Using deuterated H$_3^+$ and other molecular species to understand the formation of stars and planets

BY F. F. S. van der Tak*

SRON Netherlands Institute for Space Research, Landleven 12, 9747 AD Groningen, The Netherlands

The H$_3^+$ ion plays a key role in the chemistry of dense interstellar gas clouds where stars and planets are forming. The low temperatures and high extinctions of such clouds make direct observations of H$_3^+$ impossible, but lead to large abundances of H$_2$D$^+$ and D$_2$H$^+$ that are very useful probes of the early stages of star and planet formation. Maps of H$_2$D$^+$ and D$_2$H$^+$ pure rotational line emission towards star-forming regions show that the strong deuteration of H$_3^+$ is the result of near-complete molecular depletion of CNO-bearing molecules onto grain surfaces, which quickly disappears as cores warm up after stars have formed. In the warmer parts of interstellar gas clouds, H$_3^+$ transfers its proton to other neutrals such as CO and N$_2$, leading to a rich ionic chemistry. The abundances of such species are useful tracers of physical conditions such as the radiation field and the electron fraction. Recent observations of HF line emission towards the Orion Bar imply a high electron fraction, and we suggest that observations of OH$^+$ and H$_2$O$^+$ emission may be used to probe the electron density in the nuclei of external galaxies.

Keywords: astrochemistry; interstellar medium; stars: formation

1. Introduction

The H$_3^+$ ion plays a central role in the physics and chemistry of interstellar gas clouds where stars and planets are forming [1]. In cold parts of such clouds, where temperatures are \( \lesssim 20 \text{ K} \), H$_3^+$ is converted into its deuterated forms, which become the dominant forms of H$_3^+$ at \( T \lesssim 10 \text{ K} \). Here, H$_3^+$ can be studied directly by rotational spectroscopy of H$_2$D$^+$ and D$_2$H$^+$ in the far-infrared and submillimetre. In warm interstellar clouds (\( T \sim 30–100 \text{ K} \)), a direct study of H$_3^+$ is possible through vibrational spectroscopy in the mid-infrared, and this technique is widely used for lines of sight through the diffuse interstellar medium (see contributions by McCall, Indriolo and Geballe to this volume). To peer into highly opaque star-forming regions and to map their spatial structure, emission from indirect probes such as HCO$^+$ and N$_2$H$^+$ is used, which form by proton transfer of H$_3^+$ to CO and N$_2$, respectively.

*vdtk@sron.rug.nl

One contribution of 21 to a Theo Murphy Meeting Issue ‘Chemistry, astronomy and physics of H$_3^+$’.
The goal of this study is to review recent work on the astrophysical use of \( \text{H}^{+}_{3} \) and its deuterated forms. Because the role of \( \text{H}^{+}_{3} \) in the warm and cold regimes is so different, this review discusses them separately: §2 covers the study of \( \text{H}_2\text{D}^{+} \) and \( \text{D}_2\text{H}^{+} \) in cold clouds, while §§3 and 4 treat probes of \( \text{H}^{+}_{3} \) in warm regions. Space limitations prevent a complete coverage of all work since the previous \( \text{H}^{+}_{3} \) conference held in 2006; therefore, the content of this review is necessarily biased towards the interests of its author. In particular, this study does not cover the recent results on the ortho/para ratios of \( \text{H}_2 \) and \( \text{H}_2\text{D}^{+} \), which may constrain the ages of pre-stellar cores; see the contribution by Pagani to this volume. This work is also of interest as it marks the first use of the detailed state-to-state rate coefficients for de-excitation of \( \text{H}_2\text{D}^{+} \) in collisions with \( \text{H}_2 \) [2]. Collisions between \( \text{H}^{+}_{3} \) and \( \text{H}_2 \) may lead to reaction (fully elastic case), excitation (fully inelastic case) or both. Thus, the rates by Hugo et al. [2] are a major step forward for the interpretation of interstellar \( \text{H}_2\text{D}^{+} \) lines, compared with the scaled radiative rates used previously (see discussion by van der Tak et al. [3]). The next step up from Hugo’s statistical approach would be full quantum scattering calculations, which would require a large effort because of the reactive nature of deuterated \( \text{H}^{+}_{3} \).

