, Cotten & Mag-Jeannin 2010). Although these lines are inverted, with negative excitation temperatures, their integrated intensity approximately scales with the CH column density (Liszt & Lucas 2002). Herschel observations of the CH ground state rotational lines confirm this behavior: towards the low mass protostar IRAS16293-2422, CH probes the cold envelope (Bottinelli et al. 2014), while in more massive sources CH shows a combination of emission and absorption features (Gerin et al. 2010b), indicating that CH is present in the dense material. The methylene radical, CH$_2$, shares the same chemistry as CH. Its ground state transition has been detected by ISO (Polehampton et al. 2005) following its identification in Orion-KL (Hollis, Jewell & Lovas 1995).
Methane is best probed by infrared spectroscopy using either ground-based or space-born telescopes in the 8 μm region (Lacy et al. 1991; ¨Oberg et al. 2008). Frozen methane has an abundance ∼ 5% that of water ice, supporting a formation process through sequential hydrogenation of carbon on grain surfaces. The gas phase abundance is more uncertain and ranges between 10^{-8} and 10^{-6} relative to H_2. Even for the highest abundances, most of the interstellar methane is in solid form.

Deuterium fractionation is predicted to be very efficient for carbon hydrides, since deuterated methylum CH_2D is one of the main actors in enriching molecules in deuterium. CH_2D' is operating in lukewarm regions (T ∼ 30 – 70 K) where the kinetic temperature is too high for H_2D' to be enriched. The DCN and HDCO molecules are typical products of CH_2D' induced chemistry, with observed fractionation levels consistent with chemical models (Roueff et al. 2013). Unfortunately, no astronomical detection of the related species CD and CHD has been reported so far. Further tests involve the search for CH_3D'. Its rotational spectrum has been measured by Amano (2010), and a tentative detection has been reported towards Orion-KL by Roueff et al. (2013), which awaits confirmation from observations of a less spectrally crowded region. Because of its small dipole moment of 0.3 Debye, CH_3D' rotational lines are weak at the predicted abundance level. Deuterated methane CH_3D has a non-zero albeit small dipole moment (0.0057 D), allowing observations of rotational transitions from the ground. After a very deep integration, Sakai et al. (2012) reported a tentative detection towards the IRAS04368+2557 protostar in the L1527 core. Further searches for CH_3D are needed to confirm this detection, which implies rather large CH_3D (∼ 3 × 10^{-7}) and CH_4 (∼ 4 × 10^{-6}) gas phase abundances, and very little methane left on grain mantles.

6.3. Ammonia and nitrogen hydrides

Nitrogen hydrides are mainly formed in the gas phase through a chain of hydrogen abstraction reactions starting from N^+ + H_2 → NH^+ + H. This reaction is slightly endothermic (Fig. 2), and therefore is
more efficient for \(O-H_2\) than for \(P-H_2\). Because of the rather low formation rate in \(P-H_2\) enriched gas, a formation route on grain surfaces has also been suggested. Subsequent hydrogen abstraction reactions \(\text{NH}_2^+ + H_2 \rightarrow \text{NH}_{3+1} + H\) with \(n = 1, 2, 3\) followed by dissociative recombination reactions lead to the molecular ions \(\text{NH}_2^+\), \(\text{NH}_3^+\) and \(\text{NH}_4^+\), and the neutral hydrides \(\text{NH}, \text{NH}_2\) and \(\text{NH}_3\). The detection of \(\text{NH}, \text{D}^+\) by Cernicharo et al. (2013) nicely confirms this theoretical scheme. \(\text{NH}\) is also formed as a secondary product of the dissociative recombination reaction of \(\text{N}_2^+\) (Vigren et al. 2012). In dense clouds, the abundances of nitrogen hydrides are dominated by ammonia, with \(\text{NH}:\text{NH}_2:\text{NH}_3 = 3:1:19\) for the dense core around the protostar IRAS16293-2422 (Le Gal et al. 2014). The excess of \(\text{NH}\) over \(\text{NH}_2\) is explained by its additional formation route from the dissociative recombination of \(\text{N}_2H^+\).

Ammonia has two spin symmetry states, \(o-\text{NH}_3\) with \(K\) values multiple of three and \(P = 0\), and \(p-\text{NH}_3\) for other \(K\) values. The energy difference between \(o-\text{NH}_3\) and \(p-\text{NH}_3\) is 2.15 K, and the high temperature value of the OPR ratio is 1, while an excess of \(o-\text{NH}_3\) is expected at temperatures lower than 50 K. As a symmetric top with two equilibrium configurations, ammonia exhibits inversion transitions between equivalent rotational states. While the low energy \(\text{NH}\) inversion transitions probe the para species, the first \(o-\text{NH}_3\) state accessible from the ground is the \((J, K) = (3, 3)\) level at 120 K above ground. Therefore most \(\text{NH}_3\) measurements in dense cores only trace \(p-\text{NH}_3\), and the total ammonia column density is derived assuming an ortho-to-para ratio (OPR) of one. Using Herschel absorption data on \(o-\text{NH}_3\) and \(p-\text{NH}_3\), Persson et al. (2010) measured an anomalous value of the OPR ratio of 0.7. In \(P-H_2\) enriched gas, the chain of ion-molecule reactions forming \(\text{NH}_3\) favors the formation of \(p-\text{NH}_3\) due to spin statistics selection rules (Rist et al. 2013; Faure et al. 2013). This effect could be prominent in cold cores, with predicted OPR \(\sim 0.5\) for \(\text{NH}_3\). The deficit in \(o-\text{NH}_3\) implies a small error in the total \(\text{NH}_3\) column density deduced from \(p-\text{NH}_3\) observations. The amidogetic radical \(\text{NH}_2\) is formed in the same chain of gas phase reactions as ammonia. With two identical protons, \(\text{NH}_2\) has two spin symmetry states, the ortho state with a spin multiplicity of three is the most stable, and the para state with a spin multiplicity of one, with an energy difference of 30 K. As for ammonia, the \(\text{NH}_2\) OPR is sensitive to the presence of an excess of \(p-\text{H}_2\), and can reach values lower than 3, which are not permitted in thermal equilibrium, in \(p-\text{H}_2\) enriched gas (Le Gal et al. 2014). So far only a handful of measurements of the \(\text{NH}_3\) and \(\text{NH}_2\) OPR are available (Persson et al. 2015). Such measurements may be able to put constraints on the \(H_2\) OPR in dense and shielded gas.

