

## Hydrides in Space: Past, Present, and Future

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**Abstract.** One of the central questions of modern astrophysics concerns the life cycle of molecules in the Universe—from the diffuse interstellar medium to planetary systems—and the chemical pathways leading from simple atoms and diatomic molecules to complex organic species. In the past two decades, the Caltech Submillimeter Observatory (CSO) has contributed a number of key discoveries on these topics. Light hydrides are of particular interest for astrochemistry, as the basic building blocks of the chemical networks in both diffuse and dense clouds. Ongoing and planned submillimeter wide-field continuum surveys will yield hundreds of potential galactic targets suitable for detailed spectroscopic follow-ups. Recent advances in detector and digital spectrometer technologies promise to truly revolutionize further the field of high-resolution submillimeter spectroscopy and its application to the study of the life cycle of molecules. This will greatly improve our understanding of astrochemistry, astrobiology, the origin of life on Earth, and allow assessing the possibilities of life in other planetary systems.

## 1 Introduction

One of the fundamental questions in modern astrophysics concerns the life cycle of molecular material in the Universe.<sup>4</sup> The study of the origin of the heavy elements in stars, their processing into molecular material in interstellar clouds, incorporation into planet-forming bodies, and eventually into living material,

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<sup>4</sup> See [http://www.submm.org/sci/astro2010/Lis\\_Molecular\\_Universe\\_PSF.pdf](http://www.submm.org/sci/astro2010/Lis_Molecular_Universe_PSF.pdf)

has fascinated astronomers, planetary scientists, and biologists. A critical question in the quest to understand the origin of life on Earth and to assess the possibilities for life in other planetary environments is the source of pre-biotic and, ultimately, proto-biotic molecules. Although synthesis on Earth from atmospheric chemistry or other sources may contribute, extraterrestrial organic material is delivered to the Earth today in the form of carbonaceous chondrite meteorites and interplanetary dust particles and the process was understandably more rapid during the early evolution of the solar system. Submillimeter spectroscopy is an invaluable tool for tracing the inventory of the Molecular Universe, from diffuse interstellar clouds, through dense clouds, to protoplanetary disks and planetary systems. Simple hydride species are particularly important as basic building blocks of astrochemistry (e.g., Herbst & Klemperer 1973; Dalgarno & Black 1976) and have been shown to be excellent probes of physical conditions in interstellar and circumstellar environments. Consequently, studies of key hydrides and deuterides have constituted an integral part of the CSO research program since its early days (e.g., Menten et al. 1990a,b; Wootten et al. 1991; van Dishoeck et al. 1993). A comprehensive study of interstellar hydrides will be carried out shortly using the Heterodyne Instrument for the Far-Infrared (HIFI) aboard the Herschel Space Observatory (PRISMAS program, PI M. Gerin). The upcoming HIFI observations will write the next chapter in the hydride research. They will answer many of the outstanding questions of hydride chemistry, some of which are summarized below.<sup>5</sup>

## 2 Life Cycle of the Molecular Universe

Diffuse molecular clouds constitute the first step in the evolutionary pathway from low-density atomic hydrogen (H I) clouds to the Molecular Universe. They are transition objects between the atomic and molecular phases of the interstellar medium (ISM), and provide a relatively simple laboratory for the study of fundamental chemical processes. Such clouds are most easily studied through absorption line observations of bright, background continuum sources. The dust continuum flux steeply increases at short submillimeter wavelengths. This offers an opportunity to probe even relatively diffuse regions, characterized by several magnitudes of visual extinction. Lines of sight toward distant H II regions, such as Sgr B2 in the Galactic center, often intersect several Galactic spiral arms, thus allowing detailed investigations of the physics and chemistry of the foreground gas in clouds with a wide range of physical conditions. For the diffuse ISM, high sensitivity, exquisite spectral resolution, and immense spectral coverage are required to obtain a full chemical inventory. The known molecular content of diffuse molecular clouds consists primarily of diatomic molecules—only a few polyatomic species (e.g., HCN, HNC, C<sub>2</sub>H, H<sub>2</sub>O) having been identified to date. However, spectroscopic surveys of these objects may lead to the discovery of new molecules, in particular simple hydrides. Furthermore, the calculation of molecular column densities from absorption line equivalent widths is usually straightforward—unlike in the case of emission line observations, the column

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<sup>5</sup> The full text of the PRISMAS proposal is available at <http://astro.ens.fr/?PRISMAS>.

density determination does not depend critically upon such poorly-known quantities as the gas density and temperature (and distribution thereof) or upon the rate coefficients for collisional excitation.

