Molecular Ions in Astrophysics

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Abstract. The chemical content of the interstellar medium has been drastically revised in the last two years with the discovery of negative ions at a significant level of abundance. We emphasize the chemical processes involved in the formation and depletion of anions and the need for new laboratory work to understand them better. In addition, we comment on the detection of the first fluorine ion, CF⁺, and on hydrocarbon chemistry, specifically the recent detection of propene and a study of deuterated methylacetylene isotopomers.

1. Introduction

General overviews of interstellar molecules and their chemistry were given at the last DR meeting [1, 2] and we refer readers to these contributions for a general introduction to astrochemical modelling. There have, however, been important updates to our knowledge of the molecular content during the last two years with the detections of:

- new organic molecules such as acetamide (CH₃CONH₂) towards star-forming regions in the galactic center
- propene (C₃H₆) in the "standard" cold molecular cloud TMC 1 [3], although this stable molecule was not included in any chemical network
- the fluorine-bearing molecular ion CF⁺ in a photon-dominated region
- negative ions in a variety of sources, following their laboratory spectroscopic identification.

We display in Table 1 an up-to-date list of interstellar and circumstellar molecules without their isotopic variants. The most dramatic change from previous lists is the inclusion of negative molecular ions. The italic symbols refer to detections via absorption in electronic transitions in the UV or visible wavelength range, which are possible in diffuse or so-called translucent clouds. Molecular ions, very important tracers of the ionization state of the environment, appear in boldface. Molecules detected only in circumstellar environments are labelled with an asterisk whereas molecules detected both in the interstellar medium and circumstellar environments are labelled with two asterisks. In addition, molecules detected in external galaxies are underlined. The present inventory includes 133 neutral molecules, and 17 molecular ions including three negative species: C₄H⁻, C₆H⁻, and C₈H⁻.
Table 1. Interstellar and Circumstellar Molecules as of October 2007.

| Molecules with Hydrogen only                  | $H_2^+$ |
|-----------------------------------------------|--------|
| Molecules with Carbon and Hydrogen            | $H_3^+$ |
| CH                                            | CH$^+$ |
| $C_3$**                                       | CH$_3$ |
| $C_3$H$_2$**                                  | $C_2H_2$** |
| $C_3$H$_2$**                                  | l-$C_3H_2$** |
| CH$_4$**                                      | CH$_2$ |
| c-C$_3$H$_2$**                                | $C_2H_2$* |
| C$_5$*                                        | C$_3$H** |
| C$_5$H$_4$*                                   | l-H$_2$C$_4$** |
| CH$_3$CCH$_2$**                               | C$_6$H$_6$* |
| Molecules with Oxygen and/or Hydrogen and/or Carbon |        |
| O$_2$                                         | OH$^{**}$ |
| HCO                                           | CO$^{**}$ |
| $H_3O^+$                                      | CO$^+$ |
| H$_2$CO                                       | $C_2H_2$O |
| $C_3$H$_3$O                                   | $C_2H_4$O |
| c-H$_2$C$_3$O                                 | $C_3H_2$O |
| CH$_3$COOH                                    | CH$_2$CHO |
| CH$_3$CH$_2$CHO                                | HOCH$_2$CH$_2$OH |
| Molecules with Nitrogen and/or Hydrogen and/or Carbon |        |
| NH                                            | CN$^{**}$ |
| HNC$^{**}$                                    | N$_2$* |
| HCCN$^{**}$                                   | NH$_3$** |
| HNCCO$^{**}$                                  | HCNH$^+$ |
| CH$_2$CN                                      | HCN$^+$ |
| CH$_2$CN$^+$                                  | CH$_2$CN |
| HC$_5$N$^{**}$                                | CH$_5$N |
| HC$_7$N$^{**}$                                | CH$_7$N |
| Molecules with Nitrogen, Oxygen                |        |
| NO                                            | HNO |
| $C_3$HCONH$_2$                                | N$_2$O |
| Molecules with Phosphorus, Sulfur, Silicon, Halogen or a Metal |        |
| SH                                            | CS$^{**}$ |
| SiC                                           | SiN$^{**}$ |
| NaCl*                                         | NaCl* |
| NaCl$^+$                                      | KCl$^+$ |
| CF$^+$                                        | CP$^+$ |
| H$_2$S$^{**}$                                  | SO$_2$ |
| c-SiC$_2$*                                    | SiH$_4$* |
| C$_3$S$^{**}$                                 | SiC$_4$* |
| C$_5$S$^{*}$                                  |        |

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[2]
The remainder of the paper is organized as follows. In Section 2 we discuss fluorine chemistry, a potentially important subtopic in interstellar chemistry, interest in which has been raised by the detection of CF\(^+\) [4]. Molecular anions are then discussed in Section 3. Finally, we discuss interstellar hydrocarbon chemistry including the detection of propene in the cold cloud TMC 1 and the presence in the same cloud of different isomers of deuterated methyl acetylene.

