Negative ion excited states and the determination of their binding energy by electron detachement by an electric field

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Detachment of electrons from negative ions under the action of an external electric field $E \leq 450$ kV/cm is investigated. It is shown that there are excited metastable states with a binding energy $\epsilon < 0.2$ eV in the following ions: $He^-(^4P)$, $C^-(^2D)$, $Si^-(^2P)$, $Al^-(^1D)$. The binding energies of the states are determined on the basis of their rate of decay in a field E. For $He^-(1s2s2p\,^4P)$ the energy is 0.075 ± 0.005 eV, for $C^-(^2D)$ it is 0.037 ± 0.003 eV, for $Si^-(^2P)$, 0.035 ± 0.004 eV, and for $Al^-(^1D)$, 0.095 eV. The binding energy for the $Al^-(^3P)$ ground state (electron affinity energy) is estimated to be $\gtrsim 0.2$ eV.

INTRODUCTION

The problem of the existence of bound excited states of negative ions has been little studied to date. Most negative ions have a small binding energy (less than 1–2 eV), which is determined by the strong screening of the nuclear field and by the short-range interaction potential of the electron with the atomic core. Therefore, the number of bound excited states lying below the ground state of the atom (which is the boundary of the continuum for a negative ion), must be small.[1,2] The existence of low-lying excited states is most probable for negative ions. They should include, first of all, the levels of the fine structure of the ground term of the ion (for example, the level $^2P_{1/2}Se^-$, which lies about 0.3 eV above the ground level $^2P_{3/2}Se^-$[3]). Terms which correspond to the same electron configuration as the ground term have a somewhat greater excitation energy.

The presence of such excited terms for negative ions of certain light elements of groups III, IV and V of the periodic table has been predicted in the theoretical papers.[4-6] On the basis of the results of these studies we can expect the existence of excited terms of the ions Al^-, C^-, P^-, N^- and Si^- (see Table I). It should be noted that these excited ions are metastable, since the transition to the ground state is forbidden by the rule of spin conservation, and it can be expected that the lifetime of such states is of the order of 10^{-3}–10^{-5} sec.[7,8]

TABLE I. Low-lying excited terms and the binding energies of negative ions for Group II and III elements of the periodic table (from [5])

Electron Configuration	Term	Ion	Binding Energy, eV	Ion	Binding Energy, eV
np^2	^1S	B^-	—0.66	Al^-	—0.42
	^1D		—0.19		0.13
	^3P		0.33		0.52
np^3	^2P	C^-	—0.22	Si^-	0.02
	^2D		—0.05		0.58
	^4S		1.24		1.46
np^4	^1S	N^-	—2.55	P^-	—1.17
	^1D		—1.23		—0.05
	^3P		0.05		0.77

The existence of negative ions in which excitation is accompanied by a change in electron configuration is less probable. In such a case, one or more electrons are found in quantum states that are higher than the ground state of the ion. These ions will most likely exist for elements with completed d and f shells, especially for metals of group VIII (for example, Pt^-[9]).

It must be noted that the negative ions can exist in auto-ionization metastable states. An example is He^- in the state $1s2s2p\,^4P$.[10] The existence of ^1D auto-ionization states can also be expected for the ions N^- and P^-.

The present study was undertaken with the aim of finding and investigating weakly bound excited states of a series of negative ions, especially those of the groups III–V. The method of ionization of atomic particles by an electric field was used. This method was first applied by Riviere and Sweetman for the detection of highly excited atoms of hydrogen.[11] These same authors demonstrated the possibility of detachment of the electron from the negative helium ion under the influence of the electric field.[12] From the detachment of the electron by the electric field, we can determine the binding energy of the electron in the negative ion.[13] The method of determination of the binding energy of the electron by its detachment with the use of an electric field has definite advantages over the well-known methods of photosplitting and photoelectron spectroscopy in the case of small values of the binding energy ($\epsilon \leq 0.1$–0.2 eV).

Preliminary results of experiments on detachment of the electron by an electric field and determination of the binding energy for the ions He^- (^4P), C^- (^2D) and Si^- (^2P) were reported in our earlier papers[14-16]. In this study we have investigated detachment of the electron in an electric field from the ions He^-, C^-, Si^-, Al^-, P^-, O^- and Cl^-.

