Dissociative Recombination of O$_2^+$ Ions with Electrons

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Abstract. We have studied the dissociative recombination of O$_2^+$ ions with electrons at the temperature range of 100–230 K. Rate coefficients for this reaction were determined. This study has been performed using Cryo–FALP II apparatus based on a classic flowing afterglow design. Comparison with older results measured at the same temperature range is made and very good agreement across these experiments is observed, as well with the theory. Diagnostic with Langmuir probe and data evaluation is also discussed.

Introduction

O$_2^+$ ion is one of the most important ions found in Earth’s ionosphere, together with N$_2^+$ and NO$^+$ they are also called “terrestrial ions” [Larsson and Orel, 2008]. Dissociative recombination (DR) in general is a very important reaction and it is important in Earth’s atmosphere as well. It is a sink for electrons and also a source for airglows and highly reactive atoms [Guberman, 1997]. It is the only source for the green airglow in the nighttime F-region of the ionosphere. The DR reaction of O$_2^+$ is

$$\text{O}_2^+ + e^- \rightarrow \text{O} + \text{O},$$

where $\alpha$ is the recombination rate coefficient. One of the possible products, O($^1S$), is responsible for 557.7 nm green airglow when relaxing radiatively to the O($^1D$) state and when this state relaxes to the ground state, it produces the red airglow at 630.0 nm [Petignani et al., 2005; Bates, 1990].

History of the measurements of the DR of O$_2^+$ is very long with the first ones done in the late 40’s, for more details see the review: [Larsson and Orel, 2008]. The thermal rate coefficient is very well established and lies in the range from $1.7 \cdot 10^{-7}$ to $2.4 \cdot 10^{-7}$ cm$^3$s$^{-1}$. Temperature dependence of the coefficient is reported to be $\alpha \sim T^{-0.7}$ where $T$ refers to the electron temperature.

Agreement between various experiments [Kasner and Biondi, 1968; Mehr and Biondi, 1969; Johnsen, 1987; Peverall et al., 2001; McLain et al., 2004; Petignani et al., 2005] and theory [Guberman, 1979, 1997] across a wide temperature range is very good and this is one of the reason that DR of O$_2^+$ is used as a benchmark for DR studies. In afterglow experiments using Langmuir probe it is used in order to verify and calibrate the probe [Bilyk et al., 2004; Novotny, 2006].

Experiment

In this study we used Cryo–FALP II apparatus. It is based on a classic flowing afterglow with Langmuir probe (Abb. FALP) design [Mahdavi et al., 1971]. Buffer gas is flowing through a flow tube. Discharge (2.45 GHz, $\approx 20–25$ W) is ignited in a microwave cavity at the beginning of the flow tube. Downstream, reactant gas (or gases) are added and plasma decay is monitored by means of Langmuir probe, from which we can determine concentration and temperature of electrons $n_e$ and $T_e$. Position of the probe is converted into the decay time by known gas velocity [Kotrik et al., 2011].

In order to obtain the recombination rate coefficient, one has to evaluate absolute electron concentrations $n_e$ along the flow tube. This can be done with “i-squared method.” Voltage-current, or Langmuir probe characteristics (LP) are measured and $n_e$ can be calculated from the slope of a linear plot of $I^2$ vs. $V$ in the accelerating region of the characteristics [Novotny, 2006], where:

$$I^2 = \frac{2A^2q^2n_e^2}{\pi^2m_e}[k_BT_e + q(V - V_p)].$$

(2)
Figure 1. Drawing of Cryo–FALP II apparatus. Discharge is ignited in flowing He buffer gas in upstream glass section of the flow tube (A) which is kept at room temperature. Argon and oxygen are added downstream in stainless steel section which can be precooled by liquid nitrogen (B). Third section with movable Langmuir probe (C) is connected to a closed cycle helium cooler via copper braids (not displayed) and heating elements.

$A$ is the surface of the probe and $V_p$ is plasma potential. Then we can determine $n_e$ as

$$n_e = \sqrt{\frac{\pi^2 m_e}{2A^2 q^3} S},$$

(3)

where $S$ is the slope of the $I^2$ vs. $V$ plot. Plasma decay is driven by two processes—its dissociative recombination and ambipolar diffusion. Accounting quasineutrality of plasma and fact that we have only one dominant ion, time evolution of electron concentration $n_e$ can be described by the following equation [Chen, 1974]:

$$\frac{dn_e}{dt} = -\alpha n_e^2 - \frac{n_e}{\tau_D},$$

(4)

where $\alpha$ is the rate coefficient of dissociative recombination and $\tau_D$ is the characteristic time of ambipolar diffusion. If ambipolar diffusion is negligible, one can obtain $\alpha$ from the slope of the $1/n_e(t)$ vs. $t$ plot [Smith et al., 1975]:

$$\frac{1}{n_e(t)} = \frac{1}{n_e(0)} + \alpha t.$$

(5)

We use “integral analysis” for obtaining both of these coefficients, for details see [Korolov et al., 2008].