2. Fluorine chemistry

Three fluorine-bearing molecules have been detected so far. Of these, AlF has only been found in the circumstellar envelope IRC+10216 [5, 6], whereas both HF [7] and CF\(^+\) [4] have been detected in the Orion Bar, a well-known photon dominated region (PDR). A preliminary chemical scheme for the chemistry of fluorine-bearing species has been suggested by Neufeld, Wolfire and Schilke [8]. Theoretical and experimental work show, rather remarkably, that the chemistry can be accounted for with a relatively restricted chemical network. Because the ionization energy of atomic fluorine is larger than 23 eV, it is safe to assume that the atom is mainly neutral, even in the high-photon environment of PDR’s. Atomic fluorine (F) can react with H\(_2\) to produce HF and H. Although this well-studied reaction is exothermic, a small activation barrier in the potential energy surface moderates its reaction rate coefficient. The main destruction channels for HF in the Orion bar environment are photodissociation and reaction with C\(^+\). Photodissociation cross sections have been computed by Brown and Balint-Kurti [9], while the reaction of C\(^+\) and HF is supposed to occur at the Langevin rate and lead to CF\(^+\), a very stable molecular ion with the same electronic structure as CO. Finally, dissociative recombination and possible photodissociation are the main destruction channels of the CF\(^+\) molecular ion. The chemical pathways leading to and destroying HF and CF\(^+\) are as follows:

\[
\begin{align*}
F + H_2 & \rightarrow HF + H, \quad (1) \\
C^+ + HF & \rightarrow CF^+ + H, \quad (2) \\
HF + h\nu & \rightarrow H + F, \quad (3) \\
CF^+ + e & \rightarrow C + F, \quad (4) \\
CF^+ + h\nu & \rightarrow C^+ + F. \quad (5)
\end{align*}
\]

In their model calculation, Neufeld et al. [4, 8] estimated the DR recombination rate coefficient of CF\(^+\) to be \(2 \times 10^{-7} \ (T/300)^{-0.5} \ \text{cm}^3 \ \text{s}^{-1}\) and obtained satisfactory agreement between their observations of CF\(^+\) and their predictions. The CF\(^+\) dissociative recombination (DR) rate coefficient has now been measured by Novotny et al. [10] to be \(5.2 \pm 1.0 \times 10^{-8} \ (T/300)^{-0.8} \ \text{cm}^3 \ \text{s}^{-1}\), which is rather close to the estimated value.

In addition to CF\(^+\), other fluorine-bearing molecular ions may be of astrophysical interest. Neufeld and et al. [8] suggested that F + H\(_3^+\) could lead to FH\(_2^+\) + H, based on a study of the analogous reaction between N and H\(_3^+\) [11]. However, this latter reaction has now been shown \textit{not} to proceed [12]. Whether the F + H\(_3^+\) reaction occurs is not clear, but it is true that this process satisfies spin conservation, as opposed to N + H\(_3^+\). In any case, other formation channels exist, such as:

\[
\begin{align*}
F^+ + H_2 & \rightarrow HF^+ + H, \quad (6) \\
HF^+ + H_2 & \rightarrow H_2F^+ + H, \quad (7) \\
HF + H_3^+ & \rightarrow H_2F^+ + H_2. \quad (8)
\end{align*}
\]

The H\(_2\)F\(^+\) molecular ion may be of potential astrophysical interest, as it is quite stable and iso-electronic with H\(_2\)O. Further studies on H\(_2\)F\(^+\) would be quite relevant in the astrophysical context.
3. Negative molecular ions

