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IONS IN SPACE

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We review the detection history, observation, distribution, and reactivity of molecular ions in extraterrestrial space, with particular (though not exclusive) reference to interstellar monocations. The diversity of interstellar ion chemistry is highlighted with reaction examples, drawn from the authors' own laboratories and elsewhere, and attempt to provide an overview of this broad and increasingly divergent field. Emphasis is given to the role of ions in the synthesis of molecules, including their ability to catalyze the transformation of neutral molecules. © 2006 Wiley Periodicals, Inc., *Mass Spec Rev* 26:258–280, 2007

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I. INTRODUCTION

The title 'Ions in Space' is extremely broad—but then, so is space itself. To clarify matters somewhat, let us refine the topic. For most of the following discussion, we shall be concerning ourselves principally with *molecular monocations* in *interstellar* and *circumstellar* space, but this should not be taken to imply that these are the only kinds of ions in space. Atomic cations in many oxidation states, for example, are thought to be present (and often prevalent) in many different astrophysical environments, and indeed many stars are composed of almost nothing else (the 'almost nothing' including in large part the free electrons necessary to maintain gross electrical neutrality). Atomic anions are rather less commonplace, although they certainly feature also: for example, the opacity of the solar photosphere is largely attributable to the bound \rightarrow free transitions of the hydride ion H^- . Molecular anions and molecular dications share the characteristic of mystery, in the sense that their occurrence in space has

been the subject of some speculation but has yet to result, in either instance, in any confirmation. Concerning molecular monocations, however, the observational record is for several species unambiguous, and so it is appropriate to focus on what is most securely known of these species and their distribution. However, we will also review here the occurrence of different classes of ions in other more or less closely related space environments.

The wide variety of space environments which exist in the Universe ensures that no single review can thoroughly do justice to the topic of ion chemistry in space, and we make no pretense at an exhaustive treatment of the topic. Instead we offer a general overview interspersed with somewhat greater detail on topics of particular interest to the authors. For those who wish to delve deeper into this subject, there are several related reviews that should be highlighted. Previous overviews of the current knowledge in interstellar ion chemistry have been provided by Smith and Adams (1989), Smith (1992), and Smith and Spänel (1995) and more recently by Petrie and Bohme (2003); the latter review also surveys in detail the wide variety of mass spectrometric approaches to the study of interstellar ion chemistry, a topic also explored (from various angles) in the reviews of Smith and Rowe (2000) and Gerlich and Smith (2006). (The ubiquitous 'Smith' of the preceding sentence is, in fact, an unrelated triumvirate of experimentalists who have each pioneered distinct and important laboratory approaches to the study of astrochemistry.) The most recent broad review of interstellar chemistry (neutral and ion, gas-phase and surface chemistry) is that of Herbst (2001). Recent reviews of chemistry within particular classes of interstellar object—for example, star-forming regions—may also provide a useful background (van Dishoeck & Blake, 1998; Bergin, 2002; Herbst, 2005; Hogerheijde, 2005). Many other reviews on various aspects of interstellar chemistry, such as particular important reaction classes or processes, have also appeared over the past decade, and some of these are identified in subsequent sections as appropriate.

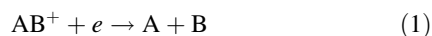
II. ABUNDANCE AND DETECTION

Molecular ions in cold astrophysical environments are always present in only trace quantities, generally in the ppb

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range or lower. These low abundances reflect several factors. A comparatively high particle density (e.g., a ‘dense’ cloud with a density of $\sim 10^4$ H_2 molecules cm^{-3}) is required to shield molecules and molecular ions from photodissociation by the interstellar radiation field or ISRF, but such shielding also cuts out photoionizing radiation, a major potential ionization source. Consequently, ionization is an inefficient process while neutralization, which for a molecular ion almost inevitably means dissociative recombination, Reaction (1), is intrinsically highly efficient.



The balance between ionization and neutralization is generally achieved at a very low ionization fraction, for example, $n(e) \sim 10^{-8} n(\text{H}_2)$.

Because interstellar molecular ions are so sparse, their detection requires methods that are highly sensitive and

unambiguous. The method that has proven most successful in detecting molecular ions in space is the same method which has dominated the detection of neutral interstellar molecules, namely radioastronomy. Radiotelescope observations of a high-density astrophysical environment can furnish a spectrum in the MHz or GHz frequency range (see, e.g., Fig. 1) in which the most prominent emission lines are often attributable to specific rotational transitions of various simple molecules or molecular ions. These spectral features can be exceptionally sharp, due to the very low temperature and (by terrestrial standards) low pressure of the interstellar clouds containing these molecules. Thermal and pressure broadening is minimal, and if the IS cloud or other object is ‘quiescent’ (i.e., is not subject to significant gravitational infall, outflow, shock waves, or other inner turmoil) then Doppler broadening may also be minimized. The sharpness of the features aids the definitive identification of species which may be present at abundances as low as $\sim 10^{-11} n(\text{H}_2)$.

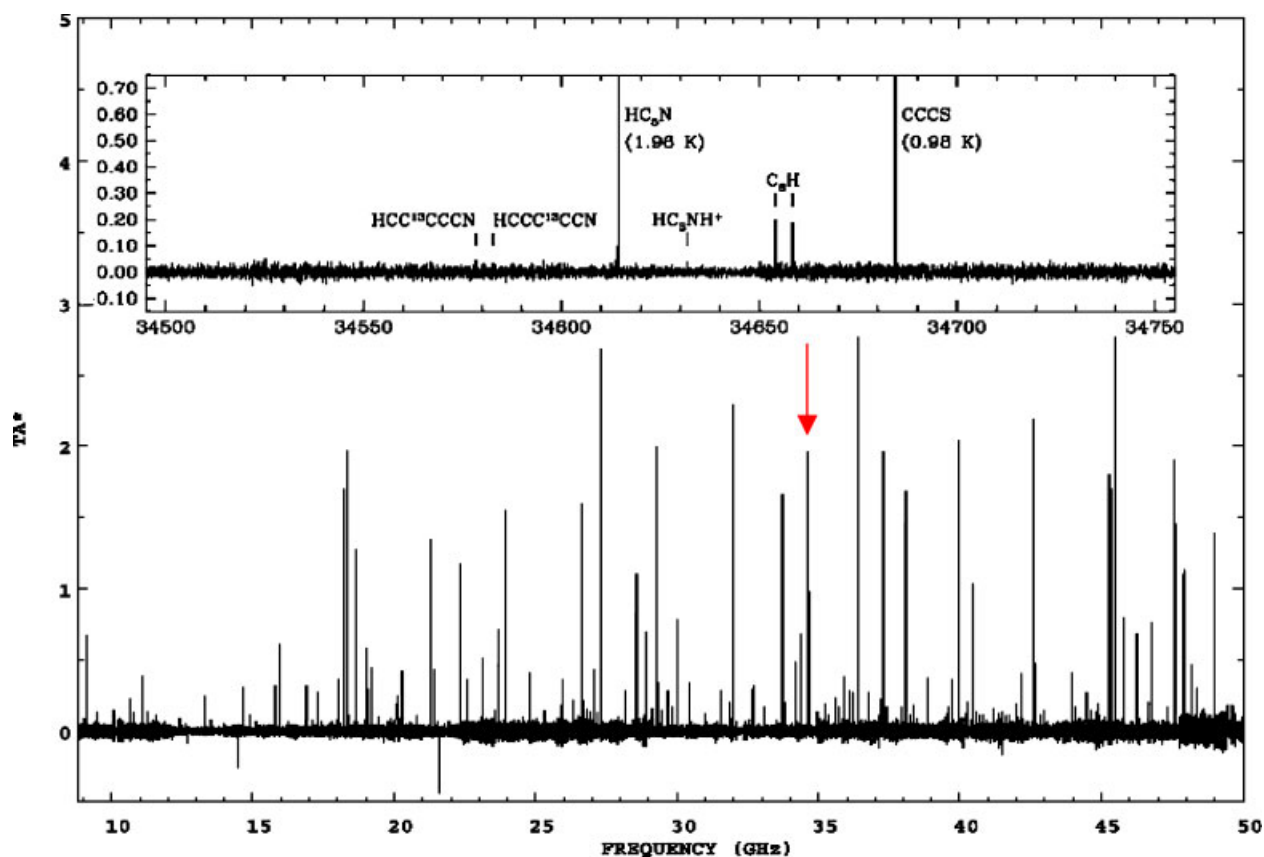


FIGURE 1. In interstellar clouds, molecules are unambiguously detected by their rotational radiofrequency spectrum. The larger spectrum here is a survey of spectral lines, between the frequencies of 8.8 and 50 GHz (corresponding to wavelengths from 6 to 34 mm) of the cold cloud TMC-1. The inset shows a high-resolution portion of the same spectrum, with frequencies in MHz; in both the full spectrum and the inset, signal strength is measured by ‘antenna temperature’ in Kelvin. Note that, at the scale of the inset spectrum, the full survey’s indicated feature (red arrow) is seen to be a pair of unrelated strong lines (due to HC_5N and CCCS , two exotic but abundant species within this object) of sufficiently differing frequency that several smaller lines may be discerned between them. Included among the spectral features visible in the inset spectrum is the unassuming signal due to the largest known interstellar ion, HCCCNH^+ . Reproduced from Kaifu et al. (2004) by permission of publications of Astronomical Society of Japan. © 2004. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

III. HISTORY OF DISCOVERY

The history of interstellar molecular ion detection began over six decades ago with the identification of observed spectral features, in visible light, due to the diatomic ion CH^+ (Douglas & Herzberg, 1941). At this time two other diatomics, the radicals CH and CN (Swings & Rosenfeld, 1937; McKellar, 1940), also had been recently identified within interstellar space. However, the detection of interstellar CH^+ appears to have had little initial impact on other research in this area. During the 1950s and 1960s the pioneering detection by Douglas and Herzberg received only two citations, both in review articles rather than in ongoing research. (It had long been known that stellar atmospheres could harbor diatomics such as CH and CN (see, e.g., Russell, 1934), and CH^+ may well have appeared merely an exotic example of an established class of astrophysical molecules.) Indeed, interstellar environments were beginning to be accepted under some conditions to provide a haven for diatomic combinations of the most cosmically abundant elements.

Almost three decades were to pass before astronomers began to report that polyatomics, also, had their place in space. The radioastronomical detection, in reasonably rapid succession between 1968 and 1970, of interstellar ammonia, water, formaldehyde, and methanol (Cheung et al., 1968, 1969; Snyder et al., 1969; Ball et al., 1970) demonstrated that very commonplace polyatomic molecules could exist in such an exotic location. Also, around this time, it began to be realized that some of the polyatomic constituents of interstellar clouds were not, from a terrestrial perspective, so commonplace. The ion HCO^+ , whose interstellar spectral lines were detected in 1970 (Buhl & Snyder, 1970), was not unambiguously identified until it had been characterized through laboratory microwave spectroscopy some years later (Kraemer & Dierksen, 1976). (Nonetheless, 1970 saw the beginning of a resurgence in interest in the prior detection of CH^+ , and the Douglas/Herzberg article has been quite heavily cited in each decade since.)

In the 35 years since the initial detection of HCO^+ , the number of known molecular ions within cool interstellar environments has now grown to 14 (see Table 1). In approximate order of discovery, these are CH^+ , HCO^+ , N_2H^+ , HCS^+ , HOCO^+ , HOC^+ , NO^+ , HCNH^+ , H_3O^+ , SO^+ , CO^+ , HC_3NH^+ , H_3^+ , and H_2COH^+ . Except for H_3^+ , which was identified through its IR spectral features (Geballe & Oka, 1996), all of the molecular ions since CH^+ have been observed by radioastronomy. The table is intended to provide a flavor of the variety of astrophysical objects in which ions have been sought, but makes no pretense to completeness in terms of the astrophysical regions in which ions have been detected. For example, some ions such as CH^+ and HCO^+ have been detected in so many objects of widely differing characteristics—including planetary nebulae and even other galaxies external to our own—that an exhaustive listing of the astrophysical objects concerned would fill up many pages (Fig. 2). (For readers who are keen to learn more about the distribution of the various interstellar ions and molecules, an excellent compilation of first-detections and important observations of astromolecules is located on the ‘Astrochymist’ website maintained by David Woon at <http://www.astrochymist.org>).

