CHARGE EXCHANGE OF ALKALI METAL IONS IN ALKALI METAL VAPOR AND INERT GASES

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The cross sections for resonant and nonresonant charge exchange of Li^+, Na^+, and K^+ ions in K and Na vapor and in the gases He, Ne, or Ar are measured at energies between 20 and 155 keV. The results for resonant charge exchange are "joined" with the results obtained at lower energies and are found to agree with the theoretical calculations. For most of the pairs investigated, the cross section is found to pass through a maximum in the case of nonresonant charge exchange. The positions of the maxima are in accord with the theoretical calculations[24] for both small and large values of ΔE.

1. INTRODUCTION

PROCESSES of single-electron charge exchange were investigated in a large velocity interval. These investigations were performed mainly with particles having relatively large ionization potentials E_i. The difference ΔE between the ionization potentials was usually small compared with the binding energy of the electron in the particle with the larger ionization potential.[1] There are few known investigations of processes of single-electron charge exchange of ions and atoms of alkali metals. Most of these investigations were carried out at low energies, but still insufficient to attain the maxima of the cross sections in the case of nonresonant charge exchange.[2-8]

So far, with the exception of [9, 11, 20], there were no investigations of the charge exchange of particles with strongly differing ionization potentials. At the same time, a study of single-electron charge exchange in the indicated cases, in a relatively large energy interval, is of great practical and also scientific interest, particularly from the point of view of comparison with the recently published theoretical calculations.

We have investigated the charge exchange of Li^+, Ne^+, and K^+ ions with Na, K, He, Ne, and Ar atoms in the energy interval 20–155 keV.

2. APPARATUS AND MEASUREMENT PROCEDURE

The charge-exchange cross sections were studied with a previously described experimental setup.[12, 13] We shall describe here only the changes and the additions made to the apparatus during the course of the described measurements.

The collision chamber, in which the necessary concentration of the sodium and potassium atoms was produced, was similar in construction to that described in [13]. For the measurements, a sealed glass ampoule containing pure metallic sodium or potassium was introduced into the chamber. This ampoule was made in a separate setup by sublimating the indicated metals in high vacuum. The ampoule was destroyed once high vacuum was attained in the collision chamber. To prevent splashing of the molten metal during the instant of destruction of the ampoule, the latter was surrounded by a screen made of thin stainless steel rolled to form a cylindrical tube. The temperature of the collision chamber was determined by a chromel-alumel thermocouple. The concentration of the metal vapor in this chamber could be varied in a wide pressure range.

The reliability with which the charge-exchange cross section is measured depends mainly on the measurement of the concentration of the alkali-metal atoms. As is well known, there are large discrepancies in the values cited by various authors for the concentrations of the alkali-metal atoms as functions of the temperature.[14] We have therefore measured directly the intensities of the fluxes of the Na and K atoms with a detector operating on the surface-ionization principle. This detector comprised a tungsten filament of 0.08 mm diameter and 30 mm long, stretched along the axis of a thin-wall nickel cylinder. The atomic beam was admitted into the cylinder through two diametrically-opposite rectangular slits (20×3.5 mm and 22×4 mm).

It is known that the surface-ionization coefficient of K on oxidized tungsten is 100%, and that of Na is also close to 100%.[15] Therefore the tungsten filament was oxidized in air under suitably chosen conditions. Prior to the oxidation, the detector filament was cleaned by heating it to high temperature in vacuum. The working temperature of the filament was selected such as to obtain saturation of the emission current. The intensity of the Na and K vapor flux from the collision chamber was determined by means of a calibrated round opening, which was located in the collision chamber in place of the output capillary. The concentration of the Na and K atoms was calculated from this intensity.

To measure the charge-exchange cross sections of the Li^+, Na^+, and K^+ ions with He, Ne, and Ar gas targets, we constructed a special collision chamber connected to the gas-supply system. The pressure in this chamber was measured with an LM-2 ionization lamp calibrated against a McLeod manometer with allowance for the pumping action of the mercury vapor. The pressure of the residual gas in the collision chamber was $(4-5) \times 10^{-6}$ mm Hg, and that in the vacuum system was $(5-6) \times 10^{-7}$ mm Hg. Since the Li^+, Na^+, and K^+ ions were obtained by us from a thermionic source, the pri-

mary beams of these ions should not contain particles in metastable states.[16] However, in the case of multiple collisions, metastable atoms might appear. To check on this possibility, we compared the charge exchange cross sections both in the region of multiple and in the region of single collisions.

