RATE COEFFICIENTS FOR O_3^+ DISSOCIATION TO O^+ AND O_2^+ BY ELECTRON IMPACT

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Abstract. In the present study we make comparison of rate coefficients for electron impact dissociation of ozone cation to singly charged oxygen ions, calculated for two sets of the cross section data. The two cross section datasets were measured by different research teams. We performed calculations of the non-equilibrium rate coefficients, using the adopted electron distribution functions from the WIND spacecraft observations in the interplanetary medium. The mean electron energies of these non-thermal distributions cover the range from 4,53 eV to 72 eV. The corresponding rates were interpolated from 4 eV to 80 eV to allow comparison with the equilibrium rates, obtained with Maxwell-Boltzmann distribution in a wide range of the mean electron energies up to 2000 eV. The contribution of the electron impact dissociation of O_3^+ to the ozone layer depletion is analyzed.

1. INTRODUCTION

Although the ozone hole in the Earth's upper atmosphere has been shrinking since the adoption of the Montreal Protocol in 1987, the environmental crisis caused by ozone depletion is likely to lasts for a long time. The most harmful ozone depleting substances are air pollutants, such as nitric oxides and chlorine and bromine compounds (Vaida and Simon 1995). But ozone layer is also vulnerable to interaction with UV radiation, and to some extent to collision with atoms, ions and electrons (Davies et al. 1993, Allan et al. 1996, Sweeney and Shin 1996). The latter one is in the focus of the present work, more precisely, the interactions of electrons originating from the solar wind with ozone. The solar-wind electrons can reach the upper atmosphere of the Earth trough the polar cusp and harm the ozone molecules. The following processes of electron impact dissociation of O_3^+ to O^+ and O_2^+ fragments are considered:

$$e^- + O_3{}^+ \rightarrow O^+ + O_2 + e^- \tag{1}$$
$$e^- + O_3{}^+ \rightarrow O + O_2{}^+ + e^- \tag{2}$$

$$e^- + O_3{}^+ \rightarrow O_2{}^+ + O^+ + e^- \quad (3)$$

The dissociative excitation processes (1) and (2) are characterized by energy thresholds of 0.64 eV and 2.19 eV, respectively. The dissociative ionization process (3) has energy threshold of 14.26 eV.

The absolute cross sections for the production of the given fragments were measured by Deng et al. (Deng et al. 2010) at Oak Ridge National Laboratory (ORNL). Five years later, Belić and coworkers (Belić et al. 2015) performed measurements at Louvain-la-Neuve (LLN) which produced absolute cross sections for electron impact dissociation of ozone cation to O^+. In their publication, Belić et al. 2015 found that their cross sections for the production of O^+ are up to a factor of three larger than those obtained by ORNL group in the region of high energies. The authors from the LLN group demonstrated that their apparent cross sections needed to be corrected by including the possible loss of signal in the experiment. The same conclusion refers to the ORNL results, as well. In their following publication (Belić et al. 2022), they have renormalized the data from ORNL group for the production of $O_2{}^+$ ions to produce the recommended absolute cross sections for the formation of this fragment ion.

In the present work we will compare the rate coefficient data published in the aforementioned paper (Belić et al. 2022) with rate coefficients that we calculated using the ORNL data for the same processes. Results obtained for equilibrium and non-equilibrium electron distribution functions are shown. The aim of making these comparisons was to evaluate the significance of the given processes to the ozone layer depletion.

2. METHOD

Rate coefficients were calculated by using the formula:

$$K(\bar{\varepsilon}) = \sqrt{2/m}\int_{\varepsilon_{th}}^{\infty} \sigma(\varepsilon)\sqrt{\varepsilon} f_e(\bar{\varepsilon},\varepsilon)d\varepsilon \quad (4),$$

where $\bar{\varepsilon}$ is the mean electron energy, ε is the electron energy, $\sigma(\varepsilon)$ is the cross section for the corresponding process, ε_{th} is the threshold energy and $f_e(\bar{\varepsilon},\varepsilon)$ is the normalized electron energy distribution function. Rate coefficients were calculated by numerical integration, with the cross sections previously numerically interpolated.

