Dissociative Recombination Data Needs for the Aeronomy Community

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Abstract.
We discuss here the dissociative recombination (DR) reactions that are of importance to various processes in the thermospheres/ ionosphere of the earth and planets, the data required to model these processes, and the desired format for these data. DR may be important for the chemistry of thermospheres/ionosphere, both as a loss process for ions and a production mechanism for minor neutrals. These neutrals may be metastable species that can participate in reactions not available to ground state species, or they may radiate, producing airglow or cooling. Because DR reactions are usually highly exothermic, they can also contribute to neutral heating. If the DR reactions are produced high enough in the atmosphere of a body with a small gravity well, the energetic neutrals formed can contribute to escape of species from the atmosphere, to the isotope fractionation of the escaping atoms, and thus to atmospheric evolution.

1. Introduction

The thermosphere and exosphere are the outermost regions of a planetary atmosphere. In the thermosphere, the neutral temperature increases with altitude above the mesopause, usually the coldest region of a planetary atmosphere, and eventually reaches a constant value, the exospheric temperature $T_\infty$. The lower E and the upper F region above it are usually superimposed on the thermosphere and exosphere, and are characterized by the presence of simple (non-cluster) positive ions and free electrons. The F and E regions are formed by ionization of the constituents by photons in the main part of the solar EUV (100-1000Å), and by soft x-rays (10-100 Å), respectively. The D-region is below the E region, and its origin is absorption of hard x-rays, those with wavelengths less than 10 Å, and, on the Earth, by photoionization of NO by the solar Lyman-α line, which penetrates to low altitudes because of an accidental “window” in the Schumann-Runge continuum of O$_2$. The terrestrial D region is formed also by the absorption of cosmic rays. Where three-body collisions are important, cluster ions are formed, and free electrons are replaced by negative ions. At low altitudes, in addition to forming cluster ions, photoionization or charge transfer to meteoric atoms (e.g., Si, Fe, Mg, Ca, Na), when present, can take place (e.g., Plane [1]; Grebowski et al. [2]).

In the E and $F_1$ regions, the major ions are molecular, and are destroyed by mainly by DR. For the minor molecular ions, ion-molecule reactions compete with DR as a loss process. In both regions photochemical equilibrium prevails, which means the direct and chemical production rates of the ions are equal to the local chemical loss rates. Above the $F_1$ region is the $F_2$ region, where the major ions are atomic. Above the $F_2$ peak, the major atomic ion loss process is downward transport, and below the peak the atomic ions are destroyed in ion-molecule
reactions. Molecular ions in this region, however, may be destroyed mainly by DR. Figure 1 from Bauer [3] shows the regions of the terrestrial ionosphere, and the major sources of ions in the various regions. These regions, while present on the dayside of all planets or satellites that have sufficiently dense atmospheres, may be smaller or larger, more or less important, or even “invisible” to some extent.

![Figure 1](image)

**Figure 1.** Electron density as a function of altitude that illustrates the regions of a planetary ionosphere by reference to the terrestrial ionosphere. The major sources of ions are also shown. Figure 48 from Bauer [3], reprinted with kind permission from Springer Science+Business Media.

In addition to its role as a loss process for molecular ions, DR is important in the $E$ and $F$-regions of planetary ionospheres for several reasons, including as a production mechanism for minor neutral species. Because of the large exothermicity of simple DR reactions, the neutral atoms and fragments produced may be electronically excited; these species may be metastable, and go on to participate in reactions that are not available to ground state species; they may also radiate, producing airglow emissions and cooling. Because the products of DR reactions are neutral fragments, DR may also contribute to neutral heating to a greater extent than ion-molecule reactions, for which the exothermicity heats both the ions and the neutral products. We have discussed the role of DR in thermospheric heating in detail previously (Fox [4]), so here we confine our comments to the data needed to determine it. When DR occurs in the upper thermospheres or exospheres of planets or satellites with small gravity wells, such as Mars or Titan (but not Earth or Venus), the energetic neutrals produced in DR may escape from the atmosphere, thus contributing to atmospheric evolution. In addition, there is usually an isotope fractionation factor inherent in the DR mechanism, which operates in addition to that produced by the different altitude distributions of the molecular ion isotopomers (e.g., Fox and Hač [5]). Escape of atoms and isotope fractionation operating over the last 3.8 Gyr (the non-catastrophic period of planetary evolution) may be expected to cause the isotope ratios in these atmospheres to evolve so that they are currently different from the terrestrial values. We describe here the data needs to describe these processes and the format that is suitable for modeling.

2. **Identifying ions for which DR is important for studies of ion chemistry**

In oxidizing ionospheres, such as those of Venus, Earth and Mars, DR is important as a loss process mainly for the “terminal ions”, which are, in general, those whose parent neutrals have
low ionization potentials (IP’s). Table 1 shows some IP’s for atmospheric species. In most ion-molecule reactions ionization flows from species whose parent neutrals have high ionization potentials to those whose parent neutrals have low ionization potentials. This is just a simple restatement of the requirement that reactions must be exothermic, and is rigorously true only for charge transfer reactions. Figure 2 illustrates a portion of the ion chemistry of oxidizing atmospheres, where the neutral species are at the top and the ions, labeled and ordered by the IP of the parent neutral, are below. The ion-neutral reactions that interchange the ions are illustrated by the arrows. Most of the arrows in this diagram point downward, although a few reactions do not follow this “rule”, such as the reaction of C$^+$ (IP$\text{C}$=11.26 eV) with CO$_2$ to produce CO$^+$ (IP$\text{CO}=14.01$ eV):

$$C^+ + CO_2 \rightarrow CO^+ + CO + 2.90 \text{ eV}. \quad (1)$$

This reaction is exothermic because of the very large binding energy of CO, 11.11 eV.