The presence of anions has been demonstrated in the last year thanks to spectroscopic studies performed in the laboratory of P. Thaddeus [13, 14, 15]. The molecular anions $C_6H^-$ and $C_8H^-$ have been found in the "standard" molecular cloud TMC 1 [15, 16] while these as well as $C_4H^-$ have been detected in the circumstellar envelope IRC+10216 [15, 16, 17, 18, 19]. Most recently, Sakai et al [20] reported the detection of $C_6H^-$ in L1527, a low-mass star-forming region. Table 2 displays the ground-state electronic structures, permanent dipole moments ($\mu$), and derived column densities (cm$^{-2}$) of the anions and their neutral counterparts in TMC-1 and IRC+10216. Whereas the neutral $C_nH$ species have an open shell structure, leading to either $2\Sigma$ or $2\Pi$ ground states, electron attachment collapses the structure and reduces the spectrum to that of a simple $1\Sigma$ molecule. Together the smaller partition function and the larger dipole moment enhance the lines of the anions relative to those of the neutral radicals by almost one order of magnitude.

| Ref symmetry | $\mu$ | TMC 1 | IRC+10216 |
|--------------|-------|-------|-----------|
| $C_4H^-$     | $1\Sigma^+$ | 6.2   | $< 8.5 \times 10^{10}$ | $7.1 \pm 2.0 \times 10^{11}$ |
| $C_4H^-$     | $2\Sigma^+$ | 0.9   | $(6.1 \pm 0.5) \times 10^{13}$ | $3 \times 10^{15}$ |
| $C_4H^- / C_4H$ |          |       | 1/4400     |           |
| $C_6H^-$     | $1\Sigma^+$ | 8.2   | $(12 \pm 2) \times 10^{10}$ | $4.1 \pm 1.5 \times 10^{12}$ |
| $C_6H$      | $2\Pi$     | 5.5   | $(750 \pm 80) \times 10^{10}$ | $6.6 \pm 2.0 \times 10^{13}$ |
| $C_6H^- / C_6H$ |        |       | $(1.6 \pm 0.3) \times 10^{-2}$ | 1/16     |
| $C_8H^-$     | $1\Sigma^+$ | 11.9  | $(2.1 \pm 0.4) \times 10^{10}$ | $1.5 \pm 0.6 \times 10^{12}$ |
| $C_8H$      | $2\Pi$     | 6.3   | $(46 \pm 4) \times 10^{10}$ | $8 \pm 3 \times 10^{12}$ |
| $C_8H^- / C_8H$ |          |       | $(5 \pm 1) \times 10^{-2}$ | 1/3.8    |

The chemistry associated with the formation of these molecular anions is not well known. Herbst [21] suggested more than 25 years ago that negative ions could be produced at low densities by radiative attachment while Petrie and Herbst [22] and Terzieva and Herbst [23] specifically addressed the formation of $C_3N^-$ and carbon cluster negative ions ($C_n^-$), respectively, in interstellar space, using phase-space theory. Petrie [24] also considered dissociative attachment of weakly-bound neutral precursors as an exothermic formation mechanism. For the detected anions, both radiative attachment; e.g.,

$$C_6H + e \rightarrow C_6H^- + h\nu,$$

and dissociative attachment of a precursor carbene; e.g.,

$$C_6H_2 + e \rightarrow C_6H^- + H$$

are likely formation processes [20].

The destruction of anions is better understood. The chemical reactions of assorted $C_n^-$ and $C_nH^-$ ions with H, H$_2$, N, and O have been studied by Barkholtz et al. [25] and Eichelberger et al. [26], who showed that these ions are not destroyed by H$_2$ but that reactions with atomic hydrogen and other atoms can be rapid. In their high-density experiment, three-body association (not applicable to the interstellar medium) is the dominant product channel for the $C_n^- +$ H.
reactions while the C$_n$H$^-$ + H reactions proceed via associative detachment, leading to HC$_n$H neutrals. Mutual ionization between cations and anions also plays a role in L1527 [20]; additional studies of this process are urgently required.

The discovery of molecular anions has generated the need to include their formation and destruction in chemical models. With estimates of the radiative attachment reaction rate coefficients for C$_n$ and C$_n$H radicals and measured and estimated anion destruction rates, Millar et al. [27] computed column densities for molecular anions in a variety of sources. They found, in agreement with observation, that the larger molecular anions detected (n = 6, 8) have higher abundances relative to their neutral precursors (see Table 2) because the radiative attachment rate increases with the number of degrees of freedom of the anion. However, their rate estimates are quite uncertain and experimental studies are highly welcome. Flower et al. [28] reported a more restricted anion chemistry to derive astrophysical constraints from the ratios of the column densities of the negative ions to their neutral counterparts. Whether their deductions concerning the actual value of the cosmic ionization rate in TMC 1 are correct remains to be demonstrated.