Since it is possible to neglect in the investigated energy interval, without incurring a large error, the influence of the loss and capture of two or more electrons, and the system can be regarded as a two-component system consisting only of neutral and singly-charged particles, the cross sections for the capture of electrons by single-charged ions in the region of multiple collisions were determined from the following formula:

$$\sigma_{10} = \frac{F_{0\infty}}{nl}\left[\ln\frac{F_{0\infty}}{F_{0\infty} - F_0}\right], \qquad (1)$$

where F_0 is the relative number of neutral particles in the beam at specified nl, n is the concentration of the target atoms, l is the effective length of the collision chamber, and $F_{0\infty}$ is the neutral component in the equilibrium beam.

In the region of single collisions, the cross sections were determined respectively from the formula

$$\sigma_{10} = \left|\frac{1}{\Sigma N_i}\frac{dN_0}{d(nl)}\right|_{nl\to 0}, \qquad (2)$$

where N_i is the number of particles of definite charge i in the beam. The differences between the charge-exchange cross sections determined by formulas (1) and (2) do not exceed 15%.

The total errors due to measurements of the concentrations of the atoms, the charge fractions, and the ion energies do not exceed 15–20%. This may be the reason why the oscillations noted in [2,3,7] were not observed in the $\sigma_{10}(v)$ curves obtained by us, since the amplitudes of these oscillations do not exceed the limits of our measurement errors.

3. MEASUREMENT RESULTS AND DISCUSSION

A. Resonant charge exchange. The dependences of the resonant charge exchange cross sections of the ions K^+ and Ne^+ on the velocity are shown in Figs. 1 and 2, respectively. The same figures show for comparison the experimental data obtained by Chkuaseli et al.,[6] Perel et al.,[3] Bukhteev and Bydin,[4] and Kushnir.[5] A comparison shows that in the case of charge exchange of potassium our data "join" the data of Chkuaseli and Perel. The data of [4] are an exception. The figures show also the theoretically calculated resonant charge exchange cross sections of the ions K^+ and Na^+ obtained by Firsov,[17] Rapp and Francis,[18] and Smirnov.[19]

As seen from the figures, the theoretically calculated curves $\sigma_{10}(v)$ agree well with the experimental curves in the investigated velocity interval. However, the theoretical curves of Rapp, Francis, and Firsov lie somewhat lower than the experimental ones. The best agreement is with the calculations of Smirnov.

Taking into account the inaccuracies in the determination of the concentration of the alkali-metal vapor, on the one hand, and the approximate character of the theoretical calculations on the other, the agreement between the theoretical calculations in the experiment can be regarded as acceptable for all the cases under consideration. It is seen from the obtained data that the cross

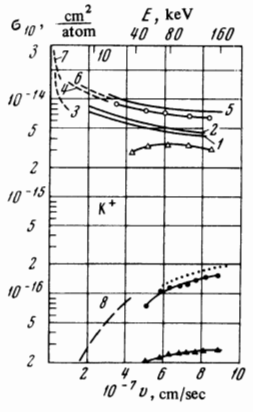

FIG. 1

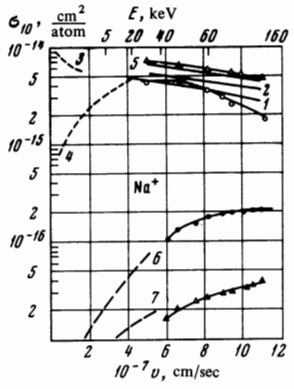

FIG. 2

FIG. 1. Velocity dependence of the effective charge exchange cross sections of K^+ ions: Δ – in Na vapor, ○ – K vapor, ▲ – Ne, ● – Ar. For comparison, data are shown on the charge exchange of K^+ in K vapor, obtained in other investigations: curve 3 – data of [4], 4 – [3], 6 – [6], 7 – [5]. Theoretical curves: 1 – calculated in accordance with the formula of Rapp and Francis [18], 2 – in accordance with Firsov's formula [17], 5 – in accordance with Smirnov's formula [19]. Dotted curve – in Ar, data of [9]; curve 8 – in Ar, data of [20].