In order to study processes which occur at temperatures below 77 K, we built a new Cryo–FALP II apparatus [Kotrik et al., 2011]. It has several unique features. Firstly, the stainless steel flow tube (40 cm in length, 5 cm in diameter) is placed in an insulation vacuum ($10^{-5}$ Pa) which minimalizes heat losses of the flow tube. Secondly, the flow tube itself is covered with thick Cu braids, which are connected to a coldhead of a closed cycle helium refrigerator with cooling power of 100 W at 40 K. Directly on a coldhead there is a copper block equipped with heating patrons and required flow tube temperature can be set in the range of 40–300 K. Whole apparatus is based on UHV technology, ultimate pressure in the apparatus is in the order of $10^{-6}$ Pa and used gases are highly purified before entering the flow tube. Purification of helium is done using molecular sieves and additionally by flowing through pipe cooled by liquid nitrogen. Purification of argon and oxygen is done by flowing through pipe which is kept at $\approx 215$ K using cooled ethanol.

Flowtube itself, which can be seen in Figure 1, is divided into the three main parts. The first part (A), where microwave discharge is ignited, is kept at room temperature. The second part (B), where reactant gases are added, can be precooled by liquid nitrogen to $\approx 110$ K temperature. The third part (C) is connected to the coldhead as described above.

Discharge is ignited in a pure helium. As reactant gases argon and oxygen are used in this study. Parameters of experiment (He flow and pressure, Ar and $O_2^+$ flows) must be set carefully in order to
Concentration of O\textsuperscript{+} are displayed.

Results and Discussion

They are listed in Table 1 together with characteristic times of the reactions based on typical experimental conditions: [He] = 5 \cdot 10^{17} \text{cm}^{-3}, [Ar] = 5 \cdot 10^{13} \text{cm}^{-3}, [O_2] = 5 \cdot 10^{13} \text{cm}^{-3}, [He\textsuperscript{m}] = 1 \cdot 10^{10} \text{cm}^{-3}, n_e = 10^9 \text{cm}^{-3}, T = 230 \text{K}. When several loss processes are included for one specie, one with the smallest characteristic time is dominant.

Table 1. List of the reactions which are included in the chemical kinetics model. Characteristic times of the reactions are based on typical experimental conditions: [He] = 5 \cdot 10^{17} \text{cm}^{-3}, [Ar] = 5 \cdot 10^{13} \text{cm}^{-3}, [O_2] = 5 \cdot 10^{13} \text{cm}^{-3}, [He\textsuperscript{m}] = 1 \cdot 10^{10} \text{cm}^{-3}, n_e = 10^9 \text{cm}^{-3}, T = 230 \text{K}. When several loss processes are included for one specie, one with the smallest characteristic time is dominant.

