Dissociative Recombination: building and destroying aspects in interstellar chemistry

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Abstract. We discuss the ionic composition of the interstellar molecular gas. Particular emphasis is put on the halogenic ions such as H\textsubscript{2}Cl\textsuperscript{+} and H\textsubscript{2}F\textsuperscript{+} for which no DR studies have been published up to now.

1. Introduction

The molecular inventory of interstellar and circumstellar environments is now close to 150 different species without counting isotopic substitutions. Most of these molecules are neutral. Amongst the 25 molecular ions detected, 6 molecular anions have now been identified thanks to the combined efforts of spectroscopists and observers. Even though their relative number is small, atomic and molecular ions trace the ionization content of the interstellar medium and play a considerable role in the stability of interstellar clouds via their coupling to the magnetic field.

Table 1 reports all the presently detected molecular ions in interstellar clouds, including various isotopologues with D, \textsuperscript{13}C and \textsuperscript{15}N nuclei. A number of new ionic detections, reported in italics, have taken place since the last DR meeting in 2007 thanks to the opening of the submillimeter domain with HIFI (Heterodyne Instrument for the Far Infrared) on board the Herschel satellite, launched in July 2009, and the ground-based APEX telescope on the Atacama plateau.

In this paper, we describe briefly the basic steps of gas phase interstellar chemistry in Section 2. Section 3 focuses on halogen chemistry in the context of new detections as well as existing theoretical and experimental studies in dissociative recombination (DR). The continuing study of isomers, such as HNCO and two higher energy isomers, may be a signature of specific branching ratios, a topic we address in Section 4. Finally, Section 5 focuses on the newly detected SH\textsuperscript{+} molecular ion, for which no DR studies have been performed.

2. General features of positive ion chemistry

We focus the discussion on positive ions as the chemistry of negative molecular ions is discussed in detail in \cite{1}. The ionization source in molecular clouds is provided both by ultraviolet radiation with photon energies less than 13.6 eV, corresponding to the ionization energy of atomic hydrogen, and by cosmic rays. External UV radiation is most important in diffuse clouds, where the radiation can penetrate. In such clouds, C\textsuperscript{+} and Cl\textsuperscript{+} are formed via this radiation. Of these, only the latter is able to react rapidly with H\textsubscript{2}. Indeed, it is remarkable that very
Table 1. List of detected interstellar molecular ions.

| 2-atoms | 3-atoms | 4-atoms | 5-atoms | 6-atoms | 7-atoms | 9-atoms |
|---------|---------|---------|---------|---------|---------|---------|
| CH⁺     | H₂⁺     | H₂O⁺   | H₂CO⁺  | HC₃NH⁺  | C₆H⁻    | C₈H⁻    |
| ^1³CH⁺  | H₂D⁺    | HCN⁺   | C₄H⁻   | HC₄H⁺   |         |         |
| OH⁺     | D₂H⁺    | HOCO⁺  |         | C₅N⁻    |         |         |
| SH⁺     | H₂O⁺    |         |         |         |         |         |
| CO⁺     | HCO⁺    |         |         |         |         |         |
| SO⁺     | DCO⁺    |         |         |         |         |         |
| CF⁺     | H¹³CO⁺  |         |         |         |         |         |
| CN⁻     | HOC⁺    | HCS⁺   | N₂H⁺   | N₂D⁺    |         |         |
|         |         |         |         | ¹⁴N¹⁵NH⁺|         |         |
|         |         |         |         | H₂Cl⁺   |         |         |

few atomic ions (Cl⁺, O⁺, F⁺) react directly and rapidly with H₂. Ionization via cosmic rays is critical for hydrogen atoms and molecules. In a molecular environment, H₂⁺, resulting from the H₂⁺ + H₂ reaction, is then able to transfer its proton to other neutral molecules such as CO and N₂, eventually forming polyatomic molecular ions. The detection of these species; e.g., HCO⁺, confirmed the first sketches of interstellar chemistry [2]. In dark clouds where hydrogen is the molecular reservoir, dissociative recombination reactions compete with possible exothermic ion-neutral reactions with neutrals. In diffuse environments, photodissociation needs also to be considered although detailed corresponding cross sections are not always available. In dense molecular clouds the fractional ionization fraction is about 10⁻⁸ whereas in diffuse gas the main ionic reservoir is ionized carbon and on the order of 10⁻⁴. From complex molecular ions, DR can lead to various neutral products. In this way, DR may have a profound impact on the formation of specific neutral molecules and isomers. We consider both of these aspects in Sections 3 and 4.

