PHYSICAL REVIEW A VOLUME 16, NUMBER 5 NOVEMBER 1977

Dissociative ionization of O_2 produced by 1-MeV H^+, He^+, and O^+

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(Received 14 April 1977)

Kinetic-energy spectra of the O^+, O^{2+}, and O^{3+} fragments produced by 1-MeV H^+, He^+, and O^+ projectiles have been obtained. The O^+ spectrum resulting from H^+ bombardment is similar to spectra obtained by electron bombardment and photoionization. In addition, an O^{2+} spectrum resulting from H^+ bombardment has been obtained. The O^+, O^{2+}, and O^{3+} spectra obtained from He^+ and O^+ bombardment show energy groups for which approximate energy assignments have been made. The relative intensities of these energy groups are dependent on the projectile, with O^+ projectile greatly enhancing the higher-energy groups relative to the ones of lower energy.

I. INTRODUCTION

Dissociative ionization of O_2 by electron bombardment and by photoionization has been studied.[1-6] Energy distributions, appearance potentials, and angular-distribution measurements of the O^+ fragments have been used to make tentative identifications of particular states through which the dissociation processes proceed.

In the present work 1-MeV projectiles of H^+, He^+, and O^+ have been used to study dissociative ionization of O_2 by measuring the energy distributions of the O^+, and O^{2+}, and O^{3+} fragments for each kind of projectile. The use of H^+, He^+, and O^+ projectiles provided a convenient means for varying the degree of excitation of the target. Since fragments with two or more electronic charges are expected to be formed through states of relatively high excitation, these experiments can provide information concerning the existence of such states and the relative probability for their formation.

II. EXPERIMENTAL PROCEDURE

The apparatus and the time-energy spectroscopy technique which were used in this experiment have been described in recent publications from this laboratory.[7-9] The dissociation fragments of O_2 which were produced by 1-MeV projectiles of H^+, He^+, and O^+ were focused into a parallel-plate energy analyzer which was located at 90° relative to the direction of the incident beam. The energy and the time-of-flight of the fragments were measured and recorded in a two-parameter (time-of-flight, energy) array in which the O^+, O^{2+}, and O^{3+} fragments intensities were stored separately.

The energy resolution of the analyzer was approximately 0.5% of the measured energy. Most of the data were obtained at an analyzing energy of 50 eV and with the target gas pressure at either 0.5 or 1 mTorr. The average current of the incident beam ranged from about 100 nA for O^+ to 200 nA for H^+. The beam pulse duration was about 150 nsec with either 16 or 32 μsec between pulses.

III. DATA REDUCTION

The energy spectra of O^+, O^{2+}, and O^{3+} fragments were obtained from the energy, time-of-flight two-parameter array with the use of a computer-assisted background-subtraction technique described previously.[7] The results are shown in Figs. 1–3. The energy scales have been corrected for two effects which displaced the zero intercept.

One of these effects was related to the ionization of the target gas which resulted from the passage of the intense pulses of current through the target cell. The peak current was approximately 200 times the average current. This effect, which will be referred to as the charged-column effect, was measured and was found to be proportional to the product of the peak current and the pressure of the gas within the target cell for each kind of projectile. Rudd and Lang[10] have reported a charged-column effect in the measurement of the energy of electrons from autoionizing states of helium. For beam pulses of approximately 150-nsec duration, at a repetition rate of 31.25 kHz, the energy shift for O^+ fragments was determined from the product of the average current in μA and the target cell pressure in mTorr. For O^+ projectiles and O^+ fragments the energy shift was determined to be 2.4 eV/μA mTorr, and for He^+ projectiles and O^+ fragments its value was 0.86 eV/μA mTorr. For the O^{2+} and O^{3+} energy distributions it was assumed that the magnitude of the charged-column effect was proportional to the charge of the fragment. The effect was not measured for H^+ projectiles because of the much smaller ionization cross section. The dissociation

