

## RESONANCE CHARGE EXCHANGE OF NEGATIVE ALKALI METAL IONS

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The process of resonance charge exchange of negative  $\text{Na}^-$ ,  $\text{K}^-$ ,  $\text{Rb}^-$ , and  $\text{Cs}^-$  ions was investigated at energies from 900 to 2400 eV. The cross sections for the process  $Q_{pn}$  were of the order of  $10^{-14}$   $\text{cm}^2$  and increased as the ion velocity  $v$  decreased. A comparison of the results with Firsov's theory was used to determine the electron affinity energy of Na, K, Rb, and Cs atoms from the slope of the  $Q_{pn}(v)$  curve.

THE phenomenon of charge exchange of negative ions in atomic collisions, i.e., the transfer of the excess electron from a negative ion to a gas atom or molecule, was first detected experimentally by Dukel'skiĭ and Zandberg.<sup>[1]</sup>

Of special interest is the study of charge exchange in collisions of monatomic negative ions with atoms of the same element—resonance charge exchange. The first work on resonance exchange was carried out by Hummer, Stebbings, Fite and Branscomb,<sup>[2]</sup> who observed the charge exchange of negative  $\text{H}^-$  ions in atomic hydrogen. Firsov<sup>[3]</sup> proposed a theory of resonance charge exchange of ions in slow collisions, which made it possible to determine, in principle, the binding energy of an electron in a negative ion (the electron affinity energy  $S$  of the corresponding atom) from measurements of the total effective cross sections  $Q_{pn}$  (as a function of the ion velocity  $v$ ) for the process of resonance charge exchange of negative ions.

The present work describes an investigation of the process of resonance charge exchange of negative alkali metal ions  $\text{Na}^-$ ,  $\text{K}^-$ ,  $\text{Rb}^-$ , and  $\text{Cs}^-$ . The measurements were made at negative-ion energies from 1000 eV (for Na, 900 eV) to 2400 eV.

It should be noted that, in the investigated range of energies, charge exchange is accompanied by electron loss from negative ions: charge exchange produces slow negative ions, and the loss process produces free electrons.

## EXPERIMENTAL SETUP

The experimental setup is shown in Fig. 1. Negative alkali metal ions were obtained from a discharge in the vapor of a salt (NaI, KBr, RbCl, CsCl). These ions were accelerated to a given energy, passed through a  $90^\circ$  magnetic mass monochromator, were subjected to additional focusing, and passed into a collision chamber C through

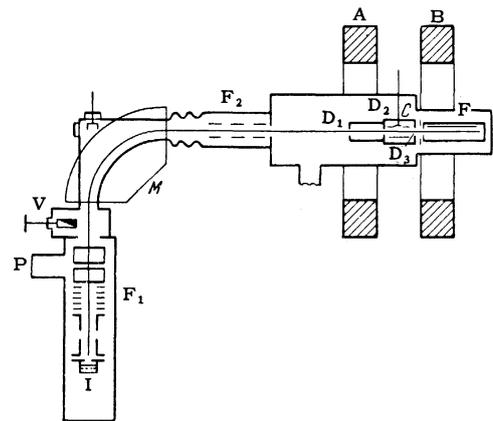


FIG. 1. Layout of the apparatus: I is the source of negative ions;  $F_1$  and  $F_2$  are focusing systems; M is the magnet of the mass monochromator; P is a tube leading to pumps; A and B are Helmholtz coils; C is the collision chamber;  $D_1$  and  $D_2$  are collimating diaphragms of 0.9 mm diameter;  $D_3$  is the exit diaphragm of 2.5 mm diameter; F is the Faraday cylinder; V is the vacuum valve.

collimating diaphragms  $S_1$  and  $S_2$ . The collision chamber could be filled with alkali metal vapor. Negative ions which have not suffered charge exchange or electron loss, as well as fast neutral atoms formed in this operation, reached a deep Faraday cylinder F, whose current I was measured with an electrometer amplifier of  $1 \times 10^{-13}$  A sensitivity per scale division.