Concerning the main environments featured in Table 1, all are interstellar clouds of varying types and are among the most widely studied objects of their class. ‘Taurus Molecular Cloud 1’ (TMC-1) is a ‘cold, dense’ molecular cloud at a distance of ~ 140 pc (~ 500 ly; ‘pc’ = parsec, ‘ly’ = light year, $1 \text{ pc} = 3.26 \text{ ly}$) (Elias, 1978; Hartquist, Williams, & Viti, 2001) with a mean particle density of $\sim 10^4$ molecule cm^{-3} and a characteristic temperature of only ~ 10 K. TMC-1 is often termed a quiescent object because it is not a region of active star formation and so has not been subject to significant hydrodynamic shock activity. In contrast, Orion KL (‘Kleinemann/Low’, also called OMC-1, ‘Orion Molecular Cloud 1’) is the site of the most recent active star formation within the larger Orion Nebula (Phillips & Beckman, 1980; Genzel & Stutzki, 1989). The Orion Nebula lies approximately 450 pc ($\sim 1,500$ ly) from Earth, and Orion KL has a particle density of $\sim 10^5$ molecule cm^{-3} and $T \sim 70$ K. The giant molecular cloud Sgr B2 (‘Sagittarius B2’) is another region of massive star formation, located only ~ 100 pc from the Galaxy’s center and approximately 8,500 pc from Earth (Nummelin et al., 1998; Hollis et al., 2003). Typical values for the particle density and temperature in Sgr B2 are $\sim 10^{10}$ molecule cm^{-3} and 200 K, respectively.

Without exception, the hydrogen-bearing ions seen in Table 1 are the protonated forms of known interstellar molecules, while the three diatomic ions are ionized forms of molecules also known in these environments. Some species— CH^+ , HCO^+ , and HCNH^+ —represent both ionized and protonated states of known interstellar neutrals.

It is also apparent that all of the polyatomic ions are closed-shell species, which contrasts with the known prevalence of open-shell polyatomic neutrals in cold astrophysical environments (e.g., C_nH ($n = 2-8$), C_nN ($n = 3, 5$), C_2X ($\text{X} = \text{O}, \text{S}$), H_nCCN ($n = 1, 2$), and $\text{M}(\text{CN})$ ($\text{M} = \text{Mg}, \text{Si}$)). This apparent disparity between the neutral and ionized populations may well have some contribution from laboratory ‘selection effects’—the detection of an ion’s microwave spectrum is generally a more experimentally demanding task than is obtaining a neutral’s spectrum. But there are also very valid ‘environmental effects’ which are expected to influence the ionized and neutral components of the interstellar environment in different fashions. Principal among these is that, while many neutral radicals are ‘protected’ by activation barriers against reaction with H_2 (invariably the dominant interstellar reagent), for radical ions the attractive long-range ion/dipole and ion/induced dipole interaction has a tendency to submerge any activation barrier below the total energy of reactants. A rapid reaction with H_2 , for an ion within such a weakly ionized environment as a dense interstellar cloud, is an almost certain guarantee that the ion will not be present in detectable quantities. Indeed, for several years the reported detection of HOC^+ (Woods et al., 1983) was viewed with considerable scepticism within some quarters of the astrochemical community because of the measurement of an apparently fatally rapid reaction of this ion with H_2 (Freeman et al., 1987). The controversy surrounding HOC^+ was ultimately resolved through the presentation of, first, unambiguous observational confirmation of its non-negligible abundance within some cold interstellar clouds (Ziurys & Apponi, 1995), and second, high-level quantum chemical calculations and kinetic modeling which demonstrated that, although HOC^+ was unarguably quite reactive with H_2 at the

TABLE 1. Summary of Known Molecular Ions in Various Interstellar Environments

Ion	Year discovered	References ^a	Detection environments ^b				Other env. type ^c
			TMC-1	Orion KL	Sgr B2	Other	
CH ⁺	1941	Douglas & Herzberg				Many sources	
HCO ⁺	1970	Buhl & Snyder Snyder et al., 1976 Langer et al., 1978 Welch et al., 1981	Y	Y	Y	Many sources	
N ₂ H ⁺	1974	Turner; Green et al. Womack et al., 1991 Womack et al., 1992	Y	Y	Y	Many sources	
HCS ⁺	1981	Thaddeus et al. Irvine et al., 1983 Blake et al., 1987	Y	Y	Y		
HOCO ⁺	1981	Thaddeus et al. Bogey et al., 1984			Y		
HOC ⁺	1983	Woods et al. Fuente et al., 2003			Y	Orion Bar	photodissociation region
HCNH ⁺	1986	Ziurys & Turner Ziurys et al., 1992	Y		Y		
H ₃ O ⁺	1986	Wootten et al.; Hollis et al.; Wootten et al., 1991		Y	Y		
SO ⁺	1992	Turner Fuente et al., 2003				IC 443G Orion Bar	shocked molecular clump photodissociation region
CO ⁺	1993	Latter et al. Fuente et al., 2003				NGC7027 Orion Bar	planetary nebula photodissociation region
HC ₃ NH ⁺	1994	Kawaguchi et al.	Y				
H ₃ ⁺	1996	Geballe & Oka McCall et al., 1998 McCall et al., 1999				GL2136, W33A Cyg OB2 W33A	young stellar objects diffuse interstellar medium dense molecular cloud
H ₂ COH ⁺	1996	Ohishi et al.		Y	Y	W51	giant molecular cloud

^aUndated references are those published in the ion's reported year of discovery. Subsequent references are only provided when the ion has been newly observed in one of the 'featured environments' TMC-1, Orion KL, or Sgr B2, or when the original tentative assignment of the ion as a carrier of an observed radioastronomical spectral feature has been subsequently substantiated.

^bBrief descriptions of the 'featured' environments can be found in the text.

^cA brief description of the 'other' environment(s) in which the ion in question has been seen.

laboratory temperature of 300K, it was very much less reactive at a representative cold cloud temperature of ~10K (Herbst & Woon, 1996). Subsequent laboratory studies in an ion trap at 25K have now substantiated the lack of reactivity between HOC⁺ and H₂ at interstellar temperatures (Smith et al., 2002). The temperature-dependent difference in reactivities of HCO⁺ and HOC⁺ means that the ratio of this isomeric pair in a particular astrophysical environment can serve as a sensitive probe of the temperature and other physical conditions in such regions (Apponi & Ziurys, 1997; Apponi, Pesch, & Ziurys, 1999; Liszt, Lucas, & Black, 2004; Savage & Ziurys, 2004).

From the chronology presented in Table 1, it seems that we are in an 'interstellar ion drought' at present, with no new ions having been identified since 1996. However, it is likely that this

drought will not continue indefinitely. Unidentified spectral features are rife in essentially all of the radioastronomical surveys which have been conducted, even for the most well-studied objects, and it is almost certain that some of the carriers of these unidentified lines are molecular ions whose identification awaits some particularly diligent (or fortunate) microwave spectroscopist. To this end, laboratory spectra of likely ion candidates are gradually accumulated. Occasionally, these spectra do result in assignments of existing 'U-lines' to a new carrier. More often, the lab spectra form the basis of subsequent high-sensitivity searches for particular spectral lines in objects such as TMC-1 and Orion KL. Sometimes such 'first searches' are successful, as was the case with protonated formaldehyde (Ohishi et al., 1996). More often, however, ions sought are not

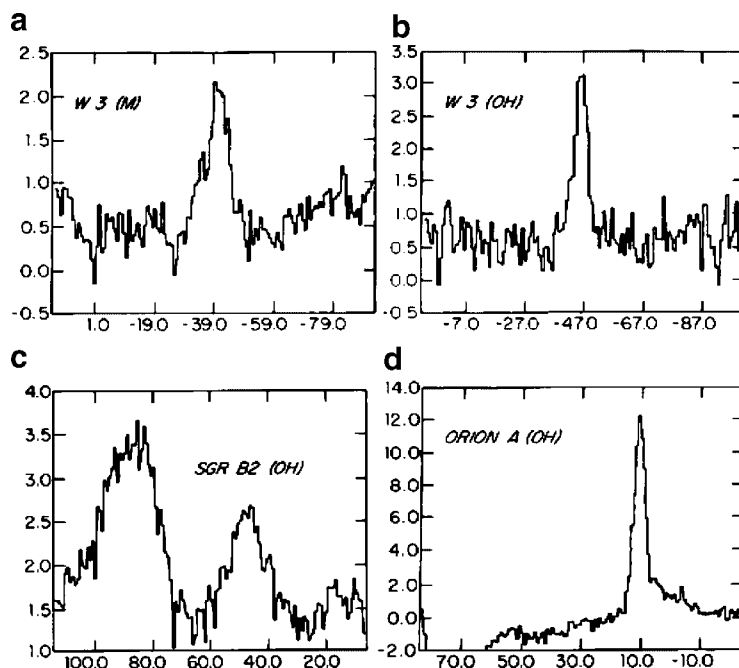


FIGURE 2. HCO^+ was observed in a very wide range of interstellar environments before its identity was confirmed through laboratory microwave spectroscopy. Shown here (in spectra a–d) are four radio-astronomical observations of a line with rest frequency 89.189 MHz, subsequently assigned as the $J(1-0)$ transition of HCO^+ , in various giant molecular clouds and star-forming regions. The vertical and horizontal axis scales show, respectively, signal strength as measured by the ‘antenna temperature’ in milliKelvins and radial velocity in km sec^{-1} . The variations in line width are indicative of differing physical conditions (temperature, pressure, etc.), while the signal strength is an approximate measure of the HCO^+ column density within the object in question. Note that the chosen line-of-sight to Sgr B2 (spectrum (c)) apparently contains two different regions, with differing redshifts, each containing appreciable HCO^+ . Reproduced from Hollis et al. (1975) by permission of the AAS © 1975.

seen. For example, searches for HC_3NH^+ , CH_3CNH^+ , and HOCS^+ (Turner, Amano, & Feldman, 1990) and for SH^+ (Millar & Hobbs, 1998) were all unsuccessful in the sense that they provided only upper limits to the respective ions in the objects searched. However, the non-detection of an interstellar ion or molecule should not generally be viewed as final, as it is quite often the case that subsequent searches in different objects, or at higher spatial or spectral resolution, in a different spectral window, or at greater sensitivity, may see something which was missed on the first pass. The eventual detection of HC_3NH^+ (Kawaguchi et al., 1994) provides a good example, as does the ultimate success in finding interstellar H_3^+ (Geballe & Oka, 1996).

The accumulation of spectroscopic data on prospective interstellar ions is by no means limited to microwave or radio-frequency measurements, although these have (to date) proven the most fruitful for ion detection in space environments. The visible and IR spectral ranges in particular have also received much laboratory attention (Shida, 1991; Maier, 1992, 1998; Bondybey, Smith, & Agreiter, 1996; Oomens et al., 2000, 2003; Salama, 2001; Schmidt & Sharp, 2005), and these windows are likely to become increasingly useful with the ongoing proliferation of space-borne observing platforms.

