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The astrochemistry of H_3^+

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The reactions of the molecular ion H_3^+ are pivotal to the chemistry of dense interstellar clouds. Produced by the cosmic-ray ionization of molecular hydrogen, H_3^+ reacts with a variety of atoms and molecules to produce species that are precursors to many of the detected molecules in dense clouds. For example, the reaction of H_3^+ with atomic O leads, eventually, to the production of water, while the reaction with HD leads to the production of a wide variety of deuterated isotopomers. In this article, the chemistry of H_3^+ and the products derived from it are discussed in the larger context of interstellar chemistry.

Keywords: interstellar clouds; astrochemistry; ion–molecule reactions

1. Introduction

Matter in galaxies is not confined to stars. Amongst the stars, material exists in a variety of phases, the best characterized and most massive of which are cool interstellar clouds (Hollenbach & Thronson 1987). These clouds are composed of both gaseous and particulate matter. The gas is chiefly hydrogen in one form or another, while the particles are tiny dust grains constituting *ca.* 1% of the mass with a distribution of sizes centred around 0.1 μm in radius. The matter in clouds derives from previous generations of stars, which, either gently or explosively, eject matter into interstellar space that eventually collects together via the force of gravity.

At the risk of oversimplification, interstellar clouds can be divided into two classes, diffuse and dense. Diffuse clouds have gas densities in the range 10^7–10^9 m^{-3} and temperatures typically in the range 50–100 K. Although partly scattered by dust particles, visual and ultraviolet radiation from background stars is able to penetrate at least partly through these sources so that absorption spectroscopy can be used to characterize the gas phase. In diffuse clouds, the gas appears to be mainly atomic in nature, with elements heavier than hydrogen being less abundant by a similar or somewhat greater extent than what is found in stellar atmospheres. For example, the carbon elemental abundance is $10^{-3.85}$ that of hydrogen, while the oxygen elemental abundance is $10^{-3.50}$ that of hydrogen (Meyer 1997). Some diatomic molecules are seen, chiefly H_2. There exists a large number of rather wide absorption features, known collectively as the diffuse interstellar bands (DIBs), which are not assigned. Current views of these features are that they arise from rather complex molecules not fully studied in the laboratory (Tielens & Snow 1995).

In dense interstellar clouds, the overall gas density is considerably higher than in diffuse clouds, but is highly heterogeneous in nature. Background starlight does not penetrate. Matter is concentrated into regions termed ‘cores’. Certain of these cores, also known as dark clouds, are typically characterized by gas densities of *ca.* 10^{10} m^{-3} and temperatures of *ca.* 10 K. Other cores, in which the collapse of material leading to the eventual formation of stars is more pronounced, can be considerably warmer and denser, as can the material surrounding them. Often the word 'protostar' is used for these regions, and there is a classification system for such objects. Indeed, even embedded stars can be found in dense clouds, although their presence is often well hidden unless they are very warm and light up the area around them, forming so-called H II regions. The formation of stars within dense clouds is in fact the chief reason why astronomers are very interested in these objects. For astrochemists, on the other hand, another major source of interest is that molecular development is much more pronounced here than in diffuse clouds. In fact, the gas is mainly molecular (van Dishoeck 1997).

Although molecular hydrogen is by far the most dominant gaseous species in dense clouds, upwards of 100 other molecules, ranging in size from 2–13 atoms, and mainly organic in nature, have been detected, chiefly by rotational transitions in emission in the microwave and millimetre-wave regions of the spectrum (Winnewisser *et al.* 1992). These molecules are listed at http://www.strw.leidenuniv.nl/ ~iau34. The second most abundant molecule, CO, has a concentration 10^{-4} that of H_2 and takes up much of the elemental abundance of carbon. Many of the molecules are highly unusual by terrestrial standards, with radicals, three-membered carbon rings, metastable isomers, and molecular ions prominent. Of chemical interest, these molecules provide, through detailed interpretation of their spectra, a way for astronomers to understand the physical conditions in clouds. In addition to molecules studied via high-resolution spectroscopy, there exists a variety of broader features, mainly in the infrared, interpretable with varying degrees of ambiguity in terms of species on dust particles as well as individual large molecules known as polycyclic aromatic hydrocarbons (PAHs) (Millar & Williams 1993). Dust particles in cold regions of dense clouds appear to consist of cores of either silicates or carbonaceous material surrounded by mantles of ices, mainly water ice.

