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Formation and destruction of molecular ions in interstellar clouds

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A brief review is given of the role of molecular positive ions in interstellar chemistry. It is indicated how the simplest ions, which are formed by photoionization and cosmic-ray ionization, are converted to polyatomic ions by sequential gas-phase ionic reaction processes such as proton transfer, carbon insertion and radiative association. The importance of H_3^+ and CH_3^+ ions in the initial stages of molecular synthesis and the analogous roles of H_2D^+ and CH_2D^+ (which are formed in the reactions of H_3^+ and CH_3^+ with HD) in the production of deuterated molecules are stressed. Recent work is also mentioned concerning the possible routes to c-C_3H_2 the first cyclic molecule to be detected in interstellar clouds. The process of dissociative recombination of positive ions with electrons is also discussed, because it is commonly invoked as the final step in the destruction of polyatomic ions and in the formation of many of the observed neutral molecules in interstellar clouds, even though the products of such reactions are currently a matter for speculation. It is stressed how spectroscopic studies of the structures and the products of reactions of molecular ions can further advance understanding in the field of interstellar chemistry.

1. Introduction

Several molecular positive-ion species have been detected in interstellar gas clouds (Winnewisser *et al.* 1979; Rydbeck & Hjalmarson 1985; Guelin 1987; Vardya & Tarafdar 1987; Irvine *et al.* 1987). The first was the diatomic ion CH^+, detected in diffuse interstellar clouds via its characteristic absorption bands in the visible region of the spectrum (Dunham & Adams 1937*a*, *b*; Douglas & Herzberg 1941, 1942). The species HCO^+, N_2H^+, HCS^+ and H_2CN^+, which are all protonated forms of known interstellar molecules, have since been detected in dense interstellar clouds via their characteristic rotational spectra, and very recently SO^+ has also been detected in dense clouds (Churchwell *et al.* 1987). There has also been a tentative identification of the ion HCO_2^+ (Thaddeus *et al.* 1981) and of the COH^+ isomer of HCO^+ (Woods *et al.* 1983). Many other molecular positive-ion species must be present in dense clouds, some in greater concentrations (number densities) than those aforementioned, including ions such as H_3^+, H_3O^+, CH_3^+, NH_4^+ and even more polyatomic species. That some ions have not been detected is simply because of their symmetry, whereas the spectra of others are not yet characterised well enough to allow detection and identification by radioastronomical techniques. Other ionic species will not be present at sufficiently high number densities to be detected until the sensitivity of the detectors associated with radio antennae are increased. It is the combination of advances in laboratory microwave spectroscopy, in ion-structure calculations and in radioastronomy that is resulting in the increase in the detection rate of interstellar molecules (including molecular ions). At the onset, it should be noted that no negative-ion species has yet been detected in interstellar clouds.

The observed interstellar molecular ions and the more numerous interstellar neutral molecules are formed by reactions between simple ions and atoms and molecules in which more complex ions are formed that can react with the electrons present in the weakly ionized interstellar clouds to produce the observed neutral molecules (Dalgarno & Black 1976; Smith & Adams 1981*a*, *b*; Herbst 1985*a*; Crutcher & Watson 1985; Adams & Smith 1987*a*; Smith 1987). Thus it is the occurrence in the gas phase of many such positive-ion–neutral reactions and positive-ion–electron dissociative recombination reactions that largely constitutes interstellar chemistry, although heterogeneous reactions on the surfaces of interstellar dust grains can also occur (Millar 1982; Duley & Williams 1984; Williams 1987). Indeed, the latter reactions are considered to generate interstellar molecular hydrogen, which is by far the most abundant molecular species (Dalgarno & Black 1976).

Certain key molecular ions are strongly implicated in interstellar gas-phase ion chemistry including H_3^+ and CH_3^+ and in the following sections their central role in the chemistry will be described. Reactions of the ions with H_2 are particularly important. Also the reactions of H_3^+, CH_3^+ and other ions with HD are important in that they result in the creation of deuterated species such as H_2D^+ and CH_2D^+ (Huntress & Anicich 1976; Watson 1976; Smith *et al.* 1982*a*; Smith & Adams 1984*a*), the subsequent chemistry of which generates the observed deuterated analogues of several interstellar molecules by the process of isotope exchange and isotope fractionation (Watson 1976; Smith *et al.* 1982*b*; Wootten 1987). Clearly, the spectroscopy of molecular ions has played, and must continue to play, a major role in interstellar physics and chemistry, not least in characterizing the rotational spectra of probable interstellar ions (Winnewisser *et al.* 1985; Thaddeus *et al.* 1985; Woods 1987), which assists in their detection and identification, and not least in the elucidation of the neutral products of dissociative recombination reactions that are currently almost totally in the realm of speculation. Some of these important topics will be discussed and highlighted by the examples given in the following sections.

2. Production and reactions of positive ions in interstellar clouds

It is now generally recognized that molecules are synthesized in interstellar clouds largely by the production and reactions of positive ions in the gas phase (Dalgarno & Black 1976; Smith & Adams 1981*a*, *b*; Herbst 1985*a*). The understanding of this gas-phase ion chemistry has resulted from astronomical observations of the nature and relative abundances of interstellar molecules (Winnewisser *et al.* 1979; Guelin 1985; Rydbeck & Hjalmarson 1985; Irvine *et al.* 1987) (which also provide the vital information on the physical conditions in the clouds), coupled with laboratory gas-phase studies of ionic reactions (Adams & Smith 1983; Smith & Adams 1984*a*), which have provided the essential rate data for detailed ion chemical models that aim to describe the overall chemistry (Millar & Freeman 1984*a*, *b*; Leung *et al.* 1984; Millar & Nejad 1985). These models have had some success in predicting relative molecular abundances that agree with observations. Several reviews are available that describe the ion chemistry of interstellar clouds and that illustrate the successes of the ion chemical models while highlighting some of the remaining problems that ion chemistry has in describing the production of some observed interstellar molecules (Millar 1985; Herbst 1987; Winnewisser & Herbst 1987; Millar *et al.* 1987). Therefore, it is not the intention here to produce another such review (valuable as they are) but rather to discuss the nature of interstellar ions and their reactivity. In doing this, the vital role of ions in the chemistry will be quite apparent. However, it is pertinent first to briefly describe the composition and the physical conditions pertaining to interstellar clouds.