FIG. 2. Velocity dependence of the effective cross sections for the charge exchange of Na^+ ions: Δ – in Na vapor, ○ – K vapor, ▲ – Ne, ● – Ar. For comparison, data obtained in other investigations are shown: curve 4 – in K vapor, data of [3]; 3 – in Na vapor, data of [4]. Theoretical curves: 1 – calculated by the formula of Rapp and Francis [18], 2 – by Firsov's formula [17]; 5 – by Smirnov's formula [19]. Curves 6, 7 – for Ar and Ne, respectively, data of [20].

section σ_{10} for the alkali metals Na and K decrease monotonically with increasing velocity of the incoming ions, and the dependence of the cross section on the velocity agrees with the equation

$$\sigma_{10}^{1/2} = a - b\ln v, \qquad (3)$$

where v is the velocity and a and b are constants. The cross section σ_{10} for K is larger than that for Na by approximately 12–15%.

This result, obtained in a relatively large interval of alkali-metal atom velocities, agrees with the existing notions concerning the corresponding connection between the cross section for resonant charge exchange and the first ionization potential of the atom.[18,21]

B. Nonresonant charge exchange. We measured the cross sections for the charge exchange of Li^+, Na^+, and K^+ ions in K and Na vapor and in He, Ne, and Ar gas targets.

Figure 3 shows the corresponding results obtained for Li^+ ions. Since there are no published data with which to make a direct comparison of our results, we have performed control experiments on He atoms and compared the results with Allison's data.[10]

As seen from the figure, the difference between the values of σ_{10} obtained by us and by Allison for He does not exceed 20%. In the region of low velocities, our results agree best with the data obtained by Kistemaker

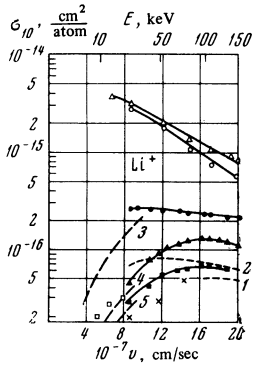

FIG. 3

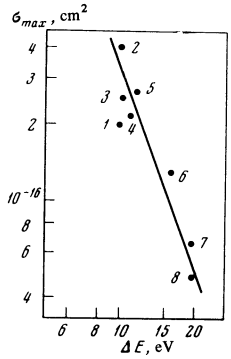

FIG. 4

FIG. 3. Velocity dependence of the effective cross sections for the charge exchange of Li^+ ions: Δ – in Na vapor; ○ – K vapor; ▲ – Ne; ● – Ar; ■ – in He; curve 1; × – in He, data of [10]; □ – in He, data of [22]; curve 2 – in N_2, data of [10]; curves 3, 4, 5 – in Ar, Ne, and He, respectively, data of [20].

FIG. 4. Dependence of the cross section for resonant charge exchange at the maximum on the quantity ΔE; 3 – (Li^+ + Ar), 4 – (Ne^+ + Ar), 6 – (Li^+ + Ne), 7 – (Li^+ + He), present data; 1 – (Al^+ + Ar), data of [11]; 2 – (Sr^+ + Ar), 5 – (K^+ + Ar), data of [9]; 8 – (Li^+ + He), data of [10].

et al.[20] In the investigated velocity region, the $\sigma_{10}(v)$ curves for the Li^+–inert gas pairs have maxima, and those for the Li^+–alkali atom pairs reveal a noticeable decrease of the cross sections with increasing velocity v.

The $\sigma_{10}(v)$ plots obtained for the interaction of K^+ and Na^+ ions with Na and K vapor, respectively, also have maxima in the investigated velocity region. The obtained data are shown in Figs. 1 and 2. The charge-exchange cross sections of these ions in Ne and Ar gas targets increase with increasing velocity v, with the exception of the case Na^+ + Ar, for which a maximum is reached. Figure 2 shows also data obtained by Perel et al.[3] We see that our data for the case Na^+ + K "join" the data of [3].

The maximum values of the charge exchange cross sections for the pairs Na^+ + K and K^+ + Na is observed practically at the same velocity, $(5.9–6.2) \times 10^7$ cm/sec. In absolute magnitude, σ_{max} for Na^+ + K exceeds the value of σ_{max} for K^+ + Na by approximately 20%.