Another important topic that this study does not discuss in detail is the observations of \( \text{H}_2\text{D}^{+} \) in protoplanetary discs. The conditions in the midplanes of such discs are somewhat similar to those in pre-stellar cores: the densities are high enough (\( \gtrsim 10^8 \text{ cm}^{-3} \)) that ultraviolet radiation does not penetrate, leading to a low temperature (\(<10 \text{ K}\)) and a low ionization fraction. The theory of chemistry in the limit of complete depletion of CNO-bearing species [4] was originally developed to describe pre-stellar cores, but may be even more applicable to protoplanetary disc midplanes. Here, all but the lightest molecular species freeze out onto grain surfaces, and \( \text{H}_2\text{D}^{+} \) is the only available ion to probe the ionization rate of the gas that controls the efficiency of interaction with the magnetic field. Because the magneto-rotational instability is thought to play a major role in the dynamics of such discs, several teams have searched for \( \text{H}_2\text{D}^{+} \) line emission. After an initial claimed detection by Ceccarelli et al. [5], only upper limits have been reported by Guilloteau et al. [6], Qi et al. [7], Chapillon et al. [8] and Öberg et al. [9]. See these papers for the quantitative implications of the limits, and the perspectives with future telescopes.

### 2. Cold gas: spatial distribution of \( \text{H}_2\text{D}^{+} \) and \( \text{D}_2\text{H}^{+} \)

As reviewed previously [10], the astrophysical use of deuterated \( \text{H}^{+}_{3} \) is based on the fact that the formation of \( \text{H}_2\text{D}^{+} \) and \( \text{D}_2\text{H}^{+} \) from \( \text{H}^{+}_{3} + \text{HD} \) is strongly enhanced at low temperatures (\( \lesssim 20 \text{ K} \)). As a result, the abundance of deuterated \( \text{H}^{+}_{3} \) peaks in the dense, cold concentrations of gas within clouds is known as cloud cores. The temperature dependence is enhanced by a second effect: the main destroyer of deuterated \( \text{H}^{+}_{3} \) is \( \text{CO} \), which freezes out onto grain surfaces under the same dense and cold conditions. These two effects make \( \text{H}_2\text{D}^{+} \) and \( \text{D}_2\text{H}^{+} \) ideal tracers of the initial conditions of star formation; see Sipilä et al. [11] for recent models of this situation. At higher temperatures (approx. 20–30 K), reactions with \( \text{CH}_2\text{D}^{+} \) and \( \text{C}_2\text{HD}^{+} \) rather than with \( \text{H}_2\text{D}^{+} \) act to enrich molecular D/H ratios [12–14].
The importance of deuterated $\text{H}_3^+$ has been realized for a long time (e.g. [15]) but whether this potential could be used remained unclear until the first detection spectra of interstellar $\text{H}_2\text{D}^+$ [16,17]. Motivated by these results, Caselli et al. [18] presented the first survey of $\text{H}_2\text{D}^+$ line emission, towards a sample of 10 starless cores and six protostellar cores. Using the Caltech Submillimeter Observatory, the $\text{H}_2\text{D}^+$ line at 372 GHz is detected in seven starless cores and in four protostellar cores. The column density of $\text{o-}\text{H}_2\text{D}^+$, derived from the 372 GHz line intensity, is also higher in starless cores than in protostellar cores. The brightest $\text{H}_2\text{D}^+$ lines are detected towards the densest and most centrally concentrated starless cores, where the CO depletion factor (measured by the ratio of CO line emission to dust continuum emission) and the deuterium fractionation (measured as the $\text{N}_2\text{D}^+$/\text{N}_2\text{H}^+$ line ratio) are also largest.

The results of this survey are consistent with the expectation that $\text{H}_2\text{D}^+$ traces very dense and cold gas, partly because the reaction of $\text{H}_3^+ + \text{HD}$ proceeds mainly in the forward direction, and partly because the main destroyer of $\text{H}_2\text{D}^+$, CO, freezes out onto grain surfaces. In particular, at gas temperatures above 15 K, low CO depletion factors and large abundance of negatively charged small dust grains or PAHs drastically reduce the deuterium fractionation to values inconsistent with those observed towards pre-stellar and protostellar cores.