3. Halogen chemistry

Halogen chemistry has received recent attention [3, 5] with the detections of HF [4], CF⁺ [6], HCl [7], and H₂Cl⁺ [8]. As quoted before, Cl⁺ is photoionized in diffuse regions and HCl⁺ is formed by the Cl⁺ + H₂ reaction as soon as some H₂ is present. H₂Cl⁺ is then obtained from the reaction of HCl⁺ with H₂. Figure 1 displays the chemical network for both chlorine (left) and fluorine (right) containing species. We see the main differences between these chemical networks: whereas HCl is mainly formed from dissociative recombination of H₂Cl⁺ and reactions of H₂Cl⁺ with neutrals, HF results from a neutral reaction between F and H₂. This highly exothermic reaction has been studied in great detail experimentally and theoretically, and is found to have a small barrier of about 1.5 kcal mol⁻¹. One of the latest studies [9] reports the reaction rate coefficient as a function of the rotational level of H₂ for J = 0 and 1, which are relatively close. The theoretical limit of the reaction rate coefficient at 0 K has been determined to be 1.3×10⁻¹² cm³ s⁻¹ as a result of resonance effects [10]. The DR of H₂Cl⁺ and H₂F⁺ has not yet been studied and corresponding product branching ratios are not known. We suggest that these branching ratios can be obtained from the general trend of the branching ratios of dihydrides as a function of energy release in the three-body channel. Such a trend was first established by [11] and a
clear correlation is obtained by plotting the branching ratio of the triatomic ions for 3-body dissociation as a function of the corresponding energy release, as shown in Fig. 2. From this correlation, we obtain that the 3-body dissociation fraction of $\text{H}_2\text{Cl}^+$ and $\text{H}_2\text{F}^+$ is respectively 0.56 and 0.40. Although the total DR rates are not available yet from experiments, a provisional value of $1.2 \times 10^{-7} \left(\frac{T}{300}\right)^{-0.85}$ is reported in [3] for $\text{H}_2\text{Cl}^+$. The rather large column density of $\text{H}_2\text{Cl}^+$ detected towards NGC 6334I and Sg B2(S), on the order of $10^{13} \text{ cm}^{-2}$ [8], remains to be understood. The observations allowed also to detect HCl at an amount of about $10^{14} \text{ cm}^{-2}$, so that the HCl over $\text{H}_2\text{Cl}^+$ ratio is about 10. It would also be interesting to determine the $\text{HF}/\text{H}_2\text{F}^+$ ratio. However, the $\text{H}_2\text{F}^+$ molecular ion has not yet been detected, due to the missing information on the microwave spectroscopy of this stable molecular ion.

4. Building the isomers

Different isomers are found in interstellar clouds, despite the very low ambient temperature in all but some star-forming regions. Table 2 displays their present observational status. The HCN/HNC problem has been extensively discussed and the similar amount of both isomers at low temperatures (e.g., 10 K) is explained in part by equivalent product branching fractions for HNC + H and HCN + H in the dissociative recombination reaction of the linear HCNH$^+$ ion. We focus instead on the 3 isomers of HNCO which have been recently detected in various interstellar clouds ranging from cold to warm (50-100 K) [12]. It is remarkable that HOCN
and HCNO, lying respectively above 24.7 and 70.7 kcal mol\(^{-1}\) above the stable HNCO isomer, are found in regions where a temperature of 10 - 20 K pertains. It is equally remarkable that in warmer regions, the HOCN isomer is detected but the HCNO isomer is not. A gas-phase chemical scenario to explain the observations is discussed in [12] where results of the chemical models rely heavily on the assumed DR branching ratios of isomeric molecular ions. Table 3 displays these reactions and the assumed DR reaction rate coefficients. However, it seems relatively well established that HCNO formation occurs via a specific gas phase mechanism, involving the neutral-neutral reaction between NO and CH\(_2\). Grain-surface chemistry may also be at work, especially in the warmer sources, and a definite conclusion is difficult to derive in view of all the underlying hypotheses and uncertainties, as discussed in [13].
Table 2. List of detected isomers.

| HCN     | HNC     |
|---------|---------|
| MgCN    | MgNC    |
| SiCN    | SiNC    |
| c-C₃H   | l-C₃H   |
| HNCO    | HOCN    |
| HNCS    | HSCN    |
| c-C₃H₂   | l-C₃H₂   |
| HC₂CN   | HC₂NC   |
| CH₃CN   | CH₃NC   |
| CH₃CHO  | c-CH₂OCH₂ |
| HCOOCH₃ | HOCH₂CHO |
| H₂CCCHCN| CH₃CN   |
| (CH₃)₂O | CH₃CH₂OH |
| (CH₃)₂CO| CH₃CH₂CHO|