4. Hydrocarbon chemistry

4.1. Propene, a new interstellar molecule

Propene, CH$_3$CH$\equiv$CH$_2$ (C$_3$H$_6$), a closed shell molecule with a low dipole moment of 0.36 D, has been found in TMC 1 by Marcelino et al. [3] with an unexpectedly large fractional abundance relative to molecular hydrogen of about $10^{-8}$, which is comparable with the main carbon-containing molecules such as C$_2$H, C$_3$H$_2$, and HCN. This molecule has not been considered, up to now, in any interstellar chemical network, because the gas-phase production of molecules with this many hydrogen atoms is often inefficient. One possibility is to first produce the precursor ion C$_3$H$_7^-$. Normal and ternary associative gas phase ion-molecule reactions of C$_n$H$_m^-$ ions with H$_2$ have been studied by McEwan et al. [29] at 300 K for various values of n and m. Although C$_3$H$_5^-$ has been found not to react associatively with H$_2$ to form C$_3$H$_7^-$, the upper limit of the association channel may still allow a reasonable radiative association rate in the cold interstellar medium. The DR of C$_3$H$_7^-$ has been studied with the CRYRING and ASTRID storage rings [30, 31]. Sixteen product channels are energetically possible, and the branching ratio leading to propene + H is a matter of debate. A value of 0.67, found by Angelova et al. [31], is used in our preliminary model calculations.

In addition to ion-molecule reactions, selected neutral-neutral reactions can be rapid at low temperatures. Canosa et al. [32, 33] have shown that CH and C$_2$ react with ethane to form propene:

$$\text{CH} + \text{C}_2\text{H}_6 \rightarrow \text{C}_3\text{H}_6 + \text{H},$$

$$\text{C}_2 + \text{C}_2\text{H}_6 \rightarrow \text{C}_3\text{H}_6 + \text{C},$$

with rate coefficients of $2 \times 10^{-11}$ and $2 \times 10^{-10}$ cm$^3$ s$^{-1}$ respectively at 23 K. Once formed, propene is destroyed by ions and, as has been recently found, by atomic oxygen [34]. Detection of this molecule in the TMC 1 environment, where many carbon chain molecules have already been found, may be a signature of a large C/O elemental ratio. We have performed model calculations including propene, using the latest information described above, for physical conditions relevant to TMC 1. The chemical network comprises 169 species, including carbon chains up to C$_8$H$_2$, the negative ions H$^-$, C$^-$, CH$^-$, OH$^-$, C$_2$H$^-$, C$_3$H$^-$, C$_4$H$^-$, C$_5$H$^-$, C$_7$H$^-$, C$_8$H$^-$, and more than 2000 chemical reactions. Figure 1 displays the time dependence of the fractional abundances of several hydrocarbon molecules relative to total hydrogen nuclei. We used two different sets of elemental abundances with differing C/O ratios. Propene peaks at about 0.1 Myr, corresponding with the decrease of C$_2$ and CH (not shown). Its maximum fractional abundance reaches $1 - 8 \times 10^{-9}$, depending strongly on the C/O ratio. More work on the corresponding chemistry is clearly needed.
4.2. Deuterated isomers
Despite a long history, deuterated molecules still represent an active topic, both for observations and modelling studies. We display detected deuterated isotopologues in Table 3; these include seven doubly-deuterated and two triply-deuterated species. As previously described [1] in

**Table 3.** Detected deuterated molecules in the interstellar medium

|       |       |       |       |
|-------|-------|-------|-------|
| HD*   | HDCO  | CH₃D₀ | D₂H⁺  |
| HDO†  | HDCS  | H₂D⁺  | D₂O   |
| DCN†  | DC₃N  | DCO⁺  | ND₂H  |
| DNC†  | CH₂DOH| N₂D⁺  | D₂CO  |
| HDS   | CH₃OD | CHD₂OH|       |
| C₂D   | DC₅N  | D₂S   |       |
| C₃D   | CH₂DCCH| D₂CS  |       |
| C₃HD  | CH₃CCD| ND₃   |       |
| NH₂D  | CH₂DCN| CD₃OH |       |

* detected in planetary atmospheres, comets and the interstellar medium via the rotational transition at 112 µm and through UV absorption in diffuse and translucent interstellar clouds as well as in front of a distant quasar where the UV Lyman transitions of HD are shifted into the visible range.
† also detected in comets
₀ only detected in planetary atmospheres
Table 4. Chemical differentiation between deuterated isomers.