Ammonia is a good tracer of both prestellar and protostellar cores, with a fractional abundance relative to \(H_2\) of \(\sim 10^{-8}\) (Bergin & Tafalla 2007). It remains undepleted in the gas phase up to relatively large densities (\(\sim 10^6\) cm\(^{-3}\)), in contrast to the case of CO. As illustrated in Figure 13 all deuterated ammonia isotopologues have been detected in the ISM: \(\text{NH}_2D, \text{ND}_2H, \text{ND}_3\) (Roueff et al. 2005), as well as the \(^{15}\text{N}\) variants: \(^{15}\text{NH}_3\) (e.g. Lis et al. 2010b) and \(^{15}\text{NH}_2D\) (Gerin et al. 2009), and even \(^{15}\text{NH}, \text{D}^+\) (Cernicharo et al. 2013). The deuterated ammonia isotopologues are better tracers of the cold inner regions of prestellar cores, where most molecules are frozen onto grains, than is \(\text{NH}_3\) itself, with fractionation levels above 10% in such regions (e.g. Daniel et al. 2013). The fractionation of ammonia and its precursors \(\text{NH}\) and \(\text{NH}_2\) is most efficient at temperatures lower than \(\sim 20\) K because it involves reactions with \(\text{HD}, \text{H}_2\text{D}^+, \text{D}_2\text{H}^+\) and \(\text{D}_3\) that are enhanced at temperatures below 20 K (Roueff, Loison & Hickson 2015). \(\text{ND}\) has been detected (Bacmann et al. 2010), with \([\text{ND}] / [\text{NH}]\) reaching \(\sim 10^{-5}\), a value similar to that observed for \([\text{NH}_2D] / [\text{NH}_3]\), but with a large uncertainty because of the difference in excitation between \(\text{NH}\) and \(\text{ND}\).

At low temperatures, nitrogen may become fractionated, leading to a possible difference between the elemental isotopic ratio \(^{15}\text{N}/^{14}\text{N}\) and the abundance ratio of nitrogen-bearing species. The topic is of interest because analysis of primitive solar system material as found in carbonaceous chondrites or in micro-meteorites have led to the identification of specific regions with isotopic ratios very different from the bulk, in either \(D/H\), \(^{15}\text{N}/^{14}\text{N}\) or both (Aléon 2010). The difference between the \(^{15}\text{N}/^{14}\text{N}\)
isotopic ratio in the Sun (and the solar system), 2.3×10⁻³, and that of the Earth, 3.8×10⁻³, also indicates that active fractionation processes were operating in the early solar system. Following the evolution of D/H and ¹⁵N/¹⁴N in interstellar molecules along the formation of a protostar and its circumstellar disk is therefore a means of constraining the chemical evolution of the star forming system and the formation of its primitive bodies. So far, measuring the ¹⁵N/¹⁴N isotopic ratio has proven to be much more difficult than D/H because of the large dynamical range required. Chemical models have investigated the coupled fractionation of hydrogen, carbon, and nitrogen, and also the dependence with time during the collapse. The prediction is that NH₃ should preserve within 20% the original nitrogen isotopic ratio, unlike other species such as HCN which could become highly fractionated (Wirström et al. 2012; Roueff, Loison & Hickson 2015). Selective photodissociation of N₂ as modeled by Heays et al. (2014) also plays a role in the nitrogen fractionation in protoplanetary disks.

6.4. Sulfur and other heavy element hydrides

Hydrogen sulfide H₂S is the main sulfur hydride in dense clouds, while SH and SH⁺ are more confined to diffuse and translucent clouds (Neufeld et al. 2015b; Crockett et al. 2014), or the UV-illuminated cloud edges as described in Section 4. The sulfur chemistry proceeds differently from that of oxygen or carbon because the hydrogen abstraction reactions between HS⁻ and H₂ are highly endothermic. The hydrogenation of sulfur atoms on grains, followed by desorption, is a possible chemical pathway to form hydrogen sulfide in dense cores, although no confirmed detection of H₂S ice has been reported so far. Singly and doubly deuterated hydrogen sulfide have been detected in a few dark clouds (van Dishoeck et al. 1995; Vastel et al. 2003) with a significant fractionation level of ~ 10%. The fractionation is sensitive to the temperature since HDS and D₂S are not detected in hot cores, despite their large H₂S column densities. For the Orion-KL region, the upper limit for the HDS/H₂S ratio is a few 10⁻³, at the same level as HDO/H₂O (Crockett et al. 2014).

The halogen hydrides HF and HCl are expected to be the main gas phase reservoirs of fluorine and chlorine in dense and well shielded gas (Neufeld & Wolfire 2009), and could be used to monitor the depletion of these elements. The detection of the J = 2 – 1 line of HF in absorption towards SgrB2 (Neufeld et al. 1997) implied a fluorine depletion close to two orders of magnitude. Surveys of hydrogen chloride also conclude that chlorine depletes on grains by at least two orders of magnitude (e.g. Peng et al. 2010; Kama et al. 2015). While many previous analysis relied on collisional cross sections with He, new calculations have been performed for the H₂-HCl system by Lanza et al. (2014), providing further confirmation of the low HCl abundance in dense gas. HCl may return to the gas phase in the hot inner region around massive protostars (Goto et al. 2013).