Astrochemists are by their nature quite imaginative creatures, so the intrinsically slow process of interstellar ion observation and identification has not greatly hindered speculation on what other ions might feasibly exist in these environments. Proposals have been made that are based on what is known of the physical and chemical properties of their parent molecules and possible mechanisms of ionization. For example, a substantial fraction of PAH molecules—proposed to be present in certain interstellar environments and which have significant electron affinities—is thought to carry a negative charge (Omont, 1986) and, by analogy, fullerene anions are also likely species within dense interstellar clouds (Millar, 1992; Petrie, Javahery, & Bohme, 1993). Positive ions such as the naphthalene cation, $\text{C}_{10}\text{H}_8^+$, have been discussed as possible contributors to the diffuse interstellar absorption bands (DIBs) (Salama & Allamandola, 1992) and to other spectral features (Sloan et al., 1999). It should be noted, however, that while there is almost unanimous agreement between astrochemists that a significant fraction of the various DIBs arise from absorption by polyatomic carbonaceous molecules and ions, there remains considerable disagreement regarding which large species are in fact responsible for the various DIBs, and to date none of the PAHs which are believed by many to be the main DIB carriers (see, e.g., Fulara & Krelowski, 2000; Salama, 2001) have been

conclusively identified as confirmed interstellar molecules or ions. This qualification applies also to the other spectral features—such as the interstellar extinction curve and the unidentified infrared bands—for which PAHs have been touted as candidate carriers.

Le Page et al. (2001a,b) have recently modeled the extent of hydrogenation and the distribution of charge states of polycyclic aromatic hydrocarbons in diffuse interstellar clouds. The model includes physical and chemical processes that are thought to form and deplete these ions. These include ionization and photodissociation in the interstellar UV field, electron recombination with PAH cations, and chemistry between PAH cations and major interstellar atoms and molecules present in diffuse clouds such as H, O, N, and H₂.

Fullerene cations including C₆₀⁺ have been proposed as the carriers of DIBs in the visible and the strong interstellar absorption at 217 nm (Leger et al., 1988; Braga et al., 1991). The latter has also been attributed to protonated fullerene species (Kroto & Jura, 1992). A strong case also has recently been made for the presence of doubly charged PAHs (Omont, 1986; Bohme, 1992a; Canosa et al., 1995) and fullerene dications (Javahery et al., 1992; Petrie, Javahery, & Bohme, 1993; Petrie & Bohme, 2000) within the interstellar environment.

IV. IONS IN PLANETARY ATMOSPHERES

The higher-energy photons of sunlight—vacuum UV and X-rays—are capable of ionizing atoms and molecules. Consequently, when raw sunlight encounters an atmosphere, it produces ions. Earth's oxygen-rich, nitrogen-dominated atmosphere is atypical of Solar System planetary atmospheres, but the general features of chemistry in the Earth's ionosphere (Ferguson, 1975; Reid, 1976; Ferguson, Fehsenfeld, & Albritton, 1979; Smith & Adams, 1980; Ferguson & Arnold, 1981; Mitra, 1981; Viggiano, 1993; Smith & Spanel, 1995; Squires, 1997; MacTaylor & Castleman, 2000; de Petris, 2002) are applicable to most planets (Mahajan & Kar, 1988; Nagy, Cravens, & Waite, 1995; Kar, 1996; Waite et al., 1997; Nagy & Cravens, 1998; Shinagawa, 2000, 2004; Majeed et al., 2004). At the highest altitudes, atmospheric gas molecules encounter photolyzing as well as photoionizing radiation, and so the predominant ions are atomic cations (O⁺ in the atmospheres of Earth, Venus, and Mars, H⁺ in the outer solar system environments). At lower altitudes, the most extreme solar photons have already been largely absorbed, so that ionization of the dominant molecules becomes important, yielding species such as N₂⁺, O₂⁺, and H₃⁺ (the latter produced by the rapid reaction of H₂⁺ with H₂). At still lower altitudes, the higher pressure facilitates bimolecular and termolecular ion/molecule reactions, leading to ionized (e.g., NO⁺) and protonated (e.g., H₃O⁺, NH₄⁺, HCNH⁺) trace components and ultimately cluster ions (hydrates; CO₂ adducts; hydrocarbon adducts; etc.). Approximate electrical neutrality is maintained by the presence of counterions; at all but the lowest edge of a planetary ionosphere, this role is principally played by free electrons, since anion formation (which occurs by an effectively termolecular mechanism) cannot proceed except at the high particle densities needed to promote cluster ion

formation. Thus the dominant negative ions, found only at the ionosphere's lower reaches, are also cluster ions, such as the hydrated NO₃⁻ ions which occur in Earth's atmosphere. All of these ion types arise from the molecules which may be considered as permanent (or at least long-lived) constituents of their respective atmospheres, and have concentrations which are highly dependent on altitude, latitude, and solar zenith angle: sunlight is not an effective ion source during the hours of darkness, and consequently ion concentrations tend to diminish overnight as neutralization processes such as dissociative recombination proceed in the absence of effective ion production. The diurnal variation depends, in turn, on the length of the night. For example, rapidly rotating Jupiter experiences a night of approximately 5 hr duration, while even the super-rotating atmosphere of slow-spinning Venus must endure an effective photochemical downtime of several days. During periods of prolonged darkness alternative upper-atmospheric sources of ionization, such as bombardment by magnetospheric electrons, can become much more significant than is typically the case during daytime.

A second family of atmospheric ions arises in a sporadic fashion, and one manifestation of these ions is the 'sporadic E' layer in Earth's ionosphere which has its counterpart also in the atmospheres of the other planets. These are the ions produced by infalling particles—meteors, comet dust, interplanetary dust grains, and latterly 'space debris'—which characteristically experience ablative heating when the atmospheric pressure climbs to approximately 1 micron. (The ablation process directly yields both atomic ions and free atoms: the latter species can subsequently give rise to the corresponding atomic ion by electron transfer processes involving pre-existing atmospheric ions (McNeil, Dressler, & Murad, 2001).) The most readily identified meteoric ions are atomic metal ions (Brown, 1973; Plane, 1991, 2003; Rietmeijer, 2000), since meteoric ablation is almost the only feasible source for such ions within the upper atmosphere. Metal ions such as Na⁺, Mg⁺, K⁺, Ca⁺, and Fe⁺ have been extensively monitored in Earth's upper atmosphere, through ground-based lidar (laser radar), satellite-borne spectrometers, and rocket-borne mass spectrometric measurements. Whereas the ion chemistry initiated by photoionization tends to be both regional and regular, depending principally on solar zenith angle, temperature, and altitude, the ion chemistry of meteoric ablation is more localized and erratic, depending on the irregular infall of meteoric particles. Meteoric ablation is important as an ionization source for several reasons, not least that it tends to produce a population of intrinsically long-lived atomic (metal) ions at an altitude well below that at which photoionization produces atomic ions. Furthermore, because ablation peaks at an altitude at which atmospheric mixing is still controlled by bulk motion ('eddy diffusion') of air masses, rather than by the molecular diffusion which occurs at higher altitudes, metal ion populations in Earth's atmosphere are often 'sculpted' into relatively intense layers with a vertical thickness as low as approximately 1 km, typically at an altitude of around 90 km. The meteoric origin of these layers in Earth's atmosphere has been established now for several decades, but it is only recently that observations of, and probes to, the planets Mars and Jupiter has established the apparent existence of comparable layers in the atmospheres of those planets (see, e.g., Fig. 3).

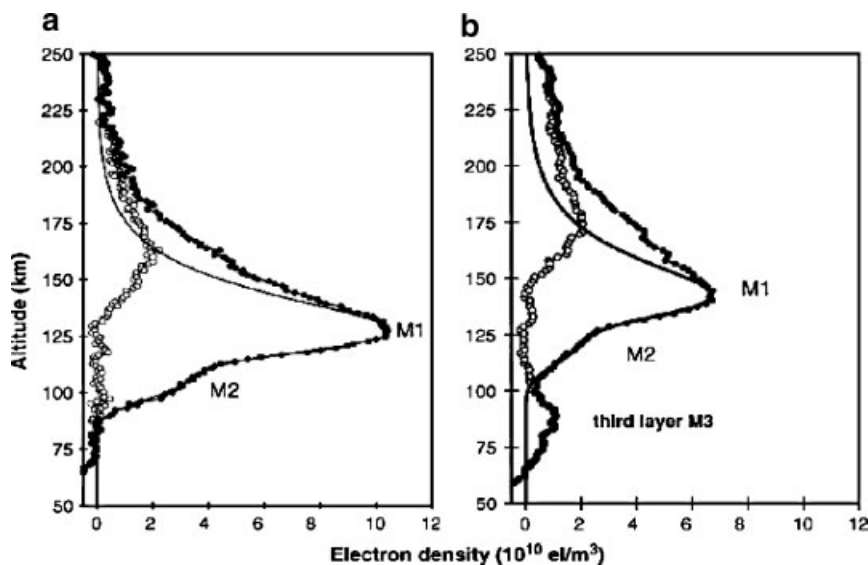


FIGURE 3. (Terrestrial) ground-based measurements of the martian atmosphere’s electron density profile, derived from signals sent by the orbiting Mars Express spacecraft. In each case, the filled circles trace the observed electron profile, the smooth curve is a calculated Chapman ionization model to the observed profile, and the open circles show the magnitude of the electron density fluctuation. In the majority of electron profile measurements which were made, only two ion layers ‘M1’ and ‘M2’ were detected (a), but in approximately 10% of the measurements a third layer, ‘M3’, centered at ~90 km altitude, was also seen (b). The location and sporadic nature of the layer M3 is consistent with ion production by the occasional infall of meteoric particles into the martian atmosphere. Reprinted with permission from Pätzold et al. (2005), science 310:837–839, © 2005 AAAS. www.sciencemag.org.

V. IONS IN COMETARY COMAE

The slow dissipation of sun-warmed comets, one of the sporadic wonders of observational astronomy, occurs in part through the production of ions within the cometary coma or ‘atmosphere.’ This photoionization process is entirely analogous to the process of ion production in upper planetary atmospheres, except that the comet is far too insubstantial to maintain gravitational control of the resulting plasma. In consequence, ions are reasonably rapidly lost from the coma and, under the influence of the prevailing solar wind, produce an often-visible ‘ion tail’ which radiates more or less directly away from the sun, and which is distinct from the comet’s dust tail which is often propagated in a substantially different direction. While many of the ions responsible for the ion tail’s visibility are long-lived atomic ions, there are also several molecular ions that are frequently observed as the comet approaches (or recedes from) the inner solar system (see, e.g., Festou, Rickman, & West, 1993a,b; Crovisier, 1998). Several of these—for example, CH^+ , CO^+ , HCO^+ , HCS^+ , HCNH^+ , and H_3O^+ —are also known interstellar ions, and serve to highlight the presumed common ground which exists between interstellar and cometary chemistry, in the sense that comets are widely considered to have received comparatively little chemical processing during, and following, the formation of the solar system from its presolar nebula (see, e.g., Charnley & Rodgers, 2002). Other cometary positive ions include OH^+ , H_2O^+ , CO_2^+ , N_2^+ , NH_4^+ , and CH_3^+ . The array of positive ions seen, all of which can arise by photoionization and/or protonation of very simple ‘primordial’ molecules, is broadly consistent with the

description of comets as largely unprocessed interstellar material. The molecular positive ion count in comets is rapidly approaching the number of different molecular ions reported to date in interstellar environments, and already comets have overtaken the interstellar ion environment in one important respect: they are known to also contain molecular negative ions, *viz.* CN^- and OH^- . The processes by which cometary negative ions arise are not fully understood, but include radiative and collisional attachment of electrons to radicals as well as radical/alkali metal atom collisions.

