Molecular ions in interstellar reaction networks

Eric Herbst
Departments of Physics, Astronomy, and Chemistry, The Ohio State University, Columbus, OH 43210, USA
E-mail: herbst@mps.ohio-state.edu

Abstract. In this review, the roles of dissociative recombination reactions and other ionic processes in the exotic environment of interstellar space are elucidated through a discussion of the interstellar medium and the chemistry that occurs in it. Both recent progress in and current challenges to interstellar ion chemistry are emphasized.

1. Introduction to the interstellar medium
Most of the matter in the universe is localized into large assemblies of stars known as galaxies. In most of the galaxies that can be studied, the space between stars is found to be not devoid of material but to contain so-called interstellar clouds, which consist of gas and dust and are embedded in a more rarefied medium. Densities and temperatures of clouds vary widely, and indeed few clouds are homogeneous.

1.1. Diffuse clouds
Perhaps the simplest clouds are known as “diffuse”; the gas and dust in such regions is not dense enough to keep out starlight, and only a trained astronomer can detect diffuse material in between bright stars and ourselves. Typical temperatures of such regions are in the vicinity of 50–100 K and total gas densities are perhaps $10^2 \text{ cm}^{-3}$ [1]. As in all clouds, the gas is mainly hydrogen in one form or another, betraying the fact that the material in clouds comes from previous generation of stars, which are also mainly hydrogen in content. Some average “cosmic” elemental abundances, normalized with respect to hydrogen, and taken from the atmospheres of nearby stars, are shown in table 1 [2]. The heavy elements in stars are depleted in interstellar gas because they also constitute the dust particles [2], which are mainly silicates and carbonaceous material [3]. Some recent elemental abundances used for a gas-phase model of diffuse clouds are also shown in table 1. By mass, the dust is typically 1% of the gas, and consists of particles ranging widely in radius from less than $\approx 1 \text{ nm}$ to more than $\approx 1 \mu\text{m}$ [4]. A standard size quoted by astronomers is 0.1 \mu m.

Although the gas phase in diffuse clouds is mainly neutral, virtually all of the carbon is ionized by ultra-violet radiation from stars, leading to a fractional ionization of $\approx 10^{-4}$ [1]. The more abundant elements hydrogen and helium cannot be ionized by stellar ultra-violet radiation because it is does not extend to high enough energies, terminating at 13.6 eV, the ionization potential of atomic hydrogen. Some ionization of hydrogen and helium comes from cosmic rays; these are mainly protons traveling at relativistic speeds. The hydrogen is typically divided evenly between neutral atomic and molecular forms; the molecules are produced not in the gas but via recombination on the surfaces of dust particles. Other than molecular hydrogen, all molecules are trace constituents of the gas. Until recently, it was thought that only diatomic species (e.g. CH, CN, OH, NH, C$_2$) are present in diffuse clouds, but the
Table 1. Elemental abundances with respect to total hydrogen. Numbers in parentheses denote powers of ten.

| Element | Cosmic | Diffuse Gas | “Low-Metal” (Dense Gas) |
|---------|--------|-------------|-------------------------|
| C       | 4.0(-04)| 1.32(-04)  | 7.3(-05)                |
| O       | 7.4(-04)| 3.2(-04)   | 1.76(-04)               |
| N       | 9.3(-05)| 7.5(-05)   | 2.14(-05)               |
| S       | 2.6(-05)| 1.86(-05)  | 8.0(-08)                |
| Si      | 3.5(-05)| 2.9(-05)   | 8.0(-09)                |

situation is now known to be more complex [1]. The most prominent molecular ion detected is probably CH⁺, which can be seen via its visible spectrum. This ion possesses a fractional abundance of only 10⁻⁷, far below that of C⁺.

1.2. Dense clouds and star formation

The chemistry that occurs in dense interstellar gas is far more complex than that of diffuse gas. Dense gas is normally associated with giant molecular clouds, which are large heterogeneous assemblies of gas and dust ranging in mass up to \( \approx 10^5 \) solar masses. At its most diffuse, the material does not extinguish visible light completely, although it is probably more proper to call the material “translucent” rather than diffuse. The dense portions, virtually black in the visible, are known as ‘cores’ and have typical temperatures of only 10 K and densities of \( \approx 10^4 \) cm⁻³, consisting overwhelmingly of molecular rather than atomic hydrogen [5]. Although some cores are termed ‘quiescent’, others are actively collapsing to form stars. The detection of molecules in regions of active star formation tells astronomers much about the physical conditions and their evolution. The earliest active stage of stellar evolution is known as a pre-stellar core; here the collapse is still isothermal but a condensation of higher density begins to form in the center as collapse occurs [6]. In this core within a core, heavy molecules condense out onto the surfaces of dust particles to form mantles of ices, and the gas becomes almost completely hydrogen and helium. In the next stage, known as a protostellar core and subdivided into various categories, the collapse turns adiabatic in the center and a warm ‘protostar’ develops [7]. Near the star, the dust grains warm sufficiently so that the mantles can evaporate and return to the gas.

