# Angular distributions of $O^+$ from $O_2^{2+}$ produced by electron impact on $O_2$

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Coincidence measurements of the angular distributions of $O^+$ dissociated from $O_2^{2+}$ produced by electron impact on $O_2$ have been made. With an incident electron energy of 55 eV, 2.6-, 3.7-, 4.5-, and 5.8-eV $O^+$ ions were detected separately using the time-of-flight and coincidence method at selected angles between 40° and 140° in 10° steps. The results show two flat, isotropic and two anisotropic angular distributions and attempts have been made to interpret these symmetries and to identify the sources of the ions. [S1050-2947(96)00909-2]

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## I. INTRODUCTION

For the last several years, a series of papers on the kinetic-energy distributions of fragment ions from $N_2$ and $O_2$ [1,2] and the angular distribution of fragment ions from $N_2$ [3] upon dissociative ionization by electron impact have been reported by the authors. Angular distributions of molecular dissociation products have been of interest since Dunn [4] reported a selection rule based on symmetry. Angular distribution measurements have been made mostly for $H_2$, $N_2$, and $O_2$, and the results at threshold have shown good agreement with the selection rule [5–14]. However, in most experiments, only singly ionized dissociation products from either of the following two processes, taking $O_2$ as an example, were detected *without using coincidence detection techniques*:

$$e + O_2 \rightarrow {O_2}^+ + 2e \rightarrow O^+ + O + 2e, \quad (1)$$

$$e + O_2 \rightarrow {O_2}^{2+} + 3e \rightarrow 2O^+ + 3e. \quad (2)$$

A few experiments [12,14,15] detected doubly ionized dissociation products and determined their angular distributions. Although some experiments [16–18] employed coincidence detection to measure the *energy* distributions of singly ionized products dissociated from doubly ionized parent molecules, no experiment, except the one by the authors [3], measured the *angular* distribution with a coincident energy-selection mechanism. This is probably due to difficulties from the very low counting rates.

Recently, there has been increasing interest in double or multiple ionization of atoms and molecules, and many experiments have been done with discharge lamps or synchrotron light sources [19–21]. There have also been some electron-impact double-ionization experiments [15–17,22–24]. However, the results are limited and less well analyzed compared to the photon-impact experiments. For the case of double ionization of molecular oxygen, there exist the photon-impact results of Curtis and Eland [25], Eland *et al.* [19], and Price and Eland [20], the electron-impact results of Feldmeier, Druchholz, and Hofmann [23] and Larsson *et al.* [24], and the theoretical results of Larsson *et al.* [24], Beebe Thulstrup, and Anderson [26], and Hurley [27]. The agreement among these data is poor and interpretations are not consistent. In the experiments [16–18] where the energy distributions of singly ionized products dissociated from doubly ionized molecules were measured, assignments of the sources of these singly ionized products showed discrepancies.

This situation spurs more intensive research on the double ionization of molecules. One way of increasing the information on the electronic states of doubly ionized molecules involved in the production of the dissociation products is measuring the angular distributions of singly ionized dissociation products and applying Dunn's selection rule to the resultant distributions as described above [3]. This information is important in assigning the electronic states of doubly ionized parent molecules from which singly ionized molecules originate. Based on the kinetic-energy distribution of $O^+$ ions obtained by the authors, coincidence measurements of the angular distributions of $O^+$ dissociated from $O_2^{2+}$ produced by electron impact on $O_2$ have now been carried out. Our previous measurement [1] of the kinetic-energy distribution of $O^+$ ions produced from doubly ionized $O_2$ by electron impact showed two dominant peaks at 3.7 and 5.8 eV with signs of the smaller peaks near 2.6 and 8.8 eV. With an incident electron energy of 55 eV, 2.6-, 3.7-, 4.5-, and 5.8-eV $O^+$ ions were detected separately using time-of-flight and coincidence techniques at selected angles between 40° and 140° in 10° steps.

## II. EXPERIMENTAL DETAILS

The experimental setup used in this experiment was the same as the one used in the previous experiment on $N_2$ [2], and only the changes will be described here. An electron beam was generated from a hot iridium filament to increase the lifetime in the oxygen environment, and was pulsed with a full width at half maximum (FWHM) of about 15 ns. The energy of the incident electrons was adjusted to 55 eV, and the currents of the dc and pulsed electron beams were maintained at about 1 $\mu$A and a few $n$A, respectively. The reason for choosing 55-eV incident energy is this: since Dunn's selection rule applies near the threshold, the electron-impact

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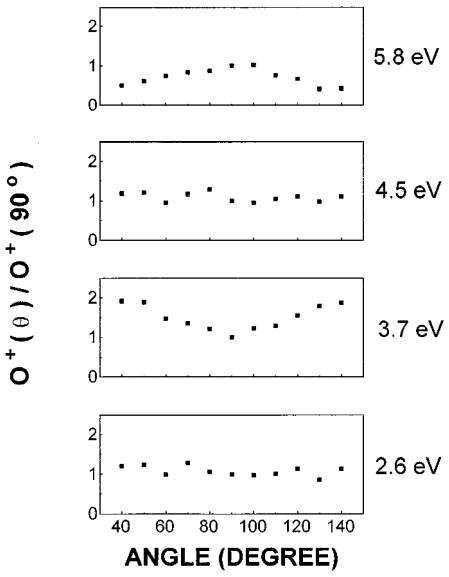


