Investigation of Two-Electron Capture in Collisions between Positive Carbon or Oxygen Ions and Gas Molecules

IA. M. FOGEL', R. V. MITIN AND A. G. KOVAL'
Physico-Technical Institute, Academy of Sciences, Ukrainian SSR
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The investigation of the processes of two-electron capture by singly-charged positive carbon and oxygen ions in collisions with He, Ne, A, Kr and Xe atoms and H_2, N_2 and O_2 molecules was carried out with the help of a double mass-spectrometer set-up. The effective cross sections for these processes were measured for the C_1^+ and O_1^+ ions in the energy range 10.7-54.5 kev.

INTRODUCTION

THE effect of the double change of the charge, i.e., the capture of two electrons in single collisions between positive ions and gas molecules has not been studied sufficiently. The first order-of-magnitude measurement of the cross section for this process was reported in Ref. 1. Two-electron capture by protons in different gases was studied in Ref. 2, and that by singly charged positive oxygen ions in hydrogen, nitrogen and oxygen in Ref. 3. The effective cross sections of the two-electron capture by triply-charged argon ions in collisions with N, Ne and A atoms were measured in Ref. 4. The main result of the above investigations was the discovery that the effective cross section of the two-electron capture is not neglibly small as compared with the one-electron capture cross section, and in some cases can attain gas-kinetic values. Further study of the two-electron capture processes, its laws and connection with other inelastic processes in collisions between fast ions and gas molecules is therefore of considerable interest.

The effective cross sections of two-electron capture in the passage of C_1^+ and O_1^+ ion beams through Ne, He, A, Kr, Xe, H_2 and O_2 were measured in the course of the present work.

APPARATUS AND EXPERIMENTAL METHODS

The investigation of two-electron capture processes in the collisions between C_1^+ and O_1^+ ions and gas molecules was carried out with the help of a double-mass-spectrometer set-up, described in detail in Ref. 3. CO_2 was passed through a bimetal valve into the high-frequency ion source in order to obtain beams of the C_1^+ and O_1^+ ions. A mass-spectrometer analysis of the ion beam revealed, besides the C_1^+ and O_1^+ ions, considerable quantities of CO^+ and CO_2^+ ions and small quantities of H_1^+, H_2^+, H_3^+ and N_1^+ ions, as well as C_1^+ and O_1^+ ions resulting from the dissociation of CO^+ ions in the drift space in front of the mass-monochromator. The dispersion of the mass-monochromator was sufficient to resolve the C_1^+ peak from the adjoining N_1^+ peak, and the peak of C_1^+ ions from dissociated CO^+, and to resolve the O_1^+ peak from the adjoining N_1^+ peak as well.

The determination of the effective cross sections of the two-electron capture by C_1^+ and O_1^+ ions was effected by the mass-spectrometric method, described in detail in Refs. 1 and 3. In order to calculate the cross section, it is necessary to determine the slope of the linear part of the curve $I^-/I^+ = f(p)$ (where I^-/I^+ is the ratio of the currents of the negative and positive components of the beam which have traversed the collision chamber, filled with a gas at pressure p). It should be taken into account that a part of the negative ions in the beam that leaves the chamber is formed by the residual impurity gases in the chamber. We have accounted for this by determining the two-electron capture cross sections from the slope of the linear part of the curve

$$(I^-/I^+) - (I^-/I^+)_\Phi = f(p - p_\Phi),$$

where $(I^-/I^+)_\Phi$ is the ratio I^-/I^+ in the beam after traversing the residual gas in the collision chamber and p_Φ is the pressure of the residual gas. The value of $(I^-/I^+)_\Phi$ depends on the composition of the residual gas. It was shown in Ref. 2 that the value of $(I^-/I^+)_\Phi$ can be reduced by an order of

magnitude by inserting a liquid air trap into the collision chamber. Such a suppression of the background is connected with the lowering of the organic vapor pressure of the various organic substances (the diffusion pump oil and its decomposition products, the vacuum grease, etc.) always present in the residual gas, and which then condense on the cool surface of the trap. Since this freezing out of organic vapors causes a considerable rise in the value of $[I^-/I^+) - (I^-/I^+)_\Phi]/(p - p_\Phi)$ and, consequently, in the accuracy of the measurements of the two-electron capture cross section, we have used this method in the present work. For this purpose the collision chamber of Ref. 3 was replaced by a new one, fitted with a trap. Besides, it was now possible to measure the beam current directly at the outlets of the input and the output channels of the collision chamber with the help of two Faraday cylinders which could be placed into, and removed from, the beam by means of magnetic control.