Interstellar clouds are extremely varied, but they can be categorized into two general types, the so-called diffuse clouds and the dense clouds. The diffuse clouds are of relatively low density consisting mainly of atomic and molecular hydrogen (overall number density of the order of 10^2–10^3 cm^{-3}) and of relatively high temperature (*ca.* 100 K). Their densities are sufficiently low for them to be partly transparent to visible and ultraviolet (UV) radiation (hence the term 'diffuse'). This allows them to be probed via absorption spectroscopy. In this way they are seen to contain elements in the atomic form e.g. H, C, N and O, and simple (diatomic and triatomic) molecules, e.g. CH, CH^+, OH, CO, CN and HCN. The ion chemistry occurring is thus relatively simple. It is initiated by the photoionization of carbon atoms by stellar UV radiation producing C^+ ions and by the ionization of H and H_2 by galactic cosmic rays producing H^+ and H_2^+ ions. Production of hydrocarbon ions can result from association of C^+ with H and H_2 terminating at CH_3^+. Another vital reaction also occurs that is central also to dense-cloud chemistry:

$$H_2^+ + H_2 \rightarrow H_3^+(v) + H. \qquad (1)$$

Reaction (1) is extremely rapid, occurring on every collision between an H_2^+ ion and an H_2 molecule, and generates the important species H_3^+ in a vibrationally excited state (see, for example, Kim *et al.* 1974). The vibrational excitation is removed from the H_3^+ in interstellar clouds either by radiation emission (in low-density regions) (Oka 1981) or by energy transfer collisions with H_2 molecules (collisional quenching) in denser regions. Relaxed H_3^+ ions are unreactive with H_2 in bimolecular collisions although at low temperatures in relatively high-pressure gas where termolecular collisions can occur they can associate with H_2 to produce H_5^+. However, in interstellar clouds, even dense clouds, termolecular collisions are totally improbable and the gas-phase chemistry proceeds only via bimolecular collisions (but, as is discussed later, bimolecular collisions can nevertheless lead to ion–molecule association). Thus the H_3^+ ions survive sufficiently long to be able to transfer protons to species such as C and O atoms that have proton affinities greater than that of H_2:

$$H_3^+ \xrightarrow{C} CH^+ + H_2 \qquad (2a)$$
$$H_3^+ \xrightarrow[O]{} OH^+ + H_2. \qquad (2b)$$

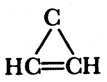
The CH^+ and OH^+ product ions of these reactions can then either be photodissociated, or react rapidly with H_2 or dissociatively recombine with the ambient electrons regenerating C and O atoms and generating H atoms. Their reactions with H_2 generates CH_2^+ and H_2O^+ ions that also react with H_2 generating CH_3^+ and H_3O^+ ions (a similar chemistry involving N atoms can also be described). The last-mentioned ions may also be photodissociated (van Dishoeck 1987) or dissociatively recombine with electrons generating small neutral molecules such as the CH and OH radicals observed in diffuse interstellar clouds (Dalgarno & Black 1976). Dissociative recombination and the likely neutral products of such reactions will be discussed more fully in §3. Detailed laboratory studies have shown that protonated ions of stable molecules such as H_3O^+ are relatively unreactive with H_2 even at low temperatures. It is obvious that such ions can therefore survive for relatively long times and may therefore be present in high enough number densities to be detected in interstellar clouds. It is because of this that HCO^+, HCS^+, N_2H^+ and H_2CN^+ are detectable via millimetre-wave emissions from dense clouds.

The gas-phase ion chemistry of dense clouds is much more complex than that of diffuse clouds. As the name implies, the gas-number densities in dense clouds are considerably higher than those in diffuse clouds being typically within the range 10^3–10^6 cm^{-3}. These dense clouds consist largely of molecular hydrogen and atomic helium (presumed to be in their cosmical abundance ratio), and 'dust' grains are dispersed throughout them assisting in rendering them opaque to visible and to shorter-wavelength electromagnetic radiation. Hence these clouds are cooler than diffuse clouds, the temperature being typically 20 K (and perhaps as low as 5 K near to the centre of some dark clouds). These lower temperatures and higher particle-number densities encourage a rich ion chemistry that is initiated by the ionization of H_2 and He by galactic cosmic rays and by which the observed complex molecules in these clouds are synthesized. Such molecules survive against photodissociation because of the shielding afforded by the ambient gas and dust grains. A current list of the molecules observed in interstellar clouds and in circumstellar shells around evolved stars is given in table 1 and includes the seven ion species (in boxes) that have definitely been identified. The most polyatomic species observed to date is $HC_{11}N$, the largest in the family of cyanopolyynes, HC_nN ($n = 3, 5, 7, 9$ and 11). The initial stages of the ion chemistry of dense clouds are quite similar to those outlined above

Table 1. Molecules detected in interstellar clouds and circumstellar shells

hydrogen
H_2

molecules containing only C and H

CH	$C\equiv C$	$C\equiv CCH$	$(C\equiv C)_2H$
$\boxed{CH^+}$	$C\equiv CH$	$(C\equiv C)_2CH$	$H_3C(C\equiv C)_2H$
*CH_4	*$HC\equiv CH$	$H_3CC\equiv CH$	
	*$H_2C{=}CH_2$		

molecules containing O

OH	$\boxed{HCO^+}$	CH_3CHO	CH_3CO_2H
H_2O	HOC^+?	CH_3OH	CH_3OCH_3
CO	H_2CO	CH_3CH_2OH	$\boxed{HOCO^+}$
HCO	CH_2CO	HCO_2H	$C\equiv CCO$

molecules containing N

CN	$\boxed{H_2CN^+}$	CH_3CH_2CN	$H(C\equiv C)_4CN$
HCN	NH_2CN	$H_2C{=}CHCN$	$H(C\equiv C)_5CN$
HNC	CH_2NH	$HC\equiv CCN$	$C\equiv CCN$
$\boxed{N_2H^+}$	CH_3NH_2	$H(C\equiv C)_2CN$	$H_3CC\equiv CCN$
NH_3	CH_3CN	$H(C\equiv C)_3CN$	$H_3C(C\equiv C)_2CN$

molecules containing O and N

NO, HNO?, HNCO, HOCN?, NH_2CHO

molecules containing S, Si and Cl

SO, $\boxed{SO^+}$, SN, CS, H_2S, SO_2, OCS, $\boxed{HCS^+}$, H_2CS

CH_3SH, HNCS, SiO, SiS, *SiC_2, *SiH_4, HCl

Molecules marked with an asterisk have been detected only in circumstellar shells. The question marks indicate tentative detections. Tentative detections of NaOH (Hollis & Rhodes 1982) and H_2D^+ (Phillips *et al.* 1985) have also been reported. $HOCO^+$ and HOCN are both possible assignments for the same lines (Thaddeus *et al.* 1981). List compiled from various sources including Winnewisser *et al.* (1979), Rydbeck & Hjalmarson (1985), Irvine (1987) and Irvine *et al.* (1987).

