

**Electron-impact dissociation of ozone cations  $O_3^+$** 

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Absolute cross sections for electron-impact dissociation of  $O_3^+$  ions yielding  $O^+$  and  $O_2^+$  fragment ions have been measured using a crossed electron-ion beams method for energies from about 3 eV to 100 eV. While the  $O_2^+$  channel dominates the dissociation cross section over the measured energy range, a strong enhancement is observed in the  $O^+$  channel at low energy.

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**I. INTRODUCTION**

Ozone constitutes only a relatively small concentration in the atmosphere but it plays an important role for human beings. On one hand, in the stratosphere layer ozone absorbs energetic ultraviolet light (UV) that is responsible for skin cancer, cataracts, and depression of the human immune system [1]. On the other hand, ozone damages the eyes and the respiratory systems of humans and other mammals if the concentration is too high [2–4].

Since its discovery by Schönbein in 1840, ozone has been extensively studied for over 100 years. Spurred by the ozone deficit problem, especially the discovery of the Antarctic ozone hole [5–7], more and more research has been focused on the study of various destruction mechanisms of the ozone molecule and the ozone cation.

In the atmosphere, ozone is created from oxygen by UV radiation or lightning, and decomposes by absorbing UV or colliding with other densely populated radicals or molecules, such as NO, NO<sub>2</sub>, HO, H<sub>2</sub>O. At the earth's surface these processes maintained a relatively stable dynamic equilibrium between ozone and oxygen, until the industrial age and massive introduction of pollutants modified these processes. Ozone is depleted efficiently by chlorine Cl, ClO, bromine Br, and BrO, which act as catalysts for ozone consumption processes [6,8]. Atomic chlorine, bromine, and their monoxides come mainly from pollutants such as the chlorofluorocarbon (CFC) and bromofluorocarbon (halon) compounds, which have small concentrations but long lifetimes in the stratosphere. Even though most of these compounds have been banned during the last decades, the released pollutants will continue to deplete the ozone layer for the next several decades. However, this is not the only channel for ozone depletion. The reactions of the ozone molecule and the ozone cation with other atoms, molecules, radicals, ions, and electrons contribute to the destruction of ozone as well.

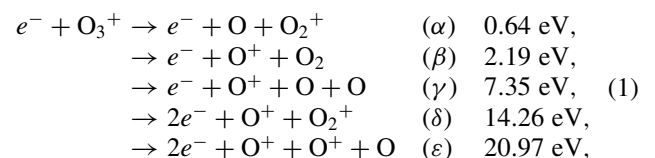
The ozone cation exists naturally and is important for our understanding of ozone depletion [9]. The ozone molecule has been studied extensively both experimentally and theoretically, but its positive ion has received little attention. The main problem for experimentalists is the lack of sources of pure  $O_3^+$  ions. Most  $O_3^+$  ion sources studied are mixed with excited states or/and oxygen ions ( $O^+$  and  $O_2^+$ ). The theoretical calculation for the electronic states of the ozone cation is

difficult due to strong electron correlation. So far, there are no detailed potential energy curves available for the ozone cation.

The  $O_3^+$  ion has a nonlinear structure and the geometry including the bond distance and angle is very different for each available electronic state. The first photoelectron spectra of  $O_3^+$  were obtained in 1974 [10], but the assignment of the states was controversial and was not clarified until 2005 [11–15]. The three lowest doublet states of  $O_3^+$  are assigned as  $\tilde{X}^2A_1$ ,  $\tilde{A}^2B_2$ ,  $\tilde{B}^2A_2$  and their energies are within 1 eV of each other. Recently, Willitsch *et al.* measured accurately that the energy difference between  $^2A_1$  and  $^2B_2$  is only 0.135 eV [13]. Most of the theoretical treatments compute the doublet states and only a few calculations have been done for the quartet states [14,15]. The calculation in Ref. [15] shows that the quartet states,  $^4A_1$ ,  $^4A_2$ , and  $^4B_2$ , are close in energy to the fourth lowest doublet state  $^2B_1$ , which is about 2 eV higher than the ground state of  $O_3^+$ .