Most of the molecular ions seen in clouds have been detected only by rotational spectra, but there are exceptions. The ion CH^+ was detected in diffuse clouds many years ago by visible absorption spectroscopy (Douglas & Herzberg 1941). The ion H_3^+, which mainly concerns us here, was detected quite recently in infrared absorption against continuum radiation emanating from a background protostar (Geballe & Oka 1996). This ion has since been detected in a variety of dense clouds as well as in diffuse clouds.

2. Interstellar chemistry and H_2

How and where are interstellar molecules produced? Although molecules are formed in certain types of stellar atmospheres of older stars and blown out into space, their time of survival in the unshielded interstellar medium is not long by astronomical standards because of photodissociation. Dust particles, also produced in stellar atmospheres, are different in this regard, since they are reasonably stable against photodegradation. If quite large molecules, such as PAHs, are produced in stellar atmospheres, they may also be stable against photons, although the minimum size of molecules needed for photostability is presently a matter of controversy. So, it is most likely that as dense interstellar clouds are formed, the matter in them consists mainly of atoms and dust particle cores. How then can the gaseous matter be converted into molecules within a reasonable time by astronomical standards?

There are two types of chemical processes that can occur: reactions in the gas phase and reactions on the surfaces of dust particles (Herbst 1995). In the gas phase, the possible types of reactions are constrained by the low temperatures and densities to binary reactions without activation energy. Although it was initially thought that such processes are almost always confined to ion–molecule reactions or reactions involving neutral atoms and radicals, it is now known that certain neutral reactions involving one stable species and one radical can also be quite rapid at low interstellar temperatures (Canosa *et al*. 1997). Gas-phase reactions are probably responsible for the syntheses of most of the detected molecules in dense clouds, but they cannot explain the formation of molecular hydrogen. The basic problem is that in order to form H_2 under interstellar conditions, two hydrogen atoms must collide and stick together by giving off the excess chemical energy in the form of a photon. This process, known as radiative association, is thought to be relatively efficient for certain classes of larger species, but is very inefficient for two H atoms.

The production of molecular hydrogen in interstellar clouds probably occurs on the surfaces of dust particles, presumably via a diffusive, or Langmuir–Hinshelwood, mechanism. One H atom strikes a dust grain, and sticks efficiently at the low prevailing temperatures. This atom then diffuses over the grain or evaporates. Meanwhile, a second H atom sticks to the same grain, and there is a finite possibility that the two H atoms can collide with one another to form a hydrogen molecule, with the excess energy this time going into thermal energy of the dust particle. Although this process has been studied in the laboratory, our current understanding of it is that the H atoms move much more slowly than previously anticipated, and that reaction before evaporation may take place only over a small temperature range for any given surface material. Still, in all likelihood, grain formation of H_2 occurs efficiently and is able to convert the gas of primarily atomic hydrogen into one of mainly molecular hydrogen within a 'reasonable' time-scale of 10^5 yr.