A large number of molecules (upwards of fifty) have been detected in the cold gas of quiescent and pre-stellar cores; these are mainly unsaturated organic molecules, with the largest being the nitrile HCN. Some observed fractional abundances in the best-studied quiescent core, TMC-1 (TMC stands for Taurus molecular cloud), are shown in table 2 [8]. It should be noted, however, that it is likely that this source is not completely quiescent although it does not show the collapse suggestive of cold pre-stellar cores either. A glance at table 2 shows that there are unusual isomers (HNC), three-membered rings (cyclic-C₃H₂), as well as molecular ions in the source. Clearly the chemistry is an unusual one.

The gas in protostellar sources shows more saturated material in the newly formed gas; this is especially true around budding stars of high mass known as “hot cores” [9]. These hot cores have temperatures in the range 100–300 K and are associated with terrestrial-like organic molecules such as methyl and ethyl alcohol, methyl formate, dimethyl ether, and others. Adding all types of molecular species together yields upwards of 120 different species, excluding isotopomers. The molecules can be found on websites such as http://astrochemistry.net/. Most of these species have been detected in dense clouds by their rotational spectral transitions, seen in emission in the millimeter-wave and microwave regions of the spectrum. Some have also been detected in the infrared, typically in absorption since infrared radiation from background stars penetrates far more efficiently than does visible radiation. In addition to high-resolution infrared features, low-resolution features are also detected; these are
Table 2. Some observed fractional abundances (with respect to H$_2$) in TMC-1.

| Species     | Abundance | Species     | Abundance |
|-------------|-----------|-------------|-----------|
| CO          | 8(−5)     | OH          | 2(−7)     |
| C$_2$H      | 9(−8)     | HCN         | 2(−8)     |
| HNC         | 2(−8)     | NH$_3$      | 2(−8)     |
| HCCCN       | 2(−8)     | cyclic-C$_3$H$_2$ | 1(−8) |
| HCO$^+$     | 8(−9)     | HCNH$^+$    | 2(−9)     |
| HCS$^+$     | 4(−9)     | HCCCNH$^+$  | 1(−10)    |

associated with the ices that constitute the mantles of grains. The most abundant form of ice is, as on the earth, that of simple water. Interestingly, the elemental abundances in the gas phase of dense clouds are not well determined since one must work backwards from molecules and depend upon model simulations. A standardly used set of abundances for important elements in dense clouds, known as “low metal” abundances,” is shown in table 1 [10]. It can be seen that the heavier elements are strongly depleted compared with stellar and diffuse cloud abundances. If these and other elements (e.g. iron) are allowed to have higher gas-phase abundances, the ionization fraction determined in models becomes too high. The elemental abundances listed in table 1 are still controversial, however.

We have still not exhausted the type of sources that are found within giant molecular clouds. In addition to the warm regions near the center of protostars, where material is evaporated gently from grain mantle to gas phase, there are more violent regions, in which jets of material are blown out strongly, causing shock waves to develop [11]. These shocks heat up molecules, sputter species from grains, and in general change the chemistry strongly. Another type of source occurs near high-mass stars that have actually formed in the dense gas. By this time, the hot core is no longer around and most of the material near the star has turned into a high-temperature plasma known as an HII region, since protons dominate the material. Although molecules are not found in HII regions, they are found right up against their border, in warm neutral gas known as “photon-dominated regions” [12]. So-called PDR’s have a rich chemistry of their own, despite the high radiation field. Finally, as low-mass stars grow to adolescence, they are often surrounded by dense disks of gas and dust known as protoplanetary disks. These objects are the precursors to planetary formation and are currently of intense interest.