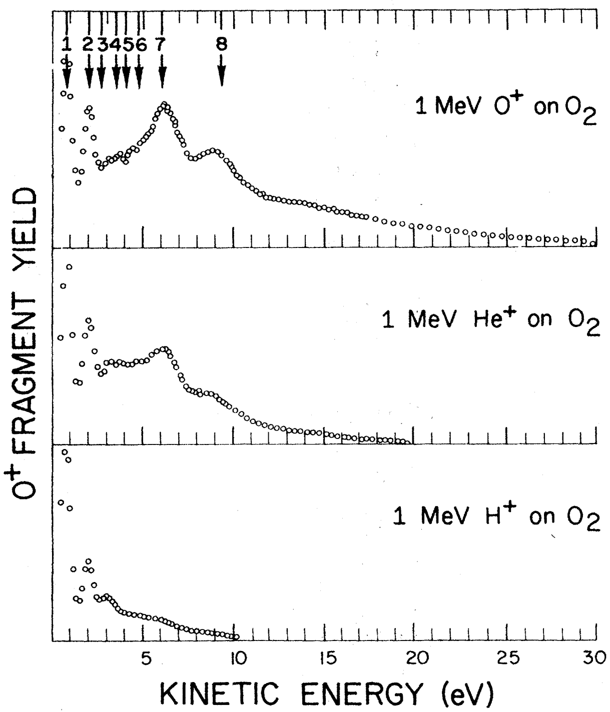

FIG. 1. O^+ fragment energy distribution for each kind of projectile. The yield is expressed in arbitrary units. The energy scales for the He^+ and O^+ projectile data have been corrected as described in the text. The energy scale for the data obtained with H^+ projectiles was obtained by normalization as described in the text. The statistical errors are less than the size of the data points. Some adjacent data points were averaged to reduce the density of points in the figure. The data represent a combination of data obtained with different sweep voltages. The total estimated uncertainty is comparable to the size of the data points.

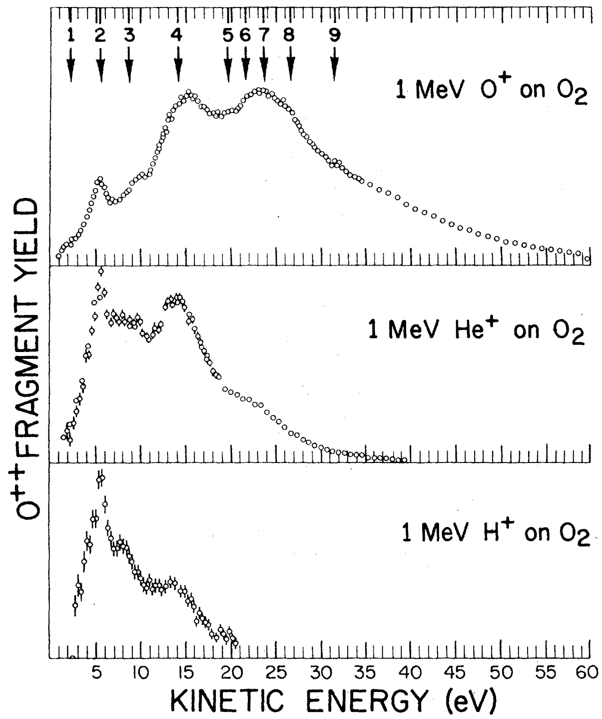

FIG. 2. O^+ fragment energy distribution for each kind of projectile. The yield is expressed in arbitrary units. The energy scales for the He^+ and O^+ projectile data have been corrected as described in the text. The energy scale for the data obtained with H^+ projectiles was obtained by normalization as described in the text. The statistical errors, except where indicated, are less than the size of the data points. Some adjacent data points were averaged to reduce the density of points in the figure. The data represent a combination of data obtained with different sweep voltages. The probable error is estimated to be less than 1.5 times the statistical standard devistion.

data for H^+ projectiles were normalized to the He^+ and O^+ projectile data over the region of the well defined 2-eV peak in the O^+ energy distribution.