Interstellar clouds are thought to evolve from diffuse to molecular phase as a result of processes that increase their column density and thus reduce photodestruction rates. We find most of the over 140 molecules discovered to date in space in dense “molecular clouds”, where gas and grain chemistry can be expected to produce a wide range of complex organic species. The dense condensations within molecular clouds, containing up to a few tens of solar masses of material at temperatures of  $\sim 10$  K, are referred to as “cloud cores” or “dense cores”. Deuterium-bearing species have been shown to be excellent probes of these cold regions prior to star formation.

Star formation occurs within cloud cores. The combination of high densities, heating by young embedded stars, and illumination by nearby sources of hard radiation drives the chemical evolution in these regions. Here, one can expect enhancement of both gas-phase chemical reactions and grain-surface chemistry. The higher temperatures open many chemical pathways, which are endothermic and therefore closed at lower temperatures. High densities (and to a lesser extent high temperatures) increase the rate of collisions of chemically interacting partners. Penetrating X-rays and UV radiation ionize atomic and molecular species, thereby greatly increasing their chemical interaction cross-sections. This radiation may also dissociate larger molecules and thus provide additional chemical pathways for producing smaller species. Hard radiation also creates radicals on grain surfaces, which—combined with the mobility due to elevated grain temperatures—leads to enhanced chemical processing. If grain reactions are sufficiently exothermic, the resulting molecules will be directly released from the grain surface. If not released at their creation, they could leave the surface later, when the grain temperature is sufficiently high. The molecules could alternatively become part of the grain’s molecular coating, influencing its optical properties, its ability to coagulate with other grains and produce larger particles (a necessary step toward planet formation), or simply be present and participate in the creation of more complex species. The chemical complexities produced by the grain-surface chemistry are revealed in “hot cores” when a massive star is born and heats the up the surrounding material to  $T \gtrsim 100$  K, leading to the evaporation of grain-mantle ices. Hot cores thus offer the best opportunity to explore and understand via theoretical models the limits of the creation of organics via interstellar chemistry. This is critical, as at this stage the ices and organics are seeded to the planet-forming disk by infall.

The accretion disks around young stars form the pivotal link between star formation and (exo)planetary science. A detailed understanding of their chemical and physical properties is essential in providing constraints on dispersal mechanisms and timescales for nebular gas and dust. Furthermore, an understanding of how various volatile species (water, carbon monoxide, methane, ammonia, nitrogen, etc.) are distributed in the outer regions of circumstellar disks is particularly important to examining the connection between interstellar and nebular processes in the formation of icy planetesimals such as comets and Kuiper Belt objects. At disk surfaces, molecules can be dissociated by UV radiation, or ionized by UV photons, X-rays and cosmic rays, and so the resulting chemistry is a

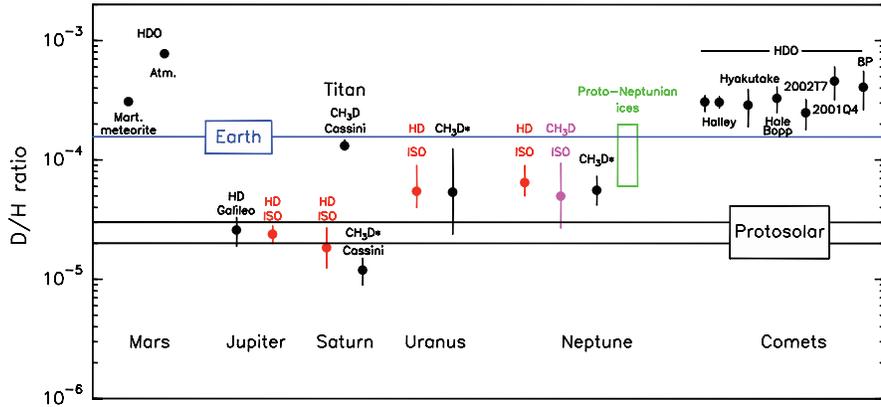


Figure 1. D/H ratio in the Solar System (see Fig. 1 of Hartogh et al. 2009). Recent Cassini measurements of Titan in  $\text{CH}_4$ , which is the main deuterium reservoir are included; the lower point, label "CH3D\*" corresponds to the D/H ratio in  $\text{H}_2$  deduced from  $\text{CH}_4$ , after correcting for the fractionation in Titan's atmosphere). The cometary measurements to date show a factor of 12 enhancement above the protosolar value in  $\text{H}_2$  and a factor of 2 enhancement above SMOW. Figure courtesy of D. Bockelée-Morvan.

combination of Photon Dominated Region-like and cosmic ray induced reaction networks at the distances where icy planetesimals are assembled.