The gas pressure in the region of the linear part of the plot $(I^-/I^+) = f(p)$, i.e., up to the pressure of $1 - 2 \times 10^{-4}$ mm Hg was measured with a Knudsen gauge, higher pressures were measured with a McLeod gauge. Changes of the I^- and I^+ currents incident on the Faraday cylinders were measured simultaneously with a mirror galvanometer and a string electrometer, which served to remove errors due to fluctuations of the primary beam intensity.

As a check of the reproducibility of the results, we measured the cross sections of the processes $H_1^+ \to H_1^-$ in argon and in helium, and $O_1^+ \to O_1^-$ in hydrogen and in oxygen, and compared the results with those obtained in Refs. 2 and 3. It was found that for the process $H_1^+ \to H_1^-$ in argon and helium the results are reproducible within the limits of the experimental error. The values obtained for the cross sections of the process $O_1^+ \to O_1^-$ in hydrogen and oxygen were 5-10 times smaller than in Ref. 3. Since the method used was different, we repeated the measurement of the cross sections of the process $O_1^+ \to O_1^-$ in hydrogen and oxygen not using the liquid air trap and obtained results consistent with those of Ref. 3 within the experimental error.

These experiments showed that the presence of condensable vapors in the residual gas of the collision chamber has a marked influence on the value of the measured cross section, which cannot be removed by determining the cross section from the plot $(I^-/I^+) - (I^-/I^+)_\Phi = f(p - p_\Phi)$. The cause is the following: a simple calculation shows that, for small gas pressures in the collision chamber, the value $(I^-/I^+) - (I^-/I^+)_\Phi$ can be represented as follows:

$$\frac{I^-}{I^+} - \left(\frac{I^-}{I^+}\right)_\Phi \tag{1}$$

$$= \left\{\sigma_{1-1} + \frac{1}{2}\left[\sigma_{1-1}\sum_{i=1}^{N}(\sigma_{10}^i + \sigma_{1-1}^i)\,p_i\,\frac{L}{kT} + (\sigma_{10} + \sigma_{1-1})\sum_{i=1}^{N}\sigma_{1-1}^i p_i\,\frac{L}{kT}\right]\right\}(p - p_\Phi)\,\frac{L}{kT},$$

where p, σ_{10} and σ_{1-1} are the pressure and the cross sections for one- and two-electron capture, respectively, for the investigated gas, and p_i, σ_{10}^i and σ_{1-1}^i the corresponding values for one of the gases present in the residual gas in the collision chamber.

The presence of the terms in the square brackets in (1) shows that the value of the cross section σ_{1-1} determined from the linear part of the relation $(I^-/I^+) - (I^-/I^+)_\Phi = f(p - p_\Phi)$ is larger than the real value because of the presence of the residual gas. The lower the pressure of residual gases in the collision chamber, the closer will be the measured value of σ_{1-1} to the real value. Using the liquid air trap in the collision chamber for the purpose of condensing the organic vapors present, we greatly reduced the pressure of the residual gas, and therefore, the systematic error.

It was shown experimentally for all ion-molecule pairs studied that further lowering of the ratio $(I^-/I^+)_\Phi$ as compared with the value reached using the liquid-air trap*, does not lead to a diminishing of the measured cross section σ_{1-1}. This means that, by using the liquid air trap, the systematic error connected with the presence in the collision chamber of gases (that are not condensing at liquid air temperature) lies within the limits of statistical errors which, in the present experiment, attained ±15%.

DISCUSSION OF EXPERIMENTAL RESULTS

The energy dependence of the two-electron capture cross section was measured for the C_1^+ and O_1^+

* This is effected by placing liquid air traps in the space before and behind the collision chamber.

ions in collisions with Ne, He, A, Kr, Xe, H_2, N_2 and O_2 molecules, in the energy interval 10.7-54.5 kev. Spectrally pure He, Ne, Kr and Xe, hydrogen filtered through palladium, 99.1% pure oxygen, 99.7% argon and nitrogen obtained from evaporation of liquid nitrogen and purified from oxygen by passage through copper filings at 600° C were used. The results obtained are shown in Figs. 1 and 2.