\begin{table}[h]
\begin{tabular}{|l|l|l|}
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reaction & $\alpha$ [cm$^{-3}$s$^{-1}$]; [cm$^{-3}$s$^{-1}$] & $\tau$ [ms] \\
\hline
He$^+$ + He + He $\rightarrow$ He$^+_2$ + He & $1 \cdot 10^{-51}$ & 0.04 & [Ikezoe et al., 1987] \\
He$^+$ + Ar $\rightarrow$ Ar$^+$ + He & $1 \cdot 10^{-13}$ & 200 & [Johnsen et al., 1973] \\
He$^m$ + Ar $\rightarrow$ Ar$^+$ + He + e$^-$ & $7 \cdot 10^{-14}$ & 0.3 & [Glosik et al., 1999] \\
He$^m$ + He$^m$ $\rightarrow$ He$^+_2$ + e$^-$ & $5 \cdot 10^{-9}$ & 20 & [Urbain, 1999] \\
He$^m$ + He$^m$ $\rightarrow$ He$^+_2$ + He + e$^-$ & $1.5 \cdot 10^{-9}$ & 67 & [Deloche et al., 1976] \\
He$^+_2$ + Ar $\rightarrow$ Ar$^+$ + 2He & $2 \cdot 10^{-10}$ & 0.1 & [Ikezoe et al., 1987] \\
He$^+$ + e$^-$ $\rightarrow$ 2He & $< 3 \cdot 10^{-10}$ & 30 & [Deloche et al., 1976] \\
Ar$^+$ + O$_2$ $\rightarrow$ O$_2^+$ + Ar & $4.5 \cdot 10^{-11} \cdot (300/T)^{0.67}$ & 0.4 & [Midey and Viggiano, 1998] \\
Ar$^+$ + e$^-$ + He $\rightarrow$ Ar + He & $3 \cdot 10^{-20}$ & 67 & [Bates and Khare, 1965] \\
O$_2^+$ + e$^-$ $\rightarrow$ O + O & $2.0 \cdot 10^{-7} \cdot (300/T)^{0.65}$ & 4.2 & this work \\
O$_2^+$ + O$_2$ + He $\rightarrow$ O$_2^+$ + He & $8.9 \cdot 10^{-31} \cdot (300/T)^{2.74}$ & 22 & [Smirnov, 1977; Boehringer et al., 1983] \\
O$_2^+$ + O$_2$ + O$_2$ $\rightarrow$ O$_2^+$ + O$_2$ & $3.7 \cdot 10^{-30} \cdot (300/T)^3$ & $47 \cdot 10^3$ & [Smirnov, 1977] \\
O$_2^+$ + e$^-$ $\rightarrow$ products & $2.3 \cdot 10^{-6}$ & 0.43 & [Kasner and Biondi, 1968] \\
\hline
\end{tabular}
\end{table}

Figure 2. A comparison of chemical kinetics model based on reactions in the table 1 with measured data at displayed conditions. After discharge ignition in helium gas, afterglow with He$^+$ and He$^+_2$ ions and He$^m$ metastable atoms are created. After addition of argon plasma is rapidly converged into the Ar$^+$ dominated plasma. Oxygen is added later and O$_2^+$ becomes dominant ion.

establish plasma with O$_2^+$ as the dominant ion and DR as the dominant ion loss process. We developed a computer chemical kinetics model which is based on known rate coefficients of the reactions. They are listed in Table 1 together with characteristic times of the reactions based on typical experimental conditions. Example result can be seen in Figure 2 where comparison with measured data is also displayed.

Results and Discussion

Temperature dependence of the rate coefficient of the dissociative recombination of O$_2^+$ was measured over a wide range of conditions. They must be set carefully with regards to several phenomenons. Concentration of O$_2$ must be high enough to assure fast O$_2^+$ formation but one has to avoid excessive O$_2^+$ formation at higher O$_2$ concentrations. Flow and pressure of He buffer gas must be set correctly in order to decrease losses caused by ambipolar diffusion. Electron number density and observation time depend on gas velocity, which can be set by varying pressure, flow, and temperature $v \sim pQ/T$. 

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Figure 3. Temperature dependence of the rate coefficient of the dissociative recombination of $O_2^+$ with electrons. Our current data marked with red stars are compared to several others experimental results [McLain et al., 2004; Alge et al., 1983; Walls and Dunn, 1974; Johnsen, 1987; Adams et al., 1984; Peverall et al., 2001]. Displayed are also data measured in our laboratory on AISA experiment [Bilyk et al., 2004] and on FALP-VT [Novotny, 2006].

Figure 4. Measurements of the rate coefficients of dissociative recombination of $O_2^+$ with electrons at 230 K (panel (a)) and 155 K (panel (b)) at several pressures of He buffer gas and over 1 order of magnitude of $[O_2]$. There is a very good agreement between the fit of the data (continuous line) and theory (dashed line).

We measured DR rate coefficient at three temperatures—230, 150 and 100 K. Measured temperature dependence can be seen in Figure 3 together with previous data [McLain et al., 2004; Alge et al., 1983; Walls and Dunn, 1974; Johnsen, 1987; Adams et al., 1984; Peverall et al., 2001; Bilyk et al., 2004; Novotny, 2006]. Very good agreement among these results is observed.

Measurement of DR rate coefficient at 230 K and 155 K at various conditions is shown in Figure 4. One can see that the coefficient does not change with $O_2$ concentration nor with pressure of He buffer gas. Measured values are in a good agreement with the theoretical ones. It means that the probe used in Cryo–FALP II is a valid diagnostic tool at typical experimental conditions (pressure, temperature).

Measurements at temperatures below 100 K are in plan and these will be the first results of its kind.

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