7. HYDRIDES AS DIAGNOSTIC TOOLS

Because the chemical pathways leading to the formation of interstellar hydrides are relatively simple and well-understood, the analysis of the observed abundances is relatively straightforward and provides key information about the physical and chemical conditions within the environments in which hydrides are found. Several examples have already been discussed. These include observations of CH⁺ and SH⁺ in diffuse molecular clouds, which trace the effects of shocks or TDRs (see Section 5), and observations of neutral hydrides such as HF, HCl and H₂O in dense clouds, which probe the depletion of heavy elements onto icy grain mantles (see Section 6 and 2). In this section, we will discuss several additional cases where observations of hydride molecules provide unique information about the ISM. In particular, we will consider how observations of specific hydrides – namely CH, H₂O, and HF – provide valuable surrogate tracers for molecular hydrogen, the dominant molecular constituent of the
ISM but one that is difficult to observe directly, while several hydride cations (including ArH\(^+\), HCl\(^+\), OH\(^+\) and H\(_2\)O\(^+\)) are most abundant in partially-molecular gas, with each molecule predicted to show a peak abundance in material with a specific molecular fraction, \(f_{N}\). We will also discuss how hydride molecules can measure the cosmic-ray (or X-ray) ionization rate in the Milky Way and other galaxies.

7.1. Hydride as tracers of H\(_2\)

Although it is the primary molecular constituent of the ISM, H\(_2\) is hard to detect because it lacks a permanent dipole moment. Absorption line observations of the ultraviolet (and dipole-allowed) Lyman and Werner bands of H\(_2\) measure the H\(_2\) column density directly, although they are limited to relatively unreddened lines-of-sight toward relatively nearby hot stars (e.g. Rachford et al. 2009). Absorption in the near-infrared quadrupole-allowed vibrational bands has also been observed toward a few highly-embedded infrared sources (Lacy et al. 1994; Kulesa 2002), but is an extremely insensitive probe (in that very large H\(_2\) column densities are needed to generate even very small optical depths). There has therefore been a considerable effort to identify surrogate observational tracers that can be used to measure H\(_2\) column densities and masses. Observations of CO emission have been widely used to measure H\(_2\) masses (Bolatto, Wolfire & Leroy 2013 and references therein), but fail to trace a significant component of the molecular ISM. This component has been called the “CO-dark” or “CO-faint” molecular gas (Grenier, Casandjian & Terrier 2005; Wolfire, Hollenbach & McKee 2010; Bolatto, Wolfire & Leroy 2013), and consists of material that is sufficiently shielded from UV radiation to have a substantial H\(_2\) fraction but not so well-shielded as to contain abundant CO. This material lies at the transition between diffuse and translucent clouds near \(A_V = 1\) mag (e.g. van Dishoeck 1998).

Three hydride molecules – CH, H\(_2\)O, and HF – exhibit remarkably constant abundance ratios relative to H\(_2\), and are therefore valuable as surrogate tracers that are sensitive to CO-dark gas. The best studied case is CH, for which optical absorption-line observations can be calibrated with respect to UV absorption-line observations of H\(_2\), yielding \(N(CH)\) and \(N(H_2)\) column densities for sight-lines with \(N(CH)\) in the range \(10^{19}\) to \(10^{21}\) cm\(^{-2}\) (e.g. Sheffer et al. 2008). The observed \(N(CH)/N(H_2)\) ratio has a mean of \(3.5 \times 10^{-9}\), shows a dispersion of 0.21 dex, and exhibits no dependence on \(N(H_2)\); moreover, the \(N(CH)/N(H_2)\) can be determined for sight-lines of even larger \(N(H_2)\) – albeit less directly from a comparison of cm-wavelength CH emission with reddening measurements – and is found to remain entirely consistent with the \(N(CH)/N(H_2)\) ratio of \(3.5 \times 10^{-9}\) cm\(^{-2}\) value for H\(_2\) column densities up to \(4 \times 10^{19}\) cm\(^{-2}\) (Mattila 1988; Liszt & Lucas 2002). State of the art steady-state chemical models reproduce the observed trend between CH and H\(_2\) correctly for densities larger than 100 cm\(^{-3}\), while for lower densities the CH production is closely related to that of CH\(^+\), as explained in Sect.

Observations of submillimeter absorption, performed with the HIFI instrument on Herschel have extended the use of hydrides as probes of \(N(H_2)\), providing access to the \(N = 1, J = 3/2 \rightarrow 1/2\) CH \(\Lambda\)-doublet at 532/536 GHz along with rotational transitions out of the ground-state of the neutral hydrides HF and H\(_2\)O. Such observations show the \(N(HF)/N(CH)\) ratio to be remarkably constant in diffuse clouds, with a typical value of 0.4, implying a mean \(N(HF)/N(H_2)\) ratio of \(1.4 \times 10^{-8}\), given a \(N(CH)/N(H_2)\) ratio of \(3.5 \times 10^{-9}\). In the limit where \(f_{N}\) \(\sim\) 1, this \(N(HF)/N(H_2)\) ratio implies that HF accounts for \(\sim 40\%\) of the gas-phase fluorine. A direct measurement of the \(N(HF)/N(H_2)\) column density ratio in the diffuse ISM has been obtained (Indriolo et al. 2013) toward a single source, the hot star HD 154368, by combining observations of the near-IR \(v = 1 \rightarrow 0\) R(0) HF vibrational transition with those of dipole-allowed UV transitions of H\(_2\). This measurement provided an independent and entirely consistent \((1.15 \pm 0.41 \times 10^{-8})\) determination of the \(N(HF)/N(H_2)\) ratio. Originally, the predictions of astrochemical models by Neufeld & Wolfire (2009) for fluorine-bearing interstellar molecules predicted a \(N(HF)/N(H_2)\) ratio roughly twice as large as the observed value. However, recent labo-
ratory measurements (Tizniti et al. 2014) of the rate coefficient for the reaction of H$_2$ with F to form HF appear to have revealed the source of the discrepancy: the original astrochemical models adopted a theoretical value for the rate coefficient at low temperature that was a significant overestimate. Revised models that assume instead the laboratory-measured value for the rate of HF formation predict $N$(HF)/$N$(H$_2$) ratios in good agreement with the astronomical observations.

Another neutral hydride that has been extensively observed with Herschel, H$_2$O, is a third potential H$_2$ tracer within the diffuse ISM. The mean $N$(H$_2$O)/$N$(HF) ratio determined from Herschel observations of the diffuse ISM is 1.73 (Sonnentrucker et al. 2015), and the standard deviation is 0.87, implying a typical $N$(H$_2$O)/$N$(H$_2$) ratio of $2.4 \times 10^{-5}$. The variation in the H$_2$O abundance is apparently somewhat larger than those in the CH and HF abundances.