Comets are occasional visitors, and thus have not enjoyed the constancy of observational attention which interstellar clouds receive. To compensate, the proximity of comets has permitted a significantly wider range of approaches than has yet proven possible in interstellar studies, most obviously including direct mass-spectrometric sampling, which has been responsible for the detection of cometary HCNH^+ and HCS^+ in Halley’s coma (Ip, 1989) and for the identification of CN^- in the same object (Chaizy et al., 1991). The bulk of the remaining ions have been identified through their visible or IR spectra, but radioastronomers have not been entirely left in the cold. Comet C/1995 O1, more popularly known as comet Hale-Bopp, was sufficiently prominent to permit the detection of radio-frequency spectral features due to CO^+ , H_3O^+ , and HCO^+ (Rauer, 1997); the comet’s coma and inner ion tail was also mapped in HCO^+ emission (Womack et al., 1997) (see Figs. 4 and 5). With cometary studies adopting a progressively more ‘hands-on’ approach as witnessed by the contrasting styles of the ‘Stardust’ and ‘Deep Impact’ missions among others, the next few years

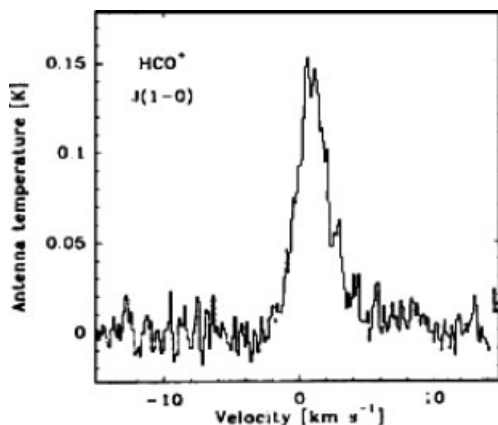


FIGURE 4. In 1995, Comet C/1995 O1 (Hale-Bopp) was sufficiently bright to permit detection of several ions by virtue of their radio-frequency rotational spectra, which is an unusual circumstance in cometary astronomy. The spectrum above shows the line profile for observations of the popular $J(1-0)$ transition of HCO^+ in comet Hale-Bopp. Reprinted from Rauer (1997) with kind permission of Springer Science and Business Media © 1997.

appear set for a rapid escalation in our understanding of comets and their ions.

VI. IONS IN THE INTERSTELLAR MEDIUM

All the interstellar clouds in which molecules have been observed are only weakly ionized. The most important primary source of ionization in the more transparent interstellar clouds is diffuse galactic starlight in the ultraviolet. In such regions elements like

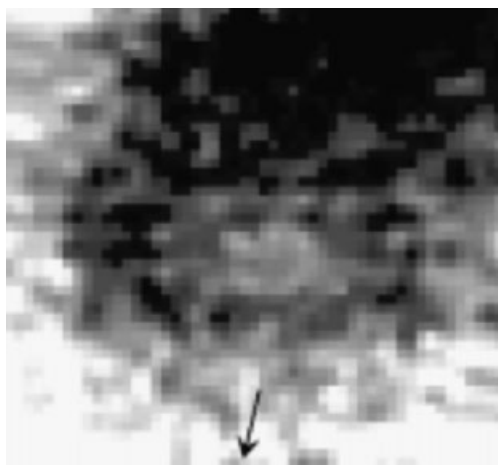
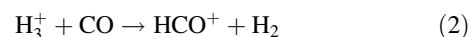


FIGURE 5. An interferometric map generated from observations of the $J(1-0)$ transition of HCO^+ in comet Hale-Bopp. In the map image, which has a side of $\sim 2.95 \times 10^5$ km, the direction of the Sun is denoted by an arrow. The map shows an apparent void (i.e., a localized region of low HCO^+ abundance) which is centered somewhat sunward of the comet's nucleus. Reprinted from Womack et al. (1997) with kind permission from Springer Science and Business Media © 1997.

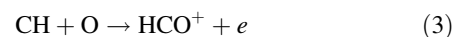
carbon, $\text{IE}(\text{C}) = 11.3$ eV, which can be ionized at lower photon energies than hydrogen, $\text{IE}(\text{H}) = 13.6$ eV, exist primarily in the ionized form. In the denser clouds, from which ultraviolet starlight is largely excluded, ionization is thought to be due to the influx of soft X-rays and galactic cosmic rays. The ionization rate deep within a dense cloud due to X-rays and cosmic rays is only one tenth to one hundredth that caused by starlight at the surface of the cloud.

Ionization by UV photons within a comparatively diffuse molecular interstellar region will predominantly produce H^+ , H_2^+ , and C^+ as primary ions. Cosmic ray ionization also produces these ions, as well as He^+ . In a dense cloud, none of these ions is expected to persist because all are reactive with the cloud's principal molecular constituents H_2 and CO . The complexity of ion/molecule chemistry of dense interstellar clouds has received considerable attention over the past three decades, and pathways to many of the observed molecular ions such as H_3^+ are well established.

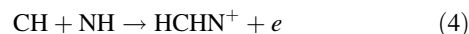
While the interaction of a precursor neutral with a sufficiently energetic photon or atomic nucleus (cosmic ray) is an obvious, important, and general source of interstellar ions, some less obvious and less general mechanisms may also be of significance. For example, it has long been appreciated that, while the dominant route to the major interstellar ion HCO^+ is through proton transfer from H_3^+ to CO , Reaction (2),



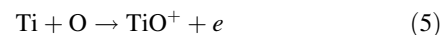
a competing mechanism (Dalgarno, Oppenheimer, & Berry, 1973) involving associative ionization of CH with O , Reaction (3),



can operate even in regions where there is no source of ionizing radiation. Such associative ionization processes require that the bond formed through combination of the neutral reactants is of a strength exceeding the product neutral's ionization energy, so that liberation of an electron becomes exothermic. There are, understandably, comparatively few reactions which conform to this requirement, but one other known interstellar ion — HCNH^+ —may arise, in part, from an analogous (exothermic) reaction (Petrie, 2001), Reaction (4),



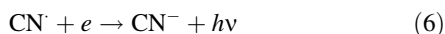
and there are a whole class of associative ionization processes involving the reactions of early transition metals such as Ti and Zr with atomic oxygen Reaction (5),



Of the transition metal/oxide reactions known to be exothermic (Petrie & Bohme, 1994a), the reaction shown with Ti is the most promising in the interstellar context (Oppenheimer & Dalgarno, 1977), since titanium has a comparatively high cosmic abundance. Nonetheless, neither TiO^+ nor any other titanium-containing species has yet been detected in interstellar space (Churchwell et al., 1980; Millar et al., 1987).

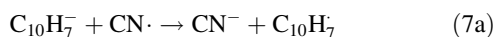
The reader may have gained an impression, thus far, that interstellar ion chemistry has focused entirely on positive ions. This is not strictly true (Dalgarno & McCray, 1973; Sarre, 1980;

Herbst, 1981), but the obvious success of astronomers in detecting over a dozen different molecular cations in many different interstellar environments does contrast with the failure, to date, of all efforts to detect a single molecular anion. There are several contributing factors here. Positive ion production, in the laboratory and in space, can be accomplished through the interaction of neutrals with particles or photons carrying an extremely wide range of energies, whereas negative ions can only arise through comparatively gentle reactions involving a spare electron (a reactant which may be difficult to come by in a weakly ionized environment such as a dense interstellar cloud). Negative ion formation requires, in the simplest circumstance, the radiative attachment of an electron to a precursor neutral, a process whose efficiency is favored by a deep potential well for electron attachment (i.e., a large electron affinity, EA) and by a large number of vibrational degrees of freedom for energy dispersal and for IR photon emission. Consequently formation of primary negative ions is most feasible for neutrals, particularly radicals (which tend to have large EA values) with many atoms. However, most interstellar radicals have far too few atoms to promote effective electron attachment. For example, calculations on CN, which has one of the highest EA values of known interstellar species, suggest that its rate coefficient for *e* attachment Reaction (6)



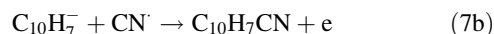
is only $\sim 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ (Petrie, 1996b), much too slow to produce detectable CN^- . Formation rates for appreciably larger, polyatomic, molecular ions may conceivably approach collisional efficiency ($k \sim 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$), but the detection of interstellar ions is biased in other respects towards small species, which have comparatively large rotational constants, hence comparatively few (but bright) radio-frequency lines in their rotational spectrum. Microwave spectroscopy is also in some sense biased towards characterization of the comparatively simple spectra for smaller species, since conditions required to generate a laboratory microwave spectrum for a polyatomic negative ion are almost certainly such that many other contaminating species will also be present in the microwave chamber during measurement of the spectrum of interest.

The combination of considerations raised above suggests that the primary negative ions are not going to be readily detectable. However, it may be that the reactions of primary ions yield secondary ions which may be more easily seen. For example, PAH radicals have sufficiently many atoms and a sufficiently high EA to suggest they will form negative ions readily, even under the tenuous conditions within interstellar clouds, but their EA is not generally as large as that of, for example, CN. Thus, exothermic electron transfer, Reaction (7a), (considering $\text{C}_{10}\text{H}_7^-$ as the polyatomic anion resulting from *e* attachment to a 'typical' PAH radical C_{10}H_7)



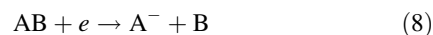
may form CN^- . Simple model calculations (Petrie, 1996b) suggest that this route is probably a much more effective path to interstellar cyanide anion than the direct electron attachment Reaction (6). But there are still hurdles for Reaction (7a); for example, the probability that PAH^- will meet and neutralize,

some positive ion before it encounters CN, as well as the generally more exothermic competing channel of associative detachment, Reaction (7b),



(The low temperature of most molecular interstellar environments also favors associative detachment, since the lifetime of the collision complex is longer, and consequently permits a greater degree of molecular reorganization, at lower *T*). So it is quite unlikely that this less direct route to small interstellar negative ions will be efficient enough to ensure their detection.

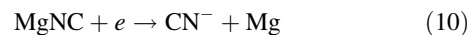
There is, however, a third path that offers some promise for detection of particular small anions in particular interstellar environments. Dissociative attachment, Reaction (8),



is the flipside of the associative ionization coin, and is only exothermic when the A–B bond strength is less than the electron affinity of fragment A. Only two known interstellar species appear to conform to this exothermicity requirement. One of them (Petrie & Herbst, 1997), which is found principally in the cold dense cloud TMC-1, is HNCCC, a very high energy (and low abundance) isomer of HCCCN. Dissociative attachment to this molecule could produce CCCN^- by Reaction (9).

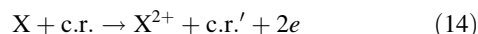
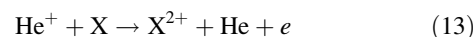
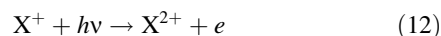
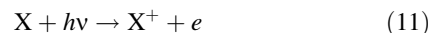


The second (Petrie, 1996b) is MgNC, a comparatively abundant metal-containing radical within the outer circumstellar envelope of the C-rich mass-losing star IRC + 10216. Dissociative attachment to this molecule could produce CN^- by Reaction (10).



It would be more than a little ironic if the first confirmed detection of a gas-phase negative ion in an interstellar environment was to occur in IRC + 10216, since there have been no detections of the otherwise ubiquitous positive ions (such as HCO^+) in this object to date.

For the moment, molecular dications occupy the same interstellar hinterland as do molecular negative ions, in the sense that no member of either class has been positively identified to date. There are, however, sound physical reasons to expect that molecular dications should be formed under various interstellar conditions. At least three general mechanisms exist for the formation of dications in the interstellar medium (Petrie & Bohme, 1994b). These include sequential photoionization, Reactions (11) and (12); reactions with the abundant IS ion He^+ , Reaction (13); and the action of cosmic radiation, Reaction (14).