The corrected energy distributions which are shown in Figs. 1–3 were obtained in a standard experimental configuration in which a lens was used to focus the fragment ions into the energy analyzer and all interior surfaces were coated with lamp black as described previously.[7] In this configuration it was found that the O^+, O^{2+}, and O^{3+} energy distributions were shifted toward lower energies in comparison with the distributions which have been observed in the electron-bombardment and photoionization experiments. This energy shift was in addition to, and was opposite in sign to, the charged-column energy shift just described. Its value, −0.32 eV for singly charged fragments, was determined by comparing the distributions obtained in the standard configuration to a measurement which was made in an *ad hoc* arrangement designed to eliminate effects which might shift the energy zero intercept. The focus elements were removed, and the front plate of the analyzer was grounded. The target cell remained at ground potential, and a grounded cylindrical shield was arranged between the target cell and the analyzer. The lamp black was removed, and all elements of the analyzer were thoroughly cleaned. Several runs were made to accumulate new energy distributions under the conditions described above. After correcting these data for the charged-column effect and the energy resolution of the analyzer, the energy of the second most energetic group in the O^+ distribution was determined to be 2.0 ± 0.1 eV in good agreement with the results of previous workers.

The energy distribution of O^+ fragments below 1.5 eV was not determined accurately in the experiment just described. Without the extraction

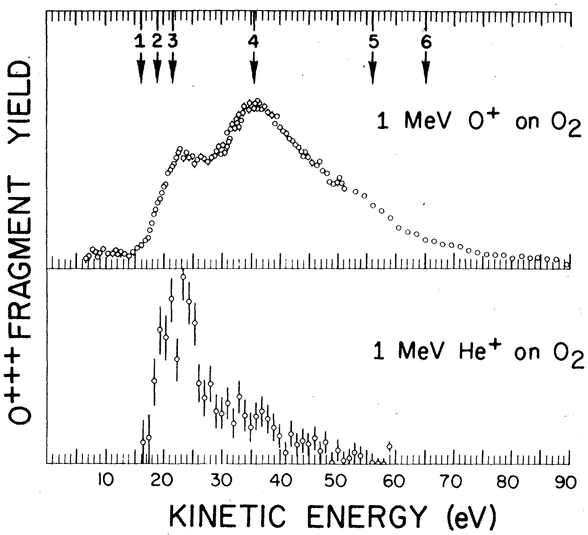

FIG. 3. O^{3+} fragment energy distribution for each kind of projectile. The yield is expressed in arbitrary units. The energy scales for the He^+ and O^+ projectile data have been corrected as described in the text. The statistical errors, except where indicated, are less than the size of the data points. Some adjacent data points were averaged to reduce the density of points in the figure. The data represent a combination of data obtained with different sweep voltages. The probable error is estimated to be less than 1.5 times the statistical standard deviation.

potential furnished by the lens, the flight times of the low-energy fragments were so large that reduction of the data could not be performed. Above 1.5 eV however, the O^+ energy distribution was in good agreement with the energy-corrected distributions obtained in the standard configuration of this work. This result is in agreement with the observations of Van Brunt *et al.*,[6] who found that surface charges influenced the transmission of O^+ fragments with energies below 1.5 eV. This effect was not investigated further in the present work, so the relative intensities of the O^+ fragments below 1.5 eV must be considered uncertain.

IV. RESULTS

The results of this experiment are presented in Figs. 1–3 and in Table I. Peaks 1 and 2 of the O^+ distributions have been seen in all the electron-bombardment experiments[2–6] and the photoionization experiment of Doolittle *et al.*[1] These two well-defined energy groups are believed to result, at least in part, from predissociation of states of O_2^+.