Understanding the complex chemical processes that take place in the astrophysical environments described above requires high-resolution spectroscopic studies, using state-of-the-art heterodyne instrumentation, with exquisite sensitivity and wide spectral coverage. Some astrophysically important molecules (such as  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , and  $\text{HF}$ ) can only be studied from space. Over the next few years, Herschel Space Observatory will be exploring the water universe and will leave a tremendous legacy for years to come. However, in order to fully understand the chemical evolution within the Molecular Universe, a high volume of supporting ground-based and airborne data is required. Observations to date have clearly demonstrated that a large fraction of the submillimeter band is accessible from high-altitude mountain sites, such as Mauna Kea or Chajnantor. CSO has played a pioneering role in these studies. In the following sections, we present recent observations of several key hydrides and deuterides in various astrophysical environments, obtained out using this facility.

### 3 D/H Ratio in Cometary Water

Comets are among the most primitive bodies left over from the planetesimal building stage of the solar nebula, and so their physical and chemical composition provides an important link between nebular and interstellar (or outer disk) processes. Here, submillimeter observations are extremely powerful, having provided the most accurate estimates of the composition of the nucleus of comets and the isotopic ratios in key species ( $\text{H}_2\text{O}$ ,  $\text{HCN}$ , e.g., Lis et al. 1997b; Bockelée-Morvan et al. 2000; Bockelée-Morvan et al. 2005). The most complex molecules

seen in comets (methyl cyanide, methyl formate, ethylene glycol) have also been detected at (sub)millimeter wavelengths (e.g. Crovisier et al. 2004). Heterodyne spectroscopy can provide an unbiased view of the submillimeter wave spectra of comets, and therefore of the composition of the nucleus itself, particularly if the observations are combined with simultaneous infrared spectra of species without permanent dipole moments, such as  $\text{CO}_2$ ,  $\text{C}_2\text{H}_2$ , and  $\text{CH}_4$ .

Deuterium fractionation in interstellar water, as compared to that measured in solar system objects (in particular in comets), is of great interest (Fig. 1). CSO provided the first ground-based observation of HDO in a comet and the corresponding measurement of the D/H ratio in cometary water (Lis et al. 1997a; Bockelée-Morvan et al. 1998). Since then, a handful of additional measurements have been obtained in long-period, Oort-cloud comets at radio–UV wavelengths (Meier et al. 1998; Hutsemékers et al. 2008; Weaver et al. 2008; Villanueva et al. 2009). The derived D/H ratio of  $\sim 3 \times 10^{-4}$  corresponds to a factor of 12 enrichment with respect to the proto-solar value in  $\text{H}_2$ , but is significantly lower than the values measured in dense interstellar clouds. This suggests that comets incorporated material reprocessed in the inner solar nebula (reducing the D/H ratio) that was subsequently transported outward by turbulent diffusion.

Late-stage cometary impacts have been suggested as a possible source of terrestrial water. However, the cometary D/H ratio is twice the Standard Mean Ocean Water (SMOW) value, which appears to rule out the delivery of the majority of terrestrial water from cometary sources. A possible alternative scenario is that the terrestrial planets accreted “wet”—the bulk of terrestrial water could have been obtained by adsorption of nebular water onto dust grains in the protosolar disk and retained during the planetary accretion phase (e.g., Drake 2005).

To date, no measurements of the D/H ratio in Jupiter-family, short-period comets have been obtained. As these comets are believed to have formed in a colder environment, outside of the turbulent zone in the protosolar nebula, they are expected to exhibit higher D/H ratios. Observations of a large sample of comets, including short-period comets, are needed to fully understand the turbulent mixing in the Solar Nebula and the origin of terrestrial water. Herschel HIFI will enable these important observations (Hartogh et al. 2009).