FIG. 1. Angular distributions of $O^+$ ions dissociated from $O_2^{2+}$ produced by electron impact on $O_2$.

energy in this experiment has to be near the threshold for double ionization of oxygen molecules. The potential-energy curves of the doubly ionized $O_2$ states in the Franck-Condon region lie mostly between 45 and 50 eV. Therefore the electron-impact energy should not be much greater than these energies. In this experiment, an electron energy of 55 eV was chosen. The preset $O^+$ energies were 2.6, 3.7, 4.5, and 5.8 eV. An estimate of the total uncertainty in the kinetic energy varies from 0.1 to 0.2 eV, depending on the time of flight.

## III. RESULTS AND DISCUSSIONS

The angular distributions of the 2.6-, 3.7-, 4.5-, and 5.8-eV $O^+$ ions dissociated from $O_2^{2+}$ produced by electron impact on $O_2$ are given in Fig. 1. In every data set, a point at 90° is normalized to 1.

As mentioned already, one angular distribution measurement must be made at one selected, preset kinetic energy of the ion, and the next measurement at the next kinetic energy. The kinetic-energy distribution of Ref. [1] was used to select these preset kinetic energies—2.6, 3.7, 4.5, and 5.8 eV—at which the angular distribution measurements were made. Our result of the kinetic-energy distribution showed peaks at 2.6, 3.7, 5.8, and 8.8 eV and was similar to that of Feldmeier, Druchholz, and Hofmann [23], even though the details do not agree in several aspects. The kinetic-energy distribution of Feldmeier, Druchholz, and Hofmann shows two dominant peaks at 3.8 and 5.3 eV, and a third peak near 8.4 eV. Our result shows two dominant peaks at 3.7 and 5.8 eV with clear signs of smaller peaks near 2.6 and 8.8 eV. The reason for taking an angular distribution at 4.5 eV even though no 4.5-eV kinetic-energy peak was observed will be discussed later.

As can be seen in Fig. 1, the angular distributions at 2.6 and 4.5 eV are isotropic while those at 3.7 and 5.8 eV are anisotropic. The one at 3.7 eV exhibits a minimum and the other at 5.8 eV a maximum near 90°.

*(i) 5.8 eV.* As mentioned above, the total uncertainty in the kinetic energy in our results is up to 0.2 eV, while Feldmeier, Druchholz, and Hofmann [23] did not give an estimate. However, since both experiments are the low-resolution electron-impact experiments, it seems that the 5.3-eV peak of Feldmeier, Druchholz, and Hofmann might correspond to our 5.8-eV peak. Neither Feldmeier *et al.* [23] nor we could identify the source of this peak from just the previous kinetic-energy distribution results. No assignment of the states to this peak had been available except that of Larsson *et al.* [24] who assigned several states to their 6.0-eV peak, which is close to our 5.8-eV distribution. However, their calculated energies of those assigned states showed big differences from the measured value of 5.8 eV.

In the photoionization experiment of Curtis and Eland [25], a total kinetic-energy release of 11.5 eV, half of which is fairly close to our 5.8-eV peak, was observed to be in great abundance, and it was postulated that the state from which this kinetic-energy release originated was near 43.9 eV. From the potential-energy curves of $O_2^{2+}$ given in the report of Larsson *et al.* [24], the possible states near 43.9 eV, which could release a total kinetic energy of 11.5 eV are $1\,^3\Delta_g$, $1\,^3\Sigma_g^-$, and $C\,^3\Pi_u$. Since the ground state of $O_2$ is $X\,^3\Sigma_g^-$, a transition to either $1\,^3\Delta_g$ or $C\,^3\Pi_u$ in the perpendicular direction with respect to the symmetry axis is allowed and a transition to $1\,^3\Pi_g^-$ is allowed in both the perpendicular and parallel directions according to Dunn's selection rule. None of these three states is excluded from contributing to the 5.8-eV kinetic-energy peak. Therefore, even though we still cannot uniquely identify the states responsible for this 5.8-eV peak, we conclude that $C\,^3\Pi_u$ and either or both $1\,^3\Delta_g$ and $1\,^3\Sigma_g^-$, a combination of which results in a flat angular distribution, are contributing based on the results of the angular distribution.