Among the many molecules detected in diffuse and dense gas are the positive molecular ions listed in table 3. Those found in diffuse gas include the classic CH$^+$, mentioned above, as well as H$_3^+$ and HCO$^+$. The latter two are more strongly associated with dense gas, and the other ions listed are only found in dense material. The ion CO$^+$ is associated especially with PDR’s, and the isomer HOC$^+$ has also been recently detected in such regions. We have included several deuterated ions since these are important indicators of the physical conditions in star formation regions, especially pre-stellar cores. Other isotopomers such as H$^{13}$CO$^+$ have not been included. The most abundant molecular ion in dense sources is, as can be seen in table 2, probably HCO$^+$ except for cold pre-stellar cores, where virtually all non-hydrogenic material is frozen out. An estimated fractional ionization in dense cores is $10^{-7}$ [13].

2. Gas-phase chemistry

Even before molecular ions were found in dense interstellar clouds, it had been suggested that these ions play a prominent role in the chemistry occurring in the gas-phase since, especially in the cold regions, the dominant processes are exothermic reactions that have no activation energy [14]. Unlike most neutral-neutral reactions, ion-molecule reactions often do not possess activation-energy barriers and so play a crucial role despite the low fractional ionization in dense clouds. The primary ion in dense clouds is H$_3^+$ because it is made early in the reaction chain and serves as a precursor for the formation of more
Table 3. Molecular ions in diffuse and dense clouds.

| Diatomic | Triatomic | Triatomic | Polyatomic |
|----------|-----------|-----------|------------|
| CH⁺      | H₃⁺       | DCO⁺      | H₃O⁺       |
| CO⁺      | H₂D⁺      | HN⁺       | HCNH⁺      |
| SO⁺      | HD₂⁺      | DN₂⁺      | HOCO⁺      |
| HCO⁺     | HCS⁺      | H₂COH⁺    |
| HOC⁺     |           | HCCCNH⁺   |

complex species [15]. Molecular hydrogen is formed on the surfaces of grains, and is released to the gas either during the reaction or by evaporation [16]. Ionization is caused by encounters with cosmic rays, typically with relativistic energies of 100 MeV or more, which lead mainly to the removal of a single electron and the formation of H⁺. This ion reacts “immediately” (within a day) with molecular hydrogen, the dominant species, to form the H₃⁺ ion:

\[
H⁺ + H₂ \rightarrow H₃⁺ + H.
\]  

The H₃⁺ does not react with H₂ and so is relatively abundant. Since it does not possess a permanent dipole moment, it does not possess a strong rotational spectrum, and so lay undetected, to the dismay of astrochemists, until technological improvements in infra-red sensitivity led to its detection in this spectral region [17]. The observed abundance in dense clouds is what had been predicted, although the more recent detection in diffuse clouds is harder to understand, as discussed below. Another primary ion is He⁺, formed by cosmic ray bombardment of abundant helium atoms, and also unreactive with H₂.

Now let us consider the role of H₃⁺ as a precursor to more complex species [18]. Consider a mainly neutral gas consisting of H₂ and atoms of the heavier elements. In addition to dissociative recombination with electrons, H₃⁺ is depleted by reactions with these heavy atoms. The reaction between H₃⁺ and primeval atomic oxygen leads to the ion OH⁺, which subsequently undergoes successive hydrogen-atom transfer reactions with H₂ to form the protonated water ion, a species that does not react with molecular hydrogen:

\[
H₃⁺ + O \rightarrow OH⁺ + H₂
\]  

\[
OH⁺ + H₂ \rightarrow OH₂⁺ + H
\]  

\[
OH₂⁺ + H₂ \rightarrow H₃O⁺ + H.
\]  

The protonated water ion is destroyed mainly by dissociative recombination with electrons, a process measured in several storage rings and a flowing afterglow apparatus. Although big physics and desktop physics do not agree on the neutral product branching fractions, we do know that OH is the major oxygen-containing product, with an uncertain amount of H₂O [19, 20].