**Figure 2.** Summary of part of the ion chemistry on the terrestrial planets. The species in the top row enclosed by circles are the neutral species from which ions in the squares are formed. Each ion is labeled by the IP of its parent neutral, and its vertical position indicates the relative values of its IP. In the presence of sufficient neutral densities the ions are transformed from those whose parent neutrals have high IP’s (near the top) to those whose parent neutrals have low IP’s (near the bottom). Therefore the ionization tends to flow downward.

Thus, although there are many production mechanisms for NO$^+$ (IP$_{\text{NO}}=9.76$ eV) and O$_2^+$ (IP$_{\text{O}_2}=12.07$ eV) in the ionospheres of Venus, Earth and Mars (hereafter the terrestrial planets), there are few loss processes. Where collisions are sufficient, the terminal molecular ions are expected to be O$_2^+$ and NO$^+$, which are then destroyed mostly by DR. In fact, loss of NO$^+$ in the E and F regions is *only* by DR, although in the lower D regions, where the neutral number
densities are large enough, NO$^+$ may form cluster ions, for which the DR rate coefficients may be necessary, by three-body recombination, or charge transfer to metal atoms (e.g., Mg, Fe, Ca, Na) and Si that are produced by ablation of meteors. The latter process usually occurs in a very narrow region, about 10 km in width, at pressures greater than 1$\mu$bar for the terrestrial planets. Table 1 shows that these species have very low IP’s.

Although O$_2$ is abundant in the terrestrial lower thermosphere, we note here that the presence of O$_2^+$ is not evidence for the presence of large abundances of O$_2$; nor is the presence of NO$^+$ evidence for large abundances of NO. Both neutral species are present in the thermospheres of Mars and Venus in only trace amounts; the major neutral species are CO$_2$ at low altitudes and O at high altitudes. High solar activity models of the Martian thermosphere and ionosphere are shown in Figure 3.

Figure 3. High solar activity models of the Martian thermosphere/ionosphere for 60° solar zenith angle. (left) Density profiles of the neutral species as a function of altitude included in the model. (right) Density profiles of important ions over the same altitude range.

The major sources of O$_2^+$ in the ionospheres of Venus and Mars are the reactions

$$\text{CO}_2^+ + \text{O} \rightarrow \text{O}_2^+ + \text{CO} \quad (2)$$

and

$$\text{O}^+ + \text{CO}_2 \rightarrow \text{O}_2^+ + \text{CO}. \quad (3)$$

Charge transfer reactions of ions to O$_2$ are negligible as sources of O$_2^+$. The major source of NO$^+$ on Venus and Mars is

$$\text{O}_2^+ + \text{N} \rightarrow \text{NO}^+ + \text{O}, \quad (4)$$

whereas the major source on Earth is

$$\text{N}_2^+ + \text{O} \rightarrow \text{NO}^+ + \text{N} \quad (5)$$

along with a few other ion-molecule reactions. Charge transfer reactions of ions to NO make up less than 10% of the production of NO$^+$ on Mars. Thus, even if we neglected the ambient NO and O$_2$ densities and charge transfer reactions for these two species, we would still predict fundamentally the same density profiles for O$_2^+$ and NO$^+$.

As shown in Table 1, the IP’s of N$_2$ and H$_2$ are large, 15.58 and 15.43 eV, respectively. This means that there are few production mechanisms for N$_2^+$, but many loss mechanisms. DR is not
important as a loss mechanism for \( \text{N}_2^+ \) or \( \text{H}_2^+ \) in the major regions of ionospheres, although it may be important at high altitudes. For example, DR becomes important as a loss process in the terrestrial ionosphere for \( \text{N}_2^+ \) only near and above an altitude of about 240 km, which is well above the \( F_1 \) peak, which appears at \( \sim 170 \) km (e.g., Dalgarno and Fox [6]). For the Mars model shown in Figure 3, the loss of \( \text{N}_2^+ \) by DR becomes important as a chemical loss mechanism in the region above \( \sim 300 \) km, but it is never dominant.

