Cross section for single and double ionization of N_2 and O_2 molecules by electron impact from threshold up to 170 eV

T. D. Märk

Institut für Atomphysik der Universität Innsbruck, A 6020 Innsbruck, Österreich
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Absolute ionization cross sections have been measured for the processes $N_2 + e \rightarrow N_2^+ + 2e$, $N_2 + e \rightarrow N_2^{++} + 3e$, $O_2 + e \rightarrow O_2^+ + 2e$, and $O_2 + e \rightarrow O_2^{++} + 3e$ as a function of electron energy up to 170 eV in a crossed molecule–electron beam apparatus. The ionization cross section curve for producing the singly charged parent ions N_2^+ and O_2^+ is found to have at least one inflection of the type first observed by Lawrence for mercury. Using nth root extrapolation the following minimum ionization potentials were derived from the low energy cross section behavior: $N_2^+(X\,^2\Sigma_g^+) = 15.6 \pm 0.1$ eV, $N_2^{++}(^3\Pi_u) = 42.9 \pm 0.3$ eV, $O_2^+(X\,^2\Pi_g) = 12.1 \pm 0.1$ eV, and $O_2^{++}(X\,^1\Sigma_g^+) = 35.6 \pm 0.3$ eV. From distinct breaks in the single ionization cross section curve the following excited states were observed; $N_2^+(B\,^2\Sigma_u^+) = 18.8 \pm 0.2$ eV, $O_2^+(a\,^4\Pi_u) = 16.0 \pm 0.2$ eV, and $O_2^+(^2\Sigma_g^-) = 21.0 \pm 0.2$ eV. In the double ionization cases, a square law was found from threshold up to some 20 eV above threshold. All results are compared with previous measurements if available.

I. INTRODUCTION

Experimental information on the electronic states of doubly ionized diatomic molecules such as N_2^{++} and O_2^{++} and the production of such ions from neutral molecules is scarce. This lack of data is due partly to the fact that for most diatomics, the doubly charged ions are unstable with respect to dissociation. In addition, for homonuclear diatomics, doubly charged parent ions and singly charged fragment ions have the same value of m/e. Nevertheless, the ionization cross sections for the double ionization of N_2 and O_2 are of much interest in radiation physics and plasma physics, as well as for astrophysical objects (polar aurorae, comet tails,[1] and auroral ionosphere[2]).

The majority of the few previous studies on N_2^{++} and O_2^{++} ions have been concerned with their appearance potentials[3-7] and with theoretical calculations of their potential energy curves.[8,9] All of the doubly ionized ionic states are metastable. Many of them, however, have potential maxima at intermediate internuclear distances sufficiently high to give them lifetimes of many seconds.

The author is aware of only three previous measurements[10-12] of the direct ionization cross section of N_2^{++}, and of none for O_2^{++}, save a rough estimate.[13] Two of these studies[10,11] of the cross section $q\,(N_2^{++}/N_2)$[14] for the reaction $N_2 + e \rightarrow N_2^{++} + 3e$ have used normalization procedures later questioned by Crowe et al.[16] References 10, 11 also reported N_2^+ ionization cross section curves quite different in shape from measurements by other authors,[4,16-19] as discussed by Crowe et al.[16] The third study of N_2^{++},[12] made by the present author with a different normalization procedure, however, was concerned only with $q\,(N_2^{++}/N_2)$ at a fixed electron energy of 70 eV. Thus, it was felt necessary to extend[20] the previous work[12] in the present study. The doubly ionized molecules were measured by monitoring in the mass spectrometer the heteroisotopic molecules with odd mass numbers, e.g., $(^{14}N^{15}N)$ and $(^{16}O^{17}O)$.

In the present study it is necessary to normalize $q\,(N_2^{++}/N_2)$ against $q\,(N_2^+/N_2)$ and $q\,(O_2^{++}/O_2)$ against $q\,(O_2^+/O_2)$. Because of the poor agreement in magnitude and shape[21] among the few studies of the absolute cross sections $q\,(N_2^+/N_2)$[4,10,11,16-19,22-24] and $q\,(O_2^+/O_2)$[18,19,24] as functions of electron energy, it was thought necessary to redetermine these dependencies.