#### 4 Carbon Chemistry: $^{13}\text{CH}^+$

$\text{CH}^+$  was one of the first molecules detected in space, by means of optical spectroscopy (Douglas & Herzberg 1941; Bates & Spitzer 1951). Its excited rotational lines were detected in the planetary nebula NGC 7027, using ISO LWS (Cernicharo et al. 1997). The ground-state rotational line of  $^{13}\text{CH}^+$  was recently detected toward G10.6-0.4 using the CSO (Falgarone et al. 2005). The formation of  $\text{CH}^+$  in diffuse clouds has remained a puzzle since the early days of molecular astrophysics. As discussed, e.g., by Black et al. (1975),  $\text{CH}^+$  is rapidly destroyed in reactions with H and  $\text{H}_2$  and its observed column densities in quiescent molecular clouds are several orders of magnitude above the gas-phase model predictions. The formation route involving  $\text{C}^+ + \text{H}_2$  is highly endothermic (4640 K), yet  $\text{H}_2$  is needed for  $\text{CH}^+$  formation. Hence  $\text{CH}^+$  has to be associated with the cold neutral medium (see Falgarone et al. 2005, and ref-

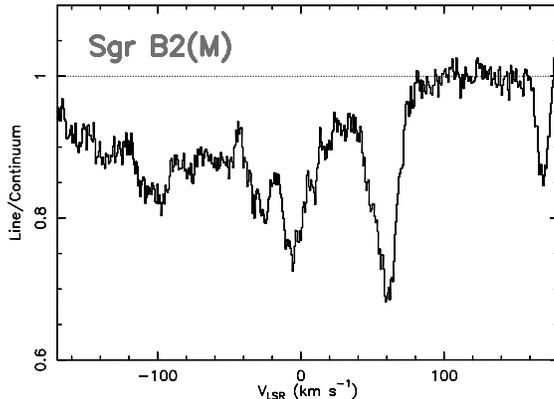


Figure 2.  $^{13}\text{CH}^+$  spectrum toward Sgr B2(M). Absorption toward the Sgr B2 envelope (at  $\sim 62 \text{ km s}^{-1}$ ) and the foreground line-of-sight clouds (at negative velocities) is seen. Note that the  $-45 \text{ km s}^{-1}$  component, most prominent in  $^{13}\text{CO}$ , is quite weak in  $^{13}\text{CH}^+$ . This shows that the two molecules trace quite different regions.

erences therein). Local temperature enhancement due to shocks, photoelectric heating of the gas in strong radiation fields, formation via a fraction of translationally hot  $\text{H}_2$ , boundary layers heated by turbulence, and transiently heated layers of hot gas from intermittent dissipation of interstellar turbulence have been suggested as possible solutions (see references in Gredel 1997; Falgarone et al. 2005; Godard et al. 2009).

$\text{CH}^+$  can be studied at visible wavelengths in low-extinction regions (total H column densities up to  $\sim 8 \times 10^{21} \text{ cm}^{-2}$ ). The fundamental rotational line of  $^{13}\text{CH}^+$  has now been observed toward several additional sources, including Sgr B2, using the CSO (Falgarone et al., in preparation; see Fig. 2), allowing a precise determination of the rest frequency of this transition. These observations offer a new avenue for investigations of the high-temperature, non-LTE chemistry in high-extinction regions (H column densities currently up to  $\sim 5 \times 10^{22} \text{ cm}^{-2}$ ). Upcoming Herschel HIFI observations of the corresponding  $\text{CH}^+$  transition will further improve upon these studies.

## 5 Nitrogen Chemistry: $\text{NH}_2$

The  $\text{NH}_2$  radical was first detected in the ISM by van Dishoeck et al. (1993), who pointed out that this simple hydride is of significant interest for testing the production pathways of nitrogen-bearing molecules, as its chemistry is directly related to that of  $\text{NH}_3$ .  $\text{NH}_2$  can be formed in the gas phase through a chain of reactions starting with  $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$  (e.g., Herbst & Klemperer 1973; Langer & Graedel 1989), which can occur at low temperatures as long as the  $\text{H}_2$  ortho-to-para ratio (OPR) is greater than a few times  $10^{-4}$  (Le Bourlot 1991). The subsequent series of abstraction reactions leads to  $\text{NH}_3^+$  and  $\text{NH}_4^+$ , which can recombine with electrons to form  $\text{NH}_2$  and  $\text{NH}_3$ .

