SOVIET PHYSICS JETP VOLUME 35(8), NUMBER 3 MARCH, 1959

ON THE APPLICABILITY OF MASSEY'S ADIABATIC HYPOTHESIS TO DOUBLE CHARGE EXCHANGE

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Submitted to JETP editor March 15, 1958

J. Exptl. Theoret. Phys. (U.S.S.R.) **35**, 565-573 (September, 1958)

The question of the applicability of Massey's adiabatic hypothesis to double charge exchange processes is considered. An analysis of the ion-velocity dependence of the cross sections for double charge exchange of some types of ions in inert gases shows that the positions of the maxima of the respective curves correspond to Massey's adiabatic criterion. In carrying out the analysis it is necessary to take into account the existence of excited ions in the primary beam as well as of the formation of slow excited doubly-charged ions. As in the case of ordinary charge exchange the constant a in the case of double charge exchange varies slightly from one ion-molecule system to another. The mean value of a for double charge exchange in inert gases is 1.5 A. The value of a for double charge exchange in molecular gases differs greatly from this value.

INTRODUCTION

AT the present time the cross sections for inelastic processes in heavy-particle collisions can be calculated quantum-mechanically for only a very limited number of cases — for particles with a small number of outer orbital electrons in slow collisions, when $v \ll v_0$, and in fast collisions, when $v \gg v_0$ (v is the relative velocity of the colliding particles and v_0 is the velocity of the electrons in the colliding particles). The theoretical literature is reviewed in reference 1.

The effective electron capture (charge exchange) cross section can also be calculated in the few instances when the potential energy curves are known for the initial and final states of the colliding particles. For such cases the cross sections are calculated by the method proposed in references 2 to 4. In all other cases the experimental results can be treated only on the basis of general theoretical considerations associated with Massey's "adiabatic hypothesis."[5] According to this hypothesis the principal quantity that determines the dependence of the cross section on the relative velocity of the particles is the adiabatic parameter $a|\Delta E|/hv$, where a is the distance at which the particles interact, ΔE is the "resonance defect" (the change of internal energy of the particles when they interact) and h is Planck's constant. For small velocities, when the condition $a|\Delta E|/hv \gg 1$ holds, inelastic cross sections are very small and increase rapidly with the velocity. The maximum cross section is reached when

$$a|\Delta E|/hv_{\max} \approx 1. \qquad (1)$$

After passing through the maximum the cross section decreases monotonically as the velocity increases.

The available experimental data show that in many instances the curves of $\sigma(v)$ are what would be expected from the adiabatic hypothesis. Thus, for example, in reference 6 it was shown that for ordinary charge exchange of singly-charged positive ions (capture of a single electron) the maximum of $\sigma_{10}(v)$* for many ion-molecule systems is given by (1), if it is assumed that the particles are in their ground states before and after the collision. a varies very little for these processes in the case of many ion-molecule systems. For some processes, however, the curve of $\sigma(v)$ is clearly not in accord with the adiabatic hypothesis. There is disagreement in two ways: (1) Two and sometimes even three maxima are observed[7] instead of a single maximum. (2) The cross sections are anomalously large at small velocities.

The fact that $\sigma(v)$ has more than one maximum does not actually conflict with the adiabatic hypothesis and results from the fact that excited particles may participate in the process in ques-

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*σ_{ik} is the cross section for the process in which a particle with charge ie is transformed into a particle with charge ke.

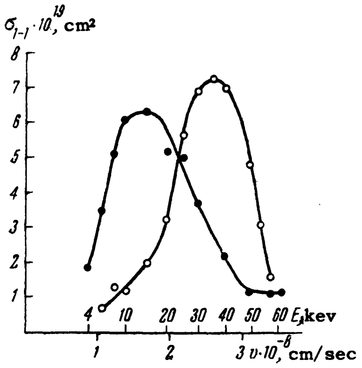

FIG. 1. ○ – H^+ – He, ● – H^+ – Ne.