The  $O_3^+$  ion is weakly bound and will dissociate by photon absorption, collision, or recombination. The dissociative recombination of ozone cation with free electrons has been investigated using the ion storage-ring method at CRYRING [16,17] detecting neutral fragments, O or O<sub>2</sub>, and is dominated at 0 eV by three-body (O + O + O) dissociation. In the present work we are only concerned with dissociative processes yielding  $O^+$  or  $O_2^+$  fragments. The photodissociation of  $O_3^+$  yielding these two fragments has been studied [18–20]. Vestal and Mauclair [18] reported that the cross section of the  $O^+$  channel is predominant in the visible light range.

In this paper, we report the measured absolute cross sections for electron-impact dissociation of  $O_3^+$  producing ion fragments. Possible channels for electron-impact dissociation of  $O_3^+$  include



where the energies given are the threshold for each channel, respectively, for the  $^2A_1$  ground state of  $O_3^+$  [21]. The first three channels are dissociative excitation (DE) processes

and the remaining channels are dissociative ionization (DI) processes.

Resonant ion pair (RIP) formation may also contribute to our measurements of ion fragments. To our knowledge, no data exist on the RIP process of ozone cations. However, for the  $\text{H}_2^+$  ion, measured RIP cross sections [22] were found to be at least two orders of magnitude smaller than those for dissociative excitation [23]. Hence we expect any contribution from RIP of  $\text{O}_3^+$  to the present measurements to be much smaller than the experimental uncertainties.

## II. EXPERIMENT

Details of the crossed electron-ion beams technique developed at Oak Ridge National Laboratory (ORNL) have been described in the literature [24,25]. The  $\text{O}_3^+$  beam was generated in the ORNL Caprice electron-cyclotron-resonance (ECR) ion source using oxygen gas. The beam was extracted at 5–10 keV and mass analyzed, then transported to the final experimental station where the ion beam was purified by an electrostatic parallel plate deflector and interacted with an electron beam at a right angle in the horizontal plane. The parent and fragment ions were separated by a double-focusing  $90^\circ$  sector analyzing magnet. The  $\text{O}^+$  and  $\text{O}_2^+$  fragments were deflected by another electrostatic deflector and collected by a discrete-dynode electron multiplier detector. Parent ions were collected in a well-characterized Faraday cup for calculation of the absolute cross section and measured to be about 8–15 nA for the incident  $\text{O}_3^+$  ion beam.

The  $^2A_1$  and  $^2B_2$  states are almost degenerate [13–15,26] and it is inevitable that the generated  $\text{O}_3^+$  ion beam from the ECR ion source is a mixture of  $^2A_1$  and  $^2B_2$ . Moreover, since the  $^2B_1$  and some quartet states are only about 2 eV higher than the ground state  $^2A_1$ , the ECR-generated  $\text{O}_3^+$  beam may also contain a small amount of those excited states, even though the microwave power injected in the source was typically less than 1 W.

The absolute cross sections  $\sigma$  at the center-of-mass electron-impact energy  $E$  are determined from the measured quantities by

$$\sigma(E) = \frac{R}{I_i I_e} \frac{q e^2 v_i v_e}{\sqrt{v_i^2 + v_e^2}} \frac{F}{\varepsilon}, \quad (2)$$

where  $R$  is the fragment signal rate,  $I_i$  and  $I_e$  are the incident ion and electron currents respectively,  $qe$  is the charge of the incident ions,  $v_i$  and  $v_e$  are the incident ion and electron velocities,  $\varepsilon$  is the detection efficiency for the product ions (estimated to be 90%), and  $F$  is the form factor that is determined from measured electron and ion beam profiles [i.e., the vertical differential distributions  $I_i(z)$  and  $I_e(z)$ ] using

$$F = \frac{\int I_e(z) dz \int I_i(z) dz}{\int I_e(z) I_i(z) dz}. \quad (3)$$

The measurements were made for collision energies from 3 eV to 100 eV. For lower energies, only weak electron currents are available and it would require excessively long times to achieve a reasonable statistical uncertainty. Calibration of the collision energy was done by measuring the electron-impact ionization cross section of  $\text{C}^+$  and comparing with the data

given by Ref. [27]. The obtained uncertainty of the collision energy is less than 0.5 eV.