3. The chemistry of H_3^+

Once molecular hydrogen is produced on grain surfaces and either evaporates from the surface into the gas or is actually ejected during the act of formation, there is a finite possibility of ionization. Since the ionization potential of molecular hydrogen is 15.4 eV ($1\ \mathrm{eV} = 96.5\ \mathrm{kJ\ mol^{-1}}$), direct photoionization by the photons present in interstellar space is impossible, since these photons range upwards in energy to 13.6 eV only, and multi-photon events are inefficient, since relaxation is more rapid than photoexcitation. In any event, the penetration of external photons into the central regions of dense interstellar clouds occurs only to a small extent. The ionization of H_2 occurs via higher energy processes. Throughout galaxies such as our own, high-energy particles known as cosmic rays exist. Travelling at relativistic speeds, these nuclei, which are in the main protons, are able to penetrate dense clouds and to afford a small degree of ionization upon collision with gas-phase species, chiefly molecular hydrogen and helium. The ionization occurs both directly and indirectly through secondary electrons produced in the primary process. In addition, the secondary electrons can excite molecular hydrogen sufficiently that fluorescence in the ultraviolet region of the spectrum results (Prasad & Tarafdar 1983). This fluorescence provides a small radiation field deep inside dense clouds, where external photons cannot penetrate. The cosmic-ray flux is not large enough to ionize a major portion of the dense-cloud gas, but does lead to a large enough ion fraction (10^{-6}–10^{-8}) so that ion–molecule reactions play a crucial role in the subsequent chemistry (Lee *et al*. 1996; Millar *et al*. 1997).

The total rate (s^{-1}) of ionization/dissociation of H_2 by cosmic rays is labelled ζ; perhaps 90% of ζ leads to H_2^+. A ‘standard’ value for ζ of *ca*. $1.3\times10^{-17}\ \mathrm{s}^{-1}$ is often used, although recent studies suggest that its value can range more than one order of magnitude in either direction from this value (Caselli *et al*. 1998). In addition to cosmic rays, ionization of molecular hydrogen can occur via X-rays in selected regions where there is a high X-ray flux. One such type of region is a young star known as a T Tauri object; these stars have not yet settled down to a stable existence and are capable of high X-ray emission. T Tauri stars embedded in objects enhance the ionization rate because of their large X-ray emissions; the enhancement can be as large as orders of magnitude, but the penetrating power of X-rays is less than that of cosmic rays, so the region of enhancement may be small. T Tauri stars can be surrounded by swirling disks of gas and solids known as proto-planetary disks; the ionization in parts of these regions is strongly influenced by the X-ray flux.

The H_2^+ produced by cosmic rays and/or X-rays is rather reactive and reacts with the first hydrogen molecule it comes in contact with to form the H_3^+ molecule:

$$H_2^+ + H_2 \rightarrow H_3^+ + H. \tag{3.1}$$

This reaction is a classic example of an exothermic ion–molecule reaction, which is known to proceed without activation energy. It occurs with a temperature-independent rate coefficient $k \approx 2\times10^{-15}\ \mathrm{m}^3\ \mathrm{s}^{-1}$, close to what is estimated based on the simple formula of Langevin,

$$k = \frac{1}{4\pi\epsilon_0} 2\pi e \left(\frac{\alpha}{\mu}\right)^{1/2}, \tag{3.2}$$

where e is the electronic charge, α is the polarizability, and μ is the reduced mass. This formula is derived by assuming that reaction occurs with 100% efficiency if the reactants are able to surmount a centrifugal barrier caused by the addition of the rotational kinetic energy to the long-range ion-induced-dipole attractive potential (Herbst 1996). Given a molecular hydrogen density of $10^{10}\ \mathrm{m}^{-3}$, the time-scale for the conversion of H_2^+ into H_3^+ is *ca*. 10^5 s, or 1 day, which is exceedingly rapid by interstellar standards.

Once H_3^+ is produced, it can be destroyed by a variety of exothermic reactions. These reactions are crucial to the chemistry of dense interstellar clouds, leading to some, if not most of, the more abundant species. The dissociative recombination reaction with electrons is discussed by Larsson in this issue. This reaction is the dominant destruction reaction for H_3^+ in diffuse clouds, where the electron fractional abundance is relatively high (*ca*. 10^{-4}). The dominant reaction pathway for reactions with neutral species (X) is proton transfer:

$$H_3^+ + X \rightarrow XH^+ + H_2. \tag{3.3}$$

In the early stages of dense-cloud evolution, proton-transfer reactions with certain neutral atoms are especially important.