The collision chamber (Fig. 2) was similar to that described earlier<sup>[4]</sup> but it was somewhat improved. It consisted of a massive (in order to increase thermal inertia) copper cylinder placed on a steatite base (used for thermal and electrical insulation). Inside the chamber, there were electrodes for measuring the current of slow charged particles produced by collisions. An electrode  $m$  of 1.9 cm length was used for the measurements (it was connected to an electrometer amplifier of  $1 \times 10^{-15}$  A sensitivity per scale division). The

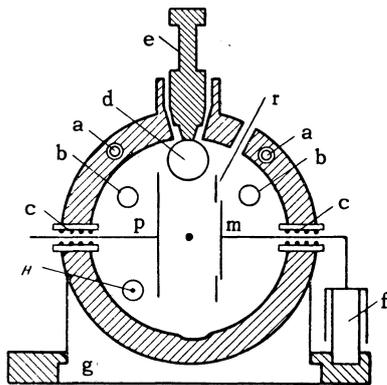


FIG. 2. Collision chamber: a, b, c are tungsten coils; d is an ampoule with an alkali metal; e is a striker; f is a quartz insulator; g is a steatite base; w is a wire for measuring alkali metal vapor pressure by the surface ionization method; p is a potential electrode; m is a measuring electrode; r is a guard electrode.

electrode m was surrounded by a guard ring r. A potential could be applied to another electrode p. Both electrodes were fixed by means of thin molybdenum rods to quartz insulators placed outside the chamber. Coils a, b, and c were used to heat the chamber and the electrodes in it. The chamber temperature was measured with a platinum resistance thermometer. An alkali metal was introduced into the chamber in a sealed glass ampoule which could be opened in vacuum. The vapor pressure of Cs, Rb and K was determined by measuring the current  $I^+$  of positive ions produced by ionizing alkali metal atoms with a heated tungsten wire (of  $25 \mu$  diameter). The wire was surrounded by a measuring cylinder and laterally placed guard cylinders.

Helmholtz coils A and B (Fig. 1) established a uniform magnetic field in the region of the collision chamber, the field being directed along the ion beam. When a given current passed through the coils, the magnetic field intensity did not vary more than 2% inside the collision chamber. The apparatus was evacuated with oil diffusion pumps. During the operation of the ion source, the pressure in the collision chamber was  $\approx 5 \times 10^{-6}$  mm Hg.

## MEASUREMENT METHOD

After a preliminary test of the apparatus, the collision chamber was heated to a given temperature and the ampoule containing an alkali metal was opened. The vapor pressure  $p$  of Cs, Rb, and K was found from the formula

$$p = I^+ \sqrt{2\pi M k T} / ea\beta, \quad (1)$$

where  $I^+$  is the current of positive ions to the

measuring cylinder,  $M$  is the mass of the alkali metal atoms,  $T$  is the absolute temperature of the alkali metal vapor,  $k$  is Boltzmann's constant,  $a$  is the area of the working surface of the wire, and  $\beta$  is the surface ionization coefficient.

Dependences of the surface ionization current on the wire temperature were recorded so that a working point could be selected for each alkali metal using the wire temperature scale. It was assumed that at the working point the coefficient  $\beta$  for Cs, Rb, and K was unity for hot tungsten.<sup>1)</sup> The vapor pressure of Na was deduced from the collision chamber temperature and from the data on the temperature dependence of the vapor pressure of Na.<sup>[5]</sup>

The collision chamber was kept at a positive potential of several volts to avoid secondary electrons from the diaphragm edges from reaching the measuring electrodes. By applying a negative potential to the electrode p, it was possible to direct electrons and slow negative ions, formed by the passage of the fast negative ion beam through the collision chamber, to the measuring electrode m. The current to the electrode m reached saturation when the potential difference which accelerated negative ions was 4–6 V; it disappeared completely on the application of a retarding potential difference of the same value. This indicated that the arrival at the measuring electrode of negative ions scattered without change of charge, the ionization of alkali metal atoms by negative ions, and the processes which might lead to electron loss from the measuring electrode (secondary emission, photoeffect), were unimportant under our experimental conditions.