Comparing their results with a chemical model, Caselli et al. [18] found that several parameters, including the cosmic ray ionization rate, the depletion of CO (and generally of neutral species), the volume density, the dust grain size distribution and the fraction of PAHs all affect the $\text{H}_2\text{D}^+$ abundance. In addition, the ortho-to-para ratio of H$_2$ is a key parameter [19]. The current data do not allow us to disentangle these effects: observations of the p-$\text{H}_2\text{D}^+$ ground state line would help us to break this degeneracy, as would detailed measurements of the temperatures and densities of the cores as a function of the radius.

The results reported by Caselli et al. [18] are corroborated by mapping of $\text{H}_2\text{D}^+$ line emission in the Oph B2 core [20]. The column density distributions of both $\text{H}_2\text{D}^+$ and $\text{N}_2\text{D}^+$ in this core show no correlation with the total H$_2$ column density. Instead, the deuterium fractionation in the Oph B2 core, again measured by the $\text{N}_2\text{D}^+$/\text{N}_2\text{H}^+$ ratio, systematically decreases with proximity to the embedded protostars, out to distances $\gtrsim 0.04$ pc.

Using the multi-pixel CHAMP+ receiver on the APEX telescope, Parise et al. [21] have successfully detected $\text{D}_2\text{H}^+$ emission at 692 GHz from the H-MM1 prestellar core located in the LDN 1688 cloud. The emission is detected on several pixels of the CHAMP+ array, hence extended on a scale of at least 40", corresponding to approximately 4800 AU. This is the first secure detection of interstellar $\text{D}_2\text{H}^+$, after the tentative detection by Vastel et al. [22]. The column densities of $\text{H}_2\text{D}^+$ and $\text{D}_2\text{H}^+$ towards this core are similar, which implies strong depletion of CO: model calculations indicate that 90–99% of CO is frozen on dust grains.

Other maps of $\text{H}_2\text{D}^+$ emission will be published soon. The region NGC 1333 IRAS4, where $\text{H}_2\text{D}^+$ was first detected, is part of the Spectral Legacy Survey at the JCMT [23], which initially covered the range 330–360 GHz but was later extended to 373 GHz. This survey provides images of molecular line emission over a $2 \times 2'$ field at 15" resolution towards four different star-forming environments. In the case of NGC 1333 IRAS4, the $\text{H}_2\text{D}^+$ emission is found to have a spatial distribution unlike that of other ions such as $\text{DCO}^+$ or $\text{N}_2\text{H}^+$ or the dust.
continuum, which peaks near the embedded protostars. The fact that H$_2$D$^+$ emission peaks away from heat sources confirms the idea that H$_2$D$^+$ is rapidly destroyed as cores warm up [24].

The first mapping survey of H$_2$D$^+$ towards pre-stellar cores is also underway. Using the JCMT, Di Francesco et al. [25] have made maps of H$_2$D$^+$ line emission towards a sample of six pre-stellar cores, selected from the N$_2$D$^+$/N$_2$H$^+$ study by Crapsi et al. [26] to have high N$_2$D$^+$/N$_2$H$^+$ ratios. For each of these cores, the H$_2$D$^+$ emission is found to peak at the core centre. The emission is extended over $\approx 30''$, as seen in the maps and confirmed by the similarity of H$_2$D$^+$ antenna temperatures between the CSO and JCMT telescopes.

3. Warm gas: reactive ions in star-forming regions

Although large abundances of interstellar H$_2$D$^+$ and D$_2$H$^+$ require low temperatures ($\lesssim 10$ K), proton transfer from H$_3^+$ to other molecules also takes place in warm gas. In particular, reactions of interstellar H$_3^+$ with species such as CO and N$_2$ lead to HCO$^+$ and N$_2$H$^+$ which are widely observed in the interstellar medium. Stable ionic species are useful as tracers of the interaction of interstellar gas with magnetic fields [27,28], whereas ions which react rapidly with H$_2$ trace other physical conditions such as the gas density and the local radiation field. The second part of this review paper discusses a few recent results in our understanding of the physics and chemistry of reactive ions in interstellar space.

