

Asymmetrical dissociative ionization of N_2^+ and O_2^+ by electron impact

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Abstract. Absolute cross sections for electron impact formation of N^{2+} from N_2^+ and O^{2+} from O_2^+ have been measured in the energy range from below threshold to approximately 2000 eV. The animated crossed beams method has been employed. The cross sections at the maximum are found to be $8.4 \times 10^{-19} \text{ cm}^2$ and $12.1 \times 10^{-19} \text{ cm}^2$, respectively, and the corresponding threshold energies are determined to be $43.7 \pm 0.5 \text{ eV}$ and $36.8 \pm 0.5 \text{ eV}$. From an energy analysis of the collected dissociation products (N^{2+} and O^{2+}), the maximum centre of mass energy available is found to be $13.0 \pm 1 \text{ eV}$ and $14.6 \pm 1 \text{ eV}$, respectively.

1. Introduction

Dissociative ionization of molecules by electron impact, resulting in the formation of atomic ions or more complex charged fragments, is an important aspect of molecular dynamics in astrophysics and in laboratory plasmas. Cross section measurements for ionization of neutral molecules in general have been carried out for more than 50 years and in particular, efforts have also been directed to the investigation of dissociative ionization processes (Märk and Dunn 1985). For molecular ions the situation is less investigated: very few cross section measurements have been performed for electron impact processes. A recent paper (Belic *et al* 1997) has demonstrated the ability of the crossed electron–ion beam method to obtain absolute values of cross sections for dissociative ionization processes. In addition, an energy scan of dissociation products allows the determination of the maximum internal energy available for these products. Results were presented for electron impact ionization and asymmetrical dissociative ionization of CO^+ .

Many studies have been concerned with the formation of doubly ionized species from molecules since the work of Hagstrum and Tate (1941). For N_2 , Kieffer and Van Brunt (1967) observed N^{2+} ions formed by electron impact. The appearance energy as well as the kinetic energy distribution were measured. Deleanu and Stockdale (1975) and Loch and Momigny (1979) repeated this experiment while Crowe and McConkey (1975) measured both the angular and the ion energy distributions, and more recently, Krishnakumar and Srivastava (1990) determined cross sections. However a large discrepancy exists between the appearance energy for N^{2+} measured by these authors. Furthermore, no thermal ions have been observed in the N^{2+} ion energy distribution although the authors have searched for them (Crowe and

McConkey 1975). Potential energy curves have been calculated for doubly positive diatomic ions such as N_2^{2+} , O_2^{2+} and NO^{2+} by Hurley (1962).

For O_2^{2+} formation from O_2 , Loch and Momigny (1979) measured the threshold energy and kinetic energy distributions and, more recently, Krishnakumar and Srivastava (1992) measured the corresponding cross section.

In this paper we present cross section measurements for electron impact asymmetrical dissociative ionization of N_2^+ and O_2^+ molecular ions. Here a doubly charged atomic ion is produced, presumably together with a neutral atom:



Reactions which produce a second charged particle instead of a neutral atom are supposed to be less abundant and are not considered here. Only atomic dications are detected and absolute cross sections are presented for reaction (1) (σ_1) and reaction (2) (σ_2), for energies from below threshold to approximately 2000 eV. The maximum kinetic energy available in the centre of mass is determined from an energy analysis of the collected dissociation products (N^{2+} and O^{2+}).

2. Experimental method and apparatus

In this experiment, the animated crossed beams method has been employed (Defrance *et al* 1981). The apparatus has been described elsewhere (Zambra *et al* 1994) and only a brief outline is given here.

N_2^+ and O_2^+ ions are extracted from a Penning ion source and accelerated to 4 keV. The ion beam is selected by means of a 30° magnetic analyser and focused into the collision region. A ribbon shaped electron beam is focused into the collision region where it crosses the ion beam at right angles. During the measurements the electron beam is swept across the ion beam in a linear see-saw motion, at a constant velocity.

Product ions are selected by means of a 90° magnetic analyser. They are additionally deflected by a spherical 90° electrostatic deflector and directed onto a channelplate detector. The primary ion beam is collected in a wide Faraday cup located inside the magnetic field. From the measured quantities the ionization cross section is determined by the following expression:

$$\sigma = \frac{v_e v_i u K}{(v_e^2 + v_i^2)^{1/2} (I_e/e) (I_i/qe)} \quad (3)$$

where u is the electron beam scanning velocity, K is the total number of events produced during one passage of electrons across the ion beam, v_e and v_i , I_e and I_i , e and qe are the velocities, currents and charges of electrons and ions, respectively.