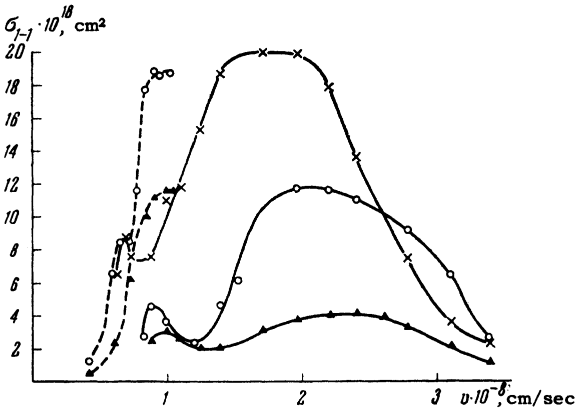

FIG. 2. —— – H^+, - - - - – C^+, ▲ – Ar, ▼ – Kr, × – Xe.

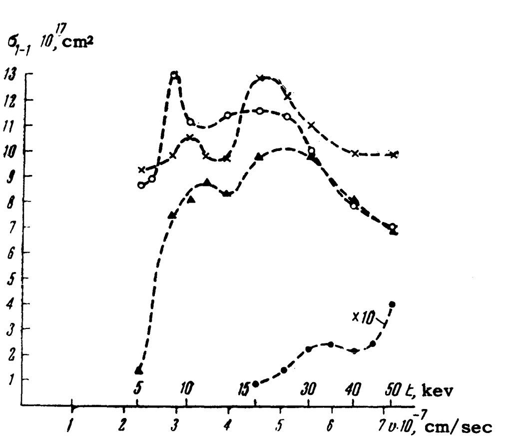

FIG. 3. ● – F^+ – Ne, ▲ – F^+ – Ar, ○ – F^+ – Kr, × – F^+ – Xe.

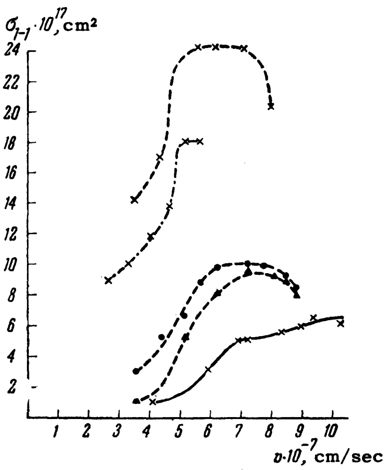

FIG. 4. —— – C^+, - - - - O^+, —·— – Cl^+, ▲ – Ar, ● – Kr, × – Xe.

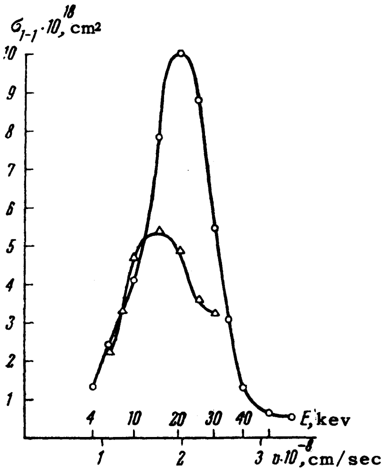

FIG. 5. ○ – H^+ – H_2, Δ – N_2.

tion as well as particles which are in their ground state.

The anomalously large inelastic cross sections at low velocities result from violations of the adiabatic condition $a\,|\Delta E|/hv \gg 1$. Such violations can occur when the potential energy curves of the initial and final states of the colliding-particle system are so close at some internuclear separation R_n that the minimum potential energy difference $\Delta U(R_n)$ becomes very small. Bates and Massey[8] have considered the cases in which violation of the adiabatic condition is probable for slow collisions.

It is of interest to determine to what extent the adiabatic hypothesis can be applied to the capture of two electrons by singly-charged positive ions, that is to processes of the type

$$A^+ + B \rightarrow A^- + B^{++}. \qquad (2)$$

The available experimental data on double charge exchange of H_1^+,[9] C_1^+, O_1^+,[10] and Cl_1^+[11], has been insufficient to determine whether the adiabatic hypothesis can be applied to these processes, because the cross sections were measured in a relatively narrow energy range. In the present article for the purpose of determining the maximum of $\sigma_{1-1}(v)$ we have measured the cross sections for a number of ion-molecule systems in a wider energy range than was used in earlier work. We have also measured the double charge exchange cross section of F^+. The next section presents these results and a discussion based on Massey's adiabatic hypothesis.