II. APPARATUS AND TECHNIQUE

The apparatus used in the present study is identical with that described fully in a previous paper from this laboratory.[25] Basically it consists of a molecular type of electron impact ion source and a high resolution double-focusing mass spectrometer, Varian MAT CH5, with a total dynamic range of 1×10^8. Great care was taken to reduce disturbing instrumental effects in the ion source in order to obtain accurate ionization cross section curves of N_2^+, N_2^{++}, O_2^+, O_2^{++} as functions of electron energy. For reference the curve was also obtained for Ar^+. Consistency checks and energy scale calibration have been reported and discussed previously.[12,25]

Normalization of the measured relative cross sections $q\,(N_2^+/N_2)$ and $q\,(O_2^+/O_2)$ to give absolute values has been made by a method described previously,[25] in which these relative cross sections are compared at a particular electron energy with that of the well known absolute cross section of Ar^+. The comparison was usually made at the cross section maximum of argon, the maximum having a value of 2.72×10^{-16} cm^2[18,26] at 110 eV electron energy. The relative measurement of the gas pressure in the collision chamber necessary for this calibration was made by means of a modified effusive flow method with an absolute capacitance manometer. According to Rapp et al.[18] and Märk et al.[25] the results thus obtained are believed to be more accurate than those based on direct McLeod-gauge measurements in each gas.

In turn, these results were used to normalize the measured relative cross sections $q\,(N_2^{++}/N_2)$ and $q\,(O_2^{++}/O_2)$. Because the double ionization cross section could be measured only through the $(^{14}N^{15}N)^{++}$ and $(^{18}O^{17}O)^{++}$ ion, the molecular isotopic abundance had to be taken into account. Moreover, in both normalization procedures corrections for the different electron multiplier gain γ for the different ions were made. The required values of γ were obtained by means of a calibration with a Far-
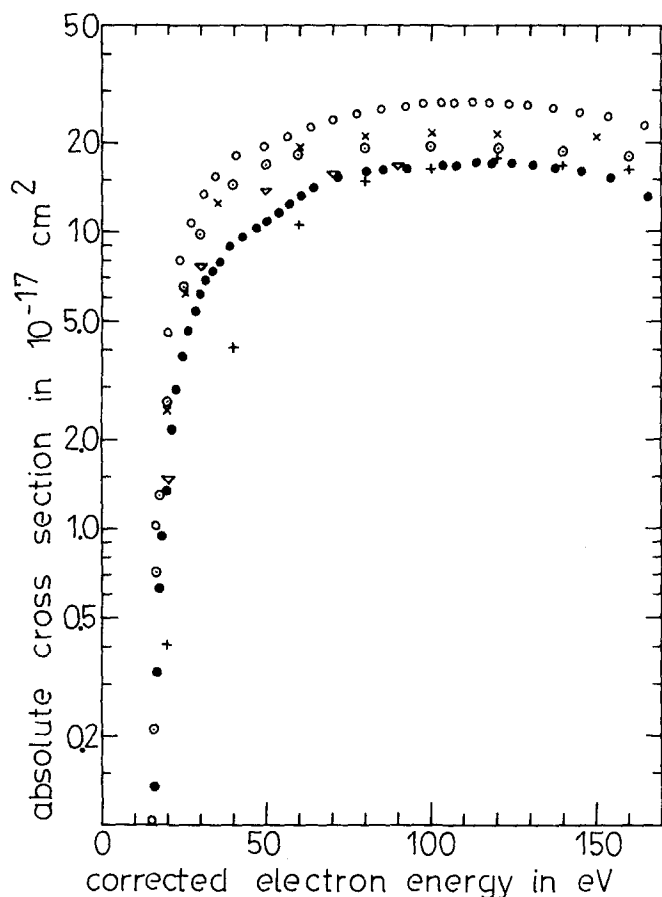
FIG. 1. Absolute ionization cross section for the production of
N_2^+: ● present data; + Daly et al.,[10] and ▽ Hagstrum et al.[4]
and Stevenson et al.[17] (all normalized to the present curve);
× Halas et al.[11] and ○ curve derived from measurements of
Rapp et al.[18,19] for $q((N_2^+ + 2N_2^{++})/N_2)$; $q(Ar^+/Ar)$ is designated
by ○ (see text for normalization procedures). The energy scale
of the present data was calibrated by means of the linear ex-
trapolation method, taking the ionization of Ar^+ as 15.76 eV
(spectroscopic value).