Taken together, submillimeter absorption line observations of CH, H$_2$O and HF provide a valuable toolset for the determination of $N$(H$_2$). Their column densities lie in the average ratio $N$(CH) : $N$(H$_2$O) : $N$(HF) = 2.5 : 1.7 : 1.0. For the spectral lines that have been most extensively observed in absorption – the 536 GHz $N$ = 1, $J = 3/2$ → 1/2 transition of CH, the 1113 GHz $J_{11} - J_{00}$ transition of $p$-H$_2$O, and the 1232 GHz $J = 1$ → 0 transition of HF – the corresponding ratio of velocity-integrated optical depths is 0.26:0.6:1.0. Thus, the HF transition provides the most sensitive probe of H$_2$ along any sight-line, followed by H$_2$O and CH. These probes are complementary because in cases where the HF absorption is optically-thick, yielding only a lower limit on the column density, the CH absorption is often optically-thin. Conversely, absorption features that are too weak to detect in observations of CH may be detectable in observations of HF. While CH, HF and H$_2$O, can be regarded as “primary” tracers of molecular hydrogen, their column densities are well correlated with other, non-hydride molecules that can be detected from the ground at millimeter wavelengths, including HCO$^+$ (e.g. Lucas & Liszt 1996) and C$_2$H (Lucas & Liszt 2000, Gerin et al. 2010b). Absorption line observations of these non-hydride “secondary” tracers can also be used to estimate $N$(H$_2$), albeit with lower accuracy. OH can

Figure 14

Distributions of molecular hydrogen fraction, $f_{H_2}$ (left panel) and cosmic-ray ionization rate, $\zeta_0$ (lower right panel), inferred from Herschel observations of OH$^+$ and H$_2$O$^+$ and reproduced from Indriolo et al. (2015). The red histogram applies to material with line-of-sight velocities within 5 km s$^{-1}$ of the systemic velocity of the background source (i.e. to material that may be in the vicinity the continuum source). The upper right panel shows the distribution of cosmic-ray ionization rates inferred (for a different set of sight-lines) from observations of H$_2^+$. 

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be added to the list of the “secondary” tracers, given the excellent correlation between the opacities of the HCO\textsuperscript{+} J = 1 → 0 and OH 1665 & 1667 MHz absorption lines (Liszt & Lucas 1996), and the moderate scatter in the OH/H\textsubscript{2}O column density ratio (Wiesemeyer et al. 2015).

Along with absorption line observations of CH, HF, and H\textsubscript{2}O, observations of CH and OH emission show considerable promise as a probe of CO-dark molecular gas (Liszt & Lucas 1996). This promise has been demonstrated recently by Allen, Hogg & Engelke (2015), who performed a sparse, high-sensitivity pilot survey near the Galactic plane for the 18 cm emission lines of OH: fewer than one-half of the multiple spectral features thereby detected were accompanied by detectable CO line emission. Further investigations, both observational and theoretical, will be needed to make quantitative use of this H\textsubscript{2} tracer.

7.2. Probes of the molecular fraction

While the neutral hydrides CH, HF and H\textsubscript{2}O are most abundant in gas with a large molecular fraction, f\textsubscript{H2}, several molecular ions show peak abundances in material with a smaller H\textsubscript{2} fraction. This behavior is particularly notable for ions that are destroyed rapidly by reaction with H\textsubscript{2}; these include ArH\textsuperscript{+}, which is destroyed by proton transfer to H\textsubscript{2} (Schilke et al. 2014), and OH\textsuperscript{+} and H\textsubscript{2}O\textsuperscript{+}, which undergo H-atom abstraction reactions to form H\textsubscript{2}O\textsuperscript{+} and H\textsubscript{2}O\textsuperscript{−} respectively. The n(OH\textsuperscript{+})/n(H\textsubscript{2}O\textsuperscript{+}) ratio is a particularly valuable probe of the H\textsubscript{2} fraction (Neufeld et al. 2010), because the reaction of H\textsubscript{2} with OH\textsuperscript{+}, which forms H\textsubscript{2}O\textsuperscript{+}, competes with dissociative recombination of OH\textsuperscript{+} with electrons; thus, the n(OH\textsuperscript{+})/n(H\textsubscript{2}O\textsuperscript{+}) ratio is larger in regions of small f\textsubscript{H2} and smaller in regions of large f\textsubscript{H2}. Through an analysis of 92 OH\textsuperscript{+} and H\textsubscript{2}O\textsuperscript{+} absorption features detected by Herschel along the sight-lines to 20 bright Galactic continuum sources, Indriolo et al. (2015) obtained the histogram of f\textsubscript{H2} values reproduced in Figure 14 (left panel). This analysis clearly reveals a substantial amount of interstellar gas with a molecular hydrogen fraction of a few percent. Of course, because the observations measure a ratio of column densities rather than volume density (i.e. N(OH\textsuperscript{+})/N(H\textsubscript{2}O\textsuperscript{+}) rather than n(OH\textsuperscript{+})/n(H\textsubscript{2}O\textsuperscript{+})), the f\textsubscript{H2} values thereby derived are really averages over the material that contributes most to the OH\textsuperscript{+} and H\textsubscript{2}O\textsuperscript{+} absorption. These f\textsubscript{H2} values may therefore differ substantially from those derived for the entire sight-line from a comparison of N(H\textsubscript{2}) and N(H).

The argonium ion, ArH\textsuperscript{+}, traces material of even smaller f\textsubscript{H2}. Because the dissociative recombination of ArH\textsuperscript{+} is unusually slow, reactions with H\textsubscript{2} become the dominant destruction mechanism for f\textsubscript{H2} ≳ 10\textsuperscript{−}4 and the ArH\textsuperscript{+} abundance starts to drop once f\textsubscript{H2} increases beyond that value. Thus, as discussed by Schilke et al. (2014), ArH\textsuperscript{+} serves as a unique probe of material that is almost purely atomic. This prediction for the behavior of ArH\textsuperscript{+} is supported by the observational finding that the distribution of ArH\textsuperscript{+} is entirely different from that of the other interstellar hydrides (see Figures 5 and 6 in Section 3 above).