Perhaps a more important sequence of reactions leads to the birth of organic chemistry [18]. Here the reaction of H₃⁺ and neutral carbon atoms leads to the production of CH⁺, which reacts with H₂ to form first CH₂⁺ and then CH₃⁺. The latter ion does not undergo an exothermic reaction with hydrogen, but there is a slower but competitive process, known as radiative association:

\[
CH₃⁺ + H₂ \rightarrow CH₅⁺ + hν,
\]  

where the intermediate complex is stabilized by emission of an infra-red photon. Dissociative recombination of the methyl ion, leading to CH and CH₂, is also possible. Once protonated methane is synthesized, it is depleted by dissociative recombination, a process studied in a storage ring and known
to lead mainly to the production of the methyl radical rather than methane [21], and by reaction with abundant CO molecules:

\[ \text{CH}_3^+ + \text{CO} \rightarrow \text{CH}_4 + \text{HCO}^+. \]  

(6)

Carbon monoxide is itself produced in a variety of ways, including radical-radical reactions between O and CH or CH$_2$. The depletion of CO occurs by reactions with ions, such as

\[ \text{CO} + \text{H}_3^+ \rightarrow \text{HCO}^+ + \text{H}_2, \]  

(7)

and

\[ \text{CO} + \text{He}^+ \rightarrow \text{C}^+ + \text{O} + \text{He}. \]  

(8)

The latter reaction is a source of atomic carbon ions, while the former reaction is the major source for protonated CO, known as the formyl ion.

Once simple hydrocarbons are produced, more complex ones can be made by a variety of types of reactions. In the realm of ion-molecule processes, the most important classes of reactions are carbon insertion, condensation, and radiative association reactions. Examples of the three categories are

\[ \text{C}^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_3^+ + \text{H}, \]  

(9)

\[ \text{C}_2\text{H}_3^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_5^+ + \text{H}, \]  

(10)

\[ \text{CH}_3^+ + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH}^+ + \text{h}v. \]  

(11)

The particular radiative association shown leads to a precursor of methanol, but has been measured to be much slower than calculated by statistical treatments [22]. All of the ions produced subsequently react with electrons to form smaller neutrals. Before the last decade, the branching fractions for almost all dissociative recombination reactions of interest were either estimated or crudely calculated via statistical methods. Now, with flowing afterglow and, more importantly, storage ring studies of the products of many relevant reactions, interstellar networks are more securely based on measurement. Among the most recent important experimental results are product determinations for the dissociative recombination of N$_2$H$^+$ [23], and an assortment of hydrocarbon ions (C$_n$H$_m^+$) [24–26], all obtained with storage rings.

The most important synthetic mechanism occurring via neutral reactions is based on carbon insertion reactions with neutral atomic carbon; viz.,

\[ \text{C} + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H} + \text{H}. \]  

(12)

This reaction and others involving a radical and a so-called stable neutral have recently been found to be rapid at low temperatures [8].

Note that the processes discussed above tend to produce unsaturated species since H atoms are often ejected as complex products are formed. This tendency is reinforced by the lack of reaction between larger hydrocarbon ions and H$_2$ unless the ions are quite unsaturated. For example, the ion C$_2$H$_3^+$ produced above does not react with H$_2$, nor does it radiatively associate rapidly. Dissociative recombination with electrons leads instead to the smaller, less saturated species C$_2$H$_2$, C$_2$H, and C$_2$. An unsaturated chemistry is indeed observed in cold regions removed from star formation.

In addition to hydrocarbons, other classes of unsaturated species are also formed. For example, the well-known cyanopolyynes are produced by both ion-molecule and radical-neutral processes; viz.,

\[ \text{N} + \text{C}_2\text{H}_3^+ \rightarrow \text{H}_2\text{C}_2\text{N}^+ + \text{H} \]  

(13)

\[ \text{H}_2\text{C}_2\text{N}^+ + \text{e} \rightarrow \text{HC}_2\text{CN} + \text{H}, \]  

(14)

\[ \text{CN} + \text{C}_2\text{H}_2 \rightarrow \text{HC}_2\text{CN} + \text{H}. \]  

(15)

The dissociative recombination reaction has not been studied, to the best of our knowledge.
It is likely that the more saturated organic species seen in dense sources, especially warm ones, arise from grain-surface chemistry followed by desorption into the gas. The best studied process is the formation of formaldehyde and methanol by successive hydrogenation of adsorbing CO by H atoms. But even the existence of this process is only partially supported by contradictory laboratory evidence [27, 28]. As opposed to warm sources, purely gas-phase models, based on large networks of reactions, both studied and unstudied, are able to reasonably account for the chemistry of quiescent and pre-stellar cores in relevant astronomical time scales \( (10^{4-8} \text{ yr}) \), although it is sometimes necessary to consider the process of accretion of heavy species in the gas onto the grains. In particular, the models reproduce the abundances of molecular ions, unusual isomers (e.g. HNC) and unusual ring species (e.g. cyclic-C\(_3\)H\(_2\)).