Grain-surface chemistry predicts high abundances of  $\text{NH}_3$ , but not  $\text{NH}_2$  in grain mantles (e.g., Hasegawa & Herbst 1993). In hot cores or shocked re-

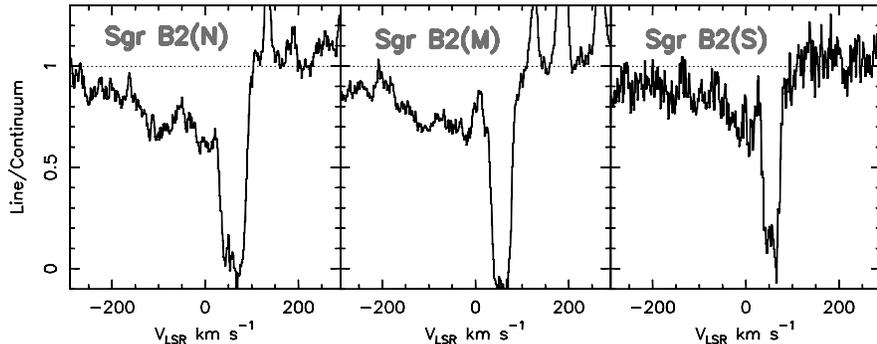


Figure 3. Spectra of the fundamental transition of  $\text{NH}_2$  toward Sgr B2(N), (M), and (S) sources, observed with CSO. The former two sources are separated by  $\sim 45''$ , compared to the CSO beam size of  $\sim 15''$  at 462 GHz.

gions, ammonia molecules can be released from grain mantles, altering the gas-phase  $\text{NH}_3/\text{NH}_2$  ratio. This scenario is consistent with the observations of van Dishoeck et al. (1993), which suggest that  $\text{NH}_2$  is present mostly in the low-density Sgr B2 envelope, and not in the embedded hot cores where grain mantle sublimation takes place. The  $\text{NH}_3/\text{NH}_2$  ratio can thus provide excellent constraints on the relative importance of the gas-phase vs. grain-surface reactions in astrophysical environments.

New, high sensitivity  $\text{NH}_2$  spectra toward Sgr B2 obtained with the CSO (Gerin et al., in preparation; Fig. 3) show spatially extended absorption from both the cloud envelope, as well as the foreground line-of-sight clouds, with the envelope absorption being much more pronounced than in  $^{13}\text{CH}^+$  (Fig. 2). Water and ammonia absorption have been detected over the same velocity range by SWAS and Odin (e.g., Neufeld et al. 2000; Hjalmarsen et al. 2005). Herschel HIFI observations of  $\text{NH}_3$  and other nitrogen-bearing hydrides (e.g.,  $\text{NH}$ ,  $\text{NH}^+$ ), combined with ground-based observations of  $\text{NH}_2$ , promise to greatly improve our understanding of the nitrogen chemistry.

## 6 Halides: HCl

HCl was the first chlorine-bearing molecule detected in space (Blake et al. 1985), using KAO. Chlorine chemistry is relatively simple in dense clouds, with atomic Cl and HCl being the main reservoirs of this element (Blake et al. 1986; Schilke et al. 1995). HCl is produced from the  $\text{H}_2\text{Cl}^+$  ion. At high densities, the main reaction is  $\text{H}_2\text{Cl}^+ + \text{CO} \rightarrow \text{HCl} + \text{HCO}^+$ , leading to an increased abundance of HCl. In OMC-1, HCl contains about one third of the available gas-phase chlorine (Schilke et al. 1995). A new Herschel theory program to re-analyze the fluorine and chlorine chemistry is currently under way (PI D. Neufeld) and laboratory measurements of the submillimeter-wave spectrum of  $\text{H}_2\text{Cl}^+$  are available (Araki et al. 2001).

The fundamental HCl transition has a high critical density and is well suited for absorption studies (e.g., Zmuidzinas et al. 1995, KAO data). Furthermore, the transition is split into three hyperfine components, allowing direct determi-

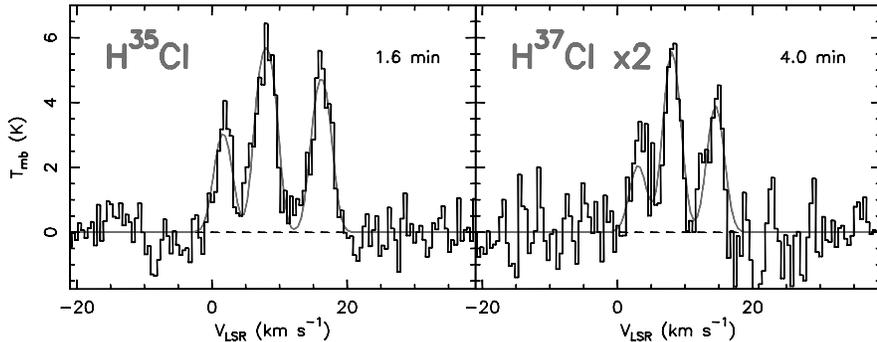


Figure 4. Spectra of  $\text{H}^{35}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$  in OMC-1 ( $0,100''$ ) with hyperfine structure fits overlaid. A preliminary  $^{35}\text{Cl}/^{37}\text{Cl}$  isotopic ratio is  $3.7 \pm 0.8$ , consistent with the solar ratio of 3.1. The spectrum is seen in emission, as there is no foreground absorbing gas on this line of sight, and the gas density is sufficient for collisional excitation.