To determine the ratio of the number of negative ions to the number of electrons appearing in the collision chamber, the slow electrons were separated from the slow ions in crossed electric and magnetic fields. A magnetic field at right angles to an electric field was produced by switching on the coils A and B. At a given potential difference between the electrodes p and m, it was possible to prevent electrons from reaching the measuring electrode m, without preventing negative ions from reaching this electrode.

Figure 3 gives, by way of example, two curves showing the dependence of the current of negative

<sup>1)</sup>Since the surface state of the hot tungsten wire was not checked directly, the surface ionization coefficient of K atoms could have been less than unity. This may have led to a systematic error in determining the vapor pressure of K, giving too low a value of this pressure (the error would not have been more than 10-15%).

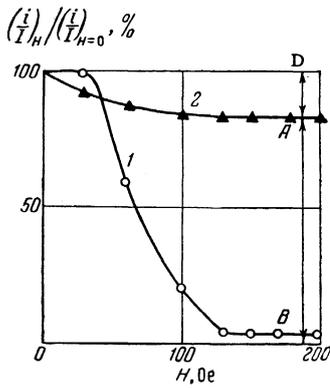


FIG. 3. Dependence of the current on negatively charged particles, reaching the electrode m, on the magnetic field intensity H: 1)  $K^-$  ions in argon; 2)  $K^-$  ions in potassium.

charged particles reaching the electrode m on the magnetic field intensity H. Curve 1 represents the case when  $K^-$  ions pass through the collision chamber filled with argon, in which charge exchange could not occur. In  $H = 150$  Oe, the current to the electrode m decreased to 0.03 of the value which was obtained with the coils not switched on. Curve 2 was recorded when the collision chamber was filled with potassium vapor; the ordinate AB corresponding to the horizontal part of curve 2 should be regarded as the current  $i_i$  of slow negative  $K^-$  ions, and the segment AD should be regarded as the current  $i_e$  of the electrons detached from negative ions. The ratios  $i_i/I$  and  $i_e/I$  were, within the limits of the experimental error, linear functions of p but independent of I, indicating that the collisions were single.

The effective cross sections for resonance

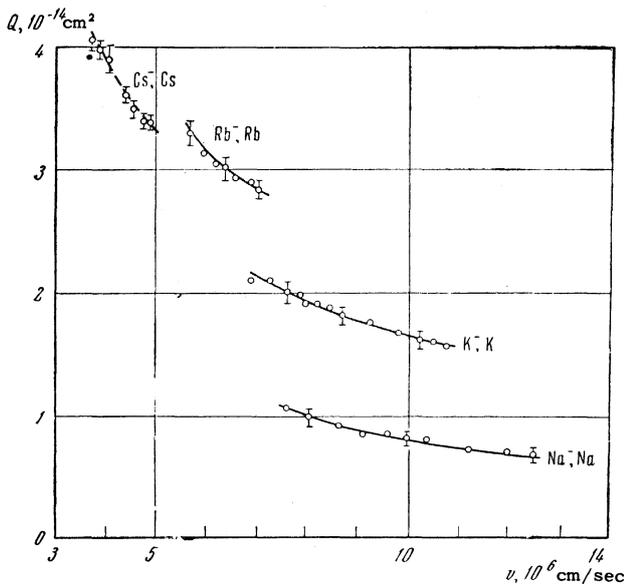


FIG. 4. Cross section for resonance charge exchange of negative  $Na^-$ ,  $K^-$ ,  $Rb^-$ , and  $Cs^-$  ions as a function of the ion velocity.

charge exchange were calculated from the formula

$$Q_{pn} = i_i \left[ I + \frac{x+L}{x} (i_i + i_e) \right] nx, \quad (2)$$

where  $n = p/kT$  is the number of alkali metal atoms per  $cm^3$ ,  $x$  is the length of the measuring electrode,  $L$  is the length of the guard electrode placed between the measuring electrode and the exit diaphragm of the collision chamber.