(*a*) *Reaction with atomic* O

The reaction with neutral atomic oxygen appears to be a straightforward proton transfer,

$$H_3^+ + O \rightarrow OH^+ + H_2, \tag{3.4}$$

although the laboratory study is rather old and at room temperature only. A recent theoretical study by Bettens *et al.* (1999) employing *ab initio* potential surfaces and classical trajectory calculations indicates that the reaction proceeds at a rate close to that of the simple Langevin theory, despite the fact that the O atom has a quadrupolar moment that enhances the long-range potential. Bettens *et al.* (1999) have found evidence that the exothermic reaction

$$H_3^+ + O \rightarrow H_2O^+ + H \tag{3.5}$$

also occurs, but with a rate coefficient approximately one order of magnitude lower. This possible reaction channel is not important in interstellar clouds because the products of reaction (3.4) themselves react efficiently via an H-atom transfer:

$$OH^+ + H_2 \rightarrow H_2O^+ + H. \tag{3.6}$$

A subsequent reaction with ubiquitous molecular hydrogen then leads to the hydronium ion:

$$H_2O^+ + H_2 \rightarrow H_3O^+ + H. \tag{3.7}$$

This ion does not react with molecular hydrogen, and so is relatively abundant. It has been detected via its rotation–inversion spectrum.

The major destruction process for H_3O^+ is via recombination with electrons, which are produced by cosmic-ray bombardment. The rate coefficients for recombination reactions are well known and large, and it is well known that the products are, in the main, neutral fragments, rather than the parent neutral, but until recently there was little information concerning the branching fractions of the various possible neutral products. Two methods of measuring the products for thermal systems are now in use: spectroscopic detection in a flowing afterglow system, and particle detection in a storage ring (see Larsson, this issue). The methods have been used to fully characterize the products of the H_3O^+–e^- reaction (Williams *et al.* 1996; Vejby-Christensen *et al.* 1997). Four exothermic channels are possible: $H_2O + H$, $OH + H_2$, $OH + 2H$ and $O + H_2 + H$. Although both methods yield the result that OH is the dominant product, they differ quantitatively concerning all four channels. In particular, the flowing afterglow results indicate that little, if any, water is produced (0–5%), while the storage-ring results show that water is produced on $33 \pm 8\%$ of reactive collisions. No explanation for the discrepancy has been offered. Although the storage-ring results are incorporated into models, recent satellite results on water show that there is less than predicted in dark clouds. A much more efficient synthesis of water occurs on grain surfaces via successive addition of hydrogen atoms to surface oxygen atoms. The water ice formed tends to remain on the grains in cold sources.

(*b*) *Reaction with atomic* C

The reaction with neutral atomic carbon has not been studied in the laboratory but has been looked at theoretically, most recently by Bettens & Collins (1998*a*), who used classical trajectory studies. This and previous work shows that the dominant process is proton transfer,

$$H_3^+ + C \rightarrow CH^+ + H_2, \tag{3.8}$$

and that the rate coefficient is near Langevin at 10 K. Bettens & Collins (1998*a*) found that the process

$$H_3^+ + C \rightarrow CH_2^+ + H \tag{3.9}$$

can occur but with a rather small rate coefficient. There are complications in (3.8) and (3.9) due to the fine structure of atomic carbon and whether or not the collisions are adiabatic with respect to fine structure. A competing process that also initiates hydrocarbon chemistry is the radiative association reaction

$$C^+ + H_2 \rightarrow CH_2^+ + h\nu, \tag{3.10}$$

which occurs on roughly one out of every 10^{6-7} collisions according to experiment and theory (Gerlich & Horning 1992). The carbon ion may be present initially or can be produced by the reaction between CO, the second most abundant interstellar molecule, and He^+, an ion produced by cosmic-ray bombardment:

$$CO + He^+ \rightarrow C^+ + O + He. \tag{3.11}$$

Once CH^+ and CH_2^+ are produced, H-atom transfer reactions with H_2 rapidly lead to the production of the methyl ion, CH_3^+. This ion does not react rapidly with H_2, since the H-atom transfer channel is endothermic by 260 kJ mol^{-1}; rather, the radiative association with H_2 produces CH_5^+:

$$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu. \tag{3.12}$$

This radiative association reaction has been studied in the laboratory (Gerlich & Horning 1992) as well as theoretically, and, to within an order of magnitude, proceeds once out of every 10^4 collisions at low temperatures. Since the reaction is not very rapid, the methyl ion retains a significant abundance and is an important precursor for many other species. The dissociative recombination reaction between CH_5^+ and electrons does not produce large amounts of CH_4 (Semaniak *et al.* 1998); rather, the dominant channel leads to $CH_3 + 2H$. Methane can be formed, however, via the reaction of CH_5^+ with CO:

$$CH_5^+ + CO \rightarrow CH_4 + HCO^+. \tag{3.13}$$

The formation of small hydrocarbons such as the methyl ion, methyl and methane sets the stage for the production of more complex hydrocarbons through three types of synthetic reactions,

(i) carbon insertion via either C or C^+,

(ii) condensation reactions between hydrocarbon ions and neutrals, and

(iii) radiative association reactions,

many of which have been studied in the laboratory, especially in the first two classes. Examples of each are found in the following sample list of synthetic reactions that occur in dense clouds:

$$C^+ + CH_4 \rightarrow C_2H_2^+ + H_2;\ C_2H_3^+ + H, \tag{3.14}$$

$$C_2H_3^+ + e^- \rightarrow C_2H_2 + H(?);\ C_2H + 2H(?), \tag{3.15}$$

$$C_2H_2^+ + H_2 \rightarrow C_2H_4^+ + h\nu;\ C_2H_3^+ + H(?), \tag{3.16}$$

$$C_2H_2^+ + C_2H_2 \rightarrow C_4H_2^+ + H_2;\ C_4H_3^+ + H, \tag{3.17}$$

$$C^+ + C_2H_2 \rightarrow C_3H^+ + H, \tag{3.18}$$

$$C_3H^+ + H_2 \rightarrow C_3H_3^+ + h\nu;\ C_3H_2^+ + H. \tag{3.19}$$

Controversy still exists concerning the relative rates of radiative association and normal product channels for several of these reactions (Gerlich & Horning 1992). It is interesting to note that hydrogen-atom transfer reactions between hydrocarbon ions and H_2 are rarely exothermic or barrier free for ions with more than a few carbon atoms, so that even with radiative association reactions, which can sometimes occur, the extent of hydrogenation is surprisingly low given the huge abundance of H_2.

It should be mentioned that neutral–neutral reactions involving neutral atomic C are also important in hydrocarbon synthesis; for example,

$$C + C_2H_2 \rightarrow C_3H + H \tag{3.20}$$

is probably the dominant route to form both known isomers of C_3H, the cyclic and the linear, although neutral–neutral reactions cannot produce the analogous isomers of C_3H_2, which are more abundant and ubiquitous in interstellar space.

(c) *Reaction with other atoms*

The proton-transfer reaction between H_3^+ and neutral atomic nitrogen is endothermic by 98 kJ mol^{-1}, so cannot occur at low temperatures. It has been claimed occasionally by experimentalists that the reaction

$$H_3^+ + N \rightarrow NH_2^+ + H \tag{3.21}$$

occurs without activation energy, but theoretical treatments have never supported this viewpoint (Bettens & Collins 1998*b*), and the latest experimental claim has just been withdrawn.

The fact that reaction (3.21) does not occur in a facile manner has profound implications for interstellar chemistry, because, if it did occur, the formation of ammonia via the sequence of reactions

$$NH_2^+ + H_2 \rightarrow NH_3^+ + H, \tag{3.22}$$

$$NH_3^+ + H_2 \rightarrow NH_4^+ + H, \tag{3.23}$$

$$NH_4^+ + e^- \rightarrow NH_3 + H, \tag{3.24}$$

would occur rapidly. Reaction (3.23) has a small entrance channel barrier. Detailed calculations show, however, that tunnelling under this barrier becomes enhanced at low temperatures (Herbst *et al*. 1991), so that the reaction is efficient at interstellar temperatures, in agreement with experimental measurements.

