Single- and double-electron-detachment cross sections for O^- collisions with rare-gas atoms

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Atomic single- and double-electron-detachment cross sections are reported for O^- ions in He, Ne, Ar, Kr, and Xe gases, at collision energies from 10 to 115 keV.

I. INTRODUCTION

The detachment of an electron from a negative atomic ion, in a collision with a single atom, has been investigated with sufficient detail (for a review see Risley[1]) that, in the low-energy region where the molecular-orbital approximation is valid, a reasonably good theoretical understanding has been achieved. The main process, direct detachment of a valence electron leaving behind the atom in its ground state, fits quite well using simple theoretical models (Lam *et al.*[2] and Gauyacq[3]). However, in detachment from negative ions without a clearly defined single valence electron, other processes such as simultaneous excitation or ionization can be important. For example, in detachment from the negative ions of the alkali metals which have two valence electrons, a mixture of final states is evident even at the lowest energies above threshold.[4] At keV energies the probability is about 30% that the second electron will be excited and about 5% that it will be detached.[5] The ratio of double detachment to single detachment is much higher for the halogen negative ions, which have a closed electron shell, particularly in I^--Xe collisions where it reaches 50% at collision energies where the molecular orbit approximation is still valid. The relative importance of double detachment seems to be partly a result of the smaller single-detachment cross section.

The mechanism for single detachment from O^- in rare-gas collisions has been examined in detail by Esaulov, Gauyacq, and Doverspike[6] in the energy region below 1 keV. Their energy-loss measurements show that the neutral oxygen atoms which are left behind after the electron has been detached are mainly in the lowest three $^3P_1$, $^1D_1$, and $^1S_1$ states. These states have configuration $1s^2 2s^2 2p^4$, so that they can be formed by direct detachment from the $2p^5$ ground state of O^-, whereas all higher states have a $2p^3nl$ configuration. However, they point out that the initial state $O^-(2p^5\,^2P^o)+\mathscr{R}(^1S_0)$ where $\mathscr{R}$ denotes a rare gas, splits, at finite separations, into two molecular configurations, one of which is $^2\Pi(\pi^3\sigma^2)$ and this can make diabatic level crossings to configurations which asymptotically become double-excited resonance states of O^-. No evidence for these shape resonances was found by Esaulov *et al.*, though the process has been identified in Cl^- detachment. Another property of double-excited configurations is that some are short lived and could also lead to double-electron decay, and so to O^+ formation and to relatively large σ_{-+} cross sections at lower energies.

Electron detachment from O^- has been the most studied of all the negative ions with the exception of H^-. The cross section for electron detachment in a single rare-gas collision has been measured by Cromer and Schulz[7] in the low-energy region up to 14 eV in helium; up to 400 eV by Wynn, Martin, and Bailey[8] in He and Ar; by Bennett, Moseley, and Petersen[9] in He and Ar between 1 and 4 keV; by Hasted[10] up to 3.6 keV in all the rare gases; by Doering[11] in Ar between 1 and 10 keV; and by Matić and Čobić[12] between 5 and 30 keV. Atomic cross sections in helium were deduced from equilibrium charge fractions by Jorgensen *et al.*[13] from 50 to 400 keV. There is also the measurement at 560 keV in He and Ar by Dmitriev *et al.*[14] Only the latter three papers experimentally separate multiple-detachment processes in a single rare-gas collision, and estimate the cross sections for two- and three-electron detachment.

II. EXPERIMENTAL METHOD

Cross sections were measured, using the initial growth method, and a differentially pumped gas target. The proportion of the ingoing negative ions which were converted into neutrals or positive ions during their passage through the target was measured as a function of its gas pressure.

The O^- beam was produced in a conventional rf ion source which was operated with the extraction voltage reversed so that negative ions produced by double-electron capture in the residual gas of the canal were accelerated. After acceleration, $_{16}O^-$ was selected by a 90°, 66-cm-radius magnet.