### Table 1. Ionization Potentials of Some Species Relevant to Planetary Atmospheres

| High \( I_P \) Species | Medium \( I_P \) Species | Ionized by Ly \( \alpha \) Species |
|------------------------|-------------------------|-------------------------------|
| \( \text{He} \) 24.59  | \( \text{H}_2\text{O} \) 12.61 | \( \text{C}_4\text{H}_2 \) 10.18 |
| \( \text{Ne} \) 21.56  | \( \text{CH}_4 \) 12.51 | \( \text{CH}_3 \) 9.84 |
| \( \text{Ar} \) 15.76  | \( \text{SO}_2 \) 12.32 | \( \text{C}_3\text{H}_6 \) 9.73 |
| \( \text{N}_2 \) 15.58  | \( \text{CH}_3\text{CN} \) 12.194 | \( \text{NO} \) 9.264 |
| \( \text{H}_2 \) 15.43  | \( \text{C}_2 \) 12.11 | \( \text{C}_6\text{H}_6 \) 9.246 |
| \( \text{N} \) 14.53  | \( \text{O}_2 \) 12.07 | \( \text{C}_2\text{H}_3 \) 8.9 |
| \( \text{CO} \) 14.01  | \( \text{C}_2\text{H} \) 11.7 | \( \text{Si} \) 8.152 |
| \( \text{CO}_2 \) 13.77  | \( \text{HC}_3\text{N} \) 11.64 | \( \text{C}_2\text{H}_5 \) 8.13 |
| \( \text{O} \) 13.618 | \( \text{C}_2\text{H}_6 \) 11.52 | \( \text{HCO} \) 8.10 |
| \( \text{H} \) 13.598 | \( \text{C}_2\text{H}_2 \) 11.40 | \( \text{N}_2\text{H}_4 \) 8.10 |
| \( \text{HCN} \) 13.60 | \( \text{C} \) 11.26 | \( \text{C}_3\text{H}_7 \) 8.09 |
| \( \text{OH} \) 13.00 | \( \text{C}_3\text{H}_8 \) 10.95 | \( \text{Fe} \) 7.87 |
| \( \text{CH} \) 10.64 | \( \text{Mg} \) 7.65 |
| \( \text{C}_2\text{H}_4 \) 10.51 | trans-HCNH 7.0^b |
| \( \text{H}_2\text{S} \) 10.45 | cis-HCNH 6.8^b |
| \( \text{CH}_2 \) 10.396 | c-C_3H_3 6.6 |
| \( \text{S} \) 10.35 | Ca 6.11 |

\(^a\) Computed with data from Lias et al. [8], except as noted.  
\(^b\) From Nesbitt et al. [9]

Titan has an atmosphere of intermediate oxidation state, and the outer planets, Jupiter, Saturn, Uranus, and Neptune all have reducing atmospheres. In these atmospheres, the terminal ions are generally those whose parent neutrals have large proton affinities (PA’s). Some PA’s are shown in Table 2, and a large compendium of PA’s can be found in Hunter and Lias [7]; see also Lias et al. [8]). Proton transfer reactions tend to be fast, near gas-kinetic (e.g., Su and Bowers [10]), and many (but not all) of the ion-neutral reactions in reducing atmospheres are proton transfer reactions from a species whose parent neutral has a lower PA to another species whose parent neutral has a higher PA. Just as for ionization, the route to the protonated species need not be a proton transfer reaction. Therefore, the existence of a protonated neutral does not imply the existence of a large abundance of the parent neutral in the planetary thermosphere.

In the thermosphere of Titan (above about 1000 km), the major species is \( \text{N}_2 \) with a small admixture of \( \sim 2.2 \% \) \( \text{CH}_4 \) and 0.4 \%\( \text{H}_2 \) (e.g., Cravens et al. [11] and the references therein). The formation of ions in the ionosphere of Titan is initiated by photoionization and/or energetic electron-impact ionization of the major species. The energetic electrons may either be photoelectrons, or they may originate from the magnetosphere of Saturn. The dominant
ions produced are N$_2^+$ and N$^+$, with small amounts of CH$^+_4$ and ion fragments produced from dissociative ionization of methane. In regions where the neutral densities are large, near the F$_1$ ion peak, the major ions produced are transformed by dissociative charge transfer and H atom transfer as well as proton transfer. For example, the following reactions have been found to have large rate coefficients:

\[
\begin{align*}
N_2^+ + CH_4 & \rightarrow CH_2^+ + N_2 + H_2, \\
& \rightarrow CH_3^+ + N_2 + H, \\
& \rightarrow N_2H^+ + CH_3, 
\end{align*}
\] (6a)

where (6b) is the dominant channel (McEwan et al. [12]). Because the proton affinity of CH$_2$ is about 8.56 eV, and that of CH$_4$ is 5.63 eV, the proton transfer reaction from CH$_3^+$ to CH$_4$, is highly endothermic. The reaction:

\[
CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2
\] (7)

is, however, fast and exothermic and results in the formation of a higher hydrocarbon ion [13]. Proton transfer reactions transform ions within groups but will not significantly increase the size of an ion. Such reactions are, of course, also limited by the availability of the neutrals to which the proton can transfer. The resulting mix of ions is, however, dominated by ions with high proton affinities.

Figure 4 shows a mass spectrum from near the peak of the Titan ionosphere recorded by the ion and neutral mass spectrometer (INMS) on the Cassini Huygens probe for three altitudes (Cravens et al. [14]). The mass/charge ratios range from 1 (H$^+$) to 99.5 (probably C$_8$H$^+_3$). The limit of the INMS instrument is 99.5 Daltons, and larger ions are present, which have been measured up to 200 Daltons by the Cassini Plasma Spectrometer (Crary et al. [15]). The ions appear to be clustered around masses that are separated by 12–14 Daltons, which represents the addition of a C or N to species in the previous cluster. In general PA’s increase with the size of the parent neutral, although the increase is not monotonic. The addition of an N atom seems to increase the PA of a hydrocarbon/nitrile molecule. The most important ions for which DR is important as a loss mechanism are the “terminal” ions in each mass group. The terminal C$_i$N$_j$H$_k^+$ species, where $i$, $j$, and $k$ are integers, that are observed appear to be those in which the parent species is a moderately unsaturated stable molecule. The DR of these large ions could be the source of large neutral hydrocarbons and nitriles that eventually form the ever-present hazes and “soot” in the lower atmosphere.