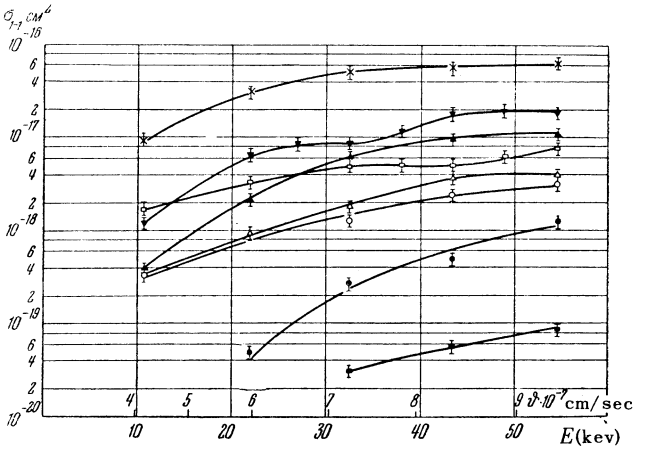

FIG. 1. $C_1^+ \rightarrow C_1^-$; ■ — He, ● — Ne, ○ — H_2, △ — N_2, □ — O_2, ▲ — Ar, ▼ — Kr, * — Xe

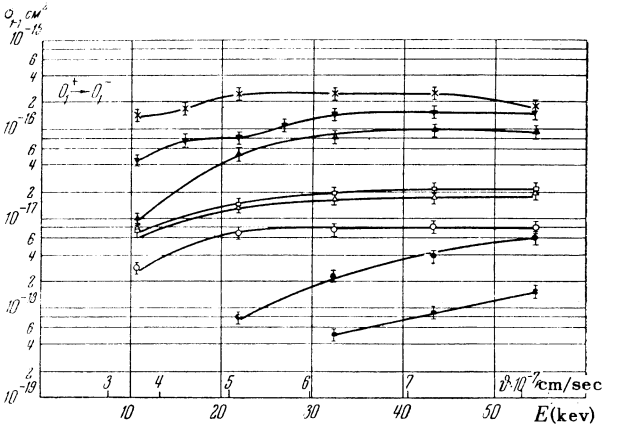

FIG. 2. $O_1^+ \rightarrow O_1^-$; ■ — He, ● — Ne, ○ — H_2, △ — N_2, □ — O_2, ▲ — A, ▼ — Kr, * — Xe

The figures show that, in the energy region under discussion, a monotonic increase in the effective cross section with the ion energy is observed for the C_1^+ ions in He, Ne, A, Xe, H_2 and N_2 and for the O_1^+ ions in He, Ne and N_2. The rate of the rise of the cross section σ_{1-1} for these ion-molecule pairs slows down with increasing ion energy, which indicates that a maximum is being approached. The cross section σ_{1-1} is constant for O_1^+ ions in A, Kr, H_2 and O_2 from about 30 kev to the upper limit of the measured inverval. Such a region of constant cross section σ_{1-1} was observed in two more cases: for C_1^+ in Kr from 27 to 32 kev and for C_1^+ in O_2 from 32 to 43 kev. In these two cases, however, the cross section increases again with the energy after the plateau. In one case only, namely, for O_1^+ in Xe, a flat maximum is observed in the measured energy interval, at about 30 kev.

The value of the cross section σ_{1-1} for a given ion changes within very wide limits: for the C_1^+ ions from 3.2×10^{-20}cm^2 (in H, at 32.4 kev) to 6.4×10^{-17}cm^2 (in Xe, at 54.5 kev) and for the O_1^+ ions from 5.1×10^{-19}cm^2 (in He, at 32.4 kev) to 2.4×10^{-16}cm^2 (in Xe, at 32.4 kev). A strong dependence of the cross section σ_{1-1} on the gas molecule from which the ions capture the electrons is observed. The cross section σ_{1-1} for the C_1^+ and O_1^+ ions of the same energy increases in the various gases in the following order: He, Ne, H_2, N_2, O_2, A, Kr, Xe. Exceptional are the $C_1^+ \rightarrow C_1^-$ processes in A and O_2 in the 10.7-28 kev region, in which the cross section σ_{1-1} is smaller for argon than for oxygen. For the same gas the same ion velocity, the cross section σ_{1-1} is as a rule larger for the O_1^+ ion than for the C_1^+.