The beam entering the gas target was collimated by two 0.8-mm-diam. apertures, placed 20 cm apart. The second aperture also defined the entrance to the gas target, so that the direction of the ions entering the cell was restricted to ±0.2°. The length of the target was defined by a 1.5-mm-diam. aperture, which was located 3.81 cm from the entrance aperture, and which was accurately aligned with the collimator apertures by machining all three from a solid piece of brass. This exit aperture was large enough to allow all particles, with scattering angles up to 2° from the central region of the target, to escape into the vacuum, where they were charge separated by a transverse electric field and then counted digitally by three channel electron multipliers (CEM's) placed side by side so as to intercept

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respectively the negative, neutral, and positive ions from the target.

The CEM's were accurately positioned so that the unscattered direction, for each charge state, was at the center of each cone. It was found that, unless precautions were taken, adjacent CEM's would sometimes count in coincidence, probably due to secondary electrons from the cone of one CEM being captured and multiplied in an adjacent CEM. To prevent this it was necessary to align the fronts of the cones, and the grounded intermediate shields, all in the same plane. The distance from the target to the CEM's was chosen so that their 1-cm-diam. cones intercepted all ions which were scattered by angles up to 2° inside the target.

The counting rates were limited to 1 kHz to avoid saturation effects which could cause gain variations. The voltages on the CEM's were kept sufficiently high that the pulse height distributions showed a deep minimum between the ion counts and the background. The discriminator threshold was set low enough in this minimum to ensure that the detection efficiency was near to 100% for all particles over the cone area,[15] but high enough so that the background count was a small correction except at the lowest target pressures.

The pressure inside the target was controlled by a thermal mechanical leak and measured by two independent capacitance manometers in the range from the background pressure to a maximum of 8×10^{-4} Torr. In this pressure range few of the negative ions made more than a single collision in their traversal of the target, and a first-order correction to the thin target approximation was sufficient.

Under these conditions a general relation for the cross section for the change of charge from an initial value i to a final value j is given by[16]

$$T\sigma_{ij}=\frac{N}{1+N/2}\left\{1+\frac{1}{2}\left[\sigma_{ji}+\sum_{k}\left[\sigma_{jk}-\sigma_{ik}-\frac{\sigma_{ik}\sigma_{kj}}{\sigma_{ij}}\right]\right]T\right\},$$

where $i=-1$ for the negative ion beam and j is either 0 or $+1$ for the single- and double-detachment cross sections, respectively. The summations exclude both $k=j$ and $k=i$. N is the ratio, for an initially pure charge i beam, of the numbers of ions of charge j to those of charge i after passing through the target.

Since σ_{ij} occurs in the correction term on the right side, values of σ_{-0} and σ_{0+} were first calculated without the corrections, and these approximate values were then used in the complete expressions. The correction cross sections σ_{+0} and σ_{+2} were obtained from Brackmann and Fite[17] for Ne and Ar. No measurements on the other targets have been reported, so the Ne values were used for He, and the Ar values for Kr and Xe. The σ_{0-} and σ_{0+} cross sections were obtained from Fogel *et al.*[18] up to 65 keV, and were extrapolated to higher energies.

The experimental cross section was extracted by making a linear least-squares fit to a graph of the right side of the equation, plotted as a function of the target-gas pressure. This pressure is proportional to the target thickness $T=nL$, where n is the atomic density of the target gas, and L is the target length.

A further correction was made for electron detachment from the negative-ion beam as it passed through the 2-m length of 5×10^{-7} Torr residual gas between the magnet and the target, so that the graphical plots did not pass through $N=0$ at zero pressure. The correction was made assuming that the residual gas has the same charge-changing cross sections as the target gas itself.