for diffuse clouds. H_3^+ is rapidly formed via reaction (1), vibrationally relaxes and then undergoes reactions such as (2) that ultimately produce the observed diatomic molecules (e.g. CO and CS) and small polyatomic molecules (e.g. H_2O, NH_3 and CH_4). Cosmic-ray ionization of He generates He^+, which rapidly reacts with CO producing C^+, which, via reactions with H_2, initiates the growth of hydrocarbon ions. Reactions can then occur between the 'primary' ions C^+ and H_3^+ and various molecules creating other species, e.g.

$$C^+ \xrightarrow{NH_3} H_2CN^+ \xrightarrow{e} HCN. \qquad (3)$$

The H_2CN^+ produced in this reaction undergoes dissociative recombination via which HCN is expected to be produced. Significantly, almost all these small molecules (and certainly the more polyatomic molecules in dense clouds) have proton affinities that exceed that of H_2 (Lias *et al.* 1984) and so they can remove a proton from H_3^+. This is largely the way in which the HCO^+, HCS^+, N_2H^+ and H_2CN^+ observed in dense clouds are produced. Numerous laboratory studies (Bohme 1975; Bohme *et al.* 1980) have shown that when proton transfer is energetically

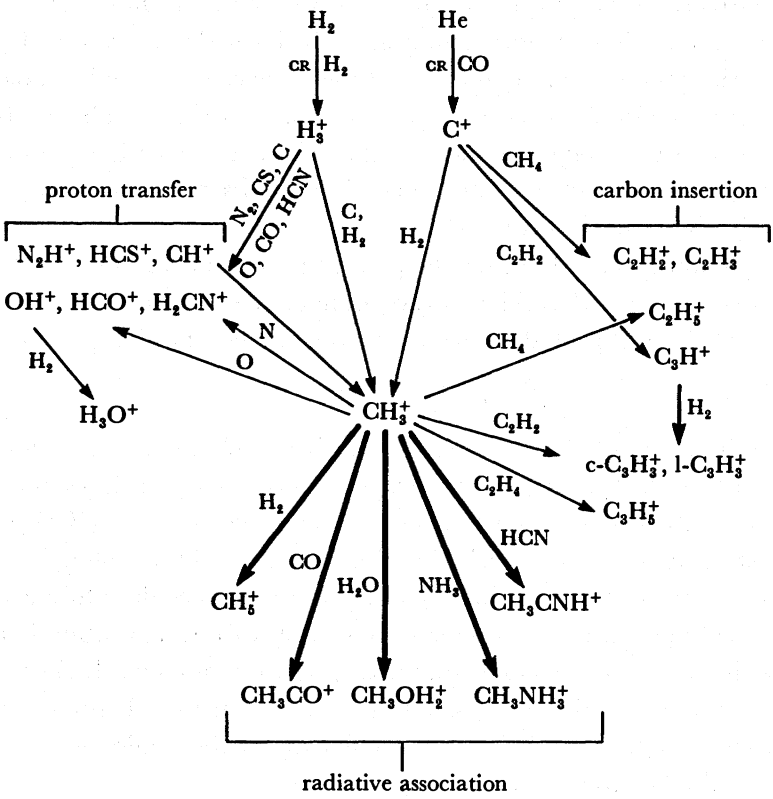


FIGURE 1. The action of cosmic rays (CR) on the abundant H_2 and He creates H_2^+ and He^+ ions, which react with H_2 and CO respectively to generate H_3^+ and C^+. The H_3^+ ions can then proton transfer to a range of atoms and molecules including C, CS and N_2 as shown generating ions such as CH^+, HCS^+, N_2H^+ etc., and the C^+ ions can undergo carbon-insertion reactions with hydrocarbon molecules generating longer-chain hydrocarbon ions. CH_3^+ ions (which are produced from H_3^+ and C^+ as indicated) undergo a variety of reactions including radiative association (indicated by thickened lines) under the low-temperature conditions of interstellar clouds, thus generating large molecular ions in a single step. The rate coefficients and product-ion distributions for many of the reactions included in the figure have been measured by various techniques and are given in the compilations by Albritton (1978) and Anicich & Huntress (1986) and in the reviews by Adams & Smith (1983, 1987*b*, *c*) that also review the experimental methods. Neutral atoms and molecules are formed from the ions via the process of dissociative recombination (see §3 of text and figure 3).

allowed, that is when the proton affinity (A_p) of a molecule exceeds that of potential protonated donor molecule, then at low temperature proton transfer will occur at every collision between the ion and the molecule (the rate coefficients for these processes are of the order of 10^{-9} cm^3 s^{-1} for non-polar molecules and, as has recently been shown, are as large as 10^{-7} cm^3 s^{-1} for polar molecules at low temperatures (Clary 1985; Adams *et al.* 1985). The relatively small A_p of H_2 (4.39 eV) ensures that H_3^+ is an excellent proton donor to most molecules (see figure 1). Also, because $A_p(N_2) = 5.13$ eV, N_2H^+ can transfer a proton to many interstellar species including CO ($A_p = 6.15$ eV), HCN ($A_p = 7.43$ eV) and CS ($A_p = 8.16$ eV). Similarly, HCO^+ can proton transfer to HCN and CS generating H_2CN^+ and HCS^+. This well-understood process of proton transfer is extremely important in gas-phase ion chemistry (Adams & Smith 1983) not least in interstellar dense clouds because it not only generates new ions but, in doing so, also creates neutral molecules. For example, in the proton transfer reaction

$$H_3O^+ + NH_3 \rightarrow H_2O + NH_4^+, \tag{4}$$

H_2O is known to be formed, whereas this may not necessarily be the case when H_3O^+ recombines dissociatively with electrons (see §3). Many other molecular ions, as yet undetected, must exist in dense interstellar clouds including those formed as a result of proton transfer reactions of H_3^+, N_2H^+, HCO^+, etc., with many of the observed interstellar molecules (listed in table 1) that have proton affinities exceeding those of H_2, N_2, CO, etc. The product ions of such reactions will have relatively long lifetimes if they do not react with H_2 and could then be present in sufficient large number densities to be observed by radioastronomy (assuming that they can radiate via rotational transitions).