Sequential photoionization is more important within diffuse regions than regions of high particle density, since the penetration of UV radiation within dense clouds is poor. Only molecules with a second ionization energy $IE(X^+) < IE(H)$ are likely to produce dications in this manner. Few, if any, small molecules meet this criterion. This condition is met by PAHs of moderate size and larger (Leach, 1986) and also by C_{60} (Petrie & Bohme, 1994b). Double ionization with He^+ requires that $IE(X) + IE(X^+) < IE(He)$ (24.587 eV). This is again more feasible with larger molecules such as PAHs and fullerenes that have substantially lower first and second ionization energies than do small molecules and radicals. Reaction (13), proposed originally for the formation of dicationic PAHs (Omont, 1986), has been experimentally observed at room temperature with naphthalene (Petrie et al., 1993b) and C_{60} (Javahery et al., 1992). Di-cation formation by cosmic-ray bombardment (Reaction 14) has no energetic restrictions, although the efficiency of such a process is not known at present. This process (if it occurs) is likely to be of some significance throughout dense IS clouds, since cosmic rays can penetrate deep within such clouds (Petrie & Bohme, 1994b).

It is worth noting that the dismal observational record of both molecular negative ions and molecular dications in interstellar space, often interpreted to mean that such species are not important in interstellar chemical evolution, may instead be due to a ‘selection effect’ which they share and which contrasts with the ‘selection effect’ for interstellar monocations. Singly charged cations appear to arise principally from the ionization of small interstellar molecules, and the limited chemical processing of these ions which precedes their neutralization ensures that the most abundant monocations are (apparently) small ions with well-characterized, unambiguous, and intrinsically strong radio-frequency spectral lines, and it is these ions which are documented in Table 1. In contrast, production of a molecular ion in a charge state of either +2 or -1 is not initiated, so far as we can tell, from small-molecule chemistry (except possibly in a few specialized instances such as the dissociative attachment examples discussed above for anions) and instead predominantly requires a pool of substantially larger molecules such as PAHs or fullerenes, yielding *classes* of ions such as PAH^{2+} or PAH^- (where PAH can be naphthalene, anthracene, tetracene, pyrene, phenanthrene, coronene, *ad nauseam* . . .) which appear beyond the reach of unambiguous identification—having so many spectral lines each by benefit of their size, any mixture of even a few PAH ions is almost certainly unidentifiable through radioastronomy, and must instead be categorized as a compound class by less species-specific spectral techniques such as IR and vis/UV spectroscopy of appropriately diffuse interstellar regions (Schmidt & Sharp, 2005).

VII. INFORMATION CONTENT OF IONS

A. Ions as Measures of Physical Conditions/Electron Density

One important virtue of molecular ion observations is that these species often provide the most direct indication of important

physical properties, such as the density of free electrons, within several classes of astrophysical object. (The importance of the electron density, to astrophysicists, is that it is thought to determine the rate of cloud collapse, and therefore of star formation (see, e.g., Shu, Adams, & Lizano, 1987)). Free electrons are not susceptible to spectroscopic detection, and while atomic ions can often be identified through their visible or UV absorption/emission line spectra, the severe attenuation of short-wavelength light by molecules and dust, in an environment such as a dark molecular cloud, ensures that atomic ions are often undetectable although they may well be present. The determination of molecular ion abundance thus provides a partial picture of the free-electron abundance required to ensure approximate electroneutrality. However, the resulting e abundance must necessarily be treated as approximate since one can never establish that all positive ions present are detectable, nor that the negatively charged species are exclusively free electrons. Within this qualification, the degree of ionization within a typical cold dense interstellar cloud such as TMC-1 can be established to be at least $1 \times 10^{-8} n(H_2)$, since this is the sum of the abundances of the identified ions HCO^+ , N_2H^+ , $HCNH^+$, HCS^+ , and HC_3NH^+ within this object (see Fig. 6).

However, the above ‘brute force’ approach of ion counting is acknowledged not to be highly accurate, since it cannot yet be determined with any confidence which ions are evading inclusion in the census. (It is also inappropriate to view any interstellar cloud as being a completely homogeneous environment, quite aside from the temperature and pressure gradients that exist. Different molecules, and very likely also different molecular ions, attain their peak abundances in spatially separate regions within a given cloud, and unless the cloud has been mapped in detail at the spectral frequencies appropriate for detection of a particular ion (Fig. 7), the signal strength observed at one point in the cloud’s geometry cannot be reliably extrapolated to any other

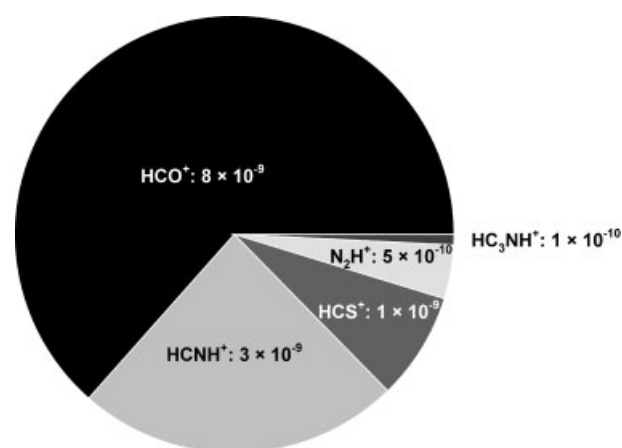


FIGURE 6. Abundances of detected molecular ions within the cold dense cloud TMC-1, expressed relative to the number density of H_2 , the predominant molecule, within this object. The sum of these values (from Hirahara et al., 1992; Ohishi, Irvine, & Kaifu, 1992; Ziurys, Apponi, & Yoder, 1992; Kawaguchi et al., 1994) provide a lower limit to the ionization fraction in this object, which is presumed also to correspond to a lower limit to the free electron abundance in TMC-1.

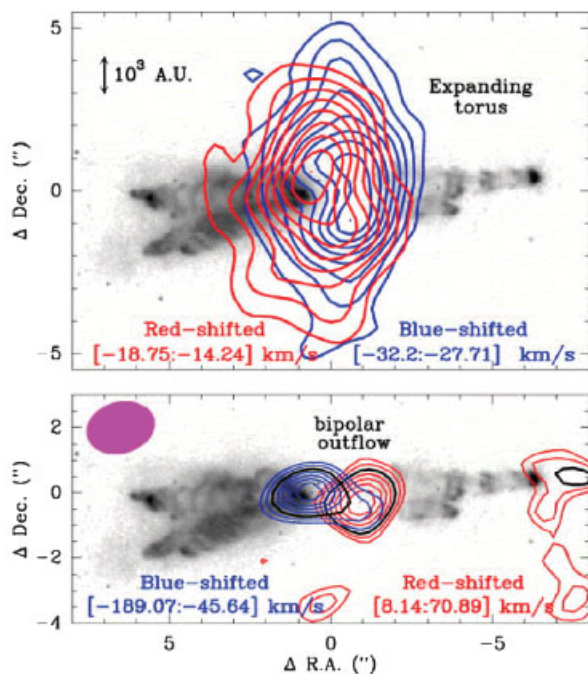


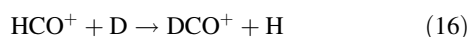
FIGURE 7. HCO^+ , widely seen in star-forming regions as shown in Figure 2, also features in observations of decomposing stars. The images above are views from an interferometric survey of the protoplanetary nebula CRL 618, again using the $J(1-0)$ transition of HCO^+ . In both images, radio signal contours are overlaid on a Hubble Space Telescope image of the nebula in visible light. The images differentiate between emission arising from an equatorial torus (upper frame) and an axial jet (lower frame) of expanding molecular material. Reproduced from Contreras and Sahai (2004) by permission of the AAS © 2004.

region within the cloud, nor satisfactorily to a bulk-averaged value for the overall cloud. A useful analogy is to consider how distorted our understanding of atmospheric chemistry would be if it were based solely on the globally averaged abundances or concentrations of ozone, atomic oxygen, nitric oxide, chlorine monoxide, and all of the other reactive species.)

Because it is highly likely that the interstellar ion census is incomplete, other approaches based on ion observation are also applied in the quest to tie down the ionization fraction in a cloud. For example, the chemistry of deuteration can be used to estimate an ion's lifetime within a cloud (Caselli, 2002), as follows. In TMC-1, the dominant (known) ion is HCO^+ , which in dense molecular clouds is formed largely through proton transfer from H_3^+ , as noted in Subsection IVA. Two important loss processes for HCO^+ are dissociative recombination, Reaction (15),



and isotopic substitution by reaction with trace atomic D, Reaction (16).



Enough of the reactants involved in this sequence have abundances which, for TMC-1, are either known through

observation—that is, CO , HCO^+ , DCO^+ —or are reasonably well-constrained in existing models—that is, H_3^+ , H , D —that the free electron abundance is also susceptible to constraint through modeling. (In truth, the modeling is rather more complicated than the above discussion suggests, because the chemistry of deuteration itself is rather convoluted and subtle. For recent detailed reviews of interstellar deuteration, the reader is referred to Herbst (2003), Millar (2003), and Roueff and Gerin (2003). In a study of several dense cloud cores (Caselli et al., 1998), an analysis based on the $\text{DCO}^+:\text{HCO}^+$ ratio found a value of $n(e) \sim 10^{-6} n(\text{H}_2)$, that is, almost a factor of 100 higher than the lower limit obtained by the ‘ion counting’ exercise undertaken in Figure 6. It turns out, in the study of Caselli et al. (1998), that TMC-1 is rather atypical of dense cloud cores, having an unusually high modeled ionization fraction (with an ‘average’ value being about an order of magnitude lower). One explanation for the higher-than-average ionization fraction in TMC-1 is that this object is atypically young and consequently has a high abundance of gas-phase metal atoms. Metals are readily ionized, and the conventional wisdom is that metal ions M^+ are lost only very slowly through electron recombination reactions. Both metal ions and metal atoms are expected also to be lost gradually through accretion onto dust grains or even large molecules, so that as a cloud ages its proportion of ‘long-lived’ atomic ions to ‘short-lived’ molecular ions is diminished, as also therefore is its ionization fraction.

Owing to the central importance of molecular ion measurements as an assay of the ionization degree and electron density (and the influence of these properties on star formation), considerable effort is ongoing in this area (Williams et al., 1998; Bergin et al., 1999; Caselli, 2002; Padoan et al., 2004).

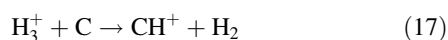
B. Ions as Tracers of Atoms and Molecules

There are instances where the detection of an ion provides a ‘missing link’ in the sense that a related neutral (and presumed parent to the ion) may be effectively invisible to radioastronomers. A commonplace example is the observed ion N_2H^+ , which almost certainly arises from the protonation of dinitrogen, mainly through proton transfer from H_3^+ , but the symmetric dinitrogen molecule lacks a permanent dipole moment and therefore also lacks a detectable rotational spectrum. The same is also true of HOCO^+ , protonated carbon dioxide. (Note that though both N_2 and CO_2 are radio-invisible, both have now been detected at shorter wavelengths: N_2 by far-UV and CO_2 by IR vibrational transitions (D’Hendecout & Jourdain de Mouzon, 1989; Knauth et al., 2004). Nonetheless, their detection in spectral windows which cannot effectively penetrate dense interstellar clouds ensures that their abundance in regions where most interstellar molecules are seen remains speculative).

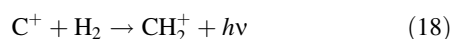
Conversely, there are also species which are readily seen in neutral form, but whose ion products may frustrate radioastronomers: a commonplace example is ammonia, which has been plainly detected, while the spherical top NH_4^+ (which is almost certainly there, and likely in significant abundance in several objects) is not observable. Another, more exotic, example is $c\text{-C}_3\text{H}_2$, cyclopropenylidene, which is widespread: a very likely route to this species is neutralization of the highly stable

aromatic cyclopropenium ion, $c\text{-C}_3\text{H}_3^+$, but, regrettably, the D_{3d} symmetry of this ion is ample to ensure its radioastronomical anonymity. There are a very few examples of even greater apparent frustration to radioastronomers: protonation of H_2 yields H_3^+ , both of which lack a dipole moment, while the longest-lived direct precursor of the spherical top CH_4 is the symmetric top CH_3^+ , which again are both rotationally inactive. In some measure, expectations have been confounded in the case of H_2 and H_3^+ , with both the neutral and the protonated form now seen in a reasonably wide variety of objects. For H_3^+ (Geballe & Oka, 1996) this has necessitated the detection of forbidden, and therefore weak, infrared features in absorption. Since dense interstellar clouds are efficient extinguishers of infrared, as well as shorter wavelength, radiation, detection of H_3^+ generally requires observation along a line of sight in which the total column density of molecules and dust is insufficient to completely cut out the infrared continuum emission from a more distant star.