It was found that there was considerable cancellation among the different corrections, but they were in all cases less than the statistical error from the least-squares fit to the line. The corrections were typically a fraction of a percent. The statistical errors, except at the lowest energy for the σ_{-+} cross section, were of the order of 2%. However, daily reproducibility was about 5%, probably due to

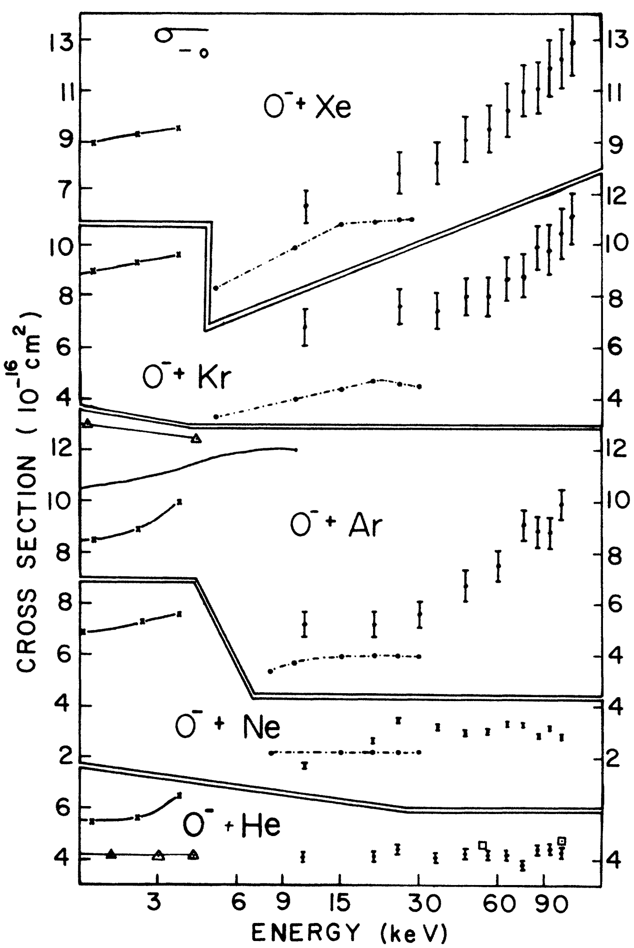

FIG. 1. Cross section for the production of neutral oxygen atoms in the collision of O^- with a rare-gas atom. The continuous lines join the data of Hasted (Ref. 10), the dot-dash lines join the data of Matić and Čobić (Ref. 12), the squares are the data of Jorgensen *et al.* (Ref. 13), and the triangles are the data of Bennett, Moseley, and Petersen (Ref. 9).

TABLE I. Cross sections for the production of oxygen atoms from O^- in single collisions with rare-gas atoms.

Energy (keV)	He	Ne	Target Ar (10^{-16} cm^2)	Kr	Xe
10.9	4.2	1.7	5.2	6.7	6.5
20		2.9	5.2		
25	4.4	3.5		7.6	7.8
30			5.7		
35	4.1	3.3		7.4	8.2
45	4.2	3.0	6.7	7.9	9.1
55	4.2	3.1		7.9	9.5
60			7.5		
65	4.2	3.6		8.6	10.3
75	3.8	3.3	9.1	8.7	11.0
85	4.4	2.9	8.9	9.9	11.1
95	4.5	3.2	8.8	9.8	11.8
105	4.4	2.9	9.9	10.0	12.2
115				11.1	12.9

short-term beam fluctuations. The accuracy of the cross sections is estimated at 10% except for the lowest energy σ_{-+} cross section where it is about 10^{-17} cm^2.

III. RESULTS AND DISCUSSION

A. Single detachment

The results are shown in Table I and compared with previous measurements in Fig. 1. There is good agreement with the data of Matić and Čobić between 4 and 30 keV and the higher-energy helium target data of Jorgensen *et al.*, but the lower-energy cross sections seem too large to extrapolate well to our data. This difference may correlate with experimental technique. The Bennett, Moseley, and Petersen data was deduced from attenuation measurements under multiple-collision conditions. Their high values may be due to incomplete collection of scattered negative ions and other charge-changing cross sections. Hasted, using the electron collection method, found that his measured cross sections changed with the way in which the negative ions were produced in his ion source, and he suggested the presence of varying proportions of metastable O^-, with configuration $(2p)^4 3s$. Bates[19] estimated the energy difference between this configuration and the $(2p)^5$ ground state as 2.0 eV, which was less than early electron affinity estimates. However, more accurate measurements[20] establish that the O^- electron affinity is 1.46 eV, so a state with this structure is likely to be unbound with a short lifetime. Our cross-section results were found to be independent of the gas pressure in the exit canal of the ion source and the energy of the O^+ ions there.