A relatively simple ion species that must be present in interstellar clouds is CH_5^+. This ion is probably the precursor ion of CH_4, which, although not detected because of its symmetry, must surely be present. CH_5^+ is most probably formed via the process of radiative association between CH_3^+ ions and H_2

$$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu. \tag{5}$$

Much has been written about the process of radiative association in relation to interstellar molecular synthesis (Smith & Adams 1977, 1978*a*; Herbst 1980*b*; Bates 1983; Barlow *et al.* 1984). In this process, the excited intermediate ion–molecule complex ($(CH_5^+)^*$ in the case of reaction (5)) must emit a photon during a time τ_d, the lifetime of the complex against unimolecular decomposition back to the reactant ion and molecule. Only a low-energy (infrared) photon needs to be emitted to prevent the complex from separating back to reactants. Thus the radiative lifetime of the excited complex, τ_r, must be sufficiently short compared with τ_d to allow the association reaction to proceed at a significant rate. Estimates of τ_d have been obtained from laboratory studies of the rate coefficients of the analogous termolecular association processes (Smith & Adams 1978*b*), e.g.

$$CH_3^+ + H_2 + He \rightarrow CH_5^+ + He, \tag{6}$$

in which the intermediate complex is stabilized in a superelastic collision with another species that exists in large concentration in the reaction cell (in this case He atoms). Theory predicts (Bates 1979, 1980; Herbst 1979, 1980*a*, *b*) and experiments confirm (Meotner 1979; Adams & Smith 1981*a*, *b*) that τ_d increases as the temperature of the reactants decreases and, for strongly bound intermediates, τ_d can greatly exceed 10^{-2} s, which is expected to be the upper-limit τ_r for infrared emissions (Herbst 1985*b*) although it may be much shorter for some polyatomic ions radiatively decaying through vibrational states near to their dissociation limit. Thus radiative association is confidently invoked as an important process for the production of complex molecular ions under the low-temperature conditions of dense interstellar clouds (Herbst *et al.* 1984). This process along with several other processes, is included in the very general scheme shown in figure 1 for the production of interstellar ions from which, ultimately, the observed interstellar neutral molecules are produced. To date, radiative emission has not been observed from ion–molecule association and there is a great need for such spectroscopic studies. More information is also required on the infrared radiative lifetimes of excited complex molecular ions. However, there is little doubt that radiative association is a reality, as the classic study of reaction (5) at low temperatures has shown in which the rate coefficient has been measured as 1.8×10^{-13} cm^3 s^{-1} at 13 K (Barlow *et al.* 1984). This is more than adequate to initiate the production of CH_5^+ from CH_3^+ in dense interstellar clouds. That CH_5^+ does not react with H_2 ensures that it will persist in the clouds. Its ultimate fate will be either to transfer its proton to another species generating CH_4 or to dissociatively recombine with electrons, perhaps again producing CH_4 or CH_3 (see §3). The relative importance of these two destruction processes will depend on the relative number density of the proton-acceptor molecules to that of electrons in the cloud and on the respective rate coefficients for the reactions.

The importance of CH_3^+ in dense interstellar cloud ion chemistry is clear from figure 1. Its relative unreactivity with H_2 means that a small but significant fraction of CH_3^+ ions are available to react with other molecules via the process of radiative association (e.g. with CO, H_2O and HCN) and via normal bimolecular fragmentation reactions such as those with N and O atoms and hydrocarbon molecules. The radiative association reactions generate ions containing N and O as well as C and H, which are the precursor ions to neutral molecules such as CH_3OH and CH_3CN. The reactions of CH_3^+ with N and O atoms are another source of H_2CN^+ and HCO^+ ions (Fehsenfeld 1976) and reactions of CH_3^+ with hydrocarbon molecules containing n carbon atoms generally produce ions with $(n+1)$ carbon atoms (Herbst *et al.* 1983). Such reactions are often termed carbon insertion reactions and, as can be seen from figure 1, reactions of C^+ with hydrocarbon molecules also result in carbon insertion. Generally, such reactions will most probably result in the extension of the carbon chain, but in the rapid reaction

$$CH_3^+ + C_2H_2 \rightarrow \text{c-}C_3H_3^+ + H_2 \tag{7}$$

the lowest energy isomer of $C_3H_3^+$ (the cyclic isomer, c-$C_3H_3^+$) is formed exclusively (Adams & Smith 1987*d*). However, the major source of interstellar c-$C_3H_3^+$ (which is probably the precursor ion of the recently discovered, yet ubiquitous, interstellar cyclic molecule c-C_3H_2, (Matthews & Irvine 1985; Thaddeus *et al.* 1985)) is probably the sequence of reactions (Herbst *et al.* 1984)

$$C \xrightarrow{C_2H_2} C_3H^+ \xrightarrow{H_2} \text{c-}C_3H_3^+,\ \text{l-}C_3H_3^+ \xrightarrow{e} \text{c-}C_3H_2,\ \text{l-}C_3H_2. \tag{8}$$

Note that both the linear and cyclic isomers of $C_3H_3^+$ are formed in the second stage, which is the association reaction of C_3H^+ with H_2. (Both l-$C_3H_3^+$ and c-$C_3H_3^+$ were observed as products of the collisional association reaction of C_3H^+ with H_2 and are presumed also to result from radiative association (Adams & Smith 1987*d*; Smith & Adams 1987).) Clearly, as the complexity of the ions increases then a greater number of structural isomers is possible. Although few experimental data exist on the structures of the ion products of gas-phase ion–molecule reactions, this is an exciting and a growing area of interest that is obviously very relevant to interstellar chemistry because other cyclic molecules must exist in interstellar clouds. The beautiful experimental techniques (Adams & Smith 1987*b*) that have been developed to study ionic reactions in the gas phase and that have provided the kinetic data that substantiate the ion chemistry summarized in figure 1, will soon, no doubt, lead to the identification of other cyclic ions that could be the precursors of other cyclic interstellar molecules.

Several interstellar molecular species are detected also containing the rare isotopes D, ^{13}C, ^{15}N, ^{17}O, ^{18}O, ^{29}Si, ^{33}S and ^{34}S. This is in itself no surprise, but what was initially surprising and very interesting was the observation that the fractional abundances of the molecules containing the rare isotope to those of the same species containing the common isotope, exceeded their terrestrial ratios. This was especially evident for the deuterated species for which the D:H ratio for a given species was greater by one or two orders of magnitude than the terrestrial ratio. The $^{13}C:^{12}C$ ratio was also greater than the terrestrial value for several species but typically only by about a factor of two. It is now appreciated that these enhanced isotope ratios in interstellar molecules are largely because of the phenomenon of isotopic fractionation in ion–molecule reactions (Watson 1976; Smith *et al.* 1982*a*, *b*; Smith & Adams 1980, 1984*a*; Adams & Smith 1981*a*, *b*, 1985) as exemplified by the elementary reaction

$$D^+ + H_2 \rightleftharpoons H^+ + HD + \Delta E, \quad \Delta E/k = 462\ \mathrm{K}. \tag{9}$$