7.3. Probes of the cosmic-ray ionization rate

Unlike the formation of CH\textsuperscript{+} and SH\textsuperscript{+}, which is driven by shocks or turbulent dissipation or enhanced in strongly FUV-irradiated gas, the formation of ArH\textsuperscript{+}, OH\textsuperscript{+} and H\textsubscript{2}O\textsuperscript{+} is initiated by cosmic-rays. ArH\textsuperscript{+} formation is driven by the cosmic-ray ionization of atomic argon, with then reacts with H\textsubscript{2} to form ArH\textsuperscript{+}; in the case of OH\textsuperscript{+} and H\textsubscript{2}O\textsuperscript{+} formation, the cosmic-ray ionization of H (or H\textsubscript{2}, in material of large f\textsubscript{H2}) is the process that initiates the relevant reaction chain. Observations of the abundances of OH\textsuperscript{+} and H\textsubscript{2}O\textsuperscript{+} in diffuse clouds, supported by detailed astrochemical calculations (Hollenbach et al. 2012), have been used to measure the cosmic-ray ionization rate in the Milky Way galaxy (Gerin et al. 2010a; Neufeld et al. 2010b; Indriolo et al. 2015).
Indriolo et al. (2015) performed an analysis of all the relevant data available from Herschel to obtain the histogram reproduced in Figure 14 (lower right panel), which shows the distribution of cosmic-ray ionization rates in the disk of the Milky Way, \( \zeta_H \), defined here as the total rate of ionization per H atom. This quantity shows a log-normal distribution, with \( \log_{10}(\zeta_H) \) having a mean of \(-15.75\) (corresponding to \( \zeta_H = 1.8 \times 10^{-16} \) s\(^{-1}\)) and standard deviation 0.29. The results for \( \zeta_H \) obtained from OH\(^+\) and H\(_2\)O\(^+\) are considerably larger than the canonical values adopted for diffuse clouds by most authors prior to 2002, but are in good agreement with estimates (e.g. Indriolo & McCall 2012) derived (for different sight-lines) from mid-IR observations of H\(_3^+\). The upper right panel in Figure 14 shows the distribution of \( \zeta_H \) derived from recent H\(_3^+\) observations.

The ionization rates inferred for material in the Galactic Center are typically 10 – 100 times as large as the average value inferred for gas in the disk, and even larger ionization rates (exceeding \( 10^{-13} \) s\(^{-1}\)) have been derived for circumnuclear regions within the ULIRGs Arp 220 and NGC 4418 (González-Alfonso et al. 2013). Because ionization by hard X-rays has similar effects on the chemistry as those of cosmic-ray ionization, it is not possible to unambiguously discriminate between these two possible ionization sources based on observations of hydrides alone.

7.4. Other diagnostic uses

In addition to those diagnostics that may be exploited by an analysis of hydride chemistry, observations of hydrides offer other tools that measure key parameters of the interstellar environment. The oblate symmetric top molecules NH\(_3\) and H\(_2\)O\(^+\) can provide physical probes of the gas temperature. For such molecules, the lowest states of a given quantum number \( K \) are metastable (and have a total angular momentum quantum number \( J = K \)). These metastable states do not undergo radiative decay, and thus their relative populations are determined by non-radiative processes. For low-lying metastable states of NH\(_3\) and H\(_2\)O\(^+\), the relative populations are determined by collisional excitation and probe the kinetic temperature of the gas, providing a “molecular cloud thermometer” (e.g. Walmsley & Ungerechts 1983). In the case of high-lying metastable states, however, the effects of “formation pumping” may complicate the interpretation of the observations (e.g. Lis et al. 2014).

The Zeeman splitting of hydride spectral lines offers another important diagnostic tool that has been used to estimate the interstellar magnetic field strength. The paramagnetic OH radical is of particular value, and absorption line observations of its 18 cm transitions have been used to determine the magnetic field in interstellar gas with densities in the range \( n_H \approx 10^2 \) cm\(^{-3}\) to \( 10^4 \) cm\(^{-3}\) (e.g. Crutcher 2012 for a review). This material is intermediate between the lower density gas probed by HI Zeeman measurements and the higher density gas probed by CN Zeeman measurements. At yet higher densities, the Zeeman splitting of OH and H\(_2\)O maser transitions has been used to measure magnetic field strengths, in extreme cases revealing fields in excess of 100 mG.

Because the 22 GHz water maser emissions from shocked regions can be extraordinarily bright, they may be observed by means of Very Long Baseline Interferometry (VLBI), providing sub-milliarcsecond resolution and the possibility of measuring parallaxes and proper motions with accuracies of \( \sim 10 \) \( \mu \)as and \( \sim 100 \) \( \mu \)as yr\(^{-1}\) respectively (e.g. Reid et al. 2009; Honma et al. 2012). Such measurements provide uniquely valuable probes of fundamental Galactic parameters such as the distance to the Galactic Center and the circular rotation speed at the solar circle.

Finally, observations of hydride isotopologues can be used to determine elemental isotope ratios, which – in turn – can provide constraints upon the star formation history and the chemical evolution. In the diffuse ISM, for example, where fractionation is generally believed to be unimportant for isotopes of elements other than hydrogen or carbon, observations of H\(_{35}\)Cl\(^+\) and H\(_{37}\)Cl\(^+\) have been used to determine the \( ^{35}\)Cl/\(^{37}\)Cl isotopic ratio, both in the Galactic disk (Neufeld et al. 2015a) and references
formation rate can reach few \( \text{M}_\odot \) yr\(^{-1}\), the average. Instead of a rate much higher than a starburst galaxy is a super-massive black hole.