Measurements of the dependence of Q on the energy T (the velocity v) of negative ions were carried out in the single-collision region at pressures of the order of  $10^{-5}$  mm Hg. The working conditions were selected so that the surface ionization current  $I^+$  in Eq. (1) was practically constant for a long time if the temperature was constant. The form of the curve  $Q(v)$  was reproducible from test to test. The absolute values of the cross sections were reproducible to within  $\pm 6\%$ .

### RESULTS OF MEASUREMENTS

Figure 4 shows the results of the measurements of the cross sections  $Q_{pn}$  for the resonance charge exchange of  $Na^-$ ,  $K^-$ ,  $Rb^-$ , and  $Cs^-$  ions as a function of the ion velocity. The cross sections are of the order of  $10^{-14} cm^2$  and increase slowly as the negative ion velocity decreases. For different ions, the velocity ranges were different, but for similar velocities the cross sections for  $Cs^-$  and  $Rb^-$  were similar in value and greater than for  $K^-$  and  $Na^-$ .

The cross section for the process of electron detachment from a negative ion  $Q_n$  was, within the experimental error, independent of the velocity v under test and amounted to  $\sim 8 \times 10^{-15} cm^2$  for  $Cs^-$ ,  $\sim 7 \times 10^{-15} cm^2$  for  $Rb^-$ ,  $\sim 5 \times 10^{-15} cm^2$  for  $K^-$ , and  $1.8 \times 10^{-15} cm^2$  for  $Na^-$ .

Figure 5 presents curves for the cross section of nonresonance charge exchange of  $Na^-$  ions in Cs and Rb vapor. These cross sections are smaller than the resonance charge exchange cross sections of  $Cs^-$  and  $Rb^-$ . The  $Q(v)$  curves for these cases have a weak maximum at an  $Na^-$  ion velocity of about  $10^7$  cm/sec.

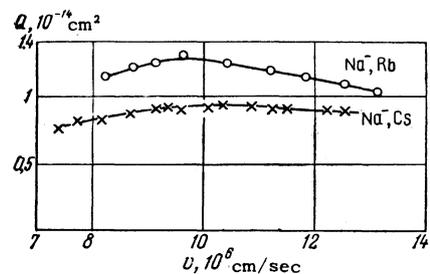


FIG. 5. Cross section for nonresonance charge exchange of  $Na^-$  ions in Cs and Rb as a function of the ion velocity.

## DETERMINATION OF THE ELECTRON AFFINITY ENERGY

The electron affinity energy  $S$  of alkali metal atoms has not yet been determined experimentally. Because this energy is small, it cannot be determined conveniently by such methods as the photo-detachment of an electron from a negative ion or negative surface ionization. The values of  $S$  quoted in the literature for alkali metals were obtained by calculation or by extrapolation of the binding energy in isoelectronic series, and they differ enormously.

On the basis of Firsov's work<sup>[3]</sup> we attempted to use our experimental data on the resonance charge exchange of negative alkali metal ions in order to determine  $S$ . Firsov's theory allows us to find  $S$  by measuring the resonance charge exchange cross section  $Q_{pn}$  and the cross section  $Q_n$  as a function of the ion velocity  $v$ . For this purpose, one uses the formulas

$$S = \hbar^2 \alpha^2 / 2m,$$

$$\alpha \approx - \left\{ \frac{1}{vdR_0/dv} + \frac{1}{2R_0} \right\} = - \left\{ \frac{d \ln v}{dR_0} + \frac{1}{2R_0} \right\},$$

$$\frac{1}{2} \pi R_0^2 = Q_{pn} + Q_n \quad (3)$$

where  $m$  is the electronic mass. In determining  $S$  from Eq. (3), we assumed for  $R_0$  its value in the middle of our range of measurements, and  $d \ln v / dR_0$  was taken to be the value of the slope of a straight line plotted by the least squares method through experimental points in coordinates  $\ln v$  and  $R_0$ . The experimental values of  $S$  obtained in this way were