As it is, ammonia is produced much more slowly from OH through N_2 via a very indirect scheme that first leads to the atomic nitrogen ion:

$$\mathrm{OH} + \mathrm{N} \rightarrow \mathrm{NO} + \mathrm{H}, \tag{3.25}$$

$$\mathrm{NO} + \mathrm{N} \rightarrow \mathrm{N_2} + \mathrm{O}, \tag{3.26}$$

$$\mathrm{N_2} + \mathrm{He^+} \rightarrow \mathrm{N^+} + \mathrm{N} + \mathrm{He}. \tag{3.27}$$

This ion must then be hydrogenated into NH_4^+. The H-atom transfer reaction between N^+ and H_2 is either slightly endothermic or possesses a small activation energy of *ca.* 0.01–0.02 eV. This can be overcome because interstellar species produced in exothermic reactions are not totally thermalized; both N^+ and H_2 have slightly excess energies, N^+ in its translational and possibly fine structure states, and H_2 in rotational levels (Galloway & Herbst 1989; Le Bourlot 1991). Since the formation of ammonia takes place so slowly, clouds in which ammonia is highly abundant are thought to be old by astronomical standards.

The final H_3^+ reaction with atoms to be considered here involves sulphur. Sulphur chemistry is thought to commence with the proton-transfer reaction

$$\mathrm{H_3^+} + \mathrm{S} \rightarrow \mathrm{SH^+} + \mathrm{H_2}, \tag{3.28}$$

which is presumably analogous to its oxygen counterpart. The product ion HS^+ cannot react exothermically with H_2, except for a possible radiative association reaction:

$$\mathrm{SH^+} + \mathrm{H_2} \rightarrow \mathrm{H_3S^+} + h\nu. \tag{3.29}$$

The rate of this reaction is uncertain. Although the three-body analogue has been studied at higher densities, conversion of the three-body to an analogous two-body rate coefficient, which can often be undertaken, is complex here because the reaction must proceed via a spin-flip (Herbst *et al.* 1989). If H_3S^+ can be formed via reaction (3.29), then dissociative recombination might lead to a sizeable abundance of H_2S. The standard assumption, however, is that gas-phase interstellar H_2S more likely derives from a grain chemistry in which successive H atoms attach to surface S atoms, followed by some mechanism for desorption from the grain surface.

(*d*) *Reaction with molecules*

In addition to its reactions with atoms, H_3^+ is able to protonate most interstellar molecules. The protonation of CO,

$$\mathrm{H_3^+} + \mathrm{CO} \rightarrow \mathrm{HCO^+} + \mathrm{H_2}, \tag{3.30}$$

is important because it produces the polar HCO^+ ion, which is, under most circumstances, the most abundant molecular ion, and is easily detectable by radio-astronomical means. The metastable ion HOC^+ is also produced in this reaction.

Finally, the protonation of HD,

$$\mathrm{H_3^+} + \mathrm{HD} \rightarrow \mathrm{H_2D^+} + \mathrm{H_2}, \tag{3.31}$$

is especially interesting. This reaction is exothermic by a small amount (*ca.* 230 K or 1.9 kJ $\mathrm{mol^{-1}}$), which is equal to the sum of the zero-point vibrational energy difference between products and reactants plus the rotational energy gained because the lowest rotational state of H_3^+ is disallowed by the Pauli principle. At low temperatures, the backwards reaction is very slow, so that the equilibrium lies far to the right, and, even though the HD/H_2 abundance ratio in dense interstellar clouds is *ca.* 4×10^{-5}, the H_2D^+/H_3^+ abundance ratio can become as high as 0.10. The high abundance of the H_2D^+ ion leads to enhanced abundances of many other singly deuterated isotopomers through ion–molecule reactions; this matter is discussed by Millar *et al.* in this issue.