The dominant contributions to the systematic uncertainties in the experiment come from product ion detection and pulse transmission, transmission of product ions to the detector, and measurement of the absolute form factor. They are given as 5%, 4%, and 4%, respectively, at a level equivalent to a 90% confidence level for statistical uncertainties. Other contributions are from the determination of the ion and electron currents (2% each), and the ion and electron velocities (1% each). The quadrature sum of these components is  $\pm 8.2\%$ . Combining this sum with the total relative uncertainties at a 90% confidence level (two standard deviations) yields the total expanded uncertainties for the measurements.

## III. RESULTS AND DISCUSSION

Absolute cross sections for electron-impact dissociation of  $\text{O}_3^+$  producing  $\text{O}^+$  and  $\text{O}_2^+$  fragment ions were measured for energies up to 100 eV. The measured cross sections are presented in Fig. 1 with one standard deviation relative error bars. At 39 eV, the outer error bars represent the total expanded uncertainties at a 90% confidence level. Both curves result from the sums of all DE and DI processes of  $\text{O}_3^+$  as given in Eq. (1). Individual DE or DI process cannot be distinguished under the current experimental conditions. No empirical formula or theoretical calculation is available for comparison and analysis for those processes.

### A. $\text{O}^+$ fragments

The open circles in Fig. 1 show the measured cross sections for the  $\text{O}^+$  fragment channel. The total expanded uncertainties

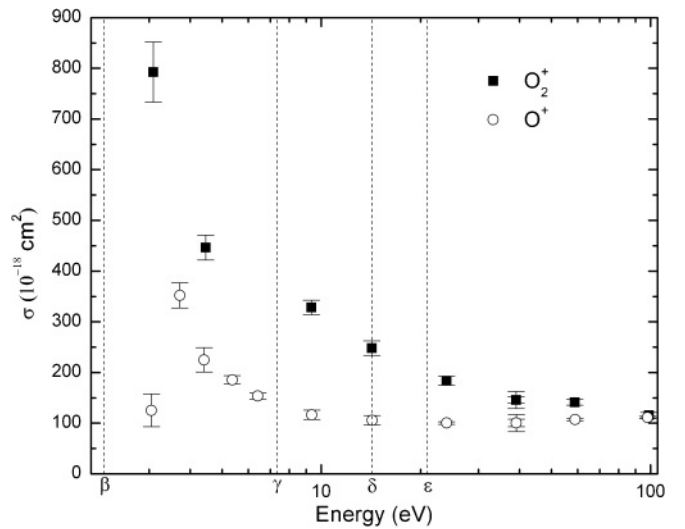


FIG. 1. Absolute cross sections versus interaction energy for electron-impact dissociation of  $\text{O}_3^+$  producing  $\text{O}_2^+$  (■) and  $\text{O}^+$  (○) fragment ions shown with one standard deviation relative error bars. The outer error bars at 39 eV represent the total expanded uncertainties at a 90% confidence level. The thresholds for different dissociation channels defined in Eq. (1) are indicated by the vertical dashed lines.

for these experimental data are typically about 10% for energies greater than 15 eV. There is a fast rise starting from 3 eV and reaching a sharp maximum at 3.7 eV followed by a smooth decrease. The cross section is almost unchanged between about 10 eV and 100 eV.

Channels  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\varepsilon$  of Eq. (1) producing  $O^+$  have dissociation thresholds of 2.19, 7.35, 14.26, and 20.97 eV, respectively. The first two are DE processes and the latter two are DI processes. The peak at 3.7 eV indicates the contribution from channel  $\beta$  which may include resonant dissociative excitation (RDE) processes. Extrapolating the first two points linearly to zero cross section a value between 2.5 and 2.8 eV can be obtained. This threshold value appears to be higher than the dissociation threshold of 2.19 eV, but the offset is consistent given the energy uncertainty of about 0.5 eV.

The threshold of 2.19 eV is for the  ${}^2A_1$  ground state, which dissociates to  $O_2^+$  as well. It has been reported that the  ${}^2B_1$  state is responsible for the formation of  $O^+$  by  $O_3^+({}^2B_1) \rightarrow O^+({}^4S) + O_2({}^3\Sigma_g^-)$  [19] and the threshold for this channel is 1.86 eV [20]. There could be a small percentage of  $O_3^+({}^2B_1)$  coming from the source. Other states such as  ${}^4A_1$  or  ${}^4B_1$  are also relevant to the dissociation of  $O_3^+$  into the  $O^+$  ion [15], but they lie at energies similar to or higher than the  ${}^2B_1$  state. The low-energy experimental data are insufficient to draw any conclusions about the contributions of the  ${}^2B_1$  and quartet states to the DE process.