The general trend of the single-detachment cross sections is from complete energy independence in helium, where the cross section is constant from 1 to 400 keV

TABLE II. Cross sections for the production of O^+ ions from O^- in single collisions with rare-gas atoms.

Energy (keV)	He	Ne	Target Ar (10^{-16} cm^2)	Kr	Xe
10.9	1.0	0.76	0.22	0.1	0.02
20	1.2	1.4	0.66		
25	1.3	1.7		0.66	0.51
30			1.1		
35	1.5	1.9		0.88	0.69
45	1.5	1.8	1.2	1.1	0.87
55	1.7	2.0		1.1	0.94
60			1.5		
65	1.6	2.0		1.2	1.2
75	1.7	2.0	1.7	1.3	1.4
85	1.8	2.2	1.8	1.5	1.5
95	2.1	2.2	1.9	1.5	1.7
105	1.8	2.0	2.3	1.7	1.7
115				1.9	2.0

within the experimental errors, to a gradually increasing cross section in the heavier targets. Even taking into account center-of-mass energy differences, the helium and neon cross sections seem to show a different behavior.

As pointed out by Champion,[21] the low-energy cross section makes possible an estimate of the collision radius at which the ^2P state of O^- crosses the ^1D and the ^3P states of oxygen in the molecular-orbital potential diagram. If the low-energy cross section has been overestimated, then the crossing probably takes place at shorter distances. At higher energies, and for the heavier targets, the adiabatic picture of molecular crossings is increasingly invalid, and other mechanisms of direct detachment begin to become important. The energy independence of the O^--He cross section is almost certainly due to a sum of different energy-dependent processes.

Andersen *et al.*[4] have compared their alkali-metal detachment cross sections to H^- detachment cross sections at the same collision velocity. They deduced an empirical factor k such that $\sigma(E)=k\sigma_H(E/M)$, where M is the projectile mass, and σ_H is the average best-fit hydrogen negative-ion detachment cross section.[1] They found that k was independent of target gas, somewhat larger than unity, and dependent slightly on the shell from which the electron was detached. Their value for the $n=2$ shell (Na^-) was $k=1.8$. Our O^- data give an equally good fit with $k=0.7$ (He), 0.8 (Ne), 0.9 (Ar), 0.8 (Kr), and 0.4 (Xe) as shown in Fig. 2. The energy dependence of our data is a better fit to the alkali-metal data than to the H^- data, which is somewhat surprising because O^- is not a quasi-two-electron system as are the alkali-metal negative ions. This and the larger electron affinity, more than double that of the alkali metals, may account for the lower magnitude of the cross sections.

B. Double detachment

The double-detachment cross-section data is shown in Table II and Fig. 3. There is good agreement with the only previous data of Matić and Čobić.[12] The cross section increases smoothly with energy in all the targets. However, these double-detachment cross-section values show a quite different target dependence from the single-detachment cross sections. The largest cross sections occur for the helium and neon targets. Heavier targets show a much lower cross section at lower energies and then a more rapid rise. At the same center-of-mass energy of 9 keV, the xenon σ_{-+} cross section is less than 10^{-17} cm^2 whereas it is 1.6×10^{-16} cm^2 in helium.

The double-detachment cross section is a non-negligible fraction of the total cross section throughout our energy range. For example, in helium, σ_{-+} exceeds 25% of the σ_{-0} cross section by 10 keV and this proportion increases with energy. It may account for the difficulties in comparing values of the single-detachment cross section which have been measured by different methods, because these include different proportions of the double-