Lack of literature on the two-electron capture by C_1^+ and O_1^+ ions makes it impossible to compare our results with other investigations.

It is impossible to calculate the effective cross sections of inelastic processes in collisions between particles with shells containing many electrons on the basis of the present theory of atomic collisions. Therefore, the discussion of our results can be made only on the basis of general theoretical considerations connected with Massey's "adiabatic hypothesis"[5]. According to this hypothesis, slow collisions between particles take place under the condition $a|\Delta E|/hv \gg 1$ (where ΔE is the resonance defect, i.e., the change of the internal energy in the given inelastic process, a is the distance at which the interaction forces between the colliding particles act, h is the Planck constant and v is the ion velocity). In the slow-collision region a sharp rise of the effective inelastic cross section with the ion velocity should be observed. The maximum value of the cross section is attained for the following condition:

$$a\,|\,\Delta E\,|\,/hv \approx 1. \qquad (2)$$

The value of the parameter $a|\Delta E|/hv$ can be estimated when a and $|\Delta E|$ are known. The value of the resonance defect for the two-electron capture processes can be easily calculated under the assumption that the colliding particles are in the ground state both before and after the collision*.

* In Refs. 2 and 3 examples of the calculation of the resonance defect are given for several ion-molecule pairs.

The resonance defect changes from 20.6 ev (in Xe) to 66 ev (in He) for the $C_1^+ \rightarrow C_1^-$ processes, and from 17.5 ev (in Xe) to 62.9 ev (in He) for the $O_1^+ \rightarrow O_1^-$ process. It should be noted that for one-electron capture processes the resonance defects are much smaller. For instance, for the $C_1^+ \rightarrow C_1^0$ process, the values vary from 0.84 ev (in Xe) to 12.4 ev (in He), and for the $O_1^+ \rightarrow O_1^0$ process, from 0.4 ev (in Kr) to 10.9 ev (in He). The value of a can be calculated from the condition (2) in the case when a maximum is attained for the cross section in the investigated energy region. In the present work, a maximum was observed only for the $O_1^+ \rightarrow O_1^-$ process in Xe at 33 kev. Calculation gives the corresponding value of a to be equal to ~1.45 A. In Ref. 2 it was found that a equals 1 and 2 A for the $H_1^+ \rightarrow H_1^-$ process in He and H_2, respectively. Hasted has shown[6,7] that in one-electron capture collision processes the value of a does not vary greatly for different ion-molecule pairs and is equal on the average to 8 A.

Under the assumption that the impact parameter varies only slightly for two-electron capture processes*, it is possible to compute the value of $a|\Delta E|/hv$, taking a to be equal to 1.45 A. For the $C_1^+ \rightarrow C_1^-$ process this value varies in the beginning of the investigated velocity interval from 1.7 (in Xe) to 3.6 (in He), and for the $O_1^+ \rightarrow O_1^-$ process from 1.8 (in Xe) to 3.3 (in He). It is therefore impossible to treat the studied velocity interval as the slow-collision region, since even for the lowest ion velocity, the criterion $a|\Delta E|/hv \gg 1$ is not fulfilled. It is possible to note, however, from Figs. 1 and 2, that the effective cross section increases with the energy more sharply for those ion-molecule pairs (C_1^+ and O_1^+ in He and Ne) for which the ratio $a|\Delta E|/hv$ is largest in the velocity interval studied. It is interesting to compare the dependence of the cross sections σ_{1-1} and σ_{10} on the

* The fact that no maximum is observed in the curves $\sigma_{1-1} = f(E)$, apart from the curve for $O_1^+ \rightarrow O_1^-$ in Xe, is a partial confirmation of the above assumption. Since the value of $|\Delta E|$ is the smallest for the $O_1^+ \rightarrow O_1^-$ process in Xe, it should be expected that for other processes the maximum cross section should be shifted in the direction of higher velocities, of only a remains constant for the processes in question.