aday cup at 3 kV ion accelerating voltage: $\gamma\ (N_2^+)/\gamma\ (Ar^+)$
$= 1.35$, $\gamma\ (N_2^{++})/\gamma\ (Ar^+) = 1.52$ and $\gamma\ (O_2^+)/\gamma\ (Ar^+) = 1.39$.
Because of the small signal of $(^{16}O^{17}O)^{++}$ in oxygen of
natural abundance it was not possible to measure γ
$(O_2^{++})/\gamma\ (Ar^+)$. Thus the correction factor of N_2^{++} had to
be applied to O_2^{++}. This was thought justifiable in light
of the similarity of the singly charged ion corrections
for both gases.

The accuracy of the ion current data was in general
better than ± 1%. For very low ion currents, i.e., O_2^{++},
however, the error could be as large as ± 5%. The ac-
curacy of the relative pressure measurement for the ab-
solute calibration of the cross sections depends on the
accuracy of measurement of p (capacitance manometer
Barocel ± 0.05%) and on the adequacy of the assumption
of effusive flow. In accordance with Rapp et al.[18] and
Märk et al.[25] the accuracy for repeated measurements
at different effusive flow conditions was found to be
about ± 4%. Thus, the estimated maximum possible er-
ror, except for the error in the Ar^+ cross section, is
~ ± 5% to 10%.

III. RESULTS AND DISCUSSION

A. Single and double ionization cross section

1. Nitrogen

The absolute cross sections obtained for the processes
$N_2 + e \rightarrow N_2^+ + 2e$ and $N_2 + e \rightarrow N_2^{++} + 3e$ are shown semiloga-
rithmically as a function of electron energy in Figs. 1
and 2, respectively. It can be seen that the N_2^+ curve
has its peak near 120 eV while the N_2^{++} curve peaks
around 130 eV. A representative set of values of all
cross sections measured in the present work is given
numerically in Table I.

Figure 1 also shows the ionization cross section curve
obtained for Ar^+ ions, which has been expressed as an
absolute ionization cross section by normalizing this
curve at its peak, viz. 110 eV. The absolute cross sec-
tion at this energy is estimated to be 2.72×10^{-16} cm^2.
In obtaining this figure the total ionization cross section
measured by Rapp et al.[18] was used. The data from Gaudin
et al.[26] were used to adjust Rapp's data to single ionization.

It should be noted that the ionization cross section
curve obtained in the present work for the singly charged
argon ion exhibited an inflection at about 50 eV electron
energy. This inflection has been reported[17,27,28] only
when great care has been taken to fulfill the require-
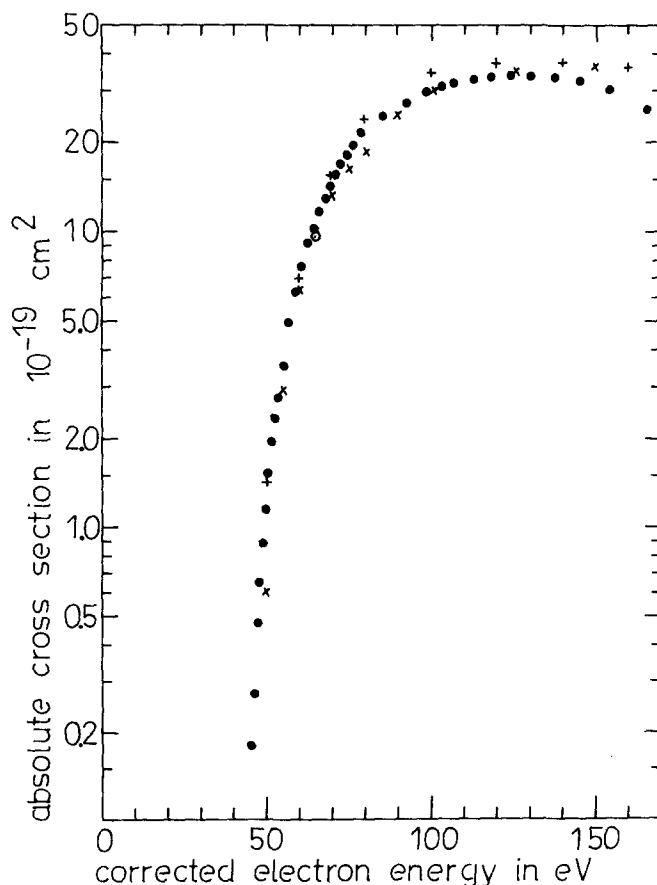ments for the measurements of accurate ionization cross

