DETACHMENT OF ELECTRONS FROM NEGATIVE ALKALINE METAL IONS IN COLLISIONS WITH INERT GAS ATOMS

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The cross sections for electron detachment from Li^-, Na^-, K^-, Rb^-, and Cs^- negative ions in collisions with He, Ne, Ar, Kr, and Xe atoms have been measured in the following energy intervals: from 900 to 9000 eV for Li^- ions, from 600 to 12,000 eV for Na^- ions, from 600 to 3000 eV for K^- ions, from 700 to 3000 eV for Rb^- ions and from 900 to 2200 eV for Cs^- ions. The results of the measurements are compared with the theory of Smirnov and Firsov.[1]

SMIRNOV and Firsov, in their theory of the interaction of negative ions and atoms,[1] consider, in particular, the process of detachment of the weakly bound excess electron from a negative ion in collisions with atoms of the inert gases with a positive scattering length (Ar, Kr, and Xe). For comparison with this part of the theory, it is convenient to use H^- ions (this case has already been discussed by us[2]) and negative alkaline metal ions, since the binding energy of the excess electron in these ions amounts to tenths of an electron volt.[3] In the present work we have measured the cross sections Q_d for the process of detachment of an electron from the negative ions Li^-, Na^-, K^-, Rb^-, and Cs^- in collisions with atoms of He, Ne, Ar, Kr, and Xe. The results of these measurements are compared with the theory of Smirnov and Firsov.[1]

A negative ion beam of a given energy was separated by means of a 90° magnetic mass analyzer. Measurements of the cross sections Q_d were carried out by counting the slow electrons which appeared on passage of the negative ion beam through a chamber filled with gas.[4,5] In the measurement region a uniform magnetic field was produced, parallel to the uniform electric field between the measuring electrodes.

The cross-section measurements were made in the energy intervals 900—9000 eV for Li^- ions, 600—12000 eV for Na^- ions, 600—3000 eV for K^- ions, 700—3000 eV for Rb^- ions, and 900—2200 eV for Cs^- ions. For Cs^- and Rb^- ions we verified (by the absence of a fast positive ion current) that the process of detachment of two electrons in one collision with a gas atom does not play an important role under the conditions of our experiments.

According to the theory of Smirnov and Firsov,[1] the cross section Q_d for detachment of a weakly bound electron from a negative ion should have a value which does not depend on ion velocity, and which is determined by the formula (in atomic units)

$$Q_d = \pi / k_1 k_2, \quad (1)$$

where $k_1 = \sqrt{2S}$, S is the electron affinity of the atom from which the negative ion was formed, and $1/k_2$ is the scattering length of an electron by an inert gas atom, which is connected with the elastic scattering cross section of very slow electrons by the relation

$$Q_{el} = 4\pi k_2^{-2}. \quad (2)$$

In the range of velocities investigated by us the observed cross sections Q_d, which have a value of the order of 10^{-16}—10^{-15} cm^2, increase with increasing ion velocity. Thus, experiment does not agree with the conclusion of the theory[1] that the cross section Q_d should be independent of velocity.

According to formula (1), the squares of the cross sections Q_d for electron detachment from a negative ion in collisions with atoms of the same inert gas are inversely proportional to the electron affinities of the atoms from which the negative ions are formed. From the point of view of the applicability of the Smirnov-Firsov theory, the most favorable case for comparison with experiment is electron detachment from negative ions of the alkali metals in Xe, since the scattering length $1/k_2$ for Xe is larger than for the other inert gases. Figure 1 shows the experimentally obtained values of Q_d in Xe as a function of the relative kinetic energy of the colliding particles W. The table lists

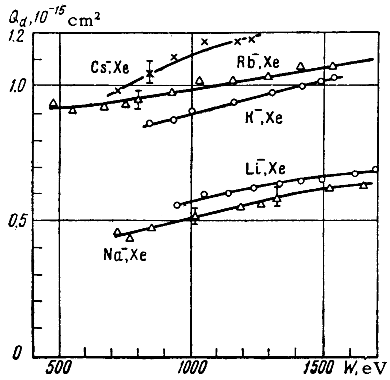

FIG. 1. Cross sections Q_d for electron detachment from negative ions of Cs^-, Rb^-, K^-, Na^-, and Li^- in collisions with Xe atoms, as a function of the relative kinetic energy of the colliding particles W.