Above 2-eV fragment energy Doolittle *et al.*[1] observed an energy group near 3 eV and one group between 4 and 5 eV; Freund[2] observed groups at 3.3 and 5.55 eV and Van Brunt *et al.*[6] reported ion groups near 3, 4, and 9 eV. Stockdale and Deleanu[3] and Schopman and Locht[5] have reported similar findings in the region below 6 eV. The data presented in Fig. 1 suggest that there are three or more energy groups which contribute to the yield between 2.5 and 5 eV for He^+ and O^+ projectiles. In order to obtain an estimate of the energies of the ion groups contributing to the yield within this region, the well-defined peaks at 2.0 eV and 6.1 eV were represented by simple triangular functions which were then subtracted from the experimental O^+ energy distribution obtained with O^+ projectiles. The reduced energy distribution was then approximated with triangular functions having peak energies at 2.7, 3.5, 4.0, and 4.7 eV corresponding to the peaks labeled 3, 4, 5, and 6 in Fig. 1. There was an indication that peak 6 may be a composite of two energy groups. These energy values must be regarded only as estimates which are consistent with the data obtained with O^+ projectiles. Similar structure is seen in the O^+ distribution obtained with He^+ projectiles, but the O^+ distribution obtained with H^+ projectiles gives evidence for excitation of only two groups in the 2.5–5-eV region. This method of data reduction was employed to obtain the energies of other ion groups indicated on the figures and in the table.

The assignment of energy values was facilitated by the availability of data obtained with the three kinds of projectiles. The figures show that the yield of the high-energy fragments increases relative to the low-energy fragments with the type of projectile going from H^+ to O^+. This feature is similar for the O^+, O^{2+}, and O^{3+} energy distribu-

TABLE I. Fragment energy (eV).

Peak	O^+	O^{2+}	O^{3+}
1	0.8	2.1[a]	16.0[a]
2	2.0	5.3	19.0[a]
3	2.7[b]	8.6	21.5
4	3.5[b]	14.0	35.3
5	4.0[b]	19.7[a]	56.0[a]
6	4.7[b]	21.6[a]	65.0[a]
7	6.1	23.6	
8	9.3	26.6[a]	
9		31.6[a]	
Estimated uncertainty of resolved peak position	±0.1 eV	±0.3 eV	±0.5 eV

[a] These peak values represent estimates of unresolved, weakly contributing, energy groups superposed on the principal energy groups of the O^{2+} and O^{3+} distributions.

[b] These peak values are estimates of the unresolved energy groups in the 2.5–5-eV region.

tion. The energy values corresponding to the positions of the peaks were determined from the distributions in which they were most prominent. This information was used to reduce the data to obtain peak values for the unresolved energy groups. The accuracy of a particular energy assignment could be judged by identifying that energy group in the two or three distributions in which it occurred; i.e. for H^+, He^+, and O^+ projectiles.

The O^+ yield for H^+ projectiles on O_2 is similar to the O^+ yield which has been observed in the low-energy electron-bombardment and photoionization experiments. The O^+ yield from H^+, however, indicates a contribution from the 6.1-eV group and a smaller contribution from the 9.3-eV group. Evidence for these two groups first appears in the results of Van Brunt *et al.*[6] for electron-bombardment energies above 150 eV. The appearance-potential measurements of Van Brunt *et al.*[6] suggest that the 9.3-eV group is the result of several processes. The increase in the yield of the 6.1 and 9.3-eV groups for He^+ and O^+ projectiles suggests that double ionization may be important. The Coulomb-repulsion energy for double ionization is about 12 eV so that double ionization could contribute to each of these groups.[6] The O^+ distribution for O^+ projectiles extends to about 30 eV and shows evidence for a group near 14 eV which has not been included in the table.

The O^{2+} distributions of Fig. 2 and the O^{3+} distributions of Fig. 3 represent dissociation processes which have not previously been observed. The energetic fragments with multiple charges are produced by dissociation through states of high excitation which have not yet been identified.

The yield of O^+, O^{2+}, and O^{3+} fragments for each kind of projectile can be compared since they were measured concurrently. In Figs. 1, 2, and 3, the full-scale values for O^+, O^{2+}, and O^{3+} yields are in the ratios 1:0.3:0.05 for O^+ projectiles, 1:0.06:0.004 for He^+ projectiles, and 1:0.008 for H^+ projectiles. For each projectile the relative yields for O^+, O^{2+}, and O^{3+} fragments were determined by integrating the energy distributions above 1.5 eV. These O^+, O^{2+}, and O^{3+} yields are in the ratios 1:0.51:0.06 for O^+ projectiles, 1:0.11:0.004 for He^+ projectiles, and 1:0.03 for H^+ projectiles. A comparison between projectiles is not possible because of charge collection uncertainties.

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