A most important success of gas-phase models with accretion has to do with deuterium fractionation [29]. In dense clouds, the reservoir of deuterium is the molecule HD, which possesses an abundance relative to H\(_2\) of \( \approx 10^{-5} \). Yet the relative abundances of singly and even multiply deuterated isotopomers of trace species are much higher than this, especially in pre-stellar cores and cold remnants of proto-stellar cores. The most important individual reaction causing this effect, which is known as fractionation, is the forward reaction of the system

\[
\text{H}_3^+ + \text{HD} \rightleftharpoons \text{H}_2\text{D}^+ + \text{H}_2,
\]

which is slightly exothermic so that, at very low temperatures (e.g. 10 K) the backward reaction does not occur appreciably. Indeed, if chemical equilibrium could be reached, there would be more H\(_2\)D\(^+\) than H\(_3^+\). Chemical equilibrium is not reached in quiescent cores because the H\(_2\)D\(^+\) ion reacts with a variety of neutral species to spread the deuteration around, and also reacts with electrons. The competitive destruction mechanisms produce ratios of singly deuterated to normal trace species of perhaps 1–10% in cold dense clouds of density \( 10^4 \text{ cm}^{-3} \), although they can become much higher at the densities that are reached in the centers of cold pre-stellar cores. In these cores, the heavy species are strongly depleted onto dust particles and the electron abundance is low, so that chemical equilibrium between H\(_3^+\) and H\(_2\)D\(^+\) can almost be reached. Although the reproduction of deuterium fractionation is a large success for gas-phase models with accretion, these models are less successful in reproducing absolute abundances of large molecules [8]. It is typical that the calculated abundances of organic species are significantly lower than observed, an effect caused mainly by the greater elemental abundance of oxygen than that of carbon. Indeed, as one approaches the size of the largest gas-phase observed species (10–13 atoms), the models can be orders of magnitude low in their predictions. This problem remains unsolved, and has even gotten worse over the years with improvements in model networks. A variety of suggestions have been made, typically having to do with a complex history of the physical conditions as well as current heterogeneity [30].

### 3. Molecular ions: Problems and uses

Until recently, the chemistry of diffuse clouds was felt to be reasonably understood via gas-phase models similar to those discussed for dense clouds with one exception: the ion CH\(^+\). This ion is destroyed rapidly by reactions with atomic and molecular hydrogen as well as electrons. Yet it can only be formed slowly via the radiative association of C\(^+\) and H. The result is that models underproduce CH\(^+\) by several orders of magnitude [1]. To come close to the observed abundance, it is necessary to posit that the endothermic reaction

\[
\text{C}^+ + \text{H}_2 \rightarrow \text{CH}^+ + \text{H}
\]

occur readily, which only happens at high temperatures (\( \geq 1000 \text{ K} \)) or non-thermal collision energies. Among the several suggestions to find suitable physical conditions are shocks along the line of sight and intermittent turbulence [31]. A problem is that such conditions also affect the calculated abundances of other species in undesirable ways.
More recently, another unwanted ion has been detected in large abundance in diffuse clouds: \( \text{H_3^+} \). To produce the requisite amount of this ion, it has been suggested that the cosmic ray ionization rate in diffuse clouds must be 1–2 orders of magnitude greater than it is in dense clouds [32]. This result can only happen if there exist unmeasured low-energy (e.g. 1 MeV) cosmic rays in the universe, since these species could not penetrate all of the way through dense clouds. Interestingly, the idea of low-energy cosmic rays was popular 30 years ago and before [14], but became suspect when increasingly accurate cosmic ray ionization rates were determined from close fits to observed abundances in diffuse clouds. A new detailed model of diffuse cloud chemistry manages to fit both the high \( \text{H_3^+} \) abundance and the abundances of other species affected by the amount of cosmic rays by adopting an intermediate ionization rate and lowering the gas-phase temperature [1].

Two other ions, the high abundances of which are difficult to explain, are \( \text{CO}^+ \) and \( \text{HOC}^+ \). Both of these species react with molecular hydrogen, the first efficiently and the second more slowly but still importantly. Although \( \text{CO}^+ \) is only found in unusual regions such as PDR’s, \( \text{HOC}^+ \), a reactive isomer of \( \text{HCO}^+ \), is found both in PDR’s and more normal environments [33].