Typical working conditions in the present experiment are: $I_e = 1$ mA, $I_i = 100$ nA, $u = 3.75$ m s $^{-1}$ and $K = 2$. All slits and apertures between the collision region and the ion detector are dimensioned to provide total ion transmission in the ionization experiments (Zambra *et al* 1994). In cases where dissociation takes place, internal energy is transferred to the products. They exhibit wider angular and energy distributions so that the transmission is not total. The angular divergence is controlled by means of an appropriate lens, but the restricted energy acceptance of the magnetic analyser prevents total ion transmission from being achieved. In order to estimate this transmission, apparent cross sections are measured as a function of the analysing magnetic field (B) both for the investigated dissociation process and for an ionization process for which total transmission of products is easily achieved. The

Table 1. Absolute cross section for asymmetrical dissociative ionization of N_2^+ by electron impact.

E_e (eV)	σ_1 (10^{-19} cm 2)	$\Delta\sigma$ (10^{-19} cm 2)	E_e (eV)	σ_1 (10^{-19} cm 2)	$\Delta\sigma$ (10^{-19} cm 2)
31.2	-0.48	0.29	91.2	7.49	0.17
36.2	0.12	0.25	96.2	7.76	0.14
42.2	-0.29	0.29	101.2	8.13	0.12
44.2	0.08	0.21	111.2	8.38	0.14
45.2	0.33	0.25	121.2	8.38	0.21
46.2	0.44	0.14	131.2	8.36	0.17
48.2	0.85	0.14	146.2	8.4	0.17
50.2	1.12	0.14	171.2	8.34	0.19
52.2	1.37	0.12	196.2	8.11	0.12
53.2	2.04	0.14	221.2	7.49	0.1
54.2	2.72	0.17	246.2	6.95	0.14
56.2	3.33	0.25	271.2	6.66	0.14
59.2	3.72	0.14	296.2	6.01	0.1
61.2	4.18	0.12	346.2	5.39	0.12
63.7	4.7	0.12	396.2	4.55	0.08
66.2	4.95	0.19	496.2	3.74	0.08
68.7	5.32	0.21	596.2	3.43	0.08
71.2	5.72	0.12	796.2	2.79	0.08
73.2	5.86	0.14	996.2	2.37	0.08
76.2	5.99	0.1	1196.2	2.08	0.08
78.2	6.2	0.17	1496.2	1.68	0.08
81.2	6.76	0.17	1996.2	1.23	0.08
86.2	7.11	0.12	—	—	—

transmission window is first determined from the apparent ionization signal profile and next, the actual transmission is obtained by estimating the percentage of ions passing through that window under measuring conditions. The values deduced from this procedure are 48% and 54% for N_2^{2+} and O_2^{2+} transmission, respectively. In addition, we have measured the field limits of the recorded profiles (B_m and B_M) which correspond to the detection of products with minimum and maximum energy available in the laboratory, that is, to ions emitted with the maximum velocity in the backward and in the forward directions, respectively. Simple kinematics calculations allow the determination of this velocity from the experimental conditions and subsequently, the maximum energy given to the dissociation products in the centre of mass. The time of flight of N_2^{2+} and O_2^{2+} ions from the collision region to the detector, is about 9 and 10 μ s, respectively.

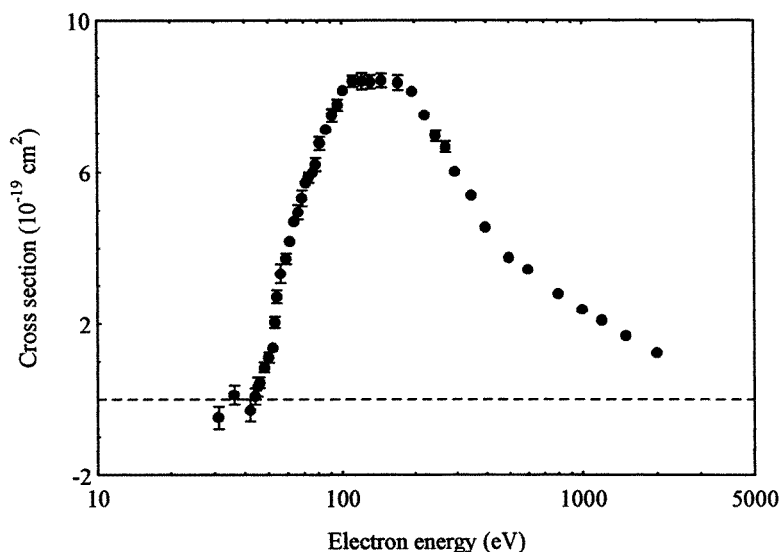
The total absolute uncertainty of the cross section is obtained as the quadrature sum of counting statistics and systematic uncertainties of all measured quantities. The total absolute uncertainty is estimated to be less than $\pm 5.5\%$ and $\pm 7.5\%$ at the cross section maximum for processes (1) and (2), respectively. The electron energy is corrected for contact potentials and for the ion velocity. The error on the true collision energy (E) is about 0.5 eV.

