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.\[1\]

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)

$$Q_d = \pi / k_2 n,$$

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

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

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 $Q_{el}$ 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

<table>
<thead>
<tr>
<th></th>
<th>Present work W=800 eV</th>
<th>W=1000 eV</th>
<th>[3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{Rb}/S_{Cs}$</td>
<td>1.21±0.15</td>
<td>1.23±0.15</td>
<td>0.3&lt;1.23&lt;2</td>
</tr>
<tr>
<td>$S_{K}/S_{Cs}$</td>
<td>1.45±0.17</td>
<td>1.5±0.17</td>
<td>0.8&lt;1.38&lt;4</td>
</tr>
<tr>
<td>$S_{Na}/S_{Cs}$</td>
<td>4.3±0.5</td>
<td>4.2±0.5</td>
<td>2&lt;3.2&lt;6</td>
</tr>
<tr>
<td>$S_{Li}/S_{Cs}$</td>
<td>3.5±0.4</td>
<td>3.4±0.4</td>
<td></td>
</tr>
</tbody>
</table>

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 ($S_{O} < S_{S}$, $S_{P} < S_{Cl}$), 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: $1.16 \times 10^{-14}$ cm$^2$ for Xe, $3.4 \times 10^{-15}$ cm$^2$ for Kr, and $7.1 \times 10^{-16}$ cm$^2$ 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 $7 \times 10^{-16}$ cm$^2$. 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.

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, $\approx 7$ keV; for H$^-$ ions, $\approx 1$–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. 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 $T$. 

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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.

In conclusion I wish to express my deep gratitude to Professor V. M. Dukel'skil for his constant attention and interest in this work. I sincerely appreciate helpful discussions with Professors O. B. Firsov, B. M. Smirnov, and Yu. N. Demkov.


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