### B. $O_2^+$ fragments

The measured cross sections for the  $O_2^+$  channel are shown with solid squares in Fig. 1. For the entire measured energy range the cross section decreases smoothly with increasing energy and there is no obvious structure. The total expanded uncertainties for these experimental data are typically about 11–12% for all energies, except the lowest one.

For this channel, there is only one DE process and one DI process. Their thresholds are 0.64 and 14.26 eV, respectively, as given in Eq. (1). The present data indicate that the DE process is dominant in  $O_2^+$  production in the measured energy range. From these data, it cannot be determined if there is any resonant dissociative excitation, because the threshold of direct dissociative excitation is lower than the lowest energy in the measurement and there is no indication of falling cross section toward lower energies.

The dissociation threshold of  $O_3^+({}^2A_1)$  ground state is 0.64 eV for the channel  $\alpha$ . In addition, the  ${}^2B_2$  and  ${}^2A_2$  excited states of  $O_3^+$  are also expected to dissociate into  $O_2^+$  ion fragments. The threshold for the  ${}^2B_2$  state was calculated to be 0.53 eV [15]. Since the  ${}^2A_1$  and  ${}^2B_2$  states are bound after formation [13], it is likely that the huge cross section at low energy is mainly due to dissociation of these states. The  ${}^2A_2$  state may also contribute to the cross section. There are more doublet states leading to the formation of  $O_2^+$  ion [28]. However, the contribution from those states is expected to be small since they are several eV ( $>3$  eV) higher than the ground state  ${}^2A_1$ , and hence lie above the dissociation limit for channel  $\alpha$ , making survival during transport from the ion source to the interaction region unlikely.

### C. Summary

The  $O_2^+$  channel dominates over the  $O^+$  channel for the entire energy range investigated. Similar phenomena have been reported in experiments on the photoionization of ozone [29,30], where the  $O_2^+$  ion has a higher yield from  $O_3$  than the  $O^+$  ion, which is partially because the subsequent dissociation of excited  $O_3^+$  contributes to the formation of  $O_2^+$  and  $O^+$  ions.

The  $O_3^+$  ion beam generated from the source is likely comprised mainly of the  ${}^2A_1$  and  ${}^2B_2$  states, partially of the  ${}^2A_2$  state, and perhaps a small amount of other higher doublet and quartet states, since the three lowest doublet states,  ${}^2A_1$ ,  ${}^2B_2$ , and  ${}^2A_2$ , lie within an energy range of 1 eV and others are at least 2 eV higher than the ground state.  $O_3^+({}^2A_1)$  dissociates to both  $O_2^+$  and  $O^+$  ions, but the  ${}^2B_2$  and  ${}^2A_2$  states exclusively dissociate to the  $O_2^+$  ion. Therefore, one might expect that the cross section for the  $O_2^+$  channel should be favored due to the populated ion beam states and because the DE threshold for producing  $O_2^+$  fragments is significantly lower than for producing  $O^+$  fragments.

During these experiments, the electron-impact ionization cross section of  $O_3^+$  resulting in  $O_3^{2+}$  was found to be negligible (less than the statistical error bar). It is possible that the ionization cross sections are themselves small, but it is also possible that the lifetime of the doubly charged ozone ion  $O_3^{2+}$  is sufficiently short (less than a few  $\mu$ s) that  $O_3^{2+}$  dissociates before it reaches the detector making the apparent yield negligible.

## IV. CONCLUSIONS

Absolute cross sections for electron-impact dissociation of  $O_3^+$  ions producing  $O_2^+$  and  $O^+$  fragment ions have been measured for energies from 3 eV up to 100 eV using a crossed electron-ion beams method. The  $O_2^+$  channel is predominant in the entire measured energy range. DE processes dominate for both  $O_2^+$  and  $O^+$  channels. For the  $O^+$  channel, the  $O_3^+({}^2A_1)$  ground state contributes to the observed low-energy peak. The  ${}^2A_1$  and  ${}^2B_2$  states are responsible for the large cross section at low energy for the  $O_2^+$  channel. Compared to DE and DI channels, ionization of  $O_3^+$  has no significant effect on the destruction of ozone cations at these energies.

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