4. The concentration of H_3^+ in interstellar clouds

What is the concentration of H_3^+ in interstellar clouds? In dense clouds, the destruction of this ion is controlled by reactions with abundant neutrals, mainly CO, and by reaction with electrons. The competition between these two destruction mechanisms is important in determining the region of bistability, as discussed by Pineau des Forêts & Roueff in this issue. The electron abundance is determined principally by the abundance of so-called 'metals' in the gas phase. The word 'metal' in astronomy often refers to every element heavier than helium (to be fair, astronomers refer mainly to the concept of 'metallicity'), although here we use it in a more restrictive sense as a group of elements consisting of actual metals as well as sulphur and silicon. Some of the typical stellar abundance of these elements is to be found on dust particles in the interstellar medium, and not in the gas phase. In standard dense-cloud models (Lee *et al.* 1996; Millar *et al.* 1997), the gas-phase concentrations of these elements relative to hydrogen are reduced strongly, since this reduction leads to better agreement with observation for many molecules and makes sense physically. Under these circumstances, the fractional electron abundance (with respect to hydrogen) is, typically, 3×10^{-8} and H_3^+ is depleted mainly by reaction with abundant neutrals such as CO. In our time-dependent models of typical cold dense-cloud cores, the concentration of H_3^+ quickly reaches a value of *ca.* $20\ \mathrm{m^{-3}}$. For a cloud of length 10 pc (*ca.* 3×10^{17} m), the predicted column density is $6 \times 10^{18}\ \mathrm{m^{-2}}$. For a cloud of length 1 pc, the column density is one-tenth of this amount. Use of a simple steady-state model in which H_3^+ is only depleted by reaction with CO leads to an ion concentration and column density a factor of a few greater. The agreement with observation (see the paper by Geballe in this issue) is good. With a reasonably high abundance for an ion, H_3^+ is a principal (if not dominant) destroyer of neutral species by protonation reactions followed by dissociative recombination of the product protonated ions to form species other than the original neutrals.

In diffuse interstellar clouds, the ion is depleted mainly by recombination with electrons. The calculated concentration and column density depend on how much of the hydrogen in the gas is in molecular form. Assuming that much of the gas in inner regions is molecular, it is easy to estimate that the H_3^+ concentration is perhaps two orders of magnitude less than in dense clouds. This result does not appear to be in agreement with the observations of Geballe *et al.* (1999), as discussed by Geballe in this issue. The interstellar chemistry of H_3^+ is still not completely understood! There is much more this most simple of polyatomic ions is telling us.

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Discussion

I. W. M. SMITH (*School of Chemistry, University of Birmingham, UK*). Can you please say a little more about the starting conditions for your time-dependent calculations and how these are chosen? Can you also comment on how the elemental atomic abundances change with time? Is there any allowance for them to be replenished from outside the cloud?

E. HERBST. For quiescent cores in dense clouds, several sets of initial conditions are used for gas-phase models. A standard density is 1–3 × 10^4 molecules cm^{-3} and a typical temperature is 10 K. These conditions are normally fixed. The overall gas density is divided among the various elements, the relative proportions of which are given by so-called 'cosmic' (near-solar) abundances with heavy elements depleted to some extent to account for the dust particles. A typical set of elemental abundances for the gas would be: $H = 1$, $He = 0.1$, $C = 7(-5)$, $O = 2(-4)$, $N = 2(-5)$. Variations in these uncertain abundances can lead to very different results. If the material is carbon rich ($C > O$), it is far easier to synthesize organic molecules. A high abundance of sulphur is conducive to the phenomenon of bistability (see the paper by Pineau des Forêts & Roueff in this issue). One can start off with the elements in the form of neutral atoms. An alternative possibility often favoured is to start with abundances that pertain to diffuse clouds; the main differences with the first view are that much of the hydrogen has already been converted into the molecular form and the carbon is in the form of the singly charged atomic cation. In truth, the real initial species are unknown, since they depend on the formation of the molecular clouds from the primeval stellar ejecta. Typical steady-state results (reached after 10^7 yr or so) are insensitive to the choices of initial conditions, although the so-called early time results, where organic molecular abundances peak, are more prominent if one starts with H_2. Although there are no models that contain replenishment of material from external sources, there are models in which large-scale motions inside clouds mix heterogeneous material from inner and outer regions. Also, there are models in which grain-surface chemistry is also included, as are the adsorption and desorption of material from the grains.