In the atmospheres of Titan and the outer planets, and at high altitudes on the terrestrial planets, H$_2^+$ may be formed by ionization of H$_2$ or, theoretically, by protonation of H. H, however, has a very small PA (2.69 eV), and there are few species with smaller PA’s (Table 2). Moreover, H$_2$ has a large IP. H$_2^+$ therefore reacts with almost any species with which it collides, including H$_2$ and H in the upper thermosphere, and with many other species present at lower altitudes. It is therefore never expected to be a terminal ion in planetary atmospheres, although Lundin et al. [16] have identified the mass-2 ion in outflow from Mars with the European Mars Express Ion Mass Analyzer as H$_2^+$.

The data that are needed to understand the loss of ions and the production of minor neutrals in the E and F$_1$ regions of ionospheres are the DR coefficients for the predicted terminal ions as a function of electron temperature, where $T_e$ ranges from ~ 100 to 5000 K. The ion temperature ($T_i$) is usually also elevated above that of the neutral temperature in the region above the peak, but its value is generally less than $T_e$. There is, of course an exception to this rule: on the nightside of Venus, anti-sunward flowing ions are accelerated by the plasma gradient force to supersonic speeds and form a shock near 150° solar zenith angle, which elevates $T_i$ above that of $T_e$ (e.g., Miller and Whitten [17]).
In order to model the formation of minor neutrals in ionospheric DR reactions, a different branching ratio for each channel is required. This is because each channel is inserted into a model as a separate reaction. Total yields of the atomic or fragment species produced in DR of a molecular ion are interesting quantities, but are useless for modeling.

Electrons are replaced by negative ions in the lower ionospheres of Earth and Titan. On the Earth, the transition from electrons to negative ions appears at about 75–80 km. (e.g., Narcisi et al., [18]). On Titan, near 1000 km, the masses of the negative ions are found to range from 6 to 5000 Daltons (e.g., Vuitton et al. [19]). In order to model these regions, recombination mechanisms for negative ions, such as mutual neutralization, or associative detachment are required. The terminal ions are, of course, those with high electron affinities.

3. Neutral heating
Since we have discussed thermospheric heating due to DR reactions in a previous DR monograph (Fox [4]), we will confine our remarks to those here. DR reactions tend to be highly exothermic, especially those of diatomic ions. The exothermicity is deposited in the neutral atomic products as electronic and translational energy. For polyatomic molecular ions, the molecular fragments produced may also be vibrationally excited. Although these fragments may be excited rotationally as well, where there are sufficient collisions, rotational excitation is more readily transformed into heat than is vibrational excitation. The DR coefficients for the largest of these ions at room temperature are of the order of a few \(10^{-6} \text{ cm}^3 \text{s}^{-1}\), about an order of magnitude larger than those of smaller ions (e.g., McLain et al. [20]; see also the review by Florescu-Mitchell and Mitchell [21]). In order to determine the heating rate due to DR reactions, in addition to DR coefficients for the various product channels as a function of \(T_e\), we need measurements (or even estimates!) of the energy that is deposited as electronic, vibrational, rotational and translational excitation of molecular fragments.

4. The production of metastable and radiating states of fragments in DR
Electronically excited states of the atoms or fragments produced in DR may radiate to lower energy levels producing airglow emissions, or survive to participate in reactions that are not available to ground state species. A familiar example of atomic products for which both phenomena are important is the DR of \(\text{O}_2^+\), which may proceed via 4 different channels, with
The exothermicities shown are for $O_2^+$ in the ground electronic, vibrational and rotational states, at zero collision energies, and they do not include the fine structure levels of the product $O(^3P)$ atoms. The DR of $O_2^+$ thus produces $O(^1D)$, which may radiate, giving rise to the visible $O$ ($^1D \rightarrow ^3 P$) red doublet at 6300, 6364 Å with a lifetime of $\sim 120$ s. Since the species is metastable, it may survive to participate in reactions that are not available to ground state $O(^3P)$, and it is also easily quenched. The $O(^1S)$ state has a radiative lifetime of less than 1 s, and is more likely to radiate to either the $O(^1D)$ state, producing the 5577 Å green line, or to the ground $O(^3P)$ state, producing the 2972 Å emission line. The ratio of these lines is determined by the ratio of the transition probabilities, which has been calculated to be about 16 (e.g., Froese-Fischer and Tachiev [22]). This ratio, however, has been questioned by several