Among other known interstellar ions, we might expect that CH^+ provides a tracer for atomic carbon. This would be valid if the principal source of CH^+ was the proton transfer to C, for example Reaction (17).



However, this reaction—which has received theoretical study (see, e.g., Bettens & Collins, 1998) but has so far eluded laboratory characterization—is thought merely to be a byway in the production of interstellar chemistry's 'first ion.' Rather, the observed CH^+ is held to form largely from radiative association of C^+ with H_2 , Reaction (18),



with subsequent conversion of CH_2^+ to CH_3^+ through an H-atom abstraction reaction with H_2 , and finally photodissociation (Black, Dalgarno, & Oppenheimer, 1975) or shock-induced fragmentation (Federman, 1982) of the CH_2^+ and CH_3^+ precursors to yield CH^+ .

It should be pointed out that, with the exceptions of N_2H^+ , HOCO^+ , and H_3^+ , ions generally have not, to date, fulfilled their apparent promise as tracers of 'invisible' molecules. It is a sad fact of electrostatics that a molecule's symmetry may doom not merely itself, but also its protonated ion, to undetectability. A useful example is dicyanogen, NCCN , which is an obvious close cousin to the cyanopolyynes HC_{2n+1}N found in many cold astrophysical environments. A study of the most plausible routes to interstellar NCCN (Petrie, Millar, & Markwick, 2003) has established that TMC-1 likely harbors this (invisible) molecule at an estimated abundance of $\sim 1 \times 10^{-11} n(\text{H}_2)$, which is comparable to that of some trace species positively identified within this object. It is conceivable that protonation of NCCN , via proton transfer from HCO^+ (for example), Reaction (19),



could produce sufficient NCCNH^+ for the detection of this polar ion. By analogy, the structurally similar ion HC_3NH^+ (a known denizen of TMC-1), probably arises mainly from a similar proton transfer process, Reaction (20).



Both NCCNH^+ and HC_3NH^+ are expected to be destroyed largely by the process of dissociative recombination. However, even if TMC-1 contains NCCN and HC_3N in equal abundance (in reality, HC_3N is likely to dominate by an order of magnitude or more), the equilibrium abundance of HC_3NH^+ will outweigh that of NCCNH^+ by a large margin. The reason for this is that the destruction of each ion by dissociative recombination likely occurs with about the same rate coefficient, while the rate coefficient for Reaction (20) exceeds that for Reaction (19) by approximately a factor of 30. The latter effect has its origin in the very great enhancement in the reaction rate for an ion with a polar molecule as the temperature is reduced from $\sim 300\text{K}$ to the TMC-1 value of $\sim 10\text{K}$, due to the strong long-range ion/dipole attraction. Similar effects assist the general detection of protonated ions whenever the parent neutral is a polar molecule, but do not operate in favor of ion detection when the parent neutral is non-polar.

We have already noted above some instances—for example, N_2 and N_2H^+ , and conversely $c\text{-C}_3\text{H}_2$ and $c\text{-C}_3\text{H}_3^+$ —which illustrate that the 'information content' of interstellar ions versus molecules can operate in either direction. A further key example, which as yet awaits a definitive resolution, concerns the gas-phase abundances of metal atoms within cold astrophysical environments. It is widely appreciated that gas-phase metals in interstellar clouds should enjoy long lifetimes as atomic cations M^+ , but while the abundance of such metal ions could be quite high—high enough, in fact, to effectively 'poison' the synthetic pathways involving reactions between molecular ions and interstellar neutrals, because a high M^+ abundance implies a high free-electron abundance, which in turn dictates a very short lifetime for any molecular ions because of the rapidity of dissociative recombination for such ions—these atomic metal ions are not themselves directly observable. Several attempts by radioastronomers to detect metal-containing molecules in interstellar clouds (and here it should be pointed out that while astronomers take a very liberal definition of the word 'metal' to mean any element heavier than helium, we use the word in its more rigorous chemical sense and exclude everything north or east of aluminum) have been consistently unsuccessful. Recently, however, an apparent direct connection between an observed circumstellar metal-containing molecule and a precursor metal ion has been established, at least tentatively. The magnesium isocyanide radical MgNC (Kawaguchi et al., 1993) features what appears to be the weakest bond in astrochemistry, and cannot arise through any known or prospective neutral/neutral reaction involving a CN-containing precursor. Despite these handicaps, this radical is quite abundant in the C-rich circumstellar envelope IRC + 10216, where it arises in cold (30K) and tenuous gas on a timescale which requires a very rapid and efficient formation reaction (Guelin, Lucas, & Cernicharo, 1993). The sole satisfactory process capable of forming sufficient MgNC to explain its observed abundance (Petrie, 1996a; Dunbar & Petrie, 2002) is the radiative association of Mg^+ with the cyanopolyynes (e.g., HC_5N and HC_7N) which are a prominent feature of this environment:



followed by dissociative recombination to yield MgNC:



While direct characterization of either of these processes has yet to be achieved in the laboratory—the problems of performing experimental studies on either radiative association or dissociative recombination, at appropriate temperatures, are considerable, even without including refractory metallic reactants—there is some corroborating circumstantial evidence which supports this mechanism, in the sense that the other two sources in which MgNC has been reported (the proto-planetary nebulae CRL 618 and CRL 2688) (Highberger et al., 2001; Highberger & Ziurys, 2003) are both objects which are also exceptionally rich in the putative cyanopolyne precursors HC₅N and HC₇N. However, while MgNC appears to show promise as a tracer for magnesium, which might well be considered a ‘typical’ metal, the chemistry of MgNC destruction, and more generally of Mg-containing species in interstellar environments, is arguably still insufficiently understood to be able to extrapolate reliably from a detection or non-detection of MgNC to an effective abundance of its precursor Mg⁺. For example, although a recent search for MgNC in the cyanopolyne-rich cold cloud TMC-1 was unsuccessful (Turner et al., 2005), this non-detection does not entirely exclude a quite high abundance of Mg⁺. Further observations, and further exploration of the chemistry concerned, is required before the problem of gas-phase metal abundances can be satisfactorily ‘put to bed.’

VIII. IONS IN MOLECULAR SYNTHESIS

With the first realization of the presence of ions in space came the proposition that ions play a key role in molecular synthesis in partially ionized interstellar gas clouds, the largest known chemical factories in the universe. Molecular synthesis induced by ions in partially ionized gases involves ionic growth by sequential ion/molecule reactions terminated by ion neutralization through electron/ion recombination or electron transfer (Bohme, 1987).

Ion-molecule reactions are especially attractive for molecular synthesis because they are often fast and proceed at, or near, the collision rate. The latter exceeds, by a factor of up to 100 at interstellar temperatures (~10K), the collision rate of analogous neutral reactions; neutral reactions often also have kinetic constraints because of the presence of activation energies. Because of the latter, ion-molecule reactions become increasingly competitive at lower temperatures. Calculations have shown that ion-molecule reactions without activation energies will compete effectively with neutral reactions having activation energies as small as only 1 kcal mol⁻¹ at a temperature of 50K and 1 ppm ionization (Bohme, 1987).

A variety of experimental techniques have been employed over the years to characterize the ion/molecule reactions of likely importance in space chemistry (Petrie & Bohme, 2003). Most of the experiments have been operated at, or near, room temperature, but a few experimental techniques now are available that allow measurements of ion/molecule reactions at very low temperatures. The latter are based either on cryogenic

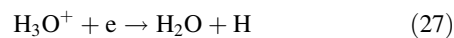
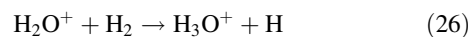
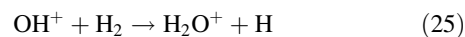
helium-cooling or aerodynamic-cooling strategies. Particularly noteworthy are ion trap techniques (see e.g., Gerlich & Horning, 1992) and the Cinétique de Reaction en Ecoulements Supersoniques Uniformes (CRESU) and the related free-jet flow techniques (Rebrion, Marquette, & Rowe, 1992).

A. Small, Large, and Biological Molecules

Interest in the formation and persistence of biologically relevant compounds in outer space has been kindled by the isolation of amino acids in meteorites as well as by the (still tentative) radioastronomical detection of the simplest amino acid, glycine, in interstellar space (Kuan et al., 2003; see also Synder et al., 2005). Within the past decade, ‘astrobiology’ has emerged as a rigorous, albeit still largely speculative, discipline in its own right, and a useful overview of space biomolecule formation and chemistry may be gleaned from the recent reviews of Ehrenfreund and Charnley (2000) and Charnley et al. (2002).

Strategies have been developed and proposed for the ionic synthesis of small molecules to large organic and biological molecules in space, including diffuse and dense interstellar clouds, circumstellar atmospheres and planetary atmospheres. Laboratory measurements of many hundreds of individual ion-molecule reactions (Anicich, 1994, 2003) have provided the experimental support for these strategies. Most measurements were performed at, or near, room temperature, but the database for rate measurements at low temperatures is growing. Numerous models of ionic synthesis have now appeared in the literature and these relate to a variety of extreme space environments. The progress that has been made in this regard merits a review on its own. Here we present only a flavor of what has been achieved in the field of the ionic synthesis of molecules.

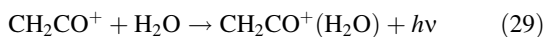
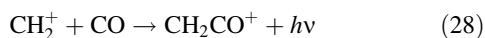
The gas-phase ionic synthesis of small molecules is reasonably well understood (Smith, 1992). This includes the synthesis of H₂O, NH₃ and other amino molecules, HCN and other cyanides, CO and various carboxy molecules, H₂S and other sulfur-bearing molecules, and CH₄ and various other hydrocarbon molecules. For example, the water molecule can be synthesized from atomic oxygen and molecular hydrogen in a reaction sequence initiated by a proton and terminated by the recombination of a hydronium ion with an electron as shown in Reactions (23)–(27).



Progress also has been made in understanding the formation of Si-containing ions and molecules through ion-molecule reactions initiated by Si⁺, especially the formation of silicon oxide, silicon sulfide, and silicon carbide molecules (Herbst et al., 1989; Bohme, 1990, 1992b). C⁺ has been reported to initiate

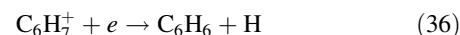
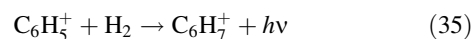
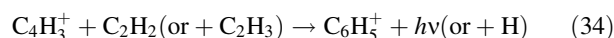
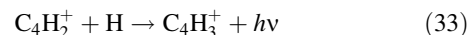
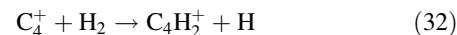
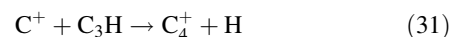
formation of carbene molecules in reactions with simple interstellar molecules. Carbenes such as methylene, completely unsaturated chain-like carbenes (some with incorporated O, N, or S atoms), slightly hydrogenated chain-like carbenes and aromatic ring carbenes can be formed and these may be building blocks for graphite-like molecules or carbonaceous grains (Bohme, 1986).