FIG. 2. Absolute ionization cross section $q(N_2^{++}/N_2)$: ● pres-
ent data, + Daly et al.,[10] × Halas et al.[11] and ○ result reported
by Märk,[12] which were recalibrated against the presently ob-
tained $q(N_2^+/N_2)$.

TABLE I. Experimentally obtained ionization cross sections versus corrected electron energy.

E eV	$q(N_2^+/N_2)$ 10^{-16}cm²	$q(N_2^{++}/N_2)$ 10^{-18}cm²	E eV	$q(O_2^+/O_2)$ 10^{-16}cm²	$q(O_2^{++}/O_2)$ 10^{-18} cm²
165.5	1.33	2.59	167	1.46	1.00
154.5	1.51	3.01	156	1.58	1.04
145.5	1.59	3.22	147	1.63	1.05
137.5	1.63	3.31	139	1.66	1.07
124.5	1.68	3.35	126	1.70	1.04
118.5	1.70	3.32	115	1.73	1.03
107.5	1.68	3.18	109	1.75	1.02
98.5	1.64	2.95	100	1.70	0.93
85.5	1.60	2.43	94.5	1.66	0.87
78.5	1.58	2.17	80	1.57	0.62
71.5	1.50	1.56	73	1.48	0.415
68.5	1.43	1.30	70	1.39	0.348
64.5	1.38	1.02	66	1.32	0.273
60.5	1.30	0.76	62	1.25	0.236
57.0	1.22	0.494	58.5	1.16	0.173
53.5	1.16	0.277	55	1.08	0.119
50.0	1.09	0.115	53	···	0.104
46.5	1.03	0.0278	51.5	0.99	0.80
44.5	···	0.0065	48	0.91	0.450
42.5	0.96	···	44	0.83	0.226
35.5	0.78	···	42	···	0.111
32.0	0.68	···	37	0.64	···
28.0	0.54	···	31.5	0.496	···
25.0	0.380	···	28	0.393	···
21.0	0.215	···	22.5	0.230	···
17.5	0.063	···	19	0.114	···
16.5	0.0335	···	17.5	0.073	···
15.5	0.0135	···	15.0	0.0290	···
15.0	0.0067	···	13.5	0.0087	···
14.5	0.0016	···	13.0	0.0049	···

Fig. 1 these values were normalized to the present curve at 90 eV. The curve in Fig. 1 designated by + is the result of measurements made by Daly et al.[10] It rises much more slowly to its peak, which lies around 120 eV. For the reasons discussed by Crowe et al.[16] it is difficult to agree with their normalization procedure (giving a peak value of $2.15 \cdot 10^{-16}$ cm²). Their values have thus been normalized to the present curve at its peak, viz. 120 eV, where the absolute cross section is 1.70×10^{-16} cm². Within the reported experimental error of all the above mentioned measurements, agreement with the present result in shape and magnitude is obtained, save a discrepancy in the energy range of 30 to 40 eV.

Figure 1 also shows q (N_2^+/N_2) reported just recently by Halas et al.[11] Their curve was obtained by normalizing the sum of their N_2^+, N^+, and N_2^{++} ionization curves to the total ionization cross section measured by Rapp et al.[18] Thus, it is somewhat astonishing that their q (N_2^+/N_2) curve lies above that derived from the measurements of Rapp et al.[18,19] This can only be explained by the fact that their measured fraction of N^+, N_2^{++}, and N^{++} is too small. According to Crowe et al.[16] this indeed seems to be the reason. It is interesting to note, however, that the shape of the q (N_2^+/N_2) curve of Halas et al.[11] is in excellent agreement with the present result. Not shown in Fig. 1 are the q (N_2^+/N_2) results by Cook et

section curves. Such structure in the ionization curve may be explained as due either to production of the ion via various channels[27,29,30] or to competition between the parent ion (e.g., Ar^+) and a new ion (e.g., Ar^{++}).[28,31] Because the apparatus used in the present work has sufficient sensitivity to reproduce the inflection in the argon curve, we believe it also is giving the N_2 and O_2 curve shapes reliably. It is interesting to observe also that the presently reported ionization cross section curve of N_2^+ (to a lesser degree O_2^+) exhibits at least one inflection above the threshold energy of N_2^{++} (see also Figs. 4 and 5).