EXPERIMENTAL RESULTS

We measured the cross sections of the process $H_1^+ \rightarrow H_1^-$ in the gases He, Ne, Ar, Kr, Xe, H_2, and N_2 over the energy interval from 3 to 65 kev, $C_1^+ \rightarrow C_1^-$ in Ar, Kr, and Xe (50 to 65 kev), $O_1^+ \rightarrow O_1^-$ in Ar and Kr (50 to 65 kev), $Cl_1^+ \rightarrow Cl_1^-$ in Xe (50 to 60 kev) and $F_1^+ \rightarrow F_1^-$ in He,

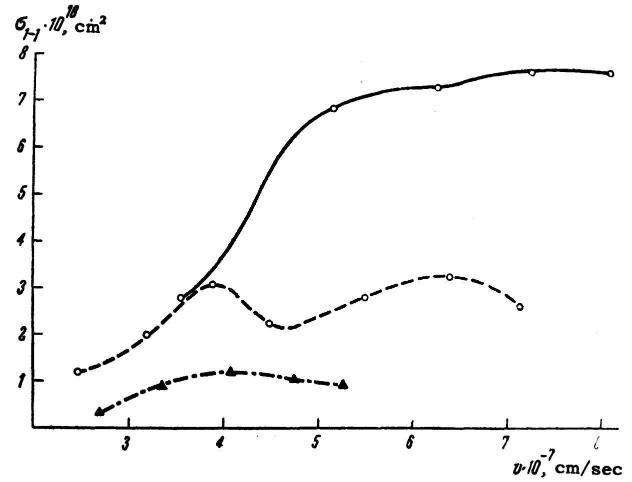

FIG. 6. - - - - - F^+, — — O^+, —·—— Cl^+, ▲ – N_2, ○ – H_2.

Ne, Ar, Kr, Xe, and H_2 (5 to 50 kev). Measurements were performed by means of a mass spectrometer similar to that which was described in detail in reference 12. Within the limits of experimental error our values of σ_{1-1} for C_1^+, O_1^+, and Cl_1^+ agreed with earlier measurements.[10,11] Our values of σ_{1-1} for $H_1^+ \rightarrow H_1^-$ are smaller by a factor of 1.5 or 2 than in reference 9. As we have shown, the cause of this discrepancy was contamination of the capillary of the McLeod gauge used in reference 9, which led to incorrect values for the pressure of the gas admitted into the collision chamber.

Figures 1 to 6 show curves of $\sigma_{1-1}(v)$ for ion-molecule systems when maxima are observed. In some figures two maxima of $\sigma_{1-1}(v)$ are observed.

We shall first analyze the curves of $\sigma_{1-1}(v)$ for double charge exchange of ions in inert gases. We shall naturally begin with the simplest case, H_1^+ and He, where the particles that participate in the double charge exchange can be only in their ground states, so that the curve of $\sigma_{1-1}(v)$ for this process can have only a single maximum, the position of which is given by (1), as is actually found to be the case. By determining v_{max} from $\sigma_{1-1}(v)$ in Fig. 1 and calculating the resonance defect of the process $H_1^+ + He \rightarrow H_1^- + He^{++}$ we can use (1) to calculate a, which for H_1^+ – He is 1.6 A.

Let us now consider double charge exchange for other ion-molecule systems. When a is identical for different systems it follows from (1) that $v_{max} \sim |\Delta E|$. We shall assume that the maxima of $\sigma_{1-1}(v)$ for the indicated systems represent double charge exchanges with all participating particles in their ground states. $v_{max}(|\Delta E|)$ as plotted under this condition is shown in Fig. 7.* The vertical bars indicate the errors in determination of v_{max}. When the curve of a cross section only reaches a plateau, the corresponding vertical line in Fig. 7 has no upper limit. The systems represented in Fig. 7 are seen to be clustered around the straight line for a = 1.5 A. This approximately constant value of a for different systems is in definite agreement with the results given in reference 6 for ordinary charge exchange except for the fact that in the latter case $a \approx 8$ A. This is a reasonable result since it is obvious that for the capture of two electrons the particles must approach closer than for the capture of a single electron.