Although the abundances of some molecular ions are still difficult to understand, the abundances of others have aided our understanding of physical conditions. In particular, fractionation models of cold dense regions in pre-stellar and cold proto-stellar sources show that in addition to reaction (16), further fractionation of \( \text{H}_2\text{D}^+ \) to produce large abundances of \( \text{D}_2\text{H}^+ \) and even \( \text{D}_3^+ \) should occur since both partially deuterated ions react exothermically with \( \text{H}_2 \) to form more deuterated isotopomers [29]. The recent detection of \( \text{D}_2\text{H}^+ \) in the cold pre-stellar source IRAS 16293E [34] and the detection of a large abundance of \( \text{H}_2\text{D}^+ \) in the best studied pre-stellar core (L1544) [6] are in excellent agreement with the model and show that our understanding of these early stages of collapse to form stars is correct. Detection of \( \text{D}_3^+ \) will be more difficult since this ion is without a permanent dipole moment and so does not possess a strong rotational spectrum.

4. Needed dissociative recombination and other experiments

It is unclear whether the temperature dependence of the rate of dissociative recombination reactions involving thermal ions and electrons is fully understood. Certainly, the latest results of flowing afterglow experiments [35] in which there is minimal or even direct temperature dependence below room temperature call into question a wide variety of experiments where the more standard \( T^{-1/2} \) dependence is seen. More work on temperature dependence is clearly needed. Also important to astrochemists are additional studies concerning the neutral products. There are a variety of metastable isomers detected in the cold dense interstellar medium, some of which are quite abundant, and the general picture is that these species are formed along with their lower-energy analogs in dissociative recombination reactions. For example, the precursor of interstellar HCN and its isomer HNC is thought to be the protonated ion \( \text{HCNH}^+ \). Although the dissociative recombination of this species has been studied in a storage ring and the relative amounts of HCN+HNC + H and CN + 2H product channels measured [36], there has been no determination of the HNC/HCN ratio. A theoretical value for this ratio of unity has been obtained by classical trajectory simulation [37]; such a value could explain the interstellar ratio of unity or above in cold dense sources if the destruction rates of the two species are similar. Another poorly understood subject is the existence of isotopic effects, especially regarding deuterium. For molecular ions that contain both hydrogen and deuterium atoms, it is important to know how the neutral product branching fractions reflect the isotopic composition. For example, for the ion \( \text{H}_2\text{D}^+ \), the channel \( \text{HD} + \text{H} \) is \( \approx3 \) times more likely than the \( \text{H}_2 + \text{D} \) channel [38] and for the ion \( \text{HD}_2\text{O}^+ \), the channel \( \text{H} + \text{D}_2\text{O} \) is more likely than \( \text{D} + \text{HDO} \) [39]. Although in each case one can argue naively that the faster velocity of the H atom makes recombination more likely, this argument cannot be generalized from the meager evidence available, nor does it tell us much about cases in which the products do not consist of an atom and a molecule. A final problem concerning products is whether or not simple radiative recombination becomes an important channel as the size of the molecular ion increases. Statistical arguments would argue that if ions become large enough they will not dissociate quickly even with a large amount of
energy, thus enhancing the prospect of radiative stabilization [40]. But there is little evidence, to the best of our knowledge, to support this claim.

Processes of interstellar interest similar to dissociative recombination, for which much less information is known, include positive ion - negative ion recombination and dissociative recombination of molecular ions on negatively charged surfaces. This latter process is relevant because grains are thought to be mainly negatively charged due to the more rapid motion of electrons in a plasma than heavy positive molecular ions.

5. Summary
Gas-phase interstellar chemistry occurs in weak plasma-type sources known as clouds, in which positively charged molecular ions are of crucial importance in low-temperature regions. Ion-molecule reactions synthesize complex ions that, if unreactive with neutrals, eventually undergo dissociative recombination reactions to form somewhat smaller neutral species. The neutral products of these reactions can be both normal and highly unusual; among the latter class are radicals and metastable isomers, both of which are prevalent in the interstellar medium. Laboratory studies of dissociative recombination reactions are crucial to a detailed understanding of interstellar chemistry; although studies of neutral products branching fractions, especially from storage rings, have proven exceedingly useful, more work is clearly needed. Among the key remaining problems are our poor understanding of isomeric product ratios (especially HNC/HCN), of isotopic effects (especially involving deuterium), and of related processes such as recombination on surfaces and radiative recombination to form complex neutrals.

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