(a) The $H_nO^+$ puzzle

The HIFI instrument is a heterodyne spectrometer onboard ESA’s Herschel space observatory that provides access to the spectral ranges between 480–1250 and 1410–1910 GHz at a resolution of $\approx 0.1$ MHz. One HIFI highlight is the discovery of interstellar OH$^+$ and H$_2$O$^+$ [29,30], which are intermediate steps in the ionic formation route of interstellar H$_2$O. This route begins with charge transfer of H$^+$ or H$_3^+$ to O, proceeds with reactions of H$_2$ with O$^+$, OH$^+$ and H$_2$O$^+$, and ends with the dissociative recombination of H$_3$O$^+$ which produces H$_2$O. Although this route dominates the formation of H$_2$O in the gas phase at temperatures $\lesssim 250$ K, which is the bulk part of the neutral interstellar medium, the abundances of OH$^+$ and H$_2$O$^+$ were predicted to be low because these species react rapidly with H$_2$, which is the bulk species of dense interstellar gas clouds. In other words, the rate-limiting steps of ionic H$_2$O formation were thought to be the formation of O$^+$ and the dissociative recombination of H$_3$O$^+$.

Observations with HIFI have revealed strong absorption by interstellar OH$^+$ and H$_2$O$^+$ on many lines of sight in our Galaxy [31], and towards nearby starburst galaxies such as M82 [32], NGC 253 and NGC 4945. The large column densities of these reactive species imply that the hydrogen in these clouds is neither purely in atomic form, because no OH$^+$ and H$_2$O$^+$ would be produced, nor in purely molecular form, because all OH$^+$ and H$_2$O$^+$ would react into H$_3$O$^+$ and H$_2$O. Previous models of the structure of molecular clouds, where clouds are either diffuse and hydrogen atomic or dense and hydrogen molecular, are inconsistent with these observations and must be rejected [33]. While PDR models are able to explain the observed amounts of OH$^+$ and H$_2$O$^+$ with diffuse gas where most
hydrogen is atomic (Gerin, this volume), the distribution of diffuse and dense gas must be reconsidered, as already indicated by millimetre-wave absorption line studies of diffuse clouds [34].

A major puzzle in the study of interstellar OH$^+$ and H$_2$O$^+$ (which I collectively call H$_n$O$^+$) is the Herschel–SPIRE spectrum of the active galactic nucleus Mrk 231, where lines of H$_n$O$^+$ appear in emission [35]. The large dipole moments and the small reduced masses of H$_n$O$^+$ imply high line frequencies and large radiative decay rates, so that excitation of their rotational levels requires extremely high densities and line emission is not expected to be observable. Since my previous discussion of this topic at the SMILES conference [36], also organized by Prof. Oka, a second report of H$_n$O$^+$ emission has appeared for the ultraluminous merger Arp 220 [37]. In this galaxy, both the OH$^+$ and the H$_2$O$^+$ lines show a P Cygni-type profile, which consists of blueshifted absorption and redshifted emission, and which is characteristic of a wind or an outflow.

One hint at the solution of this ‘H$_n$O$^+$ puzzle’ may be the HF molecule. Like H$_n$O$^+$, HF appears in absorption on most lines of sight through the interstellar medium of our Galaxy [38], which is expected from the large dipole moment and small reduced mass of the molecule. The SPIRE spectrum of Mrk 231, however, shows HF in emission [35], and the SPIRE spectrum of Arp 220 shows a P Cygni profile for the HF line [37]. This behaviour is the same as for H$_n$O$^+$, which suggests (but does not imply) a connection between these species.

(b) Detection of HF emission

In dense interstellar gas clouds, the bulk of the hydrogen is in the form of H$_2$, which is essentially unobservable at low temperatures. The common tracer for H$_2$ clouds is the CO molecule, which is abundant and chemically stable, but which photodissociates at H$_2$ column densities below \( \approx 1.5 \times 10^{21} \text{ cm}^{-2} \) [39]. While CH may be used for the intermediate (translucient cloud) regime [40], a proxy for H$_2$ at very low column densities was missing until the Herschel mission. Because the reaction of F with H$_2$ leading to HF is exothermic and HF photodissociation is slow, HF is expected to be the main carrier of fluorine in the gas phase, as long as \( \gtrsim 10^{-6} \) of hydrogen is in the form of H$_2$ [41] (figure 1).
The first confirmation of these predictions came from observations with the LWS instrument onboard the ISO satellite, which measured absorption in the $J = 2–1$ line of HF towards Sgr B2 [43]. The Herschel–HIIF instrument gives us first access to the rotational ground state of HF, and observations of widespread absorption in this line indicate an HF abundance of $(1–2) \times 10^{-8}$ in diffuse clouds, close to the interstellar (and the solar) abundance of fluorine [38]. Absorption is also observed towards dense clouds, but the implied abundance is approximately $100 \times$ lower [44], suggesting that depletion on grain surfaces plays a role.