Consider the systems H_1^+ – Ar, H_1^+ – Kr, and H_1^+ – Xe, for which $\sigma_{1-1}(v)$ has two maxima. If it is assumed that the first maximum (at the lower velocity) is associated with double charge exchange without excitation of the slow doubly-charged ion (process 2), the points of $v_{max}(|\Delta E|)$ fit well on the straight line† of Fig. 7. The second maximum of $\sigma_{1-1}(v)$ for these systems can only be associated with double charge exchange where the slow doubly-charged ion remains in an excited state, that is,

$$H_1^+ + B \rightarrow H_1^- + B^{++*}. \tag{3}$$

It is clear that $|\Delta E_2| - |\Delta E_1| = E_{B^{++}}$, where ΔE_1 and ΔE_2 are the resonance defects of processes (2) and (3) and $E_{B^{++}}$ is the excitation energy of B^{++}. Assuming that a is identical for processes (2) and (3), we can use the adiabatic criterion (1) to calculate $|\Delta E_2|$ and thus $E_{B^{++}}$. It was found that for the systems H_1^+ – Ar, H_1^+ – Kr, and H_1^+ – Xe $E_{B^{++}}$ agrees within the limits of experimental error with the third ionization potential of Ar, Kr, and Xe atoms (Table I). On the basis of the foregoing postulate we can thus assume that the second maximum of $\sigma_{1-1}(v)$ for the indicated systems results from the process

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*In plotting $v_{max} = f(|\Delta E|)$ the points for F_1^+ – Ar, F_1^+ – Kr and F_1^+ – Xe were determined on the assumption that the maximum at the higher velocity corresponds to double charge exchange when all particles are in their ground states. For H_1^+ – Ar, H_1^+ – Kr and H_1^+ – Xe it was assumed that the maximum at the smaller velocity represents this process. The justification for this procedure will appear in the discussion which follows.

†If it is assumed that the second maximum (at the higher velocity) is associated with a process for particles in their ground states, the origin of the first maximum cannot be explained by the adiabatic hypothesis since in the present instance the primary beam cannot contain excited ions.

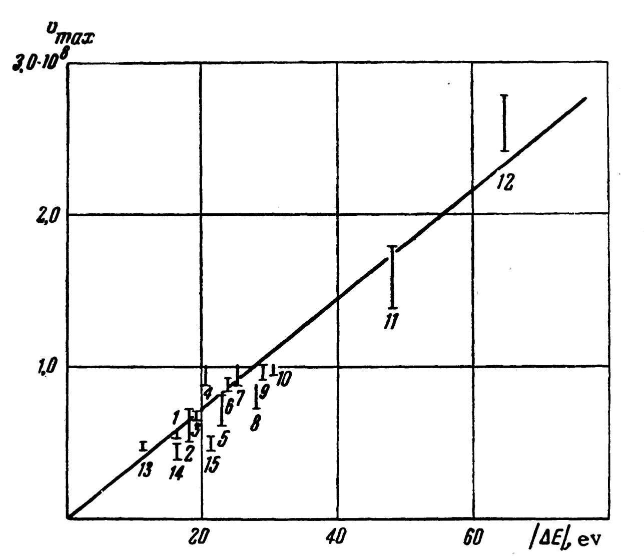

FIG. 7. v_{max} as a function of the resonance defect. 1 – Cl^+ – Xe; 2 – O^+ – Xe; 3 – H^+ – Xe; 4 – C^+ – Xe; 5 – O^+ – Kr; 6 – H^+ – Kr; 7 – C^+ – Kr; 8 – O^+ – Ar; 9 – H^+ – Ar; 10 – C^+ – Ar; 11 – H^+ – Ne; 12 – H^+ – He; 13 – F^+ – Xe; 14 – F^+ – Kr; 15 – F^+ – Ar.