This reaction is appreciably exothermic to the right ($\Delta E = 39.8$ meV; equivalent to $\Delta E/k = 462$ K, k is the Boltzmann constant) mostly because the vibrational zero-point energy (ZPE) of H_2 exceeds that of HD (Henchman *et al.* 1981). The result of this is that the reverse of reaction (9) is very slow at interstellar cloud temperatures (i.e. when $T \ll \Delta E/k$) and so the reaction proceeds only in the forward direction. This forward reaction is very efficient, occurring essentially on every collision between a D^+ ion and an H_2 molecule, and therefore it fractionates deuterium into HD. Hence, much of the D in dense interstellar clouds is in the form of HD (together with a fraction of D atoms and smaller fractions of other deuterated molecules). Detailed laboratory studies of deuterium fractionation in ion–molecule reactions have been carried out over a range of temperatures down to 80 K (Smith *et al.* 1982*a*, *b*; Smith & Adams 1984*a*; Adams & Smith 1985). From these studies has emerged a clear idea as to how most of the observed deuterated interstellar molecules are formed. Again, H_3^+ and CH_3^+ are strongly implicated in this, because they both react very rapidly with HD (but not with H_2) by

$$H_3^+ + HD \rightleftharpoons H_2D^+ + H_2, \quad \Delta E/k = 220\ \mathrm{K}\ (\text{at } T = 20\ \mathrm{K}), \tag{10}$$

$$CH_3^+ + HD \rightleftharpoons CH_2D^+ + H_2, \quad \Delta E/k = 335\ \mathrm{K}, \tag{11}$$

thus generating their deuterated analogues H_2D^+ and CH_2D^+. (Note that H_2D^+ has been tentatively identified in interstellar clouds, by Phillips *et al.* 1985.) The reverse of reactions (10) and (11), which would act to convert the deuterated ions back to H_3^+ and CH_3^+, are very slow at low temperatures (again when $T \ll \Delta E/k$), whereas the forward reactions are rapid and occur essentially on every collision between the ions and an HD molecule. Hence, the H_2D^+ and CH_2D^+ are able to react with other species in the gas clouds (in a totally analogous way to H_3^+ and CH_3^+; see figure 1) generating molecules that are enriched in deuterium. The deuterated molecules observed to date in interstellar clouds together with the elementary reactions (including reactions (9)–(11)) that are considered to generate them are shown in figure 2. Also included in figure 2 is the D–H exchange reaction

$$C_2H_2^+ + HD \rightleftharpoons C_2HD^+ + H_2, \quad \Delta E/k = 550\ \mathrm{K}. \tag{12}$$

By this reaction, deuterium is fractionated into C_2HD^+, which on recombining with an electron can generate the observed interstellar species C_2D. It is observed, somewhat surprisingly, that the $C_2D : C_2H$ ratio is greater in the Orion cloud ($T \approx 50$ K) than in the Taurus cloud, TMC-1 ($T \approx 10$ K) even though laboratory studies have clearly established that deuterium fractionation is more rapid at low temperatures. This has been explained by recognizing that both $C_2H_2^+$ and C_2HD^+ radiatively associate with H_2, which competes more effectively with reaction (12) and with dissociative recombination for the destruction of $C_2H_2^+$ and C_2HD^+ at the lower temperature of TMC-1 and hence diminishes the rate of production of C_2D (Herbst *et al.* 1987). The C_2HD^+ produced in reaction (12) may also be involved in the production of the

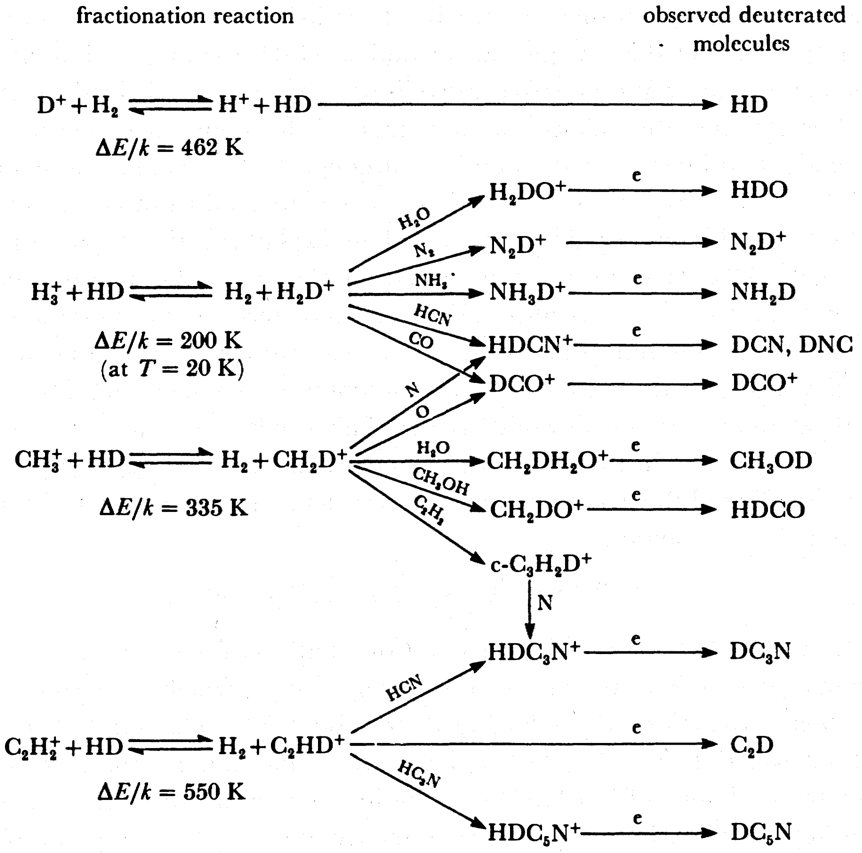


FIGURE 2. The H–D exchange (fractionation) reactions are shown as reversible reactions but because of their large exothermicities, ΔE (expressed as $\Delta E/k$ in Kelvin, where k is the Boltzmann constant), they only proceed to the right in cold dense clouds. Thus HD, H_2D^+, CH_2D^+ and C_2HD^+ are efficiently produced by the reactions indicated and then can react with the molecules shown generating the deuterated ions shown, of which both N_2D^+ and DCO^+ have been detected in dense interstellar clouds. Kinetic data on the H–D exchange reactions are given in the review papers by Adams & Smith (1983) and Smith & Adams (1984*a*). Source references for the list of deuterated interstellar molecules are given in Winnewisser *et al.* (1979) and Irvine *et al.* (1987). Dissociative recombination reactions of the other deuterated ions with electrons can produce the deuterated neutral molecules indicated, all of which have been detected in dense clouds, although it must be said that the neutral products of these recombination reactions have not yet been established experimentally (see §3 of text and figure 3).