*(ii) 4.5 eV.* Larsson *et al.* [24] obtained a noncoincident $O^+$-ion kinetic-energy spectrum following electron impact—which means that the $O^+$ dissociation products both from the $O_2^+$ states and from the $O_2^{2+}$ states were detected—and assigned the following two doubly ionized $O_2^{2+}$ states to the 4.5-eV peak:

$$B\,^3\Pi_g \rightarrow O^+(4S) + O^+(2D), \tag{3}$$

$$A\,^3\Sigma_u^+ \rightarrow O^+(4S) + O^+(4S). \tag{4}$$

However, Doolittle, Schoen, and Schubert [28] measured the kinetic-energy distribution of $O^+$ ions produced by photoionization *below the appearance potential* of $O_2^{2+}$ and noticed a peak at 4.5 eV, which means that the 4.5-eV peak is coming from a singly ionized state of $O_2$. Furthermore, neither Feldmeier, Druchholz, and Hofmann [23] nor we [1] observed any peak at 4.5 eV in the previous kinetic-energy distributions. Therefore, it is possible that the 4.5-eV peak observed by Larsson *et al.* was coming from the $O_2^+$ states instead of the $O_2^{2+}$ states.

According to Dunn's selection rule, a transition from the ground state $X\,^3\Sigma_g^-$ of $O_2$ to neither of the above two $B\,^3\Sigma_g$ and $A\,^3\Sigma_u^+$ states is allowed in both the perpendicular and parallel directions, which would result in a flat angular distribution. This supports the flatness of our 4.5-eV result of the angular distribution. Therefore it can be concluded from

the kinetic-energy distributions, as well as from the angular distributions, that a 4.5-eV kinetic-energy peak is not expected from the double ionization of $O_2$, *at least near threshold*.

*(iii) 3.7 eV.* Larsson *et al.* [24] assigned the 3.4-eV ions to the $B\ ^3\Sigma_u^-$ state. This may be the same peak as the 3.8-eV peak of Feldmeier, Druchholz, and Hofmann and our 3.7-eV peak. Dunn's selection rule allows a transition from the ground state $X\ ^3\Sigma_u^-$ of $O_2$ to the $^3\Sigma_g^-$ state in the parallel direction with respect to the symmetry axis. This agrees with the angular distribution at 3.7 eV, which shows a minimum at 90°. Therefore, our angular distribution results support the assignment of Larsson *et al.* [24]. We note that the experiment of Larsson *et al.* was a noncoincident experiment and the assignment was principally based on the potential curves alone. It is very difficult to assign a correct state among many closely spaced states to a certain kinetic-energy peak in electron-impact experiments due to their poor resolution.

*(iv) 2.6 eV.* The angular distribution of the 2.6-eV $O^+$ fragments is flat (see Fig. 1). The origin of these fragments cannot be identified even from this angular distribution result. Curtis and Eland [25] and Eland *et al.* [19] reported the observation of the total kinetic-energy release of 4.5 eV, and later Price and Eland [20] interpreted that this energy release was due to two-step photoionization processes. However, Dunn's selection rule was derived for a single-step electron-impact process and cannot be applied to the two-step photoionization process. Therefore this symmetry argument is not applicable and a possible relation between this total-energy release and our 2.6-eV feature is only tentative. Further studies using a different experimental method are required.

## IV. CONCLUSIONS

Measurements of the angular distributions of $O^+$ dissociated from $O_2^{2+}$ produced by electron impact on $O_2$ have been made employing time-of-flight and coincidence techniques. Energy-selected $O^+$ ions, 2.6, 3.7, 4.5, and 5.8 eV, were detected in coincidence for angles between 40° and 140°. The angular distributions at 2.6 and 4.5 eV are isotropic while those at 3.7 and 5.8 eV are anisotropic. The distribution at 3.7 eV exhibits a minimum and the one at 5.8 eV a maximum near 90°.

For the 5.8-eV distribution, the $1\ ^3\Delta_g$, $1\ ^3\Sigma_g^-$, and $C\ ^3\Pi_u$ state are possible candidates. Since the ground state of $O_2$ is $X\ ^3\Sigma_g^-$, a transition to either $1\ ^3\Delta_g$ or $C\ ^3\Pi_u$ in the perpendicular direction with respect to the symmetry axis is allowed and a transition to $1\ ^3\Sigma_g^-$ is allowed in both the perpendicular and parallel directions according to Dunn's selection rule. Therefore we could conclude that $C\ ^3\Pi_u$ and either or both of $1\ ^3\Delta_g$ and $1\ ^3\Sigma_g^-$ are contributing.

In the 4.5-eV case, Larsson *et al.* assigned the $B\ ^3\Pi_g$ and $A\ ^3\Sigma_u^+$ doubly ionized states as the origins of the 4.5-eV peak. However, according to the Dunn's selection rule, a transition from the ground state $X\ ^3\Sigma_g^-$ of $O_2$ to neither of the above two states is allowed in any direction, which is considered with the flatness of our 4.5-eV angular distribution. Therefore, we conclude that a 4.5-eV kinetic-energy peak is not expected, at least near threshold.

The angular distribution at 3.7 eV, which shows a minimum at 90° supports the notion that the $B\ ^3\Sigma_u^-$ state is responsible for this kinetic-energy release. The symmetry argument confirmed the result derived from potential-energy curves. The origins of the 2.6-eV ions cannot be derived from the angular distribution result.

## ACKNOWLEDGMENT

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