TABLE I

System	$\Delta E_2 - \Delta E_1$, ev	V_{iB}^{III}, ev
H_1^+ — Xe	30.0	31,3
H_1^+ — Kr	33.5	35,7
H_1^+ — Ar	39.0	40,9

$$H_1^+ + B \rightarrow H_1^- + B^{+++} + e. \qquad (4)$$

Using the terminology of reference 13, process (4) can be called ionization with capture when of the three electrons separated from particle B two are captured by a proton while the third electron passes into the continuum. The ion B^{+++} can also be produced by ordinary ionization ($H_1^+ + B \rightarrow H_1^+ + B^{+++} + 3e$) so that the cross section for the production of triply-charged ions as determined by the method developed in reference 13 is actually the sum of the cross sections for ordinary ionization and process (4), which must be kept in mind in interpreting experiments on the ionization of Ar, Kr, and Xe by protons.

It is striking that (1) for Kr and Xe the second maximum is higher than the first maximum while for Ar they are of approximately the same height, (2) the relative height of the second maximum diminishes with decreasing atomic number of the gas, and (3) there is no second maximum for Ne. At first glance the first of these facts seems incomprehensible since it is difficult to imagine that process (4), which possesses a considerably larger resonance defect than process (2), can have greater probability than the latter process. But it must be remembered that the shape of the curve of $\sigma_{1-1}(v)$ between the two maxima is determined not only by the processes (2) and (4) but evidently also by a number of processes (3) with different excitation energies of the B^{++} ions. Therefore the height of the second maximum, which is determined by the sum of the probabilities of processes (3) and process (4), can be of the same order of magnitude or even greater than the height of the first maximum. The shape of $\sigma_{1-1}(v)$ for the considered systems shows that the relative probability of processes (3) and (4) decreases compared with the probability of the principal process (2) as the atomic number of the gas decreases. This may possibly be associated with the fact that the resonance defects of processes (3) and (4) will with decreasing atomic number increase more rapidly than the resonance defect of process (2). This appears to explain the absence of a second maxima of $\sigma_{1-1}(v)$ for Ne, which we would have had to observe around 70 kev.

Our present interpretation of the shape of $\sigma_{1-1}(v)$ for double charge exchange of protons in Ne, Ar, Kr, and Xe on the basis of the adiabatic hypothesis can be justified by investigating the energy loss which occurs when a positive ion is converted into a negative ion.* Such investigations, which will provide direct proof of the possibility of applying the adiabatic hypothesis to double charge exchange, are planned for a later and more thorough state in the study of these processes.

Two maxima of the $\sigma_{1-1}(v)$ curve are also observed for the process $F_1^+ \rightarrow F_1^-$ in the gases Ar, Kr, and Xe (Fig. 3).

When it is assumed that for the systems H_1^+ — Ar, H_1^+ — Kr, and H_1^+ — Xe the maximum at the lower velocity represents process (2), the subsequent calculation of the constant a gives a value much below 1.5 A (for example, for F_1^+ — Kr the value is 0.67 A). On the other hand, the excitation energies of slow ions which are calculated from the position of the maximum at the higher velocity differ greatly from the tabulated values.† When

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*It is easily shown that when $\theta = 0$ and $\Delta E \ll T_0$ we have $\Delta E = m_2/m_1 + m_2 (\Delta T + 2\, m_1/m_2\, T_0)$, where θ and ΔT are the scattering angle and energy loss in double charge exchange, m_1 and m_2 are the mass of the ion and gas atom, respectively, T_0 is the kinetic energy of the ion. This relation enables us to use the measured value of ΔT to calculate ΔE; from ΔE we can then determine the character of the process that has resulted in the given energy loss.

†For $F_1^+ - H_2$ the maximum at the higher velocity cannot be interpreted in this manner.