S. LEPP (*UNLV, Las Vegas, NV, USA*). Regarding H_3O^+ recombination, the results may be consistent if one assumes the ring experiments are measuring predissociated states.

E. HERBST. It is certainly true that given the speed of the particles in a storage ring, they are sampled by the detector within a much shorter time than in the flowing afterglow apparatus. Thus, if the water formed by the dissociative recombination of

$H_3O^+ + e$ is metastable and predissociates in some manner, it might be detectable in the storage ring but not detectable in the flowing afterflow. For a species as small as water, however, a typical lifetime against vibrational predissociation (unimolecular decomposition) is only 10^{-13} s, so that it would not be seen in either apparatus. A larger neutral species, with more degrees of freedom, might be sufficiently metastable against vibrational predissociation to live for the *ca.* 10^{-6} s needed to reach the neutral detector in a storage ring. There remains the possibility that the water is produced in a bound but predissociative excited electronic state (e.g. a triplet state) that lives longer than the 10^{-6} s but not long enough to be detected in the flowing afterglow. This hyothesis could possibly be tested by searching for the phosphorescence, which would undoubtedly be weak.

J. B. A. Mitchell (*PALMS, Université de Rennes, France*). In your talk, you showed a transparency with the $C_3H_3^+$ ion on it. This is the dominant ion in fuel-rich flames and is seen ubiquitously in hydrocarbon plasmas but its mechanism of formation is not understood. Do you have a viable scheme to form it?

E. Herbst. The dominant formation mechanism for $C_3H_3^+$ in interstellar clouds starts with the reaction between acetylene and C^+,

$$C^+ + C_2H_2 \rightarrow C_3H^+ + H,$$

and is followed by the radiative association of C_3H^+ with H_2:

$$C_3H^+ + H_2 \rightarrow C_3H_3^+.$$

A. Suzor-Weiner (*Laboratoire de Photophysique Moléculaire, Université Paris-Sud, France*). In diffuse intrestellar clouds, you point out that two ions, CH^+ and H_3^+, have unexplained high abundances, at least with the fast rate measured for their dissociative recombination. Is there a special link between these two ions, or are they two unrelated problems?

E. Herbst. At present, they do appear to be unrelated problems. The ion CH^+ must be produced under high energy/temperature conditions, either in a shock wave or in a region of turbulence of some sort. In either situation, the reaction of importance is

$$C^+ + H_2 \rightarrow CH^+ + H,$$

which is endothermic by 0.4 eV. The H_3^+ ion is easily produced at low temperatures. It is difficult to see how high energies/temperatures can enhance its abundance significantly, although I have not done a detailed calculation on the subject.

E. F. van Dishoeck (*Leiden Observatory, The Netherlands*). It would be interesting to observe the H_3^+ line profile with high spectral resolution (a few km s^{-1}) in diffuse clouds. It would then be possible to determine observationally whether CH^+ and H_3^+ are related, since the CH^+ profile is much broader than that of other species.

M. Larsson (*Department of Physics, Stockholm University, Sweden*). The branching ratios for dissociative recombination of H_3O^+/D_3O^+ have been measured in CRYRING. The production of H_2O/D_2O was found to be 17–18%.

E. Herbst. Now that we have somewhat different values for the branching fraction of H_2O product from two different storage rings (ASTRID and CRYRING), it might be useful to look carefully at the sources of uncertainty in the values.