The large dipole moment of HF and the high frequency of its $J = 1–0$ line imply that radiative decay to the ground state is fast, which explains why the line usually appears in absorption on lines of sight through the interstellar medium [45,46]. Only very dense environments such as the inner envelopes of late-type stars show the HF line in emission [47]. The only detection of HF emission from the galactic interstellar medium so far is towards the Orion Bar, and it is a surprise because the H$_2$ density in this region is not high enough to excite the line [42]. Instead, collisions with electrons appear to dominate the excitation of HF; non-thermal excitation mechanisms seem less likely, as detailed in §4 of this paper. Line emission of HF thus appears to trace regions of molecular gas with a high electron density, which in the case of the Orion Bar is caused by strong ultraviolet irradiation by the Trapezium stars.

Excitation by electrons may also apply to active galactic nuclei where the Herschel–SPIRE spectra show HF in emission such as Mrk 231 [35] or as a P Cygni profile such as Arp 220 [37]. In contrast, the Cloverleaf quasar at $z = 2.56$ shows HF in pure absorption [48], which may imply a lower electron density. Given the importance of electron excitation for HF, the appearance of the line in emission or absorption may be a measure of the local ionization rate by ultraviolet photons (in a starburst) or by cosmic rays (in an AGN).

The similarity of the line profiles of HF and H$_n$O$^+$ in the Herschel–SPIRE spectra of Mrk 231 and Arp 220 may not be a coincidence. Electron impact excitation may also play a role for H$_2$O$^+$ in these sources. Cross sections for the inelastic collision of the e–H$_n$O$^+$ system are urgently needed to test this hypothesis. Weak OH$^+$ emission is also seen towards the Orion Bar, providing further evidence for this trend [49].

4. Alternative mechanisms to produce HF emission

(a) Infrared pumping of HF

Radiative excitation of the HF line may occur through the $v = 1–0$ vibration mode at 2.55 μm. This wavelength is too short for resonances with PAH features, which leaves dust continuum and H$_2$ line emission as options. Infrared pumping is not known to play a role for other molecular species in the Orion Bar, but most of these species occur deep in the molecular cloud where near-infrared radiation does not penetrate owing to extinction by dust. In contrast, HF readily forms at low extinction where both dust continuum and H$_2$ line emission are strong.

We have calculated the positions of the $v = 1–0$ lines of HF from the constants of Ram et al. [50] up to the $J = 10$ level. Three lines are close to a line of H$_2$; the P(1) line at 3920.312 cm$^{-1}$, the R(0) line at 4000.989 cm$^{-1}$ and the R(1)
line at 4038.962 cm$^{-1}$. Their respective partners are the H$_2$ $v = 2–1$ Q(1) line at 3920.053 cm$^{-1}$, the H$_2$ $v = 1–0$ Q(7) line at 4000.075 cm$^{-1}$ and the H$_2$ $v = 1–0$ Q(6) line at 4039.507 cm$^{-1}$. Especially the first match is close, which is encouraging because the P(1) line leads directly to the $J = 1$ level observed with HIFI, and the matching H$_2$ line is one of the strongest H$_2$ lines in Model 14 of Black & van Dishoeck [51], with an intensity of $\approx 60$ per cent of the well-known $v = 1–0$ S(1) line at 2.12 mm. However, the separations of these line pairs of 20, 69 and 40 km s$^{-1}$ exceed the widths of the H$_2$ pure rotational lines in the Orion Bar of 4–6 km s$^{-1}$ [52]. The spatial distribution of the H$_2$ pure rotational lines is similar to that of the rovibrational lines [53], so that their widths are probably similar too; Tielens et al. [54] already rule out a large contribution by shocks to the H$_2$ rovibrational line emission from the Orion Bar.