The growth of large biological molecules in extraterrestrial environments can be expected to be more complex. Of course the gas-phase synthesis of amino acids, the “building blocks of life,” has become a “holy grail” in synthetic ion chemistry. Some recent progress has been made. One plausible scenario, many features of which have been demonstrated in the laboratory, for the synthesis of glycine and β -alanine in interstellar environments is shown in Figure 8 (Blagojevic, Petrie, & Bohme, 2003). This synthesis requires the availability of acetic and propionic acid as well as hydroxylamine which has been proposed to originate from water and ammonia on irradiated interstellar ice grains, but has not yet been observed. An ionic synthesis of the required carboxylic acids also has been demonstrated in the laboratory and is attributed to a reaction sequence exemplified here for the synthesis of acetic acid cations, Reactions (28)–(30):

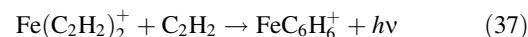


More speculative is the role of ions in the formation of PAHs that are believed to be ubiquitous in the interstellar medium because of the good match between the unidentified infrared emission features (UIRs) seen in many environments where strong UV field are present and the spectroscopic properties of PAHs. The few experimental observations available before 1990 that relate to the role of ions in the condensation of small carbon chains to form small carbon rings and the growth of polyhedral carbon cations into larger PAH cations were reviewed some 15 years ago (Bohme, 1992a) and not much progress has been made since. The emphasis in PAH research appears to have been more

on measurements of the reactions of PAH cations with atoms and small molecules (H , O , N , and H_2) (Petrie, Javahery, & Bohme, 1992; Scott et al., 1997; Snow et al., 1998) and on reactions of atomic cations (He^+ , C^+) with benzene and small PAHs (Bohme, 1992a; Canosa et al., 1995). However, a case has been made for the ionic synthesis of benzene, for example, Reactions (31)–(36), in dense interstellar clouds (McEwan et al., 1999) and for the formation of naphthalene cations from the reaction of benzene radical cation with diacetylene (Bohme et al., 1991a).



Apparently atomic metal cations also can initiate PAH formation since mass spectrometric studies have demonstrated that some sequential Fe^+ /hydrocarbon reactions can lead to cyclization (Schröder et al., 1991; Baranov, Becker, & Bohme, 1997). For example, the Reactions (37) and (38) in the acetylene chemistry of Fe^+ could play a role in the interstellar synthesis of benzene, although sequential triple addition of acetylene to Fe^+ must compete at each step with the more probable reactions with electrons or CO (Petrie et al., 1997).



B. Organometallic Molecules

The notion that gas-phase metal ions can react rapidly with large molecules has begun to infiltrate the interstellar chemistry community, but also has wider extraterrestrial implications (Petrie, 2003). As noted in Section IV, the process of meteoric ablation in Earth’s atmosphere gives rise to localized regions of high ionization and of high metal ion concentration, at altitudes of 90–100 km in Earth’s atmosphere. Precipitation of these metal ions may actually account for much of the bio-available iron and some other metals within marine environments (Johnson, 2001). Meteoric ablation also can initiate metal-ion chemistry within the hydrogen, hydrocarbon, and nitrogen-dominated atmospheres of other planets and some of their moons. Larger molecules may well play a disproportionate role in the removal of metal ions in these environments, just as they do in the envelope of IRC + 10216 (see Subsection VIIB). Metal ions entering Titan’s atmosphere encounter a cocktail of hydrocarbons and nitrogenous compounds culminating in the ‘tholins’ which form a hazy suspension of large nitrogen-containing organics. Under these conditions the reactive capture of meteoric metal ions could

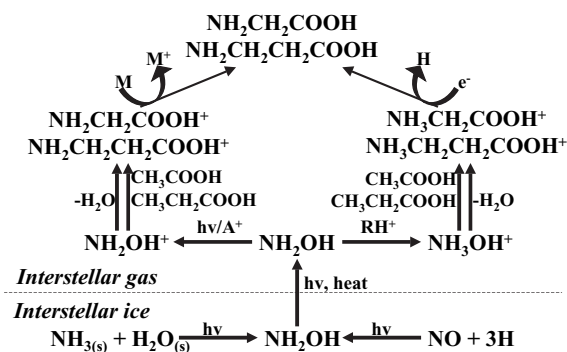
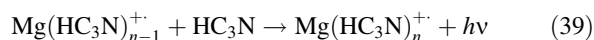


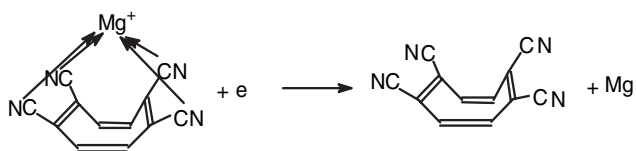
FIGURE 8. Proposed route for the synthesis of amino acids in interstellar environments. M and A represent any neutral atom/molecule with a suitable ionization energy. RH^+ represents a proton carrier with $\text{PA}(\text{R}) < \text{PA}(\text{NH}_2\text{OH})$. Reproduced from Blagojevic, Petrie, and Bohme (2003) with permission of Blackwell Publishing © 2003.

possibly lead to the formation of, for example, metalloporphyrins (Petrie, 2003, 2004). Less speculative is the very recent proposal of the formation of complex organo-magnesium ions by sequential addition reactions of type (39)



occurring in the upper atmosphere of Titan in which Mg^+ and cyanoacetylene are abundant and where subsequent electron-ion recombination may produce cyano derivatives of large unsaturated cyclic hydrocarbons such as the boat form of the CN-derivatized cyclo-octatetraene shown in Scheme 1, or of isomeric semibullvalene molecules (Milburn, Hopkinson, & Bohme, 2005). We note that the reaction sequence (39) was observed in the laboratory in helium at 0.35 Torr where termolecular kinetics is expected to prevail as may well also be the case in planetary atmospheres.

The metal-ion-initiated chemistry within a 'planetary' atmosphere such as Titan's is expected to follow a very different course from that in a circumstellar envelope such as IRC + 10216, even when the initial association chemistry apparently converges to form closely analogous complexes of the form MgNC_3H^+ (in Titan's atmosphere) and MgNC_5H^+ (in the IRC + 10216 outer envelope). In the planetary atmosphere, the ratio of reactive neutrals to free electrons is very large, so that the most probable loss process for titanian MgNC_3H^+ may well be further addition (Petrie, 2004; Milburn, Hopkinson, & Bohme, 2005). In the circumstellar envelope, however, the low temperature and the low reactive neutral: free electron ratio conspire to favor neutralization of Mg^+ /cyanopolyynes adducts such as MgNC_5H^+ , rather than the occurrence of further addition reactions. The extreme rapidity of MgNC_5H^+ dissociative recombination underpins the proposed formation mechanism for circumstellar MgNC , as discussed in Subsection VIIB, but this dissociative recombination can also feasibly break the cyanopolyynes backbone at other two-carbon-atom spaced intervals, producing also the product pairs $\text{MgNCCC} + \text{C}_2\text{H}$ and $\text{MgNCCCC} + \text{H}$ (Petrie, 1999). However, unlike MgNC , these larger 'magnesium isocyanopolyacetylides' are not the lowest-energy isomers and possess negligible barriers to isomerization to the more stable forms MgCCCN and MgC_5N (Petrie, 1999; Petrie, Kagi, & Kawaguchi, 2003). A tentative assignment of MgCCCN as the carrier of a series of unidentified spectral features in IRC + 10216, made on the basis of extremely close agreement between the observed lines and the calculated rotational constant for MgCCCN (Petrie, Kagi, & Kawaguchi, 2003), has very recently been overturned with the laboratory isolation of the spectral lines' true carrier (McCarthy, 2006), but MgCCCN , MgC_5N (and, from $\text{Mg}^+ + \text{HC}_7\text{N}$, MgC_7N) remain very promising candidates for the position of 'first identified extraterrestrial organometallic molecule.'



SCHEME 1.

Models of dense interstellar clouds estimate that Fe^+ , like Mg^+ , may account for much the total positive ion abundance within these clouds (Herbst & Leung, 1986; Millar et al., 1991). Reactions of Fe^+ with cloud molecules therefore are of much interest, including reactions initiated by Fe^+ that lead to the ionic formation of organometallic ions. For example, it has been noted (Millar, 1982) that radiative association reactions of Fe^+ and other metal ions, and subsequent "switching" reactions, are potentially very important in influencing the chemical evolution within dense interstellar clouds. Supporting laboratory measurements have been reported for room-temperature termolecular association reactions of Fe^+ with unsaturated hydrocarbons that point toward the likely occurrence of radiative association at cold cloud temperatures (Petrie et al., 1997). The neutralization of the resulting metallo-organic adduct ions by dissociative recombination with electrons can provide a route to the formation of organometallic iron-containing molecules (Fig. 9).

Reactions of the positive ions of other abundant metals (e.g., Mg^+ , Ni^+ , Ca^+ , Al^+ , Cr^+ , Mn^+ , and Ti^+) are also likely to be significant initiators of organometallic ion chemistry and hence formation of organometallic molecules if associative reactions with abundant interstellar molecules dominate over radiative recombination with electrons. However, experimental measurements of reactions of these atomic cations with organic molecules are still sparse.

IX. IONS AS CATALYSTS OR VICTIMS OF CATALYSTS

A. Ions as Catalysts of Neutral Reactions

The role of ions as catalysts for neutral reactions occurring in space environments has not yet received much attention. This is in spite of laboratory measurements that are increasingly demonstrating the ability of ions, including atomic and cluster

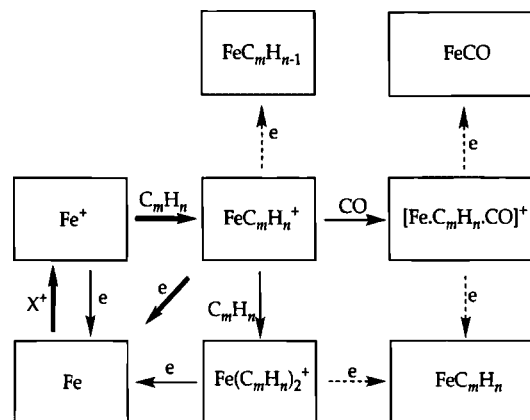
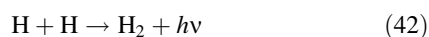
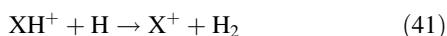
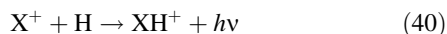


FIGURE 9. A simple network detailing probable or possible reaction pathways for the reaction of Fe^+ with hydrocarbons (principally C_2H_2 and C_4H_2) and with CO under dense interstellar cloud conditions. Speculative dissociative recombination pathways are indicated by arrows featuring dotted lines; major reaction pathways are shown by bold arrows. Reproduced from Petrie et al. (1997) by permission of the AAS © 1997.

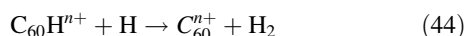
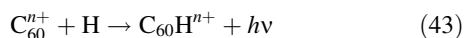
metal cations, to catalyze chemical change in the gas phase (for a review see Bohme & Schwarz, 2005).

There are some isolated proposals found in the literature that have introduced the notion of ion catalysis in space, but these are restricted primarily to the catalyzed recombination of H atoms to form molecular hydrogen, arguably the most predominant chemical bond-formation in space. The first step in this catalysis is the radiative association of a hydrogen atom to an ion, Reaction (40), which is then abstracted by a second hydrogen atom in the second step, Reaction (41). The net result is the recombination of two hydrogen atoms, Reaction (42).



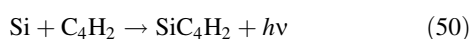
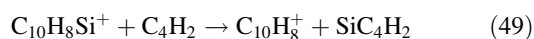
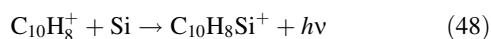
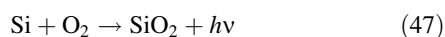
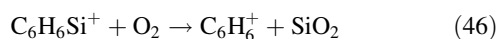
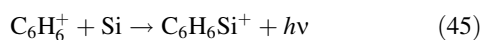
The ion catalyst X^+ must have a sufficient size (degrees of freedom) and/or hydrogen atom affinity to lead to an effective rate of radiative association. However $D(X^+-H)$ also must be less than $D(H-H)$. The occurrence of Reaction (41) recently has been demonstrated for $X = C$ and CH_3 (Luca, Borodi, & Gerlich, 2005) and may well proceed with several other hydrocarbon cations.