8. HYDRIDES IN EXTERNAL GALAXIES

As relatively abundant and ubiquitous species, hydrides are detected in external galaxies, from local objects up to high redshift systems. The list of species includes water vapor (Yang et al. 2013; Omont et al. 2013). OH, and the related ions \( \text{H}_2\text{O}^+ \), \( \text{H}_2\text{O}^- \) and \( \text{OH}^+ \); \( \text{NH}_3 \), CH and CH\(^+\), as well as HF and the chlorine bearing species HCl and H\(_2\)Cl\(^+\) (van der Werf et al. 2010; Rangwala et al. 2011, 2014; González-Alfonso et al. 2012, 2013; Kamenzetzy et al. 2012; Muller et al. 2014a, b). The hydride diagnostic capabilities can be exploited to probe the physical conditions, turbulence and radiation field including X-rays and cosmic rays in a more extreme range than what is found in the Milky Way.

8.1. Local galaxies

FIR spectroscopy, performed first with ISO, then with Herschel revealed a diversity of spectral lines, especially from hydrides that accompany the set of CO rotational lines and of atomic fine structure lines. In local galaxies (\( z < 0.1 \)), the strongest rotational lines of water vapor are the \( 2_{02} \rightarrow 1_{11} \) and \( 3_{21} \rightarrow 3_{12} \) transitions with rest frequencies 987.9 and 1162.9 GHz. Their luminosities are linearly correlated with the far infrared luminosity, \( L_{\text{FIR}} \), across a broad range of infrared luminosities, \( 1 \text{ to } 300 \times 10^{10} \text{ L}_\odot \), i.e. from normal galaxies up to very active starbursts (Yang et al. 2013). Radiative transfer models show that FIR pumping is an important source of excitation for most \( \text{H}_2\text{O} \) lines, except for those connected to the ortho or para ground states. Fully resolved line profiles have been obtained with HIFI, showing the complexity of the line profiles even in nearby galaxies: towards M82, different \( \text{H}_2\text{O} \) lines have different line profiles ranging from pure absorption to pure emission (Weiβ et al. 2010).

At moderate spectral resolution (\( \sim 200 \text{ kms}^{-1} \)), submm and FIR hydride lines appear in emission, in absorption or even with P-Cygni profiles. In galaxies hosting a compact starburst or an active galactic nucleus (AGN) the FIR radiation from the hot dust is pumping the rotational levels, leading to a variety of line profiles revealing the conditions close to the heavily buried compact source (van der Werf et al. 2010). OH lines from excited levels are especially interesting because they trace powerful outflows of molecular material (Sturm et al. 2011; González-Alfonso et al. 2012), that represent an important source of negative feedback in starburst galaxies or AGNs. In an analysis of 29 galaxies, González-Alfonso et al. (2015) clearly show that the OH 65\( \mu \text{m} \) equivalent width probes the fraction of infrared luminosity produced by a compact and warm source, i.e. closely related to the presence of an actively buried active region, which could escape detection otherwise. Absorption from excited levels of other hydrides like water vapor, \( \text{OH}^+ \) and \( \text{H}_2\text{O}^- \) can also be detected. \( \text{H}_2\text{O}^+ \) deserves a special treatment. Toward the compact infrared galaxies Arp 220 and NGC 4418, absorption from \( \text{H}_2\text{O}^+ \) lines tracing the metastable levels of this symmetric top molecule are detected up to energies of \( \sim 1300 \text{ K} \). As for the Galactic sources SgrB2 and W31C, these lines trace the formation process of \( \text{H}_2\text{O}^+ \) and can therefore be used to accurately infer the ionization rate which reaches \( \zeta_{\text{H}_2} > 10^{-13} \text{ s}^{-1} \) in both NGC 4418 and Arp 220, as compared with the mean value in the Galactic disk of \( \zeta_{\text{H}_2} = 2 \times 10^{-16} \text{ s}^{-1} \) (Indriolo et al. 2015). Non metastable lines of \( \text{H}_2\text{O}^+ \) are accessible from the ground, the strongest being the \( 3_2^+ \rightarrow 2_1^+ \) line at 364 GHz (Aalto et al. 2011).

In external galaxies hydrides are important probes of the diffuse clouds, not radiating in CO. For instance Appleton et al. (2013) report the detection of water vapor in the large shock of the Stephan’s Quintet, a group of five interacting galaxies. The ground state \( p^{+}\text{H}_2\text{O} \) transition is the brightest sub-
millimeter emission line detected in this system, excluding the FIR structure lines [CII] at 158 µm and [OIII] at 63 µm. The current generation of high resolution spectrometers operating in the visible allows measurement of CH, CH⁺ and CN absorption lines towards stars in nearby galaxies. In the Magellanic clouds, the relationships between CN, CH, CH⁺, NaI and KaI are generally consistent with those of the Milky Way but the overall CH abundance relative to H₂ is more variable, likely because of the broad range of physical conditions encountered along such sight-lines and the lower carbon abundance (Welty et al. 2006). The supernova SN2014J in M 82 (Ritchey et al. 2015) provided a bright enough background target to probe the ISM properties in the Galaxy and in M82 along this sight-line. The enhanced CH⁺/CH ratio may indicate an enhanced level of turbulence in this actively star forming galaxy.

8.2. Active Galactic Nuclei : XDR prototypes

When molecular gas is exposed to intense X-ray radiation, a specific chemistry can develop. As compared with photodissociation regions, X-ray dominated regions (XDR) show longer columns of warm molecular gas because X-rays can penetrate longer columns than UV photons. Because of the increased ionization rate due to X-rays, and the higher gas temperature, some molecular abundances are modified. This is particularly the case for the oxygen hydrides OH⁺, H₂O⁺ and H₃O⁺. In dense gas illuminated by X-rays, these species are predicted to present strong emission features, because of the increased excitation by the high electron density. The close environment of the super-massive accreting black hole in an AGN can be considered as an X-ray dominated region, even though some active galaxies also host starbursts. XDRs also exist in the close vicinity of protostars and have been modeled, for example by Stäuber et al. (2005). The Herschel/SPIRE spectrum of the Mrk 231 galaxy, an AGN template, shows prominent OH⁺ and H₂O⁺ rotational lines in emission (van der Werf et al. 2010). Other species sensitive to high X-ray irradiation are atomic carbon, H⁺, H₂O and HCN. Because S²⁺ reacts rapidly with H₂, producing SH⁺ among other species, Abel, Federman & Stancil (2008) have proposed that SH⁺ could be an excellent XDR tracer. This work remains qualitative because the reaction branching ratio towards SH⁺ is not known. A further exploration of the reactivity of doubly ionized ions with H₂ (e.g. C²⁺) and of the branching ratios towards hydrides is needed to support this new chemical route.