3. Results and discussion

The results are listed in table 1 for process (1), and in table 2 for process (2), together with corresponding electron energies and associated statistical errors which represent one standard deviation of the counting statistics, only. The data have been corrected for the non-total product ion transmission. The results are also shown in figures 1 and 2 for N_2^+ and O_2^+ asymmetrical

Table 2. Absolute cross section for asymmetrical dissociative ionization of O_2^+ by electron impact.

E_e (eV)	σ_2 (10^{-19} cm 2)	$\Delta\sigma$ (10^{-19} cm 2)	E_e (eV)	σ_2 (10^{-19} cm 2)	$\Delta\sigma$ (10^{-19} cm 2)
31.2	-0.07	0.16	106.2	12.08	0.2
33.7	0.11	0.2	116.2	12.06	0.18
36.2	-0.07	0.41	126.2	12.19	0.18
37.2	-0.02	0.22	146.2	12.08	0.18
38.2	0.37	0.2	171.2	11.84	0.13
38.7	0.68	0.22	196.2	11.54	0.13
41.2	1.44	0.29	221.2	10.86	0.17
43.7	2.05	0.24	246.2	10.54	0.15
46.2	2.79	0.31	271.2	9.95	0.17
48.7	3.81	0.28	296.2	9.51	0.11
51.2	4.18	0.24	346.2	8.82	0.15
53.7	4.96	0.24	396.2	8.07	0.13
56.2	5.9	0.24	496.2	6.72	0.09
61.2	6.99	0.31	596.2	6.07	0.09
66.2	8.1	0.17	796.2	4.99	0.11
71.2	9.12	0.22	996.2	4.22	0.11
76.2	9.88	0.2	1246.2	3.52	0.11
86.2	10.93	0.2	1496.2	3.05	0.11
96.2	11.52	0.2	1996.2	2.42	0.11

**Figure 1.** Absolute cross sections versus electron energy for electron impact asymmetrical dissociative ionization of N_2^+ . The error bars are one standard deviation statistical uncertainty.

dissociative ionization, respectively. To the best knowledge of the authors, there are no other measurements or theoretical predictions to be compared with present data.

From extrapolating the cross section to zero, respective thresholds are determined to be 43.7 ± 0.5 eV and 36.8 ± 0.5 eV. By taking into account the ionization potential of the corresponding neutral molecules (15.6 eV and 12.2 eV for N_2 and O_2 , respectively) the lower doubly ionized states reached in this experiment are found to be 59.3 eV and 49.0 eV above

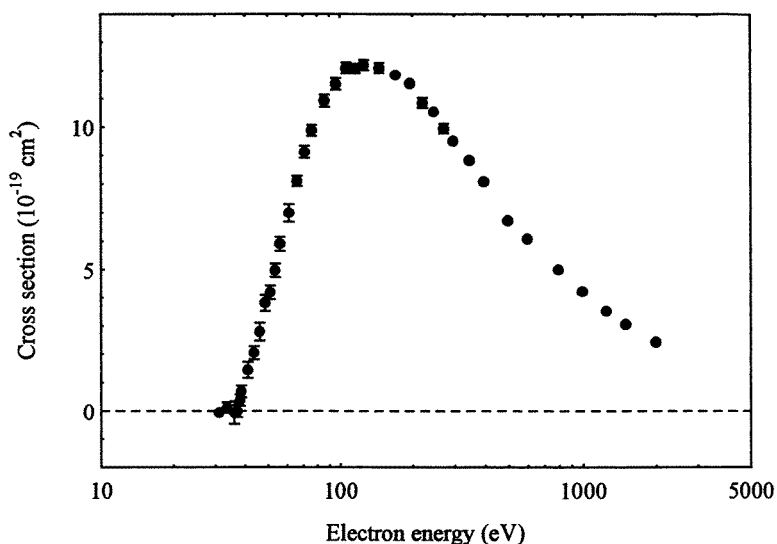


Figure 2. Absolute cross sections versus electron energy for electron impact asymmetrical dissociative ionization of O_2^+ . The error bars are one standard deviation statistical uncertainty.