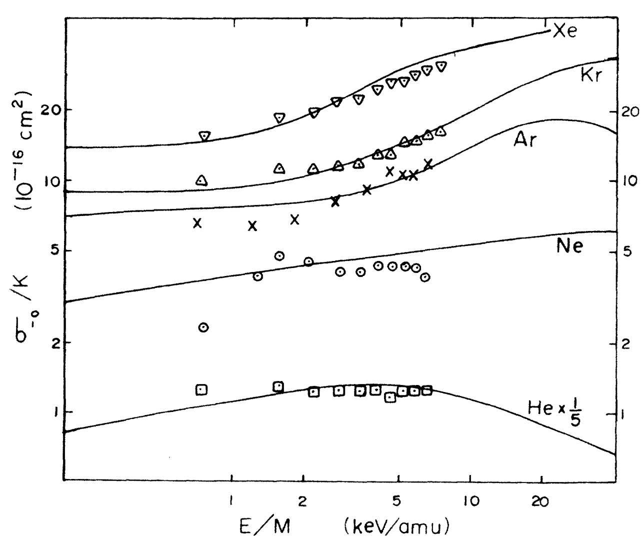

FIG. 2. Comparison of the experimental results with the averaged σ_{-0} data for H^- taken from Risley (Ref. 1): He (⊡), Ne (⊙), Ar (×), Kr (△), Xe (▽). The constant K is an empirical scale factor. For values see text.

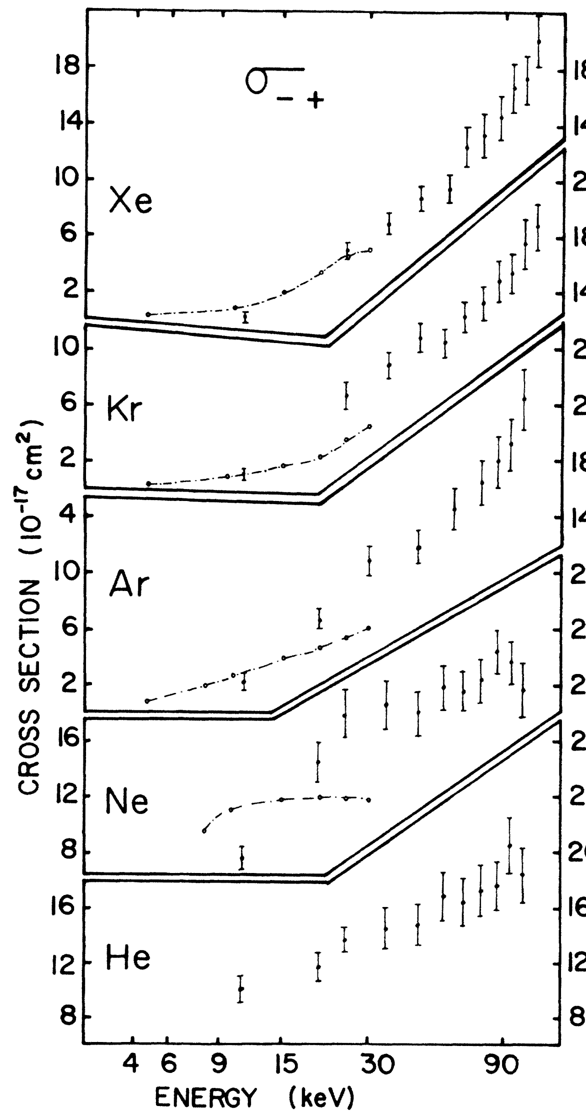

FIG. 3. Cross section for the production of O^+ ions in the collision of O^- with a rare-gas atom. The dot-dash lines join the data of Matić and Čobić (Ref. 12).

detachment cross section.

The O^- double-detachment cross sections have relative values intermediate between those of the alkali metals, where double detachment is a few percent, and the halogen negative ions, where σ_{-+} may be 50% of σ_{-0} in our energy range. These systematic variations are only in part due to the magnitude of the single-detachment cross section, and are not expected from the atomic structure of the negative ions. The two quasi-two-electron structure of the alkali metals would be expected to favor double detachment. At the other extreme the halogen negative ions have one electron outside a close shell, which must be broken to detach the second electron. In spite of this the double-detachment cross sections are larger for halogen than for alkali-metal negative ions. O^- has a p^5 configuration, with electron affinity and ionization potential intermediate between those of the alkali metals and the halogens, so that values of σ_{-+} intermediate between these two extremes are expected.

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