value of $a|\Delta E|/h\nu$. Such a comparison is possible for the pairs $C_1^+ - Xe$, $O_1^+ - Kr$ and $O_1^+ - A$, since both the σ_{1-1} cross sections measured by us and the σ_{10} cross sections measured by Hasted[6,7] correspond to such a velocity interval that the values of $a|\Delta E|/h\nu$ overlap, if we take a to be equal to 1.45 A for $ion^+ - ion^-$ processes, and to 8 A for $ion^+ - atom$ processes. The dependence of σ_{10} and σ_{1-1} on $a|\Delta E|/h\nu$ for the $C_1^+ - Xe$, $O_1^+ - A$ and $O_1^+ - Kr$ pairs is shown in Fig. 3. The corresponding curve of the σ_{10} cross section for the $H_1^+ - A$ pair is included for comparison.

Attention is drawn to the fact that fall of the cross section σ_{10} with the rise of $a|\Delta E|/h\nu$ is much slower for $C_1^+ - Xe$, $O_1^+ - A$ and $O_1^+ - Kr$ pairs than for $H_1^+ - A$. An analogous phenomenon is found in comparing the curves for the σ_{10} and σ_{1-1} cross sections. The cross section σ_{10} decreases much more slowly with increasing $a|\Delta E|/h\nu$ than does the cross section σ_{1-1}.

From the point of view of the adiabatic hypothesis, the slow decrease of the value of the σ_{10} cross section with increasing $a|<E|/h\nu$ for the $C_1^+ - Xe$, $O_1^+ - A$ and $O_1^+ - Kr$ pairs represents an anomaly. Hasted proposes to explain the large σ_{10} cross sections at low velocities by the fact that the ion beam contains some excited metastable ions. In the case of the $O_1^+ + A \rightarrow O_1^0 + A^+$ process, for instance, the resonance defect for the electron exchange between ground-state particles is equal to -2.2 ev if the O_1^+ ion is in the ^2P state, the collision process can be either $O_1^+(^2P) + A \rightarrow O_1^0(^1D) + A^+$ with $\Delta E = -0.84$ ev, or $O_1^+(^2P) + A \rightarrow O_1^0 + A^+$ with $\Delta E = 1.12$ ev. The observed dependence of σ_{10} on the ion velocity is the result of superposition of a series of curves for collision processes with different values of resonance defect and, consequently, with displaced maxima. The presence of excited ions in the beam is evidently excluded in the case of the pair $H_1^+ - A$, and, correspondingly, a sharp fall of the cross section with decreasing ion velocity can be observed.

The sharper decline of the σ_{1-1} cross section as compared with the σ_{10} cross section can be explained, on the basis of Hasted's assumption, by insignificantly small quantities of excited ions in the beam used in our experiments. This assumption is confirmed by the fact that the σ_{1-1} cross section for the $H_1^+ + H_2 \rightarrow H_1^- + H_1^+ + H_1^+$ process[2], where all particles involved can be in the ground state only, also falls sharply with diminishing velocity.

It should be noted that in two-electron capture collisions the presence of excited ions in the primary beam or the formation of excited fast or slow particles after the collision will have a lesser influence on the dependence of the cross section on velocity than in the case of one-electron capture collisions. Consequently, the relative change of the resonance defect of the two-electron capture due to the presence of excited particles in the primary beam or their creation after collision will be small. The experimental curve $\sigma_{1-1} = f(v)$ will be the result of superposition of two curves with closely-spaced maxima, which will, as a final result, distort the curve relatively slightly for small velocities.

The curves shown in Fig. 3 permit also the comparison of the numerical values of the σ_{1-1} and the σ_{10} cross sections for identical values of the adiabatic parameter $a|\Delta E|/h\nu$. It follows from this comparison that, although the cross section σ_{1-1} is much smaller than the cross section σ_{10}, yet it cannot be regarded as negligible for the studied ion-molecule pairs.