Table 2. Selected Proton Affinities (eV)

| Neutral Species | Ion Produced | Proton Affinity | Neutral Species | Ion Produced | Proton Affinity |
|-----------------|--------------|-----------------|-----------------|--------------|-----------------|
| He              | HeH$^+$      | 1.84            | H              | H$^+_1$      | 2.69            |
| N               | NH$^+$       | 3.37            | Ar             | ArH$^+$      | 3.82            |
| H$_2$           | H$_2^+$      | 4.39            | O$_2$          | HO$_2^+$      | 4.40            |
| CO              | COH$^+$      | 4.74            | O              | OH$^+$       | 5.04            |
| N$_2$           | N$_2$H$^+$   | 5.13            | CN             | HCN$^+$      | 5.36            |
| CH$_3$          | CH$_3$H$^+$  | 5.62            | CH$_4$         | CH$_4^+$     | 5.63            |
| CO$_2$          | CO$_2$H$^+$  | 5.67            | NO             | HNO$^+$      | 5.69            |
| C$_2$N          | C$_2$NH$^+$  | 5.75            | CN             | HNC$^+$      | 5.80            |
| OH              | H$_2$O$^+$   | 6.16            | CO             | HCO$^+$      | 6.16            |
| C$_2$H$_6$      | C$_2$H$_7^+$ | 6.23            | C$_3$H$_5$     | C$_3$H$_5^+$ | 6.42            |
| C               | CH$^+$       | 6.46            | C$_3$H$_8$     | C$_3$H$_8^+$ | 6.50            |
| NH              | NH$_2^+$     | 6.62            | C$_2$H$_2$     | C$_2$H$_2^+$ | 6.69            |
| C$_2$           | C$_2$H$^+$   | 6.92            | C$_3$H$_7$     | C$_3$H$_7^+$ | 7.03            |
| C$_2$H$_4$      | C$_2$H$_5^+$ | 7.05            | H$_2$O         | H$_2$O$^+$   | 7.24            |
| HCN             | HCN$^+$      | 7.46            | C$_3$H$_3$     | C$_3$H$_3^+$ | 7.56            |
| HN$_3$          | H$_2$N$^+$   | 7.76            | CH$_3$CCH      | CH$_3$CCH$^+$ | 7.78          |
| C$_4$H$_2$      | C$_4$H$_3^+$ | 7.79            | c-C$_3$H$_6$   | (c-C$_3$H$_6$)H$^+$ | 7.80 |
| C$_3$N$_2$      | C$_3$N$_2$H$^+$ | 7.81      | C$_2$H         | C$_2$H$_2^+$ | 7.95            |
| NH$_2$          | NH$_3^+$     | 8.13            | HNC            | HCN$^+$      | 8.14            |
| CH$_3$CN        | CH$_3$CNH$^+$| 8.18            | CH$_2$CHCN     | CH$_2$CHCN$^+$ | 8.23 |
| CH$_2$          | CH$_2$H$^+$  | 8.56            | NH$_3$         | NH$_3^+$     | 8.85            |
| N$_2$H$_4$      | N$_2$H$^+$   | 8.87            | CH$_3$NNCH$_3$ | CH$_3$NNCH$_3^+$ | 8.97 |
| CH$_3$CHNH      | CH$_3$CHNH$^+$ | 9.15    | CH$_2$CHNH$_2$ | CH$_3$CHNH$_2^+$ | 9.37 |
| CH$_2$NCH$_3$   | CH$_2$NHCH$_3^+$ | 9.41    |

$^a$ Computed from data taken from Hunter and Lias [7].
investigators who have measured the emissions in the airglow and aurorae, and a ratio of $9 - 10$ has been proposed (e.g., Slanger et al. [23] and references therein). The green line has been detected in the nightglow of Venus (Slanger et al. [24]), but the identification of the mechanism for its production is not yet secure. Possible sources of $O(\ ^1S)$ in the nightglows of the terrestrial planets include not only DR of $O_2^+$ (the ionospheric source) but also a mesospheric source that begins with the three body recombination of $O$ atoms to produce $O_2$ in an excited state (denoted by an asterisk)

$$O + O + M \rightarrow O_2^* + M,$$

followed by excitation transfer to $O$

$$O_2^* + O(\ ^3P) \rightarrow O_2 + O(\ ^1S)$$

in the so-called Barth mechanism [25].

The branching ratios for the various channels of $O_2^+$ DR have been measured by Kella et al. [26] for a relaxed vibrational distribution and for an extended vibrational distribution. Peverall et al. [27] measured the DR coefficient and branching ratios for DR of $O_2^+$ in the ground vibrational and electronic state at several electron energies from 0 to 300 meV. The results shows that the branching ratios are somewhat oscillatory, and therefore difficult to convert to an electron temperature dependence. More recently, Petrignani et al. [28] measured the branching fractions as a function of electron energy from 1 to 281 meV for $O_2^+$ in the vibrational ground state. The results do not appear to agree with those of Peverall, except for channel (8b), which usually has the largest yield. Those for the production of channel (8d) are the smallest, and the agreement is fair, but the yield for a collision energy of 10 meV is 2%, whereas the measurements of Peverall et al. show the yield at 11.4 and 22 meV as zero. Petrignani et al. [28] did not measure the yields in this range.