Figures 1 and 2 also show ionization cross section curves for N_2^+ and N_2^{++} reported by several other authors. Points designated ⊙ in Fig. 1 represent ionization cross section values derived from measurements by Rapp and Englander-Golden[18] and Rapp et al.[19] They made an absolute measurement of the total ionization cross section for nitrogen[18] and of the cross section for production of ions with kinetic energies > 0.25 eV in nitrogen.[19] Hence, subtraction of the energetic ion curve,[32] corrected by 5%[12,33] for dissociative ions with energies close to thermal, from the total ion curve should give the cross section for the production of $N_2^+ + 2N_2^{++}$. Also shown in Fig. 1 is the relative ionization cross section curve obtained by Hagstrum et al.[4] and Stevenson et al.[17] for N_2^+. Their values ranged from threshold up to 100 eV and in this regime the slope of their curves are in agreement with that reported by Crowe et al.[16] In
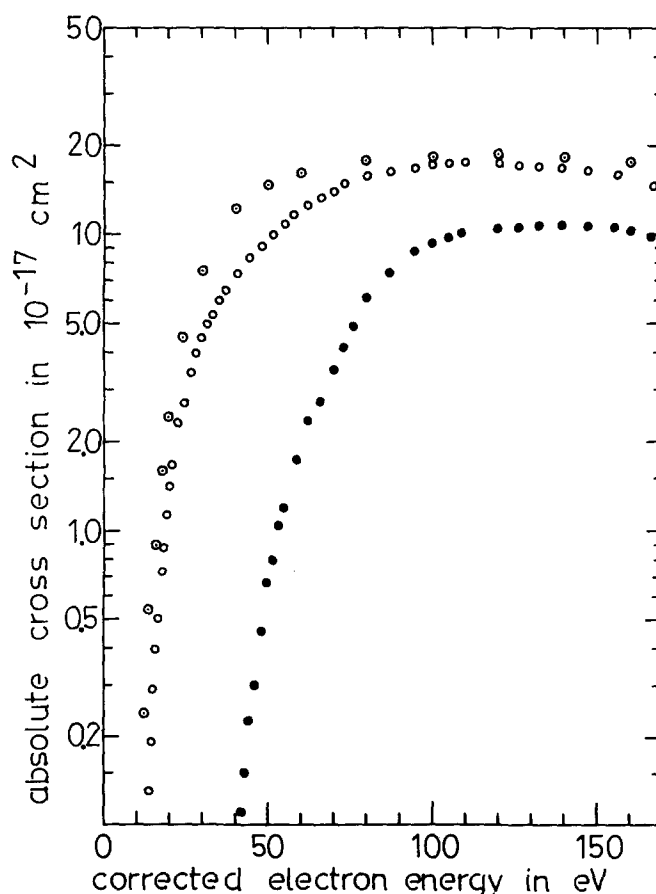