8.3. High redshift galaxies

Hydride lines at THz rest frequencies are redshifted into the (sub)millimeter range and become accessible to the ALMA and NOEMA (NOrthen Extended Millimeter Array) interferometers, offering new diagnostic capabilities of the conditions in high redshift galaxies. Figure 15 shows the ground state hydride lines accessible to ALMA with the corresponding redshift range. For water vapor, excited lines are also easily detected (Omont et al. 2013), with line strength only a factor two to three lower than CO. Nevertheless, the detection of water vapor at high redshift was achieved about two decades after that of CO, largely because the limited band-width of available receivers prohibited searching over a broad frequency range. As the CO rotational line frequencies are relatively distant from the strongest water line frequencies, targeting CO meant avoiding H₂O until recently. The tight correlation of the H₂O line luminosity with the FIR luminosity may be used to derive the star formation rate. Towards gravitationally lensed QSOs, the gas of the lensing galaxy may produce absorption lines on the continuum of the background object. The sight-line towards the radio loud QSO PKS1830-211 is particularly rich, with numerous absorption lines detected toward the two main images, sampling two lines of sight in the lensing galaxy at z = 0.89. ALMA observations enabled the detection of the same hydride lines that were seen in the Milky Way by Herschel (Muller et al. 2014b,d). Other high
redshift hydride detections include H$_2$O$^+$ in a bright submillimeter galaxy (Weiβ et al. 2013), CH in the average spectrum of 22 such objects (Spilker et al. 2014), CH$^+$ in the optical afterglow spectrum of the gamma ray burst GRB 145050A at z = 0.89 (Fynbo et al. 2014) and in three hyper luminous galaxies (Falgarone et al. 2015).

While the same species are detected at z \sim 1 as in the Milky Way, some hydrides may become undetectable at higher redshift because of the lack of the corresponding chemical element. For instance HF has been tentatively detected in Cloverleaf QSO at z = 2.56 (Monje et al. 2011) but not in the higher redshift source APM 08279+5255 at z = 3.89 (Lis et al. 2011). The absence of HF is best explained by a low fluorine abundance, since the same source exhibits bright CO and H$_2$O lines.

The comparison of carefully selected hydride line profiles provides an interesting test of the variation of two fundamental constants with time, the fine structure constant $\alpha = e^2/\hbar c$ and the proto-to-electron mass ratio $\mu = m_p/m_e$. The sensitivity of the CH doublet at 532/536 GHz to variations in $\alpha$ and $\mu$ have been computed by de Nijs, Ubachs & Bethlem (2012). These lines can be observed simultaneously with the $1_0 - 1_0$ transition of $\alpha$-H$_2$O, reducing the systematic effects when comparing lines at very different frequencies, and therefore are complementary to other diagnostics like NH$_3$, CH$_3$OH and H$_2$ discussed by Jansen, Bethlem & Ubachs (2014).

9. CONCLUSIONS AND FUTURE PROSPECTS

Since their first discovery in the diffuse interstellar medium, hydrides have been proven to exist in the wide variety of interstellar and circumstellar environments, from the most diffuse, almost purely atomic regions, up to dense cores and protoplanetary disks. Given the relative simplicity of their chemistry, and the good level of understanding of their formation processes, the diagnostic properties...
of hydrides need to be further explored in the future, taking advantage of the increasing capabilities of high spectral resolution spectrometers from UV-visible up to centimeter wavelengths. As shown in Figure 15, hydrides ground state transitions, which are mostly not accessible from ground based observatories, are redshifted to spectral regions with better atmospheric transmission in distant galaxies, where ALMA and NOEMA are operating. This offers diagnostics of the presence of molecular hydrogen, cosmic ray ionization rate, elemental abundances as well as dynamical processes in the forms of shocks, turbulence and large scale winds, from the local interstellar medium up to the most distant galaxies. The combined increase in sensitivity and spectral resolution will enable more accurate measurements of isotopic ratios, with a focus on deuterium and nitrogen, as a means to understand the origin of volatiles in the solar system, and more generally the formation of planets in circumstellar disks. It will be exciting to connect the ISM information with the measurements performed on the 67P/Churyumov-Gerasimenko comet by the Rosetta spacecraft.

At longer wavelengths, the development of powerful instruments at centimeter wavelengths offers interesting possibilities for accessing the $\Lambda$-doubling transitions of OH (both in the ground state and in excited levels), CH and the inversion transitions of NH$_3$, and for comparing the distribution of these species with that of atomic hydrogen at unprecedented sensitivity and spatial resolution. At shorter wavelengths, the launch of the JWST, and the construction of the next generation of ground-based telescopes, will provide new tools for studying the relation between ices and gas phase species, especially water, methane and associated radicals.

To obtain the best results from these upcoming facilities, several scientific issues remain to be addressed in the fields of astrochemistry and molecular physics. On the astrophysics side, a significant issue is the understanding of non equilibrium processes on the abundance and excitation of the main hydrides. As described above, for a reactive hydride like CH$^+$, both the large scale and small scale dynamics of the media, their multi-phase structure, as well as the details of the formation and excitation process all contribute to the production and excitation. A related topic is the understanding of the hydride OPR, and how these relate to the H$_2$ OPR. This requires investigations of the reaction mechanisms leading to the hydride formation and destruction, taking the spin symmetry states into account, as well as more accurate astronomical measurements.

The field of laboratory astrophysics is developing fast. The interplay between the gas phase and the solid phase is a key area for progress. With their formation through hydrogen abstraction reactions, hydride abundances are particularly sensitive to rates of the dissociative recombination of molecular ions. The new cryogenic storage ring (CSR) in Heidelberg should provide measurements of the dissociative recombination rate of rotationally cold ions such as OH$^+$. Other exciting developments in laboratory astrophysics include deeper studies of the interaction of ices with FUV and energetic radiation using synchrotron radiation sources, particle bombardment simulating cosmic ray irradiation, and advanced theoretical calculations of molecular processes. Close collaborations between molecular physicists and astronomers will remain a key asset in this area, as it has been in the past decades.