For the pairs under consideration, we estimated the nonresonant cross sections by means of the formulas given by Rapp and Francis.[18] It is interesting to note that the cross sections calculated from these formulas differ from our experimental results by not more than 30–40%. However, as shown by Skinner,[23] the accuracy of such a calculation decreases when ΔE differs from zero and drops systematically with increasing ΔE. Indeed, for the alkali ion plus atom pairs for which $\Delta E \approx E_j$ there is observed a large discrepancy between the theoretical calculations of Rapp and Francis and experiment. In the cases investigated by us, an exponential increase of the charge-exchange cross section is observed in the velocity region preceding the maximum:[1]

$$\sigma_{10} = Ae^{-B/v}, \tag{4}$$

where A and B are constants determined by the nature of each pair. It should be noted that the dropping sections of the $\sigma_{10}(v)$ curves past the maximum exhibit, in the case of the Li^+ + Na and Li^+ + K pairs can be described by Eq. (3). As seen from the figures, the cross sections σ_{10} for the charge exchange of Li^+, Na^+, and K^+ in alkali-metal vapors exceed by many times the analogous cross sections in gas targets. It is obvious that this difference is in full agreement with the large difference in the values of ΔE and $\Delta E/E_i$. For the alkali ion plus alkali atom pair, both ΔE and $\Delta E/E_i$ are small. For the alkali ion plus gas atom pair, ΔE is large and comparable with E_i of the atom.

Drukarev,[24] using the Born approximation, has shown recently that the position of the maximum on the $\sigma_{10}(v)$ curve should be determined, in the case when $\Delta E \ll E_i$, by the Massey rule

$$v_m = \frac{a}{h}\Delta E = A\Delta E. \tag{5}$$

On the other hand, in the case when $\Delta E \approx E_i$, it should be determined by the condition

$$v_m = B(\Delta E)^{1/2}. \tag{6}$$

The data obtained in this investigation, supplemented by certain results taken from[2,3,9–11], make it possible to verify their correspondence with formulas (5) and (6). Table I gives the values of the coefficients $A = v_m/\Delta E$ and $B = v_m/(\Delta E)^{1/2}$ in relative units for the alkali ion plus alkali atom pairs for which $\Delta E \ll E_i$. As seen from the table, there is no doubt that formula (5) is valid for these pairs.

Table II lists also the coefficients A and B for the ion-atom pairs with $\Delta E \approx E_i$. In these cases, in accordance with the theoretical analysis,[24] the experi-

Table I

Interacting pairs	ΔE, eV	A	B	Interacting pairs	ΔE, eV	A	B
K^+ + Rb	0.16	8.4	3.4	K^+ + Na	0.8	7.76	6.76
Rb^+ + K	0.16	8.3	3.35	Na^+ + K	0.8	7.5	6.68
Rb^+ + Cs	0.3	7.68	4.17				

Table II

Interacting pairs	ΔE, eV	A	B	Interacting pairs	ΔE, eV	A	B
Al^+ + Ar	9.78	1.43	4.14	K^+ + Ar	11.42	1.09	3.7
Sr^+ + Ar	10.09	1.23	4.08	Li^+ + Ne	16.17	0.99	3.98
Li^+ + Ar	10.37	1.12	3.67	Li^+ + He	19.19	0.866	3.84
Na^+ + Ar	10.62	1.11	3.7	Li^+ + He	19.19	0.9	3.97

mental results obtained are undoubtedly in better agreement with formula (6).

Similar conclusions were obtained in the investigation of charge exchange of protons in highly-excited states in metal vapors.[25]

From a comparison of formulas (5) and (6) it is easy to see that the distance characterizing the realization of the charge-exchange process in the cases $\Delta E \approx E_i$ decreases with increasing ΔE, viz., $a \sim 1/(\Delta E)^{1/2}$. This means in turn that the maximum cross section σ_{max} should decrease rapidly with increasing ΔE. The correctness of this conclusion is illustrated by Fig. 4, which shows a plot of σ_{max} against ΔE for the cases given in Table II. As seen from the figure, σ_{max} can be represented by the expression

$$\sigma_{max} = A(\Delta E)^{-k}. \quad (7)$$

From the velocity dependences of the charge-exchange cross sections measured by us for ion and alkali-metal atom pairs it follows, in accordance with the Massey rule, that the adiabatic parameter a is approximately equal to 30 Å. The correction for the polarization energy, in accordance with the formulas proposed by Hasted,[26] does not result in agreement with his treatment. In particular, this was noted also in [2]. Apparently, the analysis proposed in [26] does not hold for alkali metals having a large polarizability. In such cases it is apparently necessary to take into account the dynamic polarizability of the atoms. This, however, calls for a special theoretical analysis.

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