FIG. 3. Absolute ionization cross section $q(O_2^+/O_2)$, designated ○, and $100 \times q(O_2^{++}/O_2)$, designated ●; designated ○, curve for $q((O_2^+ + 2O_2^{++})/O_2)$ derived from measurements of Rapp et al.[18,19]
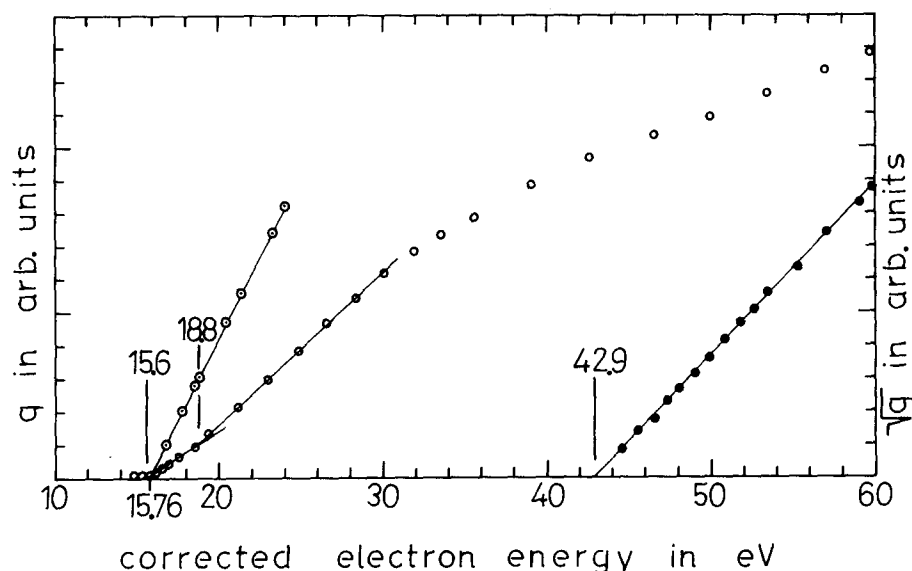
FIG. 4. Relative ionization cross section $q(N_2^+/N_2)$, designated o , and $Ar^+/Ar)$, designated o, and square root of the ionization cross section $q(N_2^{++}/N_2)$, designated ●, versus corrected electron energy.

al.,[22] Peterson,[23] and Peresse *et al.*[24] These results are quite different either in shape or in magnitude from all above mentioned measurements and are probably rather inaccurate for reasons discussed by Crowe *et al.*[16]

From Fig. 2 it can be seen that the curves for double ionization of N_2 measured by Daly *et al.*[10] and Halas *et al.*[11] show relatively good agreement in shape and magnitude with the present data. The agreement is especially good considering the fact that both have used normalization procedures which tend to make their cross sections too large.

2. Oxygen

The absolute cross sections obtained for the processes $O_2 + e \rightarrow O_2^+ + 2e$ and $O_2 + e \rightarrow O_2^{++} + 3e$ are shown semilogarithmically in Fig. 3. Also shown in Fig. 3 are ionization cross sections for the production of $O_2^+ + 2O_2^{++}$ which, just like those for nitrogen, were derived from the measurements of Rapp *et al.*[18] and Rapp *et al.*[19] Again, some discrepancy in the lower energy regime can be observed, which may also be partly due to a difference in the calibration of the energy scale. Not shown are the values of q (O_2^+/O_2) of Peresse *et al.*[23] They reach a maximum of 2.67×10^{-16} cm² at 120 eV. The relative shape, however, of their curve is in good agreement with the present results. The high parent ion cross section values appear to be a special feature of their work. This may be due to an abnormally low measured ratio $(X^+ + 2X_2^{++})/X_2^+$, probably caused by low sensitivity of their apparatus to the dissociatively produced X^+ as compared to its sensitivity to $X_2^+ = O_2^+$, N_2^+, etc.

In the case of O_2^{++} production via reaction $O_2 + e \rightarrow O_2^{++}$ $+ 3e$ only a rough estimate (within a factor of 2) of its abundance as 0.5% of the total ion yield of O_2 at 70 eV electron energy has been reported previously.[13] Using q (O_2^+/O_2 at 70 eV) $= 1.39 \times 10^{-16}$ cm² from the present work, this yields q (O_2^{++}/O_2 at 70 eV) $= 0.70 \times 10^{-18}$ cm², which differs from the present result by a factor of about 2.