DC_3N and DC_5N detected in interstellar clouds by the reactions indicated in figure 2, although this chemistry is still uncertain.

It has been shown that D–H exchange is very facile at low temperatures especially for 'symmetrical' proton-bound dimer systems including the systems $H_3^+ \cdot H_2$ (i.e. H_2—H^+—H_2, of which reaction (10) is an example), $H_3O^+ \cdot H_2O$, $NH_4^+ \cdot NH_3$ and $CH_5^+ \cdot CH_4$ etc., and this has been explained as being caused by the 'shuttling' of the proton (or deuteron) between the two chemically identical molecules, which are also able to rotate within the (strongly bound) proton-bound dimer (Adams *et al.* 1982). However, it should be noted that there are many ion–molecule interactions in which D–H exchange does not occur at a measurable rate even at a temperature of 80 K. These include the interactions of the important interstellar ions HCO^+, N_2H^+, H_3O^+, NH_4^+ and CH_5^+ with HD. For such cases, the ion–H_2 complexes are only very weakly bound, the binding energies being much less than the difference between the proton affinities of the proton donating molecules (CO, N_2, H_2O, NH_3 and CH_4) and that of H_2 (which is the smallest). This, in effect, presents an energy barrier to the motion of the proton. Thus, transfer (or shuttling) of the proton within the ion–molecule complexes cannot occur because of the presence of this energy barrier and so H–D exchange is inhibited. That the above-mentioned ions are not deuterated in collisions with HD has helped greatly in understanding and explaining the relative abundances of the deuterated species observed in interstellar clouds. It is interesting to note that, although D–H exchange occurs efficiently in reaction (12) between $C_2H_2^+$ and HD, it does not occur to a measurable degree when $C_2H_3^+$ interacts with HD. This observation has helped in explaining the apparently anomalous difference in the C_2D:C_2H ratio between the Orion cloud and the Taurus cloud discussed above (Herbst *et al.* 1987). It has also helped in characterizing the vibrational spectra of $C_2H_3^+$ (Oka, personal communication 1986). It is also worthy of note that it has recently been shown that some of those ions that do not isotope exchange with HD do, however, exchange with D atoms (Adams & Smith 1985). This needs to be taken into account when considering D–H exchange in the interstellar clouds (Dalgarno & Lepp 1984).

Isotope fractionation of the heavy isotopes of other elements also occurs in the ion–molecule reactions such as in the reaction

$$^{13}C^+ + ^{12}CO \rightleftharpoons ^{12}C^+ + ^{13}CO, \quad \Delta E/k = 40\ K. \tag{13}$$

The relatively small $\Delta E/k$ for reaction (13) means that ^{13}C fractionation only occurs to a significant extent at temperatures much lower than those at which deuterium fractionation occurs. Nevertheless, reaction (13) is largely responsible for the enhanced ^{13}CO:^{12}CO ratios (relative to the terrestrial ^{13}C:^{12}C ratio) in dense interstellar clouds (Smith & Adams 1980). The $\Delta E/k$ for the exchange of ^{14}N for ^{15}N in the interaction of N_2H^+ with N_2 is only about 10 K and thus fractionation in this system can only occur at very low temperatures (Adams & Smith 1981 *a*, *b*). The detailed laboratory studies of isotope exchange in ion–molecule reactions and the interstellar implications have been discussed in some recent reviews (Smith 1981, 1987; Smith & Adams 1984*a*; Wootten 1987).

3. Destruction of positive ions in interstellar clouds: dissociative recombination

Clearly, a given positive-ion species may be destroyed in reaction with neutral molecules as, for example, by those reaction processes that are described above and are illustrated in figure 1. The simplest and fastest of these processes is proton transfer (e.g. reactions (2) and (4)) in which predictable new molecular and ionic species are generated, and this may be the final process in the production of a particular observed interstellar molecule. For example, it has been demonstrated that proton transfer from H_2Cl^+ to CO is most probably the final step in the production of the HCl recently detected in interstellar clouds (Blake *et al.* 1985) that proceeds thus:

$$Cl^+ \xrightarrow{H_2} HCl^+ \xrightarrow{H_2} H_2Cl^+ \xrightarrow{CO} HCO^+ + HCl. \tag{14}$$

The individual reactions included in the reaction sequence (14) have all been studied in laboratory experiments (Smith & Adams 1981*a*, *b*, 1985) and the HCO^+ and HCl products of the final proton-transfer step are quite certain.

The alternative process for the destruction of positive ions in any ionized gas, including the weakly ionized interstellar clouds, is dissociative recombination. With very few exceptions (notably H_3^+, see below) molecular positive ions are neutralized by electrons and the resulting neutral excited molecule then fragments. This is the process of dissociative recombination. Sufficient energy is usually released to ensure that one or more of the neutral fragments are not only kinetically excited but also internally excited. Indeed, for simple polyatomic ions total fragmentation to atoms may occur when it is energetically allowed. This is possible for the recombination reaction of H_2Cl^+ with electrons that could produce two H atoms and a Cl atom (compare this with the final step in the reaction sequence (14)). Herein is the major problem in invoking dissociative recombination to explain the production of neutral molecules from positive ions in gas-phase ion chemistry (such as that illustrated in figure 2). Little is known about the products of such reactions except for those involving diatomic ions where the products can only be two atoms, and a few triatomic ions where the energetics dictate the nature of the products. Examples of these simple cases are given in figure 3. Clearly, the products of dissociative recombination of O_2^+ ions can only be two O atoms but interest is then directed to determining the ways in which the energy released is divided between translation and internal (electronic) modes of excitation. Experiments have shown that for O_2^+ recombination, the O atom products are distributed among the ^3P ground state and the metastable ^1S and ^1D states (Zipf 1970, 1980), but even this apparently simple case is complicated in that branching into the various states of the O atoms is very dependent on the vibrational state of the recombining O_2^+ ions (Guberman 1983). Almost all that is known about the products of recombination is indicated in the upper half of figure 3 and this has been obtained from emission and absorption spectroscopy of afterglow plasmas. In the most recent of these studies, the products of recombination of internally excited H_2O^+ ions (for which the internal state of excitation is unknown) have been investigated by detecting the product H and O atoms by vacuum ultraviolet (VUV) absorption (Rowe *et al.* 1987).