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LITERATURE CITED
Aalto S, Costagliola F, van der Tak F, Meijerink R. 2011. *Astron. Astrophys.* 527:A69
Abel NP, Federman SR, Stancil PC. 2008. *Astrophys. J., Lett.* 675:L81–L84
Agúndez M, Goicoechea JR, Cernicharo J, Faure A, Roueff E. 2010. *Astrophys. J.* 713:662–670
Alata I, Cruz-Diaz GA, Muñoz Caro GM, Dartois E. 2014. *Astron. Astrophys.* 569:A119
Aléon J. 2010. *Astrophys. J.* 722:1342–1351
Allen RJ, Hogg DE, Engelke PD. 2015. *Astron. J.* 149:123
Allers KN, Jaffe DT, Lacy JH, Draine BT, Richter MJ. 2005. *Astrophys. J.* 630:368–380
Amano T. 2010. *Astron. Astrophys.* 516:L4
Appleton PN, Guillard P, Boulanger F, Cluver ME, Ogle P, et al. 2013. *Astrophys. J.* 777:66
Arasà C, Koning J, Kroes GJ, Walsh C, van Dishoeck EF. 2015. *Astron. Astrophys.* 575:A121
Bacmann A, Caux E, Hily-Blant P, Parise B, Pagani L, et al. 2010. *Astron. Astrophys.* 521:L42
Barlow MJ, Swinyard BM, Owen PJ, Cernicharo J, Gomez HL, et al. 2013. *Science* 342:1343–1345
Bates DR, Spitzer Jr. L. 1951. *Astrophys. J.* 113:441
Batrla W, Wilson TL. 2003. *Astron. Astrophys.* 408:231–235
Beckman JE, Waite GD, White GJ, Phillips JP, Frost RL., Davis JH. 1982. *MNRAS* 201:357–364
Benz AO, Bruderer S, van Dishoeck EF, Stäuber P, Wampfler SF. 2013. *Journal of Physical Chemistry A* 117:9840–9847
Benz AO, Bruderer S, van Dishoeck EF, Stäuber P, Wampfler SF, et al. 2010. *Astron. Astrophys.* 521:L35
Bergin EA, Tafalla M. 2007. *Ann. Rev. Astron. Astrophys.* 45:339–396
Black JH. 1998. *Faraday Discussions* 109:257
Black JH, Dalgarno A. 1976. *Astrophys. J.* 203:132–142
Black JH, Dalgarno A. 1977. *ApJS* 30:405–423
Black JH, van Dishoeck EF. 1987. *Astrophys. J.* 322:412–449
Blake GA, Keene J, Phillips TG. 1985. *Astrophys. J.* 295:501–506
Bolatto AD, Wolfire M, Leroy AK. 2013. *Ann. Rev. Astron. Astrophys.* 51:207–268
Boogert ACA, Gerakines PA, Whittet DCB. 2015. *Ann. Rev. Astron. Astrophys.* 53:541–581
Boonman AMS, Doty SD, van Dishoeck EF, Bergin EA, Melnick GJ, et al. 2003. *Astrophys. J. 406:937–955
Bottinelli S, Wakelam V, Caux E, Vastel C, Aikawa Y, Ceccarelli C. 2014. *MNRAS* 441:1964–1973
Bruderer S, Benz AO, Stäuber P, Doty SD. 2010. *Astron. Astrophys.* 720:1432–1453
Butner HM, Charnley SB, Ceccarelli C, Rodgers SD, Pardo JR, et al. 2007. *Astrophys. J., Lett.* 659:L137–L140
Carr JS, Najita JR. 2008. *Science* 319:1504–
Carruthers GR. 1970a. *Astrophys. J., Lett.* 161:L81
Carruthers GR. 1970b. *Astrophys. J., Lett.* 161:L81
Caselli P, Ceccarelli C. 2012. *The Astron. Astrophys. rev.* 20:56
Caselli P, Keto E, Bergin EA, Tafalla M, Aikawa Y, et al. 2012. *Astrophys. J., Lett.* 759:L37
Cazaux S, Tielens AGGM. 2004. *Astrophys. J.* 604:222–237
Cernicharo J, Liu XW, González-Alfonso E, Cox P, Barlow MJ, et al. 1997. *Astrophys. J., Lett.* 483:L65–L68
Cernicharo J, Tercero B, Fuente A, Domenech JL, Cueto M, et al. 2013. *Astrophys. J., Lett.* 771:L10
Chastain RJ, Cotten D, Magnani L. 2010. *Astron. J.* 139:267–278
Chenoff DF, McKee CF, Hollenbach DJ. 1982. *Astrophys. J., Lett.* 259:L97–L101
Cheung AC, Rank DM, Townes CH, Thornton DD, Welch WJ. 1968. *Physical Review Letters* 21:1701–1705
Cheung AC, Rank DM, Townes CH, Thornton DD, Welch WJ. 1969. *Nature* 221:626–628

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1. The astrochymist (http://www.astrochymist.org) provides the list of detected molecules in the interstellar medium with the associated bibliographic references and related resources in astrochemistry.
2. BASECOL, a database devoted to collisional ro-vibrational excitation of molecules by colliders such as atom, ion, molecule or electron. http://basecol.obspm.fr/
3. Leiden Atomic and Molecular Database (LAMDA), a data base providing the basic atomic and molecular data for molecular excitation calculations. http://home.strw.leidenuniv.nl/ moldata/
4. Virtual Atomic and Molecular Data Centre (VAMDC). A portal for 28 databases providing atomic and molecular data. http://portal.vamdc.org/vamdc_portal/home.seam
5. The Cologne Database for Molecular Spectroscopy (CDMS). A molecular line catalog providing line frequencies, intensities and molecule partition functions. https://www.astro.uni-koeln.de/cdms
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