It is interesting to note that the maximum of q (O_2^{++}/O_2)

is smaller than the maximum of q (N_2^{++}/N_2) by a factor of about 3, although the maximum of q (O_2^+/O_2) $\cong$ the maximum of q (N_2^+/N_2). This fact may be of great importance in the theory and might be interpreted in terms of simple molecular orbital theory, where the ground state configurations are N_2 $[KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2]$ and O_2 $[KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2]$. From the MO correlation diagram[34] the two outermost orbitals are expected to be weakly bonding for nitrogen and strongly antibonding for oxygen. Removal of these electrons leads to an increase of the equilibrium nuclear separations in nitrogen and a decrease in oxygen,[9] thus raising the probability of dissociation of the doubly ionized molecule of the latter according to the Franck–Condon principle. This is further proved by the fact that the maximum cross section for dissociation of oxygen according to Rapp *et al.*[19] is 50% higher than that of nitrogen, although the maximum total ionization cross section of oxygen is only 10% higher than that of nitrogen.[18]

In addition to the study of the doubly ionized molecules a search was made for the N_2^{3+} and O_2^{3+} ions. No evidence could be detected of their existence, although they would have been observed in the mass spectrometer if the cross section for their production had been $\geq 10^{-26}$ cm².

B. Ionization potentials

From the low energy cross section behavior (Figs. 4 and 5), the minimum ionization potentials of N_2^+ and O_2^+ were derived by means of the linear extrapolation method: N_2^+ $(X^2\Sigma_g^+) = 15.6 \pm 0.1$ eV and O_2^+ $(X^2\Pi_g) = 12.1 \pm 0.1$ eV. Moreover, due to excited states of the ions with a relatively high transition probability, the ionization cross section curves exhibit distinct breaks, corresponding to the higher ionization potentials N_2^+ $(B^2\Sigma_u^+)$ $= 18.8 \pm 0.2$ eV, O_2^+ $(a^4\Pi_u) = 16.0 \pm 0.2$ eV and O_2^+ $(x) = 21.0$ ± 0.2 eV, the latter probably being identical with the not yet-identified $^2\Sigma^-$ state.[35] Values of all reported ionization potentials are in excellent agreement with previous even more detailed measurements by various methods.[36]

Figures 4 and 5 furthermore show plots of the square root of the double ionization cross section in N_2 and O_2
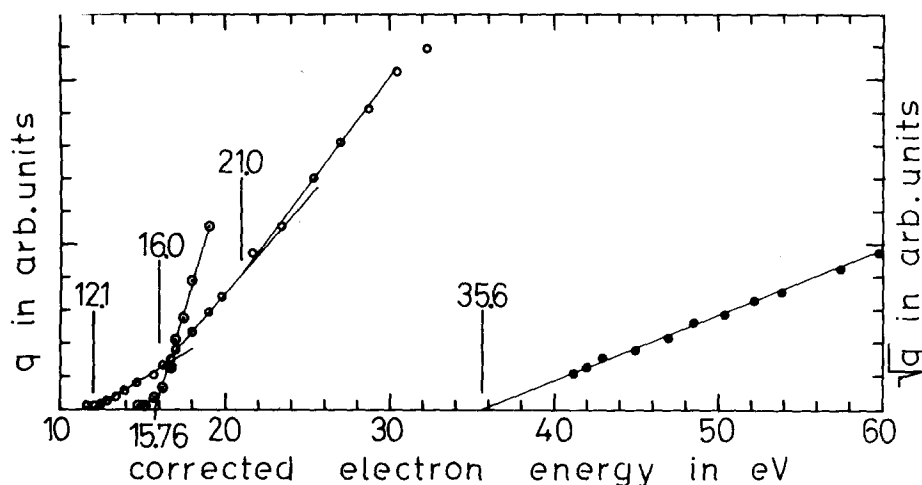
FIG. 5. Relative ionization cross section $q(O_2^+/O_2)$, designated o, and $q(Ar^+/Ar)$, designated ⊙, and the square root of the ionization cross section $q(O_2^{++}/O_2)$, designated ●, versus corrected electron energy.

as a function of electron energy. Dorman et al.[6] reported from measurements of the 1st derivative of the ionization cross section of N_2^{++} and O_2^{++} that a square law is followed for some 10–12 eV above threshold. The curves then change abruptly to a slower rate of increase. However, the authors admit that their data are not recorded with sufficient accuracy. It can be seen in the present study that in both cases a square threshold law is followed for some 20 eV above onset. This may be of great significance in theory and is in clear support of the theoretical arguments of Wannier,[37] which say that the probability for the occurrence of a process of direct n-fold ionization induced by electron impact varies above threshold as the nth power of the excess energy.