Although the data obtained for the products of O_2^+, N_2^+ and NO^+ dissociative recombination (Zipf 1970, 1980; Kley *et al.* 1977; Queffelec *et al.* 1985) are of great interest to terrestrial aeronomy, recombination of these ions with electrons (and also the CO_2^+ and H_2O^+ indicated

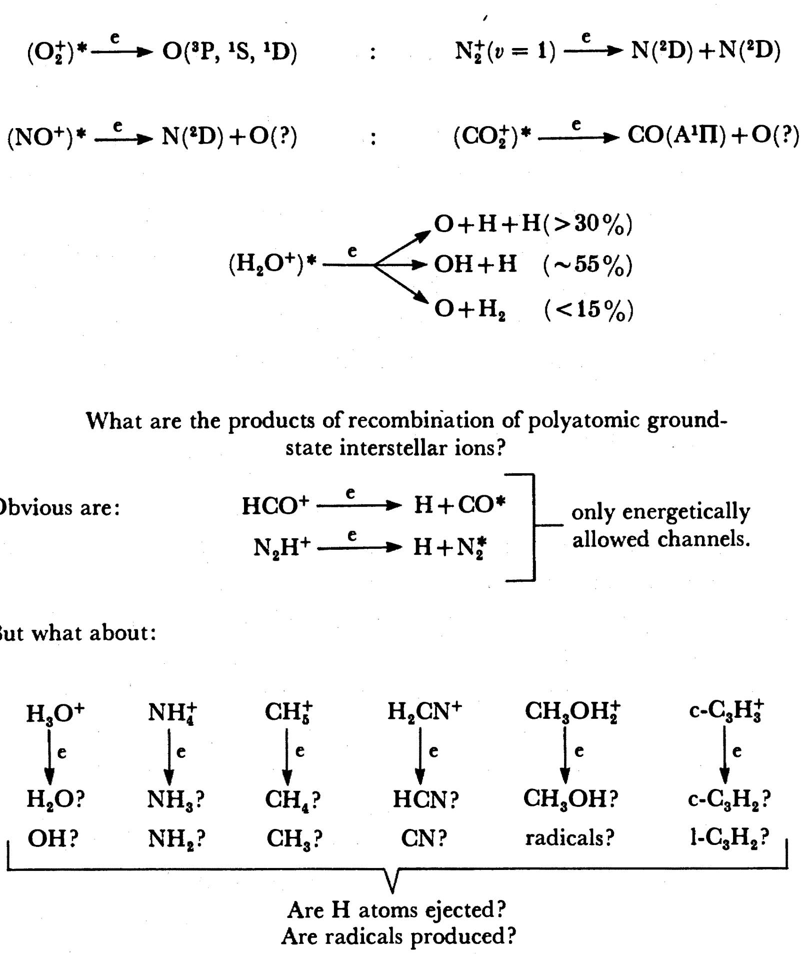


FIGURE 3. Little is known about the products of dissociative recombination reactions of interstellar ions with electrons. Some information is available (as indicated in the upper half of the figure) concerning the products of recombination of O_2^+, NO^+, CO_2^+ and H_2O^+ in unknown states of internal excitation and for $N_2^+(v = 1)$, none of which is an important interstellar ion (for references, see §3). The neutral products of HCO^+ and N_2H^+ recombinations are as indicated, these being the only energetically allowed products (the asterisks associated with the various species, including the CO and N_2, indicate that the species are internally excited). From the viewpoint of interstellar chemistry, the products of recombination of several important interstellar ions such as those indicated at the bottom of the figure (H_3O^+, --- c-$C_3H_3^+$, etc.) are urgently required. It would be particularly interesting to know whether the cyclic or linear (or both) isomers of C_3H_2 are produced when c-$C_3H_3^+$ recombines with electrons.

in figure 3) does not occur to any significant extent in interstellar clouds because either they are not formed to any significant degree (i.e. O_2^+ and NO^+) or they react much more rapidly with the abundant H_2 than with the much less abundant electrons (i.e. N_2^+, CO_2^+ and H_2O^+). This can be easily demonstrated by calculating the reaction rates by using the measured rate coefficients for the reactions of these ions with H_2 and the measured recombination coefficients. Although little is known about the products of dissociative recombination, a great many experimental data have been obtained over the last three decades concerning the recombination coefficients and their temperature dependences by using stationary afterglow methods (Bardsley & Biondi 1970; Biondi 1973). Quite recently, a flowing afterglow technique has been developed to determine recombination coefficients over a wide range of temperature for a wide variety of polyatomic ions, including many interstellar ions (e.g. H_3O^+, HCO^+ and CH_5^+)

(Smith & Adams 1984*b*, *c*). The collected results of all these studies indicate that, generally, recombination coefficients increase with increasing complexity of the recombining ion and with decreasing temperature. Thus, for most interstellar polyatomic molecular ions recombining with electrons at low temperatures, a recombination coefficient of *ca.* 10^{-6} $cm^3\,s^{-1}$ is appropriate. By using this laboratory result together with estimates of the degree of ionization of interstellar clouds, it can be shown that dissociative recombination is the most important loss process for most interstellar ions that do not react rapidly with H_2 and this includes those given in the lower half of figure 3. So, the outstanding question is: 'What are the products of recombination of such ions?' So often in interstellar ion chemical models it is assumed for expediency that an H atom is ejected following recombination leaving a stable molecule. This must indeed by the case for the recombination of HCO^+ and N_2H^+ because this is the only energetically allowed channel in both cases (see figure 3). But this is certainly not the only possibility for most other interstellar ions such as those examples given in figure 3. A statistical theory has been developed to predict the products of recombination of the important interstellar ions CH_3^+, H_3O^+, NH_4^+ and H_2CN^+ (Herbst 1978), which, for example, indicates that $CH+H_2$ will be favoured over CH_2+H as the major product of CH_3^+ recombination and that OH will be strongly favoured over H_2O in H_3O^+ recombination. However, in a more recent paper (Bates 1986), it is argued that dissociative channels involving the least rearrangement of valence bonds are favoured, and it is concluded that the predictions of the statistical theory are not valid.