| Reaction                                      | Product 1 | Product 2 | Product 3 | Product 4 |
|-----------------------------------------------|-----------|-----------|-----------|-----------|
| \( \text{H}_3^+ + \text{CH}_3 \text{CCH} \rightarrow \text{CH}_3 \text{CCH}_2^+ + \text{H}_2 \) | \( \text{H}_3^+ + \text{CH}_3 \text{CCH}_2^+ + \text{H}_2 \) | \( \text{H}_3^+ + \text{CH}_3 \text{CCH}_2^+ + \text{H}_2 \) |
| \( \text{CH}_4^+ + \text{C}_2 \text{H}_4 \rightarrow \text{CH}_3 \text{CCH}_2^+ + \text{H}_2 \) | \( \text{CH}_4^+ + \text{C}_2 \text{H}_4 \rightarrow \text{CH}_3 \text{CCH}_2^+ + \text{H}_2 \) | \( \text{CH}_4^+ + \text{C}_2 \text{H}_4 \rightarrow \text{CH}_3 \text{CCH}_2^+ + \text{H}_2 \) |
| \( \text{C}_2 \text{H}_2^+ + \text{CH}_4 \rightarrow \text{CH}_3 \text{CCH}_2^+ + \text{H}_2 \) | \( \text{C}_2 \text{H}_2^+ + \text{CH}_4 \rightarrow \text{CH}_3 \text{CCH}_2^+ + \text{H}_2 \) | \( \text{C}_2 \text{H}_2^+ + \text{CH}_4 \rightarrow \text{CH}_3 \text{CCH}_2^+ + \text{H}_2 \) |

The DR2005 conference, the abundance ratio of deuterated species to their hydrogenated counterparts is much larger than the elemental D/H ratio, which is on the order of \(1.5 \times 10^{-5}\). Deuterium enhancement is readily explained from gas phase chemical fractionation reactions involving deuteron exchange, such as \( \text{H}_3^+ + \text{HD} \leftrightarrow \text{H}_2 \text{D}^+ + \text{H}_2 \). The backward reaction is significantly slowed at low temperatures due to its endothermicity, which results from differences in the zero point energies and the extra rotational energy due to the absence of the \(0_0\) level in \(\text{H}_3^+\). Similar reaction pairs can occur with \(\text{H}_2 \text{D}^+\) and \(\text{HD}\) and \(\text{D}_2 \text{H}^+\) and \(\text{HD}\), producing \(\text{D}_2 \text{H}^+\) and finally \(\text{D}_3 \text{D}^+\). These deuterated ions then react with neutrals to form high abundances of other deuterated species, both ionic and neutral. Other efficient deuteration vectors are provided by the deuterated isotopologues of \(\text{CH}_3^+\) and \(\text{C}_2 \text{H}_2^+\) ions, which do not react rapidly with \(\text{H}_2\) but can exchange a deuteron with \(\text{HD}\).

The study of the abundance ratio between abundances of different deuterated versions of polyatomic molecules, such as the isotopomers \(\text{CH}_3 \text{CCD}\) and \(\text{CH}_2 \text{DCCH}\) of methyl acetylene, is most probably linked to subtle chemical processes, where care has to be taken with the various mechanisms. Markwick et al. [35] suggest the occurrence of the chemical reactions shown in Table 4, under the assumption that deuterons cannot transfer between functional groups. Experimental studies by Angelova et al. [31] on the DR reaction of protonated methyl acetylene have shown that the product channel leaving the carbon skeleton intact occurs with an 87% probability. If, in addition, ejection of \(\text{H}\) is more likely than ejection of \(\text{D}\) for the deuterated precursor ions, the abundances of the deuterated isotopologues in TMC 1 can reasonably be accounted for. But deuterium fractionation can also occur on grain mantles with the products subsequently released into the gas phase by thermal and non-thermal processes. Whether gas-phase mechanisms or surface processes dominate is still an open question, and more work is needed on these topics, such as the extent to which non-equilibrium effects reduce the gas-phase fractionation.

5. Conclusions
We have given some examples showing the relevance of dissociative recombination and other ion processes for astrophysical modelling. The recent discovery of molecular anions demonstrates the need to improve our knowledge of assorted classes of reactions such as electron attachment, dissociative attachment, associative detachment, and mutual neutralization, all processes for which the theoretical and experimental DR community has the appropriate expertise. Finally, we recall the need for studying specific isotopic processes. For example, whether \(\text{H}\) or \(\text{D}\) atoms are more easily ejected during DR has a profound influence on the model results.

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