On the assumption that the nth power rule is correct, the methods commonly in use[38] for determining the threshold energy for processes of direct single ionization, no longer can be expected to give correct results.[39] In order to obtain reliable results one would like to use a method which takes into account the specific form of the ionization cross section curve, as is the case for single ionization with the linear extrapolation method. Extension of this method, namely the nth root extrapolation has been proved fairly accurate.[39] Thus, in the present study the minimum double ionization potential was taken as the point to which the square root of the double ionization cross section extrapolated to the energy axis, yielding N_2^{++} $(^3\Pi_u) = 42.9 \pm 0.3$ eV and O_2^{++} $(X^1\Sigma_g^+) = 35.6 \pm 0.3$ eV. Data from previous electron im-

pact studies are given in Table II.

Both ions have not been identified by optical spectroscopy, save the 0–0 transition of the $d^1\Sigma_u^+-a^1\Sigma_g^+$ system of N_2^{++},[40] but have been observed in mass spectrometers directly or indirectly. Hagstrum et al.[4] deduced their minimum ionization potentials as I.P. $(N_2^{++}) = 49.5 \pm 0.5$ eV and I.P. $(O_2^{++}) = 50.0 \pm 0.5$ eV from breaks in the ionization cross section curves for ions of $m/e = 14$ and $m/e = 16$, respectively. Dorman et al.[5] measured the first derivative of the ionization cross section curve of N_2^{++} using the isotopic molecule with odd parent mass. They derived from it I.P. $(N_2^{++}) = 43.5 \pm 0.3$ eV. In a latter work[6] they used enriched O_2 with 2% ^{17}O and obtained by means of the square root extrapolation method an I.P. $(O_2^{++}) = 36.3 \pm 0.5$ eV. In a reexamination[6] of the first derivative of ionization curve for N_2^{++} they obtained the two ionization potentials I.P. $(N_2^{++}) = 42.7 \pm 0.1$ eV and I.P. $(N_2^{++}) = 43.8 \pm 0.1$ eV. Daly et al.[7] used a charge transfer reaction in a gas cell to detect O_2^{++}, and obtained observed by means of the square root extrapolation method an ionization potential of 37.2 ± 0.5 eV.

The present I.P. (N_2^{++}) is in excellent agreement with the lower results of Morrison et al.,[6] whereas in the case of oxygen the present I.P. (O_2^{++}) is below the results of Morrison et al.[6] and Daly et al.[7] However, when comparing the present I.P. (N_2^{++}) and I.P. (O_2^{++}) with theoretical predicted spectroscopic constants from Hurley,[9] excellent agreement for both values is evident. Hurley

TABLE II. Summary of values of minimum ionization potentials for N_2^{++} and O_2^{++} obtained by electron impact studies (EIS) and by theoretical calculations (TC).

I.P. (N_2^{++}) in eV	Reference	I.P. (O_2^{++}) in eV	Reference
49.5 ± 0.5	Hagstrum et al. 1941,[4] EIS	50.0 ± 0.5	Hagstrum et al. 1941,[4] EIS
43.5 ± 0.3	Dorman et al. 1961,[5] EIS	36.3 ± 0.5	Dorman et al. 1963,[6] EIS
42.7 ± 0.1	Dorman et al. 1963,[6] EIS	37.2 ± 0.5	Daly et al. 1967,[7] EIS
41.32	Hurley et al. 1961,[8] TC	35.88	Hurley et al. 1961,[8] TC
42.63	Hurley 1962,[9] TC	35.48	Hurley 1962,[9] TC
42.9 ± 0.3	Present result	35.6 ± 0.3	Present result

et al.[8] established an integral form of the quantum mechanical virial theorem leading to an approximate relationship between potential curves of the doubly charged ion and a related neutral molecule. From this the relevant ionization potentials of the ground state curve were obtained,[9] i.e., N_2^{++} $(X\,^3\Pi_u) = 42.63$ and O_2^{++} $(X\,^1\Sigma_g^+) = 35.48$ eV.

No evidence of higher ionization potentials that correspond to excited states of the doubly ionized molecules could be found in the present study. A discussion of this, however, is not justified at the present time, because the data are not obtained with sufficient accuracy, especially those for the lower parts of the oxygen curves. Use of isotopically highly enriched gases could prove to be an adequate remedy.

ACKNOWLEDGMENTS

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