Clearly, theoretical calculations of the products of recombination of polyatomic ions are particularly difficult and experiments are necessary to answer the questions posed at the bottom of figure 3. In this regard, spectroscopy on the neutral products offers the best hope of success and collaborative experiments are underway between the Universities of Rennes, France (B. Rowe and J. L. Queffelec), and Birmingham, England (N. G. Adams and D. Smith) that will surely provide the answers to these questions for some ions. These new experiments rely on the fact that H_3^+ ions in the ground vibrational state do not recombine with electrons at a measurable rate (it is interesting to note that the Birmingham group have shown that HeH^+ also does not recombine with electrons). This remarkably important result for interstellar chemistry has only quite recently been demonstrated experimentally (Smith & Adams 1984*b*) and substantiated by theory (Michels & Hobbs 1984). It has made it necessary to reappraise the ion–chemical models of interstellar chemistry and the method of predicting electron densities in dense clouds (Smith & Adams 1984*b*). The new laboratory experiments are essentially based on the Birmingham FALP apparatus (Smith & Adams 1984*c*; Adams & Smith 1987*c*) to which spectroscopic diagnostics are being added to detect the products of recombination of vibrationally relaxed ions (e.g. H and O atoms by VUV absorption and product molecular fragments, e.g. OH and CN radicals by laser-induced fluorescence). The first stage in the experiment is to create an H_3^+–electron flowing afterglow plasma. This is achieved by adding H_2 in excess to a helium afterglow plasma consisting of largely He_2^+ ions, metastable helium atoms and electrons. Charge exchange between the He_2^+ and H_2 and Penning ionization of H_2 by helium metastables both create H_2^+, which rapidly reacts with H_2 producing H_3^+ and an H atom. The latter is detected by Ly-α absorption and effectively calibrates the experiment. A proton-acceptor molecule, e.g. H_2O, can then be added to the H_3^+ plasma producing (via proton transfer) H_3O^+ ions, which are rapidly recombining species. If on recombination H atoms are generated then these are detected as an increase in the Ly-α absorption. In this way, the number of H atoms produced per recombining ion can be determined. Additionally, if radicals such as OH are generated then these can be detected by laser-induced fluorescence. Very preliminary results on the Ly-α experiment have indicated that valuable data on the products of recombination of several molecular ions (importantly in their ground states) will soon be obtained. Such will be a major contribution to interstellar chemistry and also provide much valuable fundamental data on dissociative recombination. Perhaps it might be possible to answer the intriguing question posed at the bottom of figure 3, which is whether cyclic neutral molecules (e.g. c-C_3H_2) are generated when cyclic ions (e.g. c-$C_3H_3^+$) recombine with electrons!

4. Summary and concluding remarks

Positive ions are created in interstellar clouds by the action of electromagnetic and cosmic radiation on the ambient gas. The simple (primary) ions thus produced then react with ambient atoms and molecules by a variety of mechanisms generating polyatomic ions (see figure 1). Those ions that are reactive with H_2 are relatively quickly destroyed because of the preponderance of H_2 in interstellar clouds, but those that are unreactive with H_2 have a longer lifetime. Significantly, as laboratory work has shown, those ions that have been detected in dense interstellar clouds do not react with H_2 at significant rates even at low temperatures. It is clear from the ion chemistry outlined in this paper that many more ionic species must exist in interstellar clouds than have so far been detected. Other species will undoubtedly be detected as their spectra are determined and as the detection sensitivities of radio antennae are increased. Those molecular ions that are unreactive with ambient neutrals are eventually destroyed via the process of dissociative recombination with electrons. This is probably the final process by which most of the neutral molecules detected in interstellar clouds are formed (see table 1). Dissociative recombination is generally an efficient reaction process but because the ionization density in dense interstellar clouds is low ($[e]/[H_2] \approx 10^{-7}$) (Smith & Adams 1984*a–c*; Dalgarno & Lepp 1984), then the number densities of several ionic species should be large enough for them to be detected, notably those ions that are formed efficiently and that do not react with H_2. The recent recognition that ground-state H_3^+ recombines only slowly, if at all, (Smith & Adams 1984*b*, 1987) with electrons means that its reactions with neutrals to generate other ion species takes on a greater significance than had previously been thought. Also, the recent recognition that its proton-transfer reactions with polar molecules are much more rapid at low temperatures than had previously been assumed (Adams *et al.* 1985) means that ions that essentially are protonated interstellar polar molecules, are prime candidates for detection. Significantly, H_2CN^+ has recently been detected in concentrations consistent with ion-chemical predictions based on the new realizations concerning the reactions of H_3^+ ions (Millar *et al.* 1985; Ziurys & Turner 1986). It is well worth noting that this understanding of interstellar ion chemistry can be put to good use in creating laboratory plasmas consisting of particular ion species and in facilitating the generation of ion beams for spectroscopic studies. Hopefully, it will also stimulate spectroscopists to select for study some of those ions that are identified as being involved in interstellar chemistry.

Isotope exchange in ion–molecule reactions, particular H–D exchange, is a very interesting phenomenon both fundamentally and from the viewpoint of interstellar chemistry. Laboratory studies have shown that several of the important ions involved in interstellar molecular synthesis, including H_3^+ and CH_3^+, undergo H–D exchange in reaction with HD. This process is very efficient at low temperatures and is responsible for the fractionation of the heavy isotopes of some elements into interstellar ions and neutral molecules. All of the deuterated molecules so far detected in interstellar clouds (see figure 2) are enriched in deuterium to varying degrees and, significantly, H_2D^+ has recently been (tentatively) detected in interstellar clouds. However, laboratory studies have also shown that some important interstellar ions do not D–H exchange with HD (including HCO^+, H_3O^+, NH_4^+ and $C_2H_3^+$) and this is valuable additional information in the efforts to elucidate the synthetic routes to interstellar molecules. Again it can be a help to spectroscopists in identifying the spectra of certain ions.

It is clear that molecular spectroscopy has a vital role to play in the further study of molecular ions in the gas phase, and thus in the field of interstellar chemistry. The accurate characterization of the rotational and vibrational spectra of more ion species is required before they can be usefully sought in interstellar clouds. It seems likely that structural isomers of some ions (e.g. $C_3H_3^+$) must exist in interstellar clouds and, if the spectra of these could be separately characterized in laboratory experiments, it would be a great step forward. It has been postulated (§2) that radiative association is a major reaction process in the synthesis of interstellar molecules, yet a major uncertainty in quantitatively accounting for this process in interstellar ion–chemical models lies in the magnitudes of the radiative lifetimes of excited ion complexes. Spectroscopic work is urgently required as a guide in this area. Indeed, it would be of great value if the structures of the ions formed in certain ion–molecule reactions, including some association reactions, could be ascertained since this is also a major area of doubt. It has already been stressed how important it is to the proper understanding of interstellar molecular synthesis to be able to specify the neutral products of dissociative recombination of polyatomic positive ions. Again in this, as in so much of the interstellar research, spectroscopic studies are the best and often the only hope of gaining the required understanding. Interstellar physics and chemistry is both a mission field and an exciting stimulus to spectroscopy.

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