TABLE II

System	Calculated excitation energy in ev	Ion state	Energy of state in ev
$F^+ — Xe$	3.6±0.9	$2s^2\,2p^4\,{}^3P_{2,1,0}$	0
$F^+ — Kr$	6.5±1.6	$2s^2\,2p^4\,{}^1D_2$	2.6
$F^+ — Ar$	6.9±1.9	$2s^2\,2p^4\,{}^1S_0$	5.6
$F^+ — Ne$	20.4±2.5	$2s^2\,2p^4\,3s\,{}^5S_2{}^0$	22.0

we assume that the maximum at the higher velocity represents process (2), the value of a does not differ greatly from 1.5 A (see the points for $F_1^+ — Ar$, $F_1^+ — Kr$, and $F_1^+ — Xe$ in Fig. 7). The maxima at the lower velocity for these systems can be explained by the presence of metastable excited ions in the primary beam. The excitation energy E_{A^+} can be calculated as the difference $|\Delta E_1| - |\Delta E_2|$, where ΔE_1 is the resonance defect of process (2) and ΔE_2 is the resonance defect of the process $A^{+*} + B \rightarrow A^- + B^{++}$.

Assuming that the value of a for double charge exchange of an excited ion is the same as for process (2), we can calculate ΔE_2 and the excitation energy E_{A^+}. The excitation energy of F_1^+ corresponding to the maximum of $\sigma_{1-1}(v)$ for $F_1 — Ne$ can be calculated if we assume that a for this system is the same as for $F_1^+ — Ar$, $F_1^+ — Kr$, and $F_1^+ — Xe$. For $F_1^+ — Ne$ we use a = 1.2 A, which is the average for the systems that have been mentioned, and obtain $E_{F^+} = 20.4$ ev. Table II gives the calculated fast-ion excitation energies compared with the tabulated excitation energies of F_1^+.* These values are seen to agree within the limits of experimental error. The $\sigma_{1-1}(v)$ curve for $F_1^+ — Xe$ shows an additional maximum associated with the fact that the beam contains F_1^+ in the state $2s^22p^4\,{}^1D$, additional maxima for $F_1^+ — Ar$ and $F_1^+ — Kr$ associated with the excited state $2s^22p^4\,{}^1S$ of F_1^+ and, finally, a maximum for $F_1^+ — Ne$ associated with the excited state $2s^22p^33s^5S$ (the state $2s2p^5\,{}^3P$ is not metastable). The fact that the curves of $\sigma_{1-1}(v)$ for $F_1^+ — Ar$ and $F_1^+ — Kr$ do not contain a maximum for the state $2s^22p^4\,{}^1D$ evidently means that this maximum is not distinct from the principal maximum.

Thus the data in Table II do not disagree with the hypothesis that the low-velocity maxima of $\sigma_{1-1}(v)$ for the systems given in the table are associated with the presence of excited ions in the primary beam. Keeping in mind the fact that the shape of $\sigma_{1-1}(v)$ can depend on the fraction of excited ions in the beam,* we varied the conditions under which the high-frequency ion source operated in order to determine the effect of such variation on the shape of $\sigma_{1-1}(v)$ near the maximum at the lower velocity for $F_1^+ — Ar$ and $F_1^+ — H_2$. The power of the high-frequency generator was varied from 150 to 300 watts and the extracting potential was varied from 2 to 4 kv without affecting the cross sections for $F_1^+ — F_1^-$ in Ar and H_2. This result indicates that the fraction of excited ions in the F_1^+ beam issuing from a channel in the cathode of the high-frequency source does not depend on the operating parameters of the source within the indicated limits.

It must be remembered, however, that excited ions can also be produced by collisions of ions in the primary beam with molecules of residual gas. In order to determine the influence of the composition of the primary beam on the shape of $\sigma_{1-1}(v)$ it would be desirable to investigate the shape of these curves when it is definitely known that the beam from the source does not contain excited ions (a thermionic source), for comparison with the curves obtained in the present work. We shall continue our work in this direction.