nation of the line optical depth. Simultaneous observations of the corresponding  $^{37}\text{Cl}$  line allow a direct measurement of the  $^{35}\text{Cl}/^{37}\text{Cl}$  isotopic ratio. Measurements of the HCl abundance can serve as a valuable probe of depletion (as in the case of HF; Neufeld et al. 1997). In the diffuse ISM, chlorine is depleted by a factor of 2–3, with the depletion increasing steeply with density (Salez et al. 1996). Figure 4 shows recent CSO spectra of  $\text{H}^{35}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$  in OMC-1 (Peng et al., in preparation). Sensitive observations of HCl with HIFI will further improve our understanding of Cl depletion in high-extinction regions.

## 7 Low Temperature Deuteration: $\text{H}_3^+$ and Ammonia

Deuterated species are of particular interest for molecular astrophysics and astrochemistry. On the one hand, they are probes of peculiar, low-temperature non-equilibrium chemistry (fractionation). But more importantly, they are excellent tracers of the physical conditions at the early stages of star formation. Dust emission is a good mass tracer, but provides no information about gas kinematics. At the same time, the abundant molecular tracers have been recently shown to deplete onto dust grains under conditions characteristic of prestellar cores and mid-planes of protoplanetary disks (Bergin et al. 2002; Bacmann et al. 2002, 2003). The non-depleting tracers, such as  $\text{H}_3^+$ , are often symmetric molecules and have no allowed transitions. Substituting one or more deuterium atoms breaks the symmetry and allows the deuterated species to be studied by means of rotational spectroscopy.

The cosmic abundance of deuterium is  $\sim 1.5 \times 10^{-5}$ , yet D/H ratios of order 0.1 are often measured in heavy molecules, in the cold, dense ISM. The detections of multiply deuterated molecules, in particular triply deuterated ammonia (Lis et al. 2002; van der Tak et al. 2002), have led to significant revisions of the gas-phase deuterium chemistry. The fundamental realization was that deuteration of  $\text{H}_3^+$ , has to be extended beyond  $\text{H}_2\text{D}^+$ , to  $\text{D}_2\text{H}^+$ , and  $\text{D}_3^+$  (Phillips & Vastel 2003; Roberts et al. 2003). Shortly after,  $\text{D}_2\text{H}^+$  was detected using the CSO (Vastel et al. 2004).

Deuterium chemistry is closely related to the freeze-out of abundant gas-phase species onto dust grains. Molecular differentiation is now firmly established in starless cores (e.g., Bergin et al. 2002). At low temperatures, the “classical” molecular tracers, such as CO and CS, deplete onto dust grains at densities above a few  $\times 10^4 \text{ cm}^{-3}$ . Nitrogen bearing species, such as  $\text{N}_2\text{H}^+$  are unaffected by depletion up to a few  $\times 10^5 - 10^6 \text{ cm}^{-3}$ , while ammonia abundance has been shown to be enhanced in the central regions (Tafalla et al. 2002, 2004). Recent chemical calculations (e.g., Walmsley et al. 2004) suggest that at densities above a few  $\times 10^6 \text{ cm}^{-3}$  even the nitrogen-bearing species should eventually condense onto dust grains. Under such conditions, the  $\text{H}_3^+$  ion and its deuterated isotopologues become the only tracers of  $\text{H}_2$ . However, as the density threshold is model- and time-dependent, good observational constraints are needed. Observations of  $\text{H}_2\text{D}^+$  (e.g., Vastel et al. 2006; Caselli et al. 2008) and the fundamental submillimeter lines of ammonia isotopologues are of particular interest as probes of evolved cores (Lis et al. 2006, 2008).

The degree of deuteration of molecular ions and neutrals is further complicated by the molecular hydrogen spin statistics, and hence the chemical and thermal history of the gas (Flower et al. 2006). Protostars forming in young ( $< 10^6 \text{ yr}$ ) clouds are not expected to display high levels of deuteration, since in such clouds a high  $\text{H}_2$  OPR is an indication of its relatively recent formation. It is thus important to study both ortho- and para- transitions of  $\text{H}_2\text{D}^+$  and  $\text{D}_2\text{H}^+$  to accurately derive total column densities of these molecules. Current observations are limited to specific nuclear spin states (ortho- $\text{H}_2\text{D}^+$  and para- $\text{D}_2\text{H}^+$ ). Herschel HIFI will provide measurements of the fundamental ortho- $\text{D}_2\text{H}^+$  transition at 1.48 THz. Unfortunately, the para- $\text{H}_2\text{D}^+$  transition at 1.37 THz is not observable, as it falls in the frequency gap between HIFI bands 5 and 6.