Atom:	Na	K	Rb	Cs
$S_{\text{exp}}$ :	$0.41 \begin{smallmatrix} +0.06 \\ -0.02 \end{smallmatrix}$	$0.22 \begin{smallmatrix} +0.08 \\ -0.06 \end{smallmatrix}$	$0.16 \pm 0.06$	$0.13 \begin{smallmatrix} +0.07 \\ -0.06 \end{smallmatrix}$

The limits of the values of  $S$  (governed by the random experimental errors) were based on the highest and lowest values of the slopes of the straight lines passing through the experimental points in the plot of  $R_0(\ln v)$  within the limits of the rms error in the determination of  $R_0$ .

Systematic errors may have been committed in this work in measuring the absolute values of the cross sections  $Q_{pn}$  and  $Q_n$ . The main error may have been due to an inaccuracy in measuring the vapor pressure of the alkali metals. The values of the vapor pressures of Cs and Rb, obtained by the method of surface ionization, should be regarded as

more reliable than the values for K and Na.<sup>2)</sup> This error may have distorted somewhat values of  $S$  determined from the experimental data; however, the order of magnitude of  $S$  is probably correct. For comparison, one can quote the electron affinity energy of sodium given in Edlén's work<sup>[6]</sup>:  $S = 0.47$  eV. The extrapolation method used in the present study gave for  $C^-$ ,  $O^-$ ,  $F^-$ ,  $S^-$ , and  $Cl^-$  binding energies which were in good agreement with reliable experimental data.

To obtain more accurate values of the electron affinity energy of alkali metals, one needs to study the dependence of the cross sections  $Q_{pn}$  and  $Q_n$  on the velocity over a wider range of the latter (preferably including low velocities) and to determine more accurately the absolute values of  $Q_{pn}$  and  $Q_n$ . It is desirable also to develop further the theory and to extend it to processes of nonresonance charge exchange of negative ions. This would then make it possible to determine the electron affinity of atoms by investigating nonresonance charge exchange of pairs for which there are reliable electron affinity energy data for one of the partners.

In conclusion, the author wishes to express his deep gratitude to Professor V. M. Dukel'skiĭ for his constant interest in this work and for his valuable advice in carrying it out. The author is also most grateful to Professor O. B. Firsov and B. M. Smirnov for valuable discussions, and to S. S. Pop for help in making the measurements.

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<sup>2</sup>Hummer, Stebbings, Fite, and Branscomb, Phys. Rev. 119, 668 (1960).

<sup>3</sup>O. B. Firsov, JETP 21, 1001 (1951).

<sup>4</sup>Yu. F. Bydin and A. M. Bukhteev, ZhTF 29, 12 (1959), Soviet Phys. Tech. Phys. 4, 10 (1959).

<sup>5</sup>S. Dushman, Scientific Foundations of Vacuum Technique, 1949 (Russ. Transl., IIL, 1950).

<sup>6</sup>B. Edlén, J. Chem. Phys. 33, 98 (1960).

<sup>7</sup>Marino, Smith, and Caplinger, Phys. Rev. 128, 2243 (1962).

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<sup>2)</sup>To check this point, the cross sections for  $(Cs^+, Cs)$  charge exchange  $Cs^+, Cs$  were measured at several energies under the same conditions and simultaneously with  $(Cs^-, Cs)$  charge exchange cross sections. The results of these measurements were close to those of Marino et al.,<sup>[7]</sup> who measured the cross section for resonance charge exchange  $(Cs^+, Cs)$  more carefully.