The differences between the various measurements are difficult for modelers to ascertain or interpret; it is also difficult to determine the branching ratios as a function of $T_e$, especially when the largest collision energy is of the order of 300 meV. Of course, the measurements may be interpolated, extrapolated and then convolved with a Maxwell-Boltzmann distribution to give an electron temperature dependence, but doing so requires making the assumption that it is proper to do so. It would be better for the original investigators to carry out this exercise, in order to convert their results into a form that could be used by atmospheric modelers. Moreover, the applicability of the data to atmospheres is questionable when the measurements are confined to $O_2^+$ ($v = 0$). Models have shown that $O_2^+$ is vibrationally excited in the thermospheres of Venus, Mars, and Earth (e.g., Fox and Hać [29,5] and references therein).

Petrignani et al. [30] reported the branching fractions and cross sections for DR of $O_2^+$ in vibrational levels $v = 0, 1, 2$ at zero collision energy. They showed that the branching ratio for production of $O(\ ^1S)$ (channel (8d)) is greatly enhanced for vibrationally excited $O_2^+$, although the cross section decreases as a function of vibrational level. Thus, there is clearly an abundance of data relating to DR of $O_2^+$, but in practice the available data are difficult to incorporate into models in which there are simultaneous variations in both $T_e$ and in the vibrational distributions. Again, modelers require DR coefficients for each channel as a function of $T_e$ and vibrational level simultaneously. Only when these data are available will it be possible to reliably predict the production rates of $O(\ ^1D)$ and $O(\ ^1S)$, the heating due to the DR reaction, the emission rates of the red, green and 2972 Å lines, and the escape rates or coronal populations of $O$ atoms.

### 5. Excited electronic states of CO in CO$_2^+$ DR

DR of CO$_2^+$:

$$CO_2^+ + e \rightarrow CO(X^1\Sigma^+) + O(\ ^3P) + 8.32 \text{eV}$$

(11)
is sufficiently exothermic to produce CO in excited electronic states, including $A^{1}\Pi$ state, which is the upper level of the CO Fourth Positive bands, and the $a^{3}\Pi$ state, which radiates to the ground state in the CO Cameron band system. The Cameron bands are the brightest features in the UV dayglows of Mars and Venus. Jongma et al. [31] found that the radiative lifetime of the CO($a^{3}\Pi, v = 0, J = 1$) state is about 3 ms. DR of CO$_2^+$ may also produce CO in the excited triplet states $a^3\Sigma^+, d^3\Delta,$ and $e^3\Sigma^-$, which may cascade into the CO($a^3\Pi$) state in the Asundi, Triplet, and Herman band systems, respectively. The branching ratios for production of excited states of CO are not well known, but it is clear that a significant fraction of the CO fragments are formed in excited states. Experimental identification of the branching ratios for the various excited states has not even begun to converge. Gutcheck and Zipf [32] found that 5\% of the dissociative recombinations of CO$_2^+$ produce the CO($A^{1}\Pi$) state, while Tsuji et al. [33] suggested that this state is populated only 0.33\% of the time. Wauchop and Broida [34] reported that 55\% of the recombinations of CO$_2^+$ form CO in the $a$ state, 0.8\% in the $d$ state, and 0.04 in the $a'$ state. Skrzypkowski et al. [35] found that the yield of CO($a^3\Pi$) was 29\%, including cascading from the higher triplet states. Further studies showed that the yields of the $a'$, $d$ and $e$ states were approximately 18, 20, and 0.3\%, respectively, and therefore about 38\% of the total CO($a^3\Pi$) yield is due to cascading (Rosati et al. [36]). Tsuji et al. [37] suggested that the yields of the $a'$, $d$ and $e$ excited triplet states in DR of CO$_2^+$ are 60\%, 40\% and 0.83\%, thus producing Cameron band emission 100\% of the time. In order to compute the emission rates of the Cameron bands and Fourth Positive bands in the dayglows of Mars and Venus, we need some consensus for the branching ratios for these excited states. Because of an accidental resonance of the solar Lyman alpha line with the (14,0) band of the CO Fourth Positive system, fluorescent scattering of the solar Lyman alpha line leads to emission in the (14,$\nu''$) progression (e.g., Durrance et al. [38]). Although this progression dominates the Fourth Positive emission in the airglow of Venus, and to a lesser extent in the airglow of Mars, other bands in the fourth positive spectrum may arise from DR of CO$_2^+$, if the yield is large. Therefore, studies of the aeronomy of Venus and Mars would benefit from accurate determinations of the absolute yields of excited states of CO from CO$_2^+$ DR, the measurements of which currently conflict.

6. DR and escape of species from light bodies

Bodies that have substantial atmospheres and small gravitational wells, such as Mars, Titan, Triton, and Pluto, are subject to escape of heavy atoms and molecules. The escape may be thermal (Jeans escape and hydrodynamic escape), or non-thermal. Non-thermal escape may be physical, such as pickup ion escape, sputtering, or ion outflow (cf., Fox [39] and references therein). Photochemical escape includes photo- and electron-impact processes, such as dissociation and dissociative ionization, and exothermic reactions that occur at high altitudes, including DR. For example, on Mars, even though DR of N$_2^+$ is not important for determining the ion density, it is important as an escape mechanism for N. We have discussed this in detail in previous DR proceedings (e.g., Fox [4], and references therein).