Alternatively, the infrared pumping of HF may take place by continuum radiation from dust. Following Carroll & Goldsmith [55], efficient pumping requires that $A_{vib} \epsilon f / (e^{h\nu/kT_d} - 1)$ exceeds $A_{rot}$, where $A_{vib}$ and $A_{rot}$ are the vibrational and rotational Einstein A coefficients, $\epsilon$ is the dust emissivity (assumed to be unity in the mid-infrared), $T_d$ is the dust temperature and $f$ is the geometric filling factor of the dust. Because the vibrational frequency of 3961.4 cm$^{-1}$ is high ($h\nu/k \gg T_d$), the expression simplifies to $f e^{-h\nu/kT_d} > A_{rot}/A_{vib}$, where the right-hand side is about $1/100$ using $A_{vib} = 203$ s$^{-1}$ from Ram et al. [50].

If the dust radiation field fills the entire sky as seen from the HF cloud ($f = 1$), the lower limit for the dust temperature is 1170 K. While such warm dust could exist locally in the Orion Bar, this temperature seems unreasonably high as an average over a 7200 AU region. Even transiently heated mini-grains will rarely get so warm. Smaller filling factors exacerbate this problem: for example, 50 per cent sky coverage means a dust temperature of at least 1380 K, and 10 per cent coverage implies $T_d > 2340$ K. Hence, continuum radiation cannot do the pumping either.

Finally, we consider the possibility that the excitation of HF in the Orion Bar is influenced by radiation from the Trapezium stars. The brightest of these stars is $\theta^1$C Ori, which is 127$''$ away from the HIFI position [56]. Assuming that both objects lie 414 pc from us [57], the stellar continuum flux at the Orion Bar is 2.6 million times stronger than at the Earth. For the 2.5 $\mu$m flux density, we adopt the K band magnitude of 4.14 [58], which corresponds to 11.5 Jy at Earth and 30.3 MJy at the Bar. Dividing this flux density by $4\pi$ gives an angle-averaged radiation field $J_\nu$ of $2.4 \times 10^{-17}$ erg s$^{-1}$ cm$^{-2}$ Hz$^{-1}$ sr$^{-1}$. Setting this equal to the Planck function at a radiation temperature $T_R$, we obtain $T_R = 209$ K at $\lambda = 2.5 \mu$m, which is only slightly larger than the intensity owing to average galactic starlight at the Sun’s location. The corresponding pumping rate in the HF vibrational fundamental is of order $A_{vib}/\{\exp(h\nu/kT_R) - 1\} = 1.8 \times 10^{-10}$ s$^{-1}$, which is much less than the collisional excitation rates by H$_2$ and electrons. We conclude that infrared pumping does not play a role for HF in the Orion Bar.

(b) Formation pumping of HF

Besides infrared pumping, an alternative non-thermal excitation mechanism of HF would be chemical pumping. In this scheme, the excitation of HF is out of thermal equilibrium because the formation and destruction rates are as fast as radiative decay. This mechanism is plausible for the Orion Bar because of the
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high ultraviolet radiation field, which leads to a large amount of material in the regime where \( \text{H}_2 \) is abundant but the HF destruction rate by photodissociation and reaction with \( \text{C}^+ \) is of the order of the maximum formation rate.

Assuming optically thin emission, the observed HF line flux of 7.8 K km s\(^{-1} \) = 1.5 \times 10^{-5} \text{ erg cm}^{-2} \text{ s}^{-1} \text{ sr}^{-1} requires a column density of \( N_{J=1} = 9.5 \times 10^{11} \text{ cm}^{-2} \) in the \( J = 1 \) state of HF. To obtain this by chemical pumping, the HF formation rate \( R = k n(\text{H}_2)n(\text{F})/n(\text{HF}) \) must fulfil \( R/A_{10} \times N_{\text{HF}} \geq 9.5 \times 10^{11} \text{ cm}^{-2} \), where \( A_{10} \) is the Einstein A coefficient of the HF \( J = 1 \) line. The formation of HF is dominated by the reaction of \( \text{H}_2 \) with \( \text{F} \), the rate coefficient of which is given in table 2 of Neufeld & Wolfire [41] and equals \( k = 4.6 \times 10^{-12} \text{ cm}^{3} \text{ s}^{-1} \) at \( T = 80 \text{ K} \). In strong radiation fields, destruction of HF is dominated by photodissociation, at a rate of \( \zeta_{\text{d}} = 1.2 \times 10^{-10} \text{ s}^{-1} \) in the standard Draine field, so that \( \zeta_{\text{d}} = 6 \times 10^{-6} \text{ s}^{-1} \) for the Orion Bar (\( \chi \sim 50000 \)). The HF abundance follows from balancing its formation and destruction rates (\( \zeta_{\text{d}} = R \)),