Table 3. Assumed DR reaction rate coefficients of H₂NCO⁺⁺ isomers at 300K.

|                      | eV   | cm³s⁻¹       |
|----------------------|------|--------------|
| H₂NCO⁺⁺ + e⁻ → HNCO  + H | 6.21 | 1.5·10⁻⁷     |
| H₂NCO⁺⁺ + e⁻ → NCO  + H₂ | 5.93 | 1.5·10⁻⁷     |
| HNCOH⁺⁺ + e⁻ → HNCO  + H | 7.03 | 1.5·10⁻⁷     |
| HNCOH⁺⁺ + e⁻ → HOCN  + H | 5.96 | 1.5·10⁻⁷     |
| HCOOH⁺⁺ + e⁻ → HCNO  + H | 6.66 | 1.5·10⁻⁷     |
| HCNOH⁺⁺ + e⁻ → HONC  + H | 6.04 | 1.5·10⁻⁷     |
| H₂OCN⁺⁺ + e⁻ → HOCN  + H | 8.82 | 1.5·10⁻⁷     |
| H₂OCN⁺⁺ + e⁻ → NCO  + H₂ | 9.61 | 1.5·10⁻⁷     |
| H₂CNO⁺⁺ + e⁻ → HCNO  + H | 7.00 | 1.5·10⁻⁷     |

5. The SH⁺ molecular ion
Amongst the new hydrides detected recently with high frequency heterodyne receivers (Herschel, APEX), some of which are discussed in the contribution Herbst & Roueff [1], we now focus on SH⁺, which has been detected towards the galactic center in both dense components near the galactic center and diffuse clouds in spiral arms surrounding it [14]. As already pointed out in [15], the reaction between S⁺ and H₂ giving SH⁺ + H is endothermic by a significant value of about 0.84eV. In diffuse regions, where S is ionized and where the kinetic temperature is about 40-80 K, additional energy input is required to allow the reaction to proceed. MHD shocks or turbulence driven processes may provide such a chemical impetus. In dense regions, the S + H₃⁺ reaction is supposed to form SH⁺, in a reaction analogous to O + H₃⁺. The specificity of SH⁺ is that the reaction of SH⁺ with H₂ giving H₂S⁺ + H is also endothermic, with an endothermicity of 0.73eV, so that dissociative recombination may become the dominant destruction channel in such environments (see below). This is different from CH⁺, another important astrophysical ion, which is produced by an endothermic reaction between C⁺ and
Figure 3. Comparison of column density ratios observed in various cloud components towards Sgr B2, as reported in [14].

H$_2$ but destroyed straightforwardly by H$_2$. Another channel of formation of SH$^+$, suggested by Abel et al. [16], involves the doubly charged sulfur ion, which reacts with H$_2$ to produce SH$^+$ and H$^+$ amongst other possible exothermic channels. Again, some energy input is required to form S$^{++}$, which can be due to X rays but cannot be provided by UV photons, as the ionization energy of S$^+$ is larger than 23eV.

The dissociative recombination rate coefficient of SH$^+$ has not been studied either theoretically nor experimentally. The usually assumed reaction rate coefficient of $2 \times 10^{-7}$ (T/300)$^{-0.5}$ cm$^3$ s$^{-1}$ needs to be checked. We may point out that this value is significantly larger than the DR rate coefficient of OH$^+$ ($0.375 \times 10^{-7}$ (T/300)$^{-0.5}$ cm$^3$ s$^{-1}$) and NH$^+$ ($0.43 \times 10^{-7}$ (T/300)$^{-0.5}$ cm$^3$ s$^{-1}$), as given in [17]. An even smaller value, $(6.3 \pm 0.7) \times 10^{-9}$ (T/300)$^{-0.48}$, of the OH$^+$ DR rate has been calculated theoretically by Guberman [18]. We have displayed in Fig 3 the column density ratios of SH$^+$/CH$^+$ as a function of SH$^+$/HCO$^+$ and SH$^+$/c-C$_3$H$_2$ given in [14]. We see that SH$^+$/CH$^+$ is always smaller than 1 except in one case, which occurs, however, for an average value of the other ratios but is somewhat larger than the elemental sulfur to carbon ratio. Values of SH$^+$/HCO$^+$ span a range between 0.1 and 2.5, whereas SH$^+$ is almost always larger than c-C$_3$H$_2$. The chemical significance of these data is not clear yet.

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6. References
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