Maxima of $\sigma_{1-1}(v)$ are also observed for some cases of double charge exchange in molecular gases (see the curves for $H_1^+ — H_2$, $O_1^+ — H_2$, $F_1^+ — H_2$, $H_1^+ — N_2$, and $Cl_1^+ — N_2$ in Figs. 5 and 6). In discussing double charge exchange in molecular gases it must be remembered above all that this process can take two different forms represented schematically by the formulas

$$A^+ + B_2 \rightarrow A^- + B_2^{++}; \tag{5}$$

$$A^+ + B_2 \rightarrow A^- + B^+ + B^+. \tag{6}$$

The resonance defect of process (5), in which a slow doubly-charged molecular ion† is produced, can be calculated in the usual way (reference 12). The resonance defect of process (6) can be calculated from

$$\Delta E = V_{iA}^I + S_A - (E_{\text{dis}} + 2V_{iB}^I + E_{\text{п}}), \tag{7}$$

where E_{dis} is the dissociation energy of molecule B_2 and E_p is the potential energy of the two B^+ ions which are produced. It is easily

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*The excitation energy of F_1^+ was taken from reference 14.

*If the primary beam contains excited ions with only a single excitation energy, it is easily shown that the measured cross section σ'_{1-1} is expressed by $\sigma'_{1-1} = k\sigma^*_{1-1} + (1-k)\sigma_{1-1}$, where k is the fraction of excited ions in the beam and σ^*_{1-1} and σ_{1-1} are the cross sections for double charge exchange of excited and unexcited ions, respectively.

†Process (5) can naturally occur only when B_2^{++} is stable.

seen that double charge exchange in hydrogen can occur only according to (6). The resonance defect in this case can be calculated unambiguously since E_p is known for the two protons formed from the unexcited H_2 molecule.[15] For other molecular gases E_p is unknown, so that the resonance defect can be calculated only for process (5) and then only when the first and second ionization potentials of B_2 are known.

TABLE III

Ion-molecule system	a, Angstroms
$H^+ - H_2$	2.3
$O^+ - H_2$	0.9
$F^+ - H_2$	0.9
$H^+ - N_2$	2.0
$Cl^+ - N_2$	0.5

Table III gives the values of a calculated from (1) for the cases of double charge exchange in molecular gases when a maximum of $\sigma_{1-1}(v)$ is observed.* For $H_1^+ - N_2$ and $Cl_1^+ - N_2$ it was assumed that the double charge exchange proceeded according to (5), and in calculating the resonance defect we used the potential for the appearance of N_2^{++} which was determined in reference 16.

Table III shows that a for double charge exchange in molecular gases varies within broad limits and is considerably different from the average value, 1.5 A, which is characteristic of atomic gases. The calculation of the excitation energy of F_1^+ from the maxima of $\sigma_{1-1}(v)$ for $F_1^+ - H_2$ yields 11.1 ev, which does not agree with any of the actual excitation energies of this ion (Table II). The hypothesis that a is constant for double charge exchange of unexcited and excited F_1^+ ions in hydrogen is clearly not confirmed.

It follows from the foregoing discussion that the study of the true shape of the curve $\sigma_{1-1}(v)$ at low velocity is complicated by the presence of excited ions in the primary beam, which leads to additional maxima that distort the curve for $\sigma_{1-1}(v)$ in this region. However, there are some double charge exchange processes, namely $H_1^+ \rightarrow H_1^-$ in He and H_2 as well as $Li^+ \rightarrow Li^-$ with a Li^+ beam from a thermionic source,[17] for which we can assume that $\sigma_{1-1}(v)$ is undistorted at low velocities. In all of these cases, the cross section σ_{1-1} is observed to decrease rapidly as the velocity decreases, as can be expected from the adiabatic hypothesis.

For these cases we can affirm that the potential curves of the initial and final states of the system of colliding particles do not intersect. In order to determine whether this is a general law, we must continue the study of double charge exchange at low velocities as far as the threshold for those cases in which we can eliminate the possibility of the presence of excited ions in the primary beam.

In conclusion, we wish to thank Professor A. K. Val'ter for his continued interest.

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*For $F_1^+ - H_2$, a was calculated for the maximum at the higher velocity, and for $O_1^+ - H_2$ the lower limit of a was determined since $\sigma_{1-1}(v)$ only reaches a plateau.

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Translated by I. Emin
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