\[
n(\text{HF})\zeta_{\text{d}} = kn(\text{H}_2)n(\text{F}),
\]

where the sum of the abundances \( X(\text{HF}) + X(\text{F}) \) is constrained by the total amount of fluorine, 1.8 \times 10^{-8} relative to H. The product \( R/A_{10} \times X(\text{HF}) \) reaches its maximum of 4.5 \times 10^{-12} for very high densities, leading to a maximum \( N_{J=1} = 4.5 \times 10^{11} \text{ cm}^{-2} \) when assuming a total gas column density of \( 10^{23} \text{ cm}^{-2} \). For gas densities of \( 10^{6} \text{ cm}^{-3} \), this drops by a factor of 2, for a gas density of \( 10^{5} \text{ cm}^{-3} \) by another factor of 10. Higher temperatures lower the required densities approximately proportionally.

The computation above assumes that every molecule formation leads to an excitation of the \( J = 1 \) state. This premise is reasonable, if not intuitive. The formation of HF releases 1.36 eV in each reaction, which is well above the energy of the \( v = 1 \) state, so that all rotational levels in the vibrational ground state will be about equally populated. The relative fraction of molecules formed in \( J = 0 \) will be very small, and the radiative decay of all other molecules passes through the \( J = 1 \) state so that they contribute to the observed \( J = 1 \) \text{-} 0 emission.

We have calculated the formation rate of HF in a self-consistent model of fluorine chemistry using the KOSMA-\( \tau \) code [59]. The rate equations are solved for a spherical clump of gas and dust with a density of \( n_H = 10^5 \text{ cm}^{-3} \) at the outer radius (\( A_V = 0 \)) and increasing to \( 1.1 \times 10^6 \text{ cm}^{-3} \) at the clump centre, so that the total clump mass is \( 1 M_\odot \). The dust model is number 7 of Weingartner & Draine [60], equivalent to \( R_V = 3.1 \), and the formation of \( \text{H}_2 \) is according to Cazaux & Tielens [61] with formation on PAH surfaces suppressed. The total abundance of fluorine in the Orion region is taken as \( 6.68 \times 10^{-9} \) [62], which is lower than the average value from Neufeld & Wolfire [41] by about a factor of 3.

Figure 2 shows the results of our calculations, which consider both ground state and vibrationally excited \( \text{H}_2 \). Collision of \( \text{F} \) with \( \text{H}_2 \) (\( v > 0 \)) dominates the formation of HF until \( A_V = 0.0036 \), after which point ground state \( \text{H}_2 \) takes over. The full model confirms the numbers from the estimate above with a formation rate \( R \) of about \( 10^{-5} \text{ s}^{-1} \), and approximately half of the fluorine in the form of HF in the reactive zone between \( A_V \approx 0.01 \ldots 2 \) containing most of the mass. Hence, we find that chemical pumping of the HF 1–0 transition is effective in the Orion Bar, but that estimates based on current molecular data fall short by a factor of a few. This could be due to uncertainties in the total fluorine abundance, or higher temperatures and radiation fields in the interclump gas.

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Figure 2. Chemical model of the Orion Bar as a function of $A_V$, using the UMIST reaction rates (dashed lines) or the $\text{H}_2 + F$ rate from Neufeld et al. [63] (solid lines). (a) Formation rate of HF by reactions of F with $\text{H}_2$ in its $v = 0$ and $v = 1$ states. (b) Absolute densities of $\text{H}_2$ and HF. The apparent dip in the HF abundance near $A_V = 3$ when using UMIST rates is due to incorrect temperature dependence of the $\text{H}_2 + F$ reaction rate. (c) Calculated temperatures of gas and dust. The distribution of HF is unlike that of $\text{OH}^+$ and $\text{H}_2\text{O}^+$, which peak at low $A_V$ and disappear where $\text{H}_2$ and HF are abundant [29]. The observational similarity between $\text{H}_2\text{O}^+$ and HF is thus likely to be related to the non-uniform structure of the ISM and similar excitation requirements, rather than chemical similarities. (Online version in colour.)
5. Conclusions and future work