For estimates of the escape due to DR, aeronomers need not only the rate coefficients, but the branching ratios of the various channels, and the variation of these parameters with $T_e$. For DR of homonuclear diatomics, such as O$_2^+$ and N$_2^+$, vibrationally resolved rate coefficients and branching ratios are required. DR coefficients for vibrationally excited heteronuclear ions such as NO$^+$ and CO$^+$ are interesting, but are not relevant to planetary atmospheres, since these molecular ions relax radiatively before they recombine. For example, the radiative lifetime of vibrational levels of NO$^+$ $v = 1$ to $v = 5$ have been measured by Wytttenbach et al. [40], and the values have been found to decrease from 90 ms to 19 ms. The lifetime of NO$^+$ against DR near the peak electron density at $\sim 135$ km for the Martian high solar activity model shown in Figure 3 is $\sim 13$ s, that near 100 km is $\sim 38$ s, and that near 200 km is $\sim 104$ s. Therefore there is ample time for vibrationally excited NO$^+$ to radiate to the ground state over the entire thermosphere.
before it can undergo DR. NO$^+$ may also be vibrationally quenched, and an estimate of the lifetime against this process is about 0.2 s at 100 km, where quenchers are abundant. Models of the NO$^+$ density and the production of translationally and electronically excited N$(^2D)$ atoms require DR coefficients that pertain to the ground vibrational and electronic states of the ions.

7. Isotope effects

Because DR processes may be isotope dependent, data for the analogous processes for the common isotopomers are also needed. Kella et al. [41, 26] measured the branching ratios for DR of $^{15}$N$^{14}$N$^+$ and $^{18}$O$^{16}$O$^+$ in ion storage ring experiments. In some of these studies, the heteronuclear isotopic species are used rather than the homonuclear species $^{14}$N$^{14}$N$^+$ and $^{16}$O$^{16}$O$^+$, because they are more likely to relax radiatively before undergoing DR. Guberman [42], however, carried out calculations of the DR coefficients for production of O$(^1S)$ (channel (8d)) from $v = 0$ of the $X^2Π_{1/2}$ state for $^{18}$O$^{16}$O$^+$ and $^{16}$O$^{16}$O$^+$. He reported that the DR coefficient of the isotopomer exceeds that of the more common species homonuclear ion over the $T_e$ range from about 100 to 3000 K, by a factor which ranges from $\sim 1.4$ to $\sim 2.6$. Thus the use of isotopomers as proxies for the homonuclear species is apparently questionable to an extent that is unknown, but should be measured.

The relative escape rates of $^{18}$O and $^{16}$O (as well as $^{15}$N and $^{14}$N, and $^{13}$C and $^{12}$C) are important to the evolution of the Martian atmosphere. Dissociative recombination of O$^+_2$ is probably the most important escape mechanism for O in the Martian atmosphere at the current epoch. DR of O$^+_2$ is sensitive to vibrational excitation, both through changes in the rate coefficients, and in the branching ratios of the channels, for which there is conflicting data, as we have discussed above. Fox and Hać [5] have carried out a computation of the vibrational distribution on Mars as a function of altitude for both $^{32}$O$^+_2$ and $^{34}$O$^+_2$, and the results are shown in Figure 5. It is clear that $^{32}$O$^+_2$ is vibrationally excited for altitudes above about 180 km, but that $^{34}$O$^+_2$ is found to be overwhelmingly in the $v = 0$ ground state over the range from about 80 to 400 km. Because collisions are frequent at the lower altitudes, the vibrational levels of both isotopes are in equilibrium with the local thermospheric temperature, which ranges from about 130 to 250 K from 80 to 160 km. At higher altitudes radiative decay of the isotopic species limits the ion to mostly $v'' = 0$. The radiative lifetimes of levels $v'' = 1$–10 have been computed to range from 25.06 to 3.29 s (Amitay et al. [43]).

In addition to the different vibrational distributions, there are small differences in the energies of the O atoms produced in DR in the center-of-mass frame. In DR of $^{16}$O$^{16}$O$^+$, the $^{18}$O carries away a fraction 16/34 of the total energy released, whereas in DR of $^{16}$O$^{16}$O$^+$, the $^{16}$O carries away half the energy. The exothermicities of the $^{32}$O$^+_2$ channels (8) differ from those of $^{32}$O$^+_2$ by only $\sim 0.02$ eV, which is much smaller than the other uncertainties in the model. The computed nascent kinetic energy distributions and the escape energies of $^{18}$O and $^{16}$O due to DR of O$^+_2$ for the two isotopes at four altitudes are shown in Figure 6.

There is an isotope effect of a factor of 2 in DR reactions simply because there is one $^{18}$O atom produced in DR of $^{18}$O$^{16}$O$^+$, but there are two $^{16}$O atoms produced in DR of $^{16}$O$^{16}$O$^+$. In addition, the escape energy of an $^{18}$O is larger than that of a $^{16}$O atom. We have carried out Monte Carlo calculations of the escape probabilities of both isotopes, in which we follow the energetic O atoms from their altitude of production from collision to collision until they either escape or their velocity falls below the escape velocity. We modeled the escape processes for two assumptions about the differential cross sections in the center-of-mass frame. In the first model, the scattering is assumed to be isotropic, and in the second model, the scattering is strongly forward peaked. We have also compared our results to the exobase approximation. The exobase is the boundary of the “collisional” and the “collisionless” regions of the atmosphere. In the exobase approximation all atoms produced above the exobase, with velocity vectors oriented in the upward hemisphere, and with magnitudes greater than the escape speed, are
Figure 5. Computed fractional population of $^{32}\text{O}_2^+$ vibrational levels, $v = 0$, 1, 2, 3, 4, and 5 as a function of altitude from 80 to 400 km (solid curves). The fraction of $^{34}\text{O}_2^+$ in $v = 0$ is shown with a dashed curve. From Fox and Hać [5].