Ratios of electron affinities of Rb, K, Na, and Li atoms to the electron affinity of Cs

	Present work		[3]
	W=800 eV	W=1000 eV	
S_{Rb}/S_{Cs}	1.21±0,15	1.23±0.15	0.3<1.23<2
S_K/S_{Cs}	1.45±0,17	1.5±0.17	0.8<1.38<4
S_{Na}/S_{Cs}	4.3±0,5	4.2±0.5	2<3.2<6
S_{Li}/S_{Cs}	3.5±0,4	3.4±0.4	

the ratios of the electron affinities of Rb, K, Na, and Li to that of Cs, obtained according to formula (1), on the basis of the ratios of the values of the cross sections Q_d in Xe, taken for the same value of relative kinetic energy W. The table also shows the values of these same ratios obtained from data on the resonant charge exchange of negative alkali metal ions.[2] As we can see from the table, $S_{Cs} < S_{Rb} < S_K < S_{Na}$, but $S_{Li} < S_{Na}$. A similar phenomenon occurs in the sixth and seventh columns of the periodic table ($S_O < S_S$, $S_F < S_{Cl}$), in which the electron affinity of the lightest element is also less than the one following it.

The absolute values of the cross sections Q_d calculated from formulas (1) and (2) (if we take for Q_{el} the values given by Massey and Burhop:[6] 1.16×10^{-14} cm² for Xe, 3.4×10^{-15} cm² for Kr, and 7.1×10^{-16} cm² for Ar) in Xe and Kr (0.1 eV < S < 1 eV) turn out to be larger than the experimentally obtained values in the energy region studied by us, and in Ar—close to them.

According to formula (1), the cross section Q_d should be proportional to the scattering length of the gas atom with which the negative ion collides (or proportional to $\sqrt{Q_{el}}$). For the values of Q_d obtained experimentally by us for Cs^- and Rb^- ions, a correlation is observed between Q_d and the scattering lengths. It is known that the greatest values of the scattering lengths occur for the alkali metal atoms, smaller values for Ar, Kr, and Xe, and still smaller for He and Ne. The values of Q_d are similarly distributed. For example, the cross section Q_d for the pair Rb^-, Rb amounts to about 7×10^{-15} cm².[2] The cross section Q_d for Rb^- ions in the inert gases are shown in Fig. 2. It is evident from the figure that the cross sections Q_d in He and Ne are noticeably smaller than in Ar, Kr, and Xe.

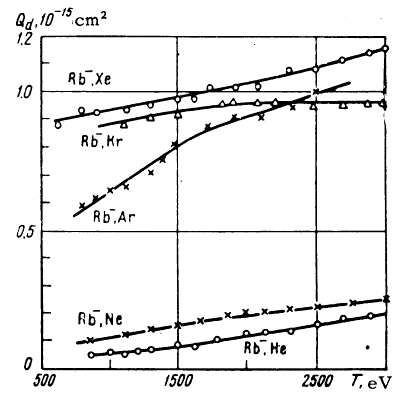

FIG. 2. Cross sections Q_d for electron detachment from negative ions of Rb^- in collisions with atoms of He, Ne, Ar, Kr, and Xe, as a function of the negative ion kinetic energy T.

If there were a quantitative connection between Q_d and the elastic scattering cross section for very slow electrons, we would expect that the cross section Q_d would depend nonmonotonically on v for negative ion velocities close to the electron velocities at which the Ramsauer effect is observed in Ar, Kr, and Xe (for Li^- ions, ≈7 keV; for H^- ions, ≈1–2 keV). However, for Li^- and H^- ions, for which these energy intervals were carefully examined, the electron detachment cross sections increase monotonically with v, and significant irregularities in the dependence of Q_d on v are not observed.

Part of the discrepancies between theory and experiment can be explained by experimental errors in determination of Q_d and insufficient accuracy of the values of Q_{el} used in the calculation. Another part is evidently due to the approximate nature of the theory. It is also possible that the electron affinity of the alkali metal atoms is insufficient for strict fulfillment of the criterion for applicability of the Smirnov-Firsov theory. However, this theory apparently gives correctly the order of magnitude of the cross section Q_d and indicates its connection with the electron affinity S

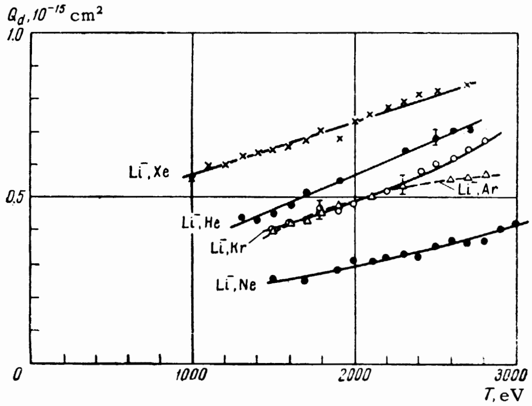

FIG. 3. Cross sections Q_d for electron detachment from negative ions of Li^- in collisions with atoms of He, Ne, Ar, Kr, and Xe, as a function of the negative ion kinetic energy.

and with the elastic scattering cross sections for very slow electrons.

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