The study of interstellar deuterated H$_3^+$ has come a long way in the past 16 years, and the conferences that Prof. Oka has organized every 6 years provide clear milestones of this progress. At the 88th birthday of the discovery of H$_3^+$ in 2000, the first detection of interstellar H$_2$D$^+$ was announced [16], which followed shortly after the discovery of interstellar H$^+_3$ itself [64]. The 94th birthday saw the first report of strong H$_2$D$^+$ emission from cold pre-stellar cores [17], the first H$_2$D$^+$ map of LDN 1544 by Vastel et al. [65] and the first tentative detection of interstellar D$_2$H$^+$ [22]. This year, at the 100th birthday, we are seeing the confirmation of interstellar D$_2$H$^+$ [21], the first survey of H$_2$D$^+$ emission [18], and mapping surveys of H$_2$D$^+$ are ongoing.

The natural question to ask now is: what will the 106th birthday in 6 years’ time bring? The most likely development in the next years are high-resolution maps of pre-stellar H$_2$D$^+$ with the ALMA interferometer, which is now about halfway completed and has started its Early Science programme. In fact, the tuning range of the ALMA receivers was especially extended to include the 372GHz line of o-H$_2$D$^+$, following the CSO detection of strong emission in this line in the pre-stellar core LDN 1544. The ALMA telescope will also probably make the first detection of H$_2$D$^+$ in a protoplanetary disc, and hence constrain the ionization fraction of the disc midplane. Another possibility is a survey of the p-D$_2$H$^+$ line at 692GHz in pre-stellar cores with ALMA, although the emission is probably quite weak in many cases. Third is the new capability of the GREAT receiver on the SOFIA airborne observatory, which gives access to the p-H$_2$D$^+$ ground state line near 1370GHz. The science operations of SOFIA started in 2011, and GREAT is among the first-light instruments.

The GREAT instrument may also be used for searches for the ground-state line of o-D$_2$H$^+$ at 1477 GHz. A search for this line with HIFI in the framework of the CHESS programme [66] was unsuccessful (C. Vastel 2012, personal communication). Both the p-H$_2$D$^+$ 1370 GHz line and the o-D$_2$H$^+$ 1477 GHz line are unlikely to appear in emission: their upper level energies of approximately 70 K and radiative decay rates of approximately $3 \times 10^{-3}$ s$^{-1}$ imply that their excitation requires higher densities and temperatures than occur in regions where the species are abundant. However, it is possible that the GREAT observations will reveal absorption by p-H$_2$D$^+$ and o-D$_2$H$^+$ near 1400GHz. Appearance in absorption requires a source of background continuum, which the warm central regions of young protostellar cores may provide, as well as sufficient abundance of H$_2$D$^+$ and D$_2$H$^+$ in the cold outer layers of these cores. Such conditions may well occur along some lines of sight, as the example of H$_2$D$^+$ absorption at 372 GHz towards IRAS 16293 shows [67]. These observations would be a new astronomical use of deuterated H$_3^+$ to probe physical conditions in star-forming regions.

In warm regions of the interstellar medium, hydride molecules such as HF and reactive ions such as OH$^+$ and H$_2$O$^+$ will continue to play an important role in characterizing the physical conditions of the gas. Mapping the spatial distribution of HF in the Orion Bar and other photon-dominated regions with Herschel–HIFI will help to clarify the contributions by atomic and molecular layers to the HF emission. The Herschel–SPIRE spectra of other galactic nuclei will help us to understand the origin of OH$^+$ and H$_2$O$^+$ emission by probing a
range of environments. After the end of the Herschel mission in \( \approx \) March 2013, ground-based observations of OH\(^+\) such as pioneered by Wyrowski et al. [68] will be invaluable as probes of interstellar physics and chemistry, supported by other reactive ions that are observable from the ground such as SH\(^+\) [69], CO\(^+\) [70] and HOC\(^+\) [71]. Clearly, the use of deuterated H\(_3^+\) and other molecular ions to probe star-forming regions has a bright future!

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