## 8 High-Temperature Deuteration: $\text{CH}_3^+$

Low-temperature deuteration is driven by the  $\text{H}_3^+$  ion. However, some deuterated species are detected in warm ( $\sim 50 \text{ K}$ ) environments (e.g., Wootten 1987). The DCN/HCN abundance ratio in OMC-1 is 0.01–0.06 (Schilke et al. 1992), and in the Orion Bar 0.007–0.009 (Leurini et al. 2006). The persistence of DCN at high temperatures has been interpreted as a consequence of a high  $\text{CH}_2\text{D}^+/\text{CH}_3^+$  ratio (Roueff et al. 2007), resulting from an exothermicity involved in the  $\text{CH}_3^+ + \text{HD}$  reaction (394 K, as compared to 230 K for the reaction of  $\text{H}_3^+ + \text{HD}$ ). As  $\text{CH}_3^+$  cannot be detected directly, due to its zero dipole moment,  $\text{CH}_2\text{D}^+$  offers an excellent opportunity to probe such a deuterium fractionation scenario. Roueff et al. (in preparation) have recently obtained a tentative detection of  $\text{CH}_2\text{D}^+$  toward Orion IRc2 using the CSO. Spectral features at the frequencies of both para- $\text{CH}_2\text{D}^+$  ( $1_{0,1} - 0_{0,0}$ ) at 278.7 GHz (Fig. 5) and ortho- $\text{CH}_2\text{D}^+$  ( $2_{1,1} - 2_{1,2}$ ) at 201.8 GHz are present, when the nearby strong contaminating lines are carefully removed. The implied fractional abundance of  $\text{CH}_2\text{D}^+$  with respect to molecular hydrogen is  $\sim 10^{-10}$ , consistent with the Roueff et al. gas-phase chemical models, and the OPR is that expected from equilibrium at a temperature of about 50 K (the lowest ortho- $\text{CH}_2\text{D}^+$  state is 18.5 K above the ground state). The best-fit  $\text{CH}_2\text{D}^+$  rest frequencies are 278.6918 GHz and 201.7542 GHz, close to the predictions of Roesslein et al. (1991). From the astrochemical point of

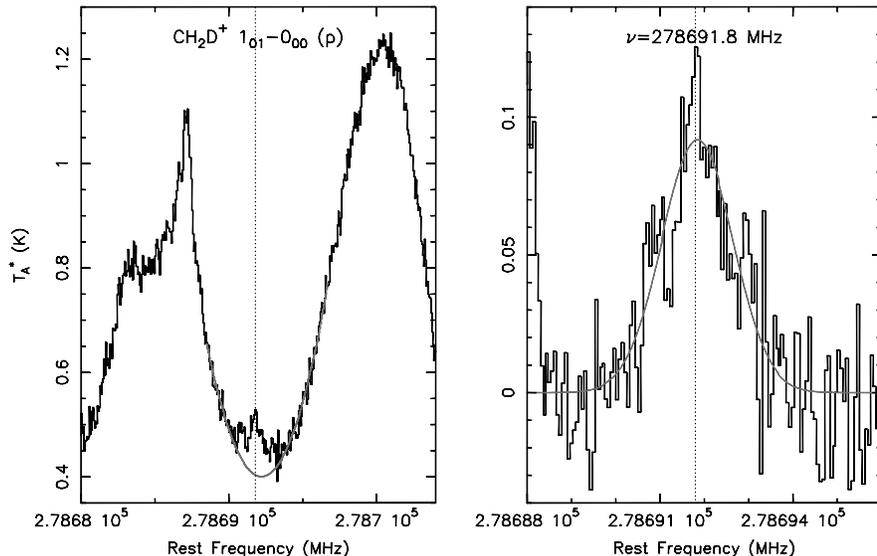


Figure 5. Spectrum at the frequency of the  $(1_{0,1} - 0_{0,0})$  para- $\text{CH}_2\text{D}^+$  transition toward Orion IRC2. The left panel shows the original spectrum, without a baseline subtracted. The thin line shows a second order polynomial baseline used to subtract the emission from the neighboring strong lines. The right panel shows the final baseline-subtracted spectrum with a Gaussian fit superposed. The best-fit rest frequency is 278691.8 MHz.

view, this result, if confirmed, provides strong support for active gas-phase chemistry involving  $\text{CH}_3^+$  and its deuterated isotopologues. Herschel HIFI will enable observations of additional transitions of  $\text{CH}_2\text{D}^+$ .