In the case of the equilibrium conditions, $f_e(\bar{\varepsilon},\varepsilon)$ in Equation (4) is the Maxwell-Boltzmann distribution:

$$f_e(\bar{\varepsilon},\varepsilon) = \frac{2}{\sqrt{\pi}}\left(\frac{3}{2\bar{\varepsilon}}\right)^{\frac{3}{2}}\sqrt{\varepsilon}\exp\left(-\frac{3\varepsilon}{2\bar{\varepsilon}}\right) \quad (5).$$

Non-equilibrium rates were calculated by using electron energy distributions obtained at mean energy values of 4.53 eV, 6.4 eV, 46.2 eV and 71.7 eV, taken from measurements performed on the WIND spacecraft (Lin 1997).

As it was already stated, the cross sections we used in calculations are from the publication Deng et al. 2010. We extrapolated those cross sections in the range of high energies, since the non-thermal distributions possess a wide bulk, reaching 500 eV. The obtained rate coefficient results were interpolated in energy interval from 4 to 80 eV.

3. RESULTS

In Figure 1 we present rate coefficient results for O^+ and O_2^+ production, as well as the total rate coefficients for the production of singly charged fragments. Figure 1(a) shows equilibrium rate coefficients, while Figure 1 (b) presents non-equilibrium rate coefficients. Data herein calculated for the ORNL cross sections are presented with dashed lines and data presented in the publication Belić et al. 2022 are shown with full lines. A mutual comparison of the rates obtained for different cross section datasets reveals that using ORNL cross sections leads to much lower values of the corresponding rates than it is the case when cross sections from Belić et al. 2015 and Belić et al. 2022 are used. The difference between rate coefficient values for the two cross section sets is up to 3 times higher in the case of non-equilibrium conditions and up to 6 times higher in the case of equilibrium conditions.

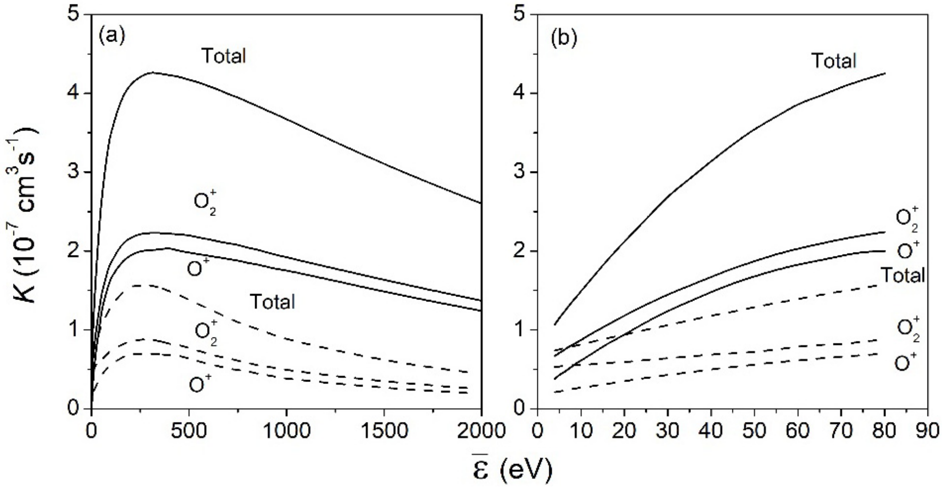

Figure 1: Equilibrium rate coefficients (a) and non-equilibrium rate coefficients (b); full lines – Belić et al 2022, dashed lines – results obtained for ORNL cross sections.

4. CONCLUSION

The comparison of the results show that cross section data from Belić et al. 2015 and Belić et al. 2022 give rise to much greater rate coefficients for both fragment ions than those from ORNL, which underestimate the contribution of the O^+ and O_2^+ production due to a loss of signal. It was also found that the non-equilibrium rates exceed the equilibrium ones. All this indicates a much greater importance of the contribution of the O_3^+ dissociation by the solar-wind electrons to the ozone layer depletion than it is expected.

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