Figure 6. Examples of nascent energy spectra of $^{16}\text{O}$ (solid curves), and $^{18}\text{O}$ (dotted curves) due to DR of $^{32}\text{O}_2^+$ and $^{34}\text{O}_2^+$ for the high solar activity model at four altitudes. The panels are labeled by the altitudes. Also shown as vertical solid and dotted lines are the escape energies of the two isotopes. From Fox and Hać [5].

assumed to escape. The exobase approximation has been used extensively in the past, but is now outdated; the transition from collisional to collisionless conditions occurs gradually. We consider the forward scattering model to be superior to either the isotropic model or the exobase approximation.

In Figure 7 we show the resulting escape probabilities for $^{18}\text{O}$ and $^{16}\text{O}$ as a function of altitude
of production for the three models, and for low and high solar activity. The ratio of escape probabilities of $^{18}$O to $^{16}$O is the isotope fractionation factor inherent in the DR mechanism, and it varies from about 0.20 to 0.37 as a function of altitude for the forward scattering model. This large fractionation factor operates in addition to that which arises from the different altitude distributions of $^{18}$O$^{16}$O$^+$, and $^{16}$O$^{16}$O$^+$. Since no fractionation (within about 5%) of the Martian O isotopes with respect to terrestrial isotope ratio has been found (e.g., Owen [44] and references therein), there must be effects operating in the Martian atmosphere that act over time to reverse or dilute the isotope fractionation that arises from preferential escape of the lighter isotope. This result has implications for processes that preferentially remove $^{18}$O from the atmosphere; those due to exchange of the atmospheric isotopes of O with (large) unfractionated reservoirs of O, such as the polar caps or the regolith; the interaction of atomic O with the crust, or its incorporation into rocks.

**Figure 7.** Computed O escape probabilities as a function of altitude for isotropic, forward scattering and exobase approximations. (left) $^{18}$O escape probabilities. (right) $^{16}$O escape probabilities. Note the differences in the scales for the left and right panels. From Fox and Hač [5]

Presumably, we will find similar isotope effects for escape of N in DR of N$_2^+$. The Martian atmospheric $^{15}$N/$^{14}$N ratio is observed to be fractionated by a factor of about 1.62 with respect to the terrestrial value, due probably to preferential escape of $^{14}$N operating over billions of years. Unlike O, however, there are several photochemical escape processes operating for N in addition to N$_2^+$ DR, such as photodissociation of N$_2$. The latter process cannot be computed with low resolution cross sections, and its role in escape of N from Mars has not yet been quantified.

8. Summary
Ionospheric modelers require DR coefficients for determining the loss rate of terminal ions, and for production rates of atoms or molecular fragments. Branching ratios of the allowed channels are required, including those which produce metastable or emitting fragments. For homonuclear diatomics, there is a need for vibrationally resolved DR coefficients and branching ratios. For heteronuclear diatomic ions, the DR coefficients and branching ratios must pertain to the ion in the ground vibrational level. For isotope evolution calculations of Mars (or other bodies), modelers need DR coefficients and branching ratios for the homonuclear molecules, such as O$_2^+$ and N$_2^+$, and their isotopomers, as well as lifetimes of the vibrationally excited ions and quenching coefficients. Above all, modelers need the expertise of the DR community in resolving discrepancies in the results of different measurements and computations, providing recommendations relative to which data are most appropriate and how best to incorporate the
data into models. Rate coefficients are preferable to cross sections, and $T_e$ dependences are preferable to collision energies.

Dave Barry [45] tells a story about an incident that occurred in 2009 on the Metromover, the public transportation system in Miami. Apparently one evening two men carried a live six-foot shark onto the Metromover, with the idea of selling it to a wholesaler in downtown Miami. When the men got to their intended stop, they carried the now-dead shark onto the street, but the wholesaler declined to purchase the fish. They then left the shark on the street, where it remained for several hours before it was removed. Bystanders were apparently unconcerned about the situation, partly because they were relieved that it was a shark and not a dead body, and partly because weirder things had happened in Miami. Barry points out, however, that for a while there was a live shark on the Metromover, and “had it been a little more alive, there is a very real possibility that it could actually have bitten somebody”, which would “have been tragic”. Therefore Barry recommends that the public “exercise caution when boarding public transportation”, and further explains what he means when he says “exercise caution”: “carry a speargun”.

One might ask what this has to do with this chapter. I cannot count the number of times that experimentalists and theoreticians have admonished modelers to “use caution” in adopting DR data, but do not further explain what they mean, or make suggestions about what modelers should actually do with the apparently questionable data. The next time I see this phrase, you might see me with a spear-gun at my side as I am incorporating DR information into a model (Figure 8). Please, give me something I can use!

![Figure 8. Using caution while inputting DR data into a model.](image)

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10. References
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