## 9 Future Prospects

The Herschel Space Observatory was launched on 14 May 2009. With its 3.5 m primary mirror, it is the largest and most sensitive space facility operating at submillimeter/far-infrared wavelengths. The HIFI instrument, providing almost complete frequency coverage from 488 to 1903 GHz, offers unparalleled spectroscopic capabilities, providing a clear view of the Molecular Universe, unobstructed by the Earth's atmosphere. Key hydrides and deuterides containing the heavy elements C, N, O, F, and Cl will be studied within the PRISMAS and HEXOS programs. These observations will address the role of high-temperature, non-equilibrium reactions in the formation of interstellar molecules, and the question of how such reactions are driven. They will also improve our understanding of the role of grain-surface reactions in formation of interstellar molecules and the growth of large carbon chains, bridging the gap between molecules and aggregates.

However, in order to fully understand the chemical evolution within the Molecular Universe, a large volume of supporting ground-based and airborne data will be required. Observations to date have clearly demonstrated that a large fraction of the submillimeter band is accessible from high-altitude moun-

tain sites, such as Mauna Kea or Chajnantor (e.g., CSO, JCMT, APEX). Sub-orbital platforms (including SOFIA and balloons) will provide additional opportunities to study key species that are not accessible from the ground (e.g., HD, C II, H<sub>2</sub><sup>18</sup>O, OH), well beyond the lifetime of Herschel. ALMA, when it becomes operational in the next decade, with its unparalleled sensitivity and angular resolution, will offer outstanding spectroscopic capabilities. This instrument will be perfectly suited for studies of the chemical composition of the compact hot core regions in the immediate vicinity of the newly formed stars, where the intense heating causes ice-mantle sublimation, driving rich, complex chemistry. Nevertheless, even with ALMA, complete spectroscopic surveys of hundreds of sources over the full wavelength range will be prohibitive in terms of time required. Moreover, the extended emission will be largely resolved out in the interferometric data. Since the roots of the chemical complexity of the hot core sources can be related to the initial conditions within the envelopes surrounding the cores as well as to their earlier history, a program of sensitive, high spatial resolution spectral survey of all relevant spatial scales is needed. A new generation of wideband heterodyne array receivers, covering full atmospheric windows, or multiple windows simultaneously, will make this feasible in the next decade. More advanced calibration techniques, improved sideband deconvolution, and the large numbers of lines from the same species, will provide the opportunity to extract much more definitive results than previously obtained. The line shapes and intensities from the spectroscopic surveys will provide hundreds to thousands of constraints on physical and chemical models of sources and of the molecular astrophysics as well. For a relatively simple physical model of some component of a source, the physical parameters of the astronomical region can be determined using the multiple line spectra of simple, well-characterized molecules. However, more complex models will be required to properly model the temporal and spatial variations of source conditions, and these models will rely on the spectral map data that this program will provide.

The observational data complementary to that provided by ALMA can be supplied by large single-dish telescopes (e.g., Green Bank Telescope, GBT; Institut de Radioastronomie Millimétrique, IRAM 30-m Telescope; Large Millimeter Telescope, LMT; and Cornell-Caltech Atacama Telescope, CCAT), equipped with large-format heterodyne arrays, with bandwidths covering full atmospheric windows. Arrays with as many as 64 pixels are currently under construction and next generation instruments with hundreds of pixels can be envisioned. Recent progress in digital spectrometer technology has largely solved the problem of high-resolution spectroscopic analysis of multiple pixel systems. SOFIA will also be a platform for proving new spectroscopic imaging capabilities at wavelengths not accessible from the ground and in this respect, it complements future large ground based telescopes.

Analysis and interpretation of the vast quantities of data that will be collected will require coordinated efforts in laboratory spectroscopy (line identification) and theoretical modeling (chemistry and radiative transfer, incorporated into dynamical cloud, core, and disk models). There is the critical need for collisional rate coefficients along with spectroscopic identifications, as well as laboratory and theoretical studies of fundamental chemical processes (e.g., to determine bimolecular reaction rates). This work is already partly under way in preparation for Herschel, SOFIA, and ALMA.

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