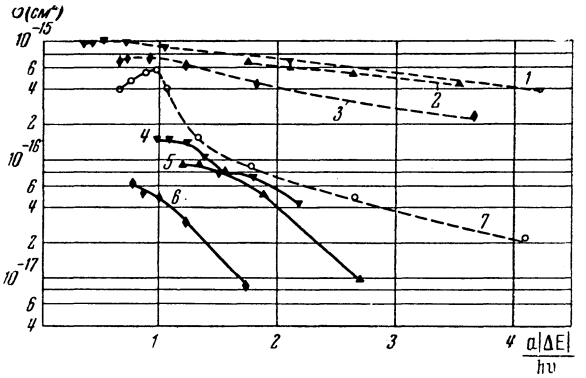

FIG. 3. 1 — $O_1^+ \rightarrow O_1^0$, Kr; 2 — $O_1^+ \rightarrow O_1^0$, A; 3 — $C_1^+ \rightarrow C_1^0$, Xe; 4 — $O_1^+ \rightarrow O_1^-$, Kr; 5 — $O_1^+ \rightarrow O_1^-$, A; 6 — $C_1^+ \rightarrow C_1^-$, Xe; 7 — $H_1^+ \rightarrow H_1^0$, A

It was mentioned above that there exists a strong dependence of the effective cross section σ_{1-1}

on the nature of both the ion and the molecule which collide. It is of considerable interest to find which physical values characterize the connection between the value of the cross section $\sigma_{1\text{-}1}$ with the nature of the ion and of the molecule. It is natural to assume that a certain role should be played by the binding energy of electrons both in the negative ion formed in the collision process and in the molecule from which they are captured. The resonance defect in the investigated two-electron capture processes $A^+ + B \to A^- + B^{++}$ (B is assumed to be an atomic particle) can be written in the form:

$$\Delta E = (V_A^{\mathrm{I}} + S_A) - (V_B^{\mathrm{I}} + V_B^{\mathrm{II}}), \qquad (3)$$

where V_A^{I} and S_A are the first ionization potential and the electron affinity of the particle A, and V_B^{I} and V_B^{II} are the first and the second ionization potentials of the particle B. As it can be seen from (3) the binding energy of the exchanged electrons in the capturing and in the losing particle enter into the value of ΔE. Therefore, it is logical to find the connection between ΔE and $\sigma_{1\text{-}1}$.

The dependence of the cross section $\sigma_{1\text{-}1}$ on $|\Delta E|$ for the processes $O_1^+ \to O_1^-$ and $C_1^+ \to C_1^-$ for one and the same velocity of the O_1^+ and C_1^+ ions, equal to 7.55×10^7 cm/sec, is shown in Fig. 4. The points for the different processes lie on different smooth curves (only the points for the $C_1^+ - O_2$ and $O_1^+ - H_2$ pairs fail to coincide), corresponding to the monotonic decrease of the cross section $\sigma_{1\text{-}1}$ with increasing absolute value of the resonance defect. Since the value of $V_A^{\mathrm{I}} + S_A$ for each of these curves is constant (equal to 12.74 and 15.77 ev for the $C_1^+ - C_1^-$ and the $O_1^+ - O_1^-$ processes, respectively), they represent the dependence of the cross section $\sigma_{1\text{-}1}$ on the electron binding energy in the particle losing them. The following can be deduced from these curves: 1) The cross section $\sigma_{1\text{-}1}$ decreases with increasing binding energy of electrons in the losing particle; 2) The cross section $\sigma_{1\text{-}1}$ increases with increasing electron binding energy in the negative ion, formed in the collision; 3) The resonance defect is not a universal parameter, determining the two-electron capture cross section for a ion-molecule pair. Further study of this process for a large number of ion-molecule pairs will show whether these conclusions are generally valid.

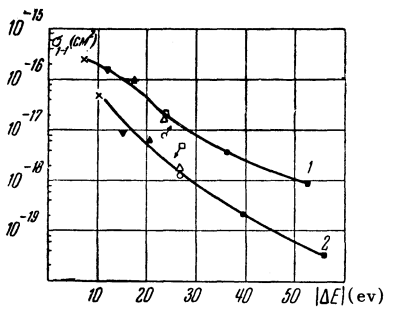

FIG. 4. *1* — $O_1^+ \to O_1^-$, *2* — $C_1^+ \to C_1^-$; ■ — He, ● — Ne, ○ — H_2, △ — N_2, □ — O_2, ▲ — A, ▼ — Kr, * — Xe

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