the N_2 and O_2 ground states in the Franck–Condon region. For N^{2+} production, the value is in good agreement with the results obtained from electron impact ionization of neutral N_2 molecules by Briglia (1963), 62 ± 0.2 eV, Crowe and McConkey (1973), 60.3 ± 2.0 eV and Kieffer and Van Brunt (1967), 62 eV. These values are much higher than the spectroscopic value (53.9 eV) for the dissociation limit, $N^{2+}(^2P) + N(^4S)$, from the ground state and even higher than the double photoionization threshold (43.0 eV, Dawber *et al* 1994). For O^{2+} ion production, the present result clearly disagrees with the results obtained from electron impact ionization of O_2 (54 ± 1 eV, Krishnakumar and Srivastava 1992), and totally with the one 60.5 ± 0.8 eV, obtained by Loch and Momigny (1979). The double photoionization threshold was determined to be 35.5 eV (Dawber *et al* 1994) above the ground state of the neutral molecule. In addition the presently observed threshold is found to be located below the dissociation limit, $O^{2+}(^3P) + O(^3P)$ (53.7 eV, Hierl and Franklin 1967), a result which can be accepted only if a long-lived metastable excited state population is assumed to be present in the primary ion beam. The $a^4\Pi_u$ state is located 4 eV above the ground state (Herzberg 1950) and its population can explain the above-mentioned discrepancy as well as the disagreement with the threshold obtained for electron impact ionization of O_2 .

Additional information is deduced from the analysis of the product energy spectra in the laboratory frame, which can be deconvoluted in order to obtain the corresponding energy spectra in the centre of mass frame. This experiment does not allow the determination of this kind of detailed information, but the maximum kinetic energy transferred to dissociation products is obtained from a magnetic field scan of apparent cross sections, used to determine the ion transmission. According to this procedure (see section 2), these energies are determined to be 13.0 ± 1 eV and 14.6 ± 1 eV for N^{2+} and O^{2+} , respectively. These values correspond to the upper limit of the Franck–Condon transition region.

For N^{2+} production, the experimentally determined threshold is located above the corresponding lowest dissociation limit (53.9 eV). The difference (5.4 eV) corresponds to the minimum kinetic energy distributed between the dissociation products. According to the maximum kinetic energy (13.0 eV) transferred to these products, the energy range available in

Franck–Condon transitions is 7.6 ± 1.0 eV. For O^{2+} , it is not possible to determine the lower limit of the Franck–Condon region because of the presence of excited states.

The potential energy curves leading to asymmetrical dissociation have not been studied in detail so far, and therefore no information can be given concerning the states in the present discussion.

For atomic ions, the scaling of results along an isoelectronic sequence provides information on the respective role of various ionization mechanisms. For molecular ions, such a scaling is valid for a limited number of situations only. N_2^+ and CO^+ , previously studied (Belic *et al* 1997), belong to the same isoelectronic sequence so that the respective results obtained for asymmetrical dissociative ionization can be compared with each other. In the CO^+ case, two channels are to be considered (C^{2+} and O^{2+} formation) instead of one only for N_2^+ . The thresholds for the processes in question are very close to each other and the shapes of the curves look very similar. The ratio of the respective total asymmetrical dissociative ionization cross sections for CO^+ and N_2^+ is found to be almost constant above 80 eV. This ratio is evaluated to be 0.60 ± 0.06 , a figure which is much smaller than unity.

This fact cannot be explained by the size of the molecular ions: their internuclear distances are nearly identical. The reason is probably found in the electronic structure which is very different for CO^+ and N_2^+ . The type, order and number of the highest excited states of dications are strongly affected by changes in the charges of nuclei and by the electronic structure of dissociation fragments. As a consequence, the corresponding repulsive potential curves are very different from each other. This should explain the low value of the above-mentioned cross section ratio. In addition, the different lifetimes of the respective doubly charged molecular ions will certainly affect the formation of the corresponding doubly charged atomic ions.

4. Summary

Absolute cross sections for electron impact asymmetrical dissociative ionization of N_2^+ and O_2^+ molecular ions are reported. The cross sections at the maximum are found to be 8.4×10^{-19} cm² and 12.1×10^{-19} cm² for N^{2+} and O^{2+} formation, respectively. For N_2^+ , the Franck–Condon region is clearly determined to extend from 5.4 to 13 eV above the dissociation limit. For O^{2+} , only the upper limit (14.6 eV) of the Franck–Condon region can be determined, due to the presence of O_2^+ ions probably formed in the long-lived a $^4\Pi_u$ excited state.

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