Ions with higher charge states may also may promote such a catalysis as has been proposed, for example, for multiply charged fullerene cations, according to Reactions (43) and (44).



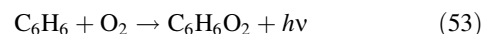
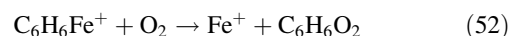
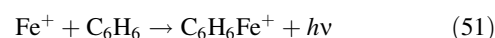
Reaction (44) is exothermic by 37 kcal mol⁻¹ with $n = 1$ (Petrie, Javahery, & Bohme, 1992). Repeated addition of atomic hydrogen to fullerene cations, dications, and trications has been demonstrated in the laboratory, but the occurrence of the second step could not be resolved (Petrie & Bohme, 1994c; Petrie et al., 1995).

Another example of the catalytic action of an ion substrate in a neutral transformation can be drawn from measurements of ion/molecule reactions of XSi^+ generated by the addition of Si^+ to $X =$ benzene and naphthalene (Bohme, Wlodek, & Wincel, 1989, 1991). The kinetic results obtained for the reactions of XSi^+ with oxygen and diacetylene, for example, suggest the likely catalytic cycles indicated in the coupled Reactions (45) + (46) and (48) + (49).



It remains to be established whether these specific examples are prototypes of more general catalytic cycles involving, as a first step, the “chemisorption” of an atom or molecules to an ionized atom, molecule, PAH, molecular cluster, grain, etc., followed by a “surface reaction” with an incoming atom or molecule.

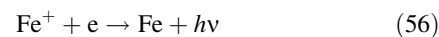
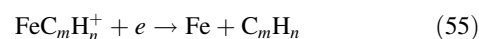
Examples also are known of another closely related variant in which an attached ion activates the substrate to which it is attached and induces a chemical change in this substrate upon subsequent reaction. A catalytic cycle results when this reaction is coupled to the attachment of the atomic ion to the substrate, for example by radiative association. This is illustrated by the reaction Sequence (51) and (52) in which Fe^+ catalyses the oxidation of benzene with molecular oxygen, probably to catechol which is the most exothermic result (Caraiman & Bohme, 2002, 2003). At least two other metal cations, Cr^+ and Co^+ , appear to do the same (Caraiman & Bohme, 2002).



This interesting mimic of heterogeneous catalysis has also been reported for the oxygenation of benzene by N_2O to ethanol (Ryan, Stöckigt, & Schwarz, 1994). Both catalytic cycles are examples of “bond-activation catalysis”: the ionic substrate activates the attached molecules to promote chemical reaction with another incoming molecule (Bohme & Schwarz, 2005). Bond-activation catalysis was first demonstrated in atmospheric chemistry for the reduction of ozone and N_2O_5 by NO catalyzed by atomic alkali-metal cations (Rowe et al., 1982).

B. Neutrals as Catalysts of Ion Neutralization

The increasing probability for radiative association of ions with increasing size of the neutral adduct can increase the probability of the neutralization of the ions by dissociative recombination with electrons. This has been realized for atomic ions that have been shown to attach to organic molecules. When Fe^+ , for example, attaches to unsaturated hydrocarbons, subsequent electron-ion recombination can lead to neutral Fe as indicated in Reactions (54–56).



In this catalytic cycle the neutral hydrocarbon molecule C_mH_n serves as a catalyst for the neutralization of Fe^+ . Such catalytic cycles with atomic metal cations generally have the capacity to reduce the degree of ionization of an interstellar cloud (Petrie et al., 1997) and so also to “poison” the ionic synthesis of organometallic molecules within these clouds by “removing” the metal ion. Atomic metal cations are especially suited as “victims” of such poisoning since their low electron recombination energies assure that other competing reaction channels in

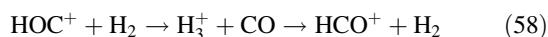
Reaction (54) are unlikely. However, it is worth noting that what is poison to one ion, such as Fe^+ , may provide meat to another, such as HCO^+ , since atomic metal ions themselves are widely viewed by astrochemists as having a ‘poisoning’ effect on ion-molecule chemistry. By drastically cutting short the otherwise very long life of an atomic metal ion, the associative promotion of Fe^+ neutralization also has the effect of reducing the free electron abundance and indirectly increasing the lifetime of other ions such as HCO^+ , with the result that HCO^+ is more likely to survive long enough to actively participate in further chemical evolution such as proton transfer to a larger interstellar neutral such as HC_3N .

C. Neutrals as Catalysts of Ion Isomerization

The effortlessness of the proton transfer Reaction (57),

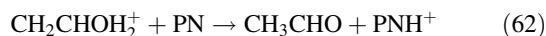
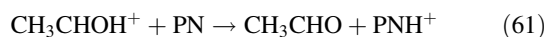
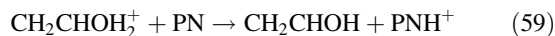


a process which is almost always highly efficient when exothermic by even only a small margin, has some interesting connotations for interstellar chemistry. For example, as noted in Section III, it was long held in some astrochemical quarters (see, e.g. Freeman et al., 1987) that the ion HOC^+ would be doomed to a very low interstellar abundance by virtue of the apparent efficiency of process (Reaction 58)



in which both sequential proton transfer steps appear to occur at approximately the collision rate at room temperature. (As related in Section III, it subsequently transpired that proton transfer from HOC^+ to H_2 was, at 10K, satisfactorily slow enough to allow the ion HOC^+ to exist under cold cloud conditions, but the general mechanism of ion isomerization through proton-transport catalysis remains viable (Bohme, 1992c)). It is perhaps notable that, while several sets of neutral interstellar isomers are now known, including HCN/HNC , linear and cyclic forms of both C_3H and C_3H_2 , and vinyl alcohol/acetaldehyde/ethylene oxide (all $\text{C}_2\text{H}_4\text{O}$) to name but a few, HOC^+ and HCO^+ remain the sole known example of isomeric interstellar ions, despite considerable observational effort. It may well be that higher-energy isomeric ions are, in general, too rapidly lost through isomerization to permit their detection.

One interesting variant on the general mechanism of proton-transport catalysis has recently come to light (Petrie, 2005). Among feasible formation mechanisms for interstellar vinyl alcohol CH_2CHOH , the association reaction between H_3O^+ and C_2H_2 is thought to produce a mixture of isomeric adduct ions including an ion of the formula $\text{CH}_2\text{CHOH}_2^+$. This ion might reasonably be described as protonated vinyl alcohol, except that the preferred site of vinyl alcohol protonation is not the O atom but rather the β -C atom, with the structure CH_3CHOH^+ . The latter ion, while being the lowest-energy protonated form of vinyl alcohol, is also the lowest-energy form of protonated acetaldehyde. Quantum chemical calculations have established that, with a reactant neutral of appropriate basicity such as phosphorus nitride, PN, a known interstellar molecule, the sequence of proton-transfer Steps (59)–(61) are all individually exothermic and viable:



Thus, O-protonated vinyl alcohol is expected to react with interstellar PN to produce neutral acetaldehyde, by virtue of a proton-transfer ‘triple play.’

We should include here also a very recent suggestion of a possible role for grains of water ice in promoting the isomerization of the H_2O adduct of ketene cations $[\text{CH}_2\text{CO} \cdot \text{H}_2\text{O}]^+$ into the acetic acid cation (Orlova, Blagojevic, & Bohme, 2006). Proton transport also is crucial in this catalysis. The proposal is based on the observation of the gas-phase addition of water to the ketene radical cation to form the enolic $\text{CH}_2\text{C}(\text{OH})_2^+$ cation in a reaction second-order in H_2O . Furthermore, the presence of ice also can promote electron-ion recombination to form acetic acid according to Reaction (63).



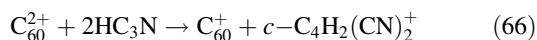
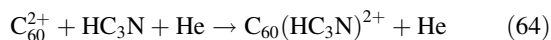
Icy surfaces would readily be available in hot cores and dense molecular clouds in which neutral acetic acid already has been detected.

X. A CHEMICAL ROLE FOR MULTIPLY CHARGED IONS?

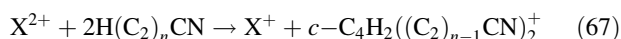
The likely prospect for the formation of multiply charged cations in interstellar environments raises questions about the chemistry of such ions in these environments. Laboratory measurements of reactions of multiply charged cations already have revealed several interesting chemical properties for such ions that may impact on the chemical evolution of dense interstellar clouds that contain such ions. We have already discussed their possible role as catalysts for H-atom recombination (Subsection IXA).

In this closing section we note especially the unique ability of multiply charged cations to undergo charge separation reactions that can feature in the production of internally cold, but translationally hot, ions that can provide the driving force for the subsequent occurrence of neutral reactions. For example, hydrogen-atom abstraction reactions with the dominant dense-cloud species H_2 can be initiated in this way (Petrie & Bohme, 1994b).

Multiply charged ions can also be effective in promoting unique cluster-ion chemistry. This has been demonstrated in SIFT experiments with C_{60}^{2+} which show that this ion has the ability to transform two cyanoacetylene molecules into a dicyanocyclobutadiene cation. This cation may neutralize by electron transfer or recombination with electrons to form the corresponding cyclic neutral molecule (Milburn, Hopkinson, & Bohme, 1999). The reaction sequence observed in the laboratory is shown in Equations (64) and (65) and would involve radiative, rather than collisional, association as a first step in the interstellar medium.



The same mechanism should apply to the higher homologs of cyanoacetylene and so lead to formation of derivatized cyclobutadienes. Furthermore, any doubly charged substrate, be it another doubly charged molecule such as PAH^{2+} or a double-charged cluster or grain, capable of bonding with the N-terminus of a cyanopolyacetylene should exhibit the generalized transformation given in Equation (67).



More generally, SIFT experiments with C_{60}^{2+} , which perhaps is a useful model of a doubly charged interstellar carbonaceous dust particle, have shown this carbonaceous cation to be effective in “docking” a large variety of molecules, a form of chemical absorption, and so to expose them to further chemistry with other incoming molecules. This chemistry exhibits a marvelous variety including proton transfer, cyclization (as we have seen), and chain propagation (Petrie, Javahery, & Bohme, 1993; Bohme, 1999; Petrie & Bohme, 2000).

XI. CONCLUDING REMARKS

We have not attempted, and certainly have not achieved, a complete overview of the subject of ‘ions in space’ within the present work, but we hope that we have provided some insight into the richness of this subject. The knowledge gained on this subject over the past several decades has been achieved through the close collaboration of astronomers, spectroscopists, mass spectrometrists, kineticists, theoreticians, modelers, and practitioners of diverse other fields within the physical sciences and engineering.

The elucidation of ion chemistry occurring in regions that we cannot yet hope to visit is a powerful exercise in scientific exploration, and one which perhaps holds the promise of particularly exciting and far-reaching discoveries. Ion chemistry in deep space may hold the key to the rate of star formation, and it may also provide the spark needed to generate the stuff from which life assembles itself. By studying these ideas, and others, we learn much about the small charged particles with which we share the Universe, and more generally about the nature of the Universe that we inhabit.

XII. NOTE ADDED IN PROOF

In a sign that the ‘interstellar ion drought’ identified in section III may have ended, the detection of the CF^+ ion in the Orion Bar has been very recently reported (Neufeld et al., *Astron Astrophys* 454: L37–L40).

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