1. METHOD OF DETERMINATION OF THE BINDING ENERGY OF THE ELECTRON BY MEANS OF ITS DETACHMENT BY AN ELECTRIC FIELD

In this method, the dependence of the attenuation of a beam of particles in a given change state is measured as a function of the field intensity E:

$$I(E) = i(E)/i_0, \tag{1}$$

where i_0 is the beam intensity at E = 0 and i(E) is the beam intensity after passage through a field E.

The relative population of states decomposed by the field can be determined experimentally directly from the I(E) dependence. However, to find the binding energy, it is necessary to know the relation between the probability of electron detachment W and the quantities ϵ and E.

A. Probability of Detachment of the Electron from Negative Ions in an Electric Field

When an external electric field acts on an atomic particle, a unilateral lowering of the potential barrier occurs and decay of the atomic particle takes place through the penetration of the electron through this potential barrier. The probability of such a transition for negative ions has been considered by Demkov and Drukarev[13] and by Smirnov and Chibisov.[17]

In[13] the problem was solved for an ion in which the weakly bound electron is in the s state, in the approximation of zero effective radius of the forces. Smirnov and Chibisov[17] solved this problem for an electron with different quantum numbers l, under the assumption that the penetration of the electron takes place at large distances from the nucleus in directions that are close to the direction of the electric field. They used a wave function with a radial part which has the following asymptotic form:

$$\Psi(r)=Ar^{z/\gamma-1}e^{-\gamma r}, \tag{2}$$

where z is the charge of the atomic core, $\frac{1}{2}\gamma^2 = |\epsilon|$ is the binding energy of the electron, and A is a constant which takes into account the effect of the atomic core on the behavior of the electron.

The result obtained by Smirnov and Chibisov shows that in the single-electron approximation the decay probability w of an atom or ion depends in particular on the projection of the orbital momentum of the weakly bound electron onto the direction of the field $|m_l|$. For a p electron, the probabilities have the following form (in atomic units):

$$l=1, m=0: \; w_{10}=\frac{3}{4}A^2\frac{E}{\gamma^2}\exp\left\{-\frac{2}{3}\frac{\gamma^3}{E}\right\}; \tag{3}$$

$$l=1, |m|=1: \; w_{11}=\frac{3}{4}A^2\frac{E^2}{\gamma^5}\exp\left\{-\frac{2}{3}\frac{\gamma^3}{E}\right\}. \tag{4}$$

In a later paper[18], these same authors extended this result to the case of atoms or ions which have several equivalent outer electrons. Here the scheme of angular momentum addition of Racah was used, giving for the decay probability

$$W_{LM}=N[G_{LS}^{L'S'}]^2\sum w_{lm}\begin{bmatrix} l & L & L' \\ m & M' & M \end{bmatrix}^2. \tag{5}$$

Here N is the number of valence electrons, $G_{LS}^{L'S'}$ is the genealogical coefficient, $\begin{bmatrix} l & L & L' \\ m & M' & M \end{bmatrix}$ are the Clebsch-Gordan coefficients, w_{lm} are the single-electron probabilities, which are determined for the p electron from (3) and (4); L, S are the orbital and spin angular momenta of the ion; L′, S′ are the same quantities for the atomic core.

B. Determination of the Value of the Binding Energy

As is well known, the Stark effect takes place in an external electric field, leading to a shift of the levels and also to their splitting. In the case of an outer s electron, splitting does not occur and there is only a single state. However, for outer electrons with $l \geq 1$, there are several Stark states with different projections of the angular momentum. In this case, the damping of the beam I in the field is linked to the corresponding decay probabilities by the relation

$$I(E)=\sum_{k=1}^{n} f_k e^{-W_k(E,\epsilon)t}, \tag{6}$$

where W_k is the probability of decay of the kth state, f_k the fraction of ions in the state k, and t the time of flight of the negative ions through the region with the field.

Here the decay probability W_k cannot be found by simply taking the logarithm of I, as was done in[17]. Experience shows that more exact results can be obtained if we use the differential dependence

$$D(E)=dI(E)/dE \tag{7}$$

as the basic experimental dependence.

For each individual state, the dependence of the form (7) represents a kind of "line," and the D(E) dependence as a whole a "field" spectrum. The positions and widths of the lines in such a spectrum depend on the time of flight of the ions through the region of action of the electric field. In certain cases the lines which correspond to the various Stark states of the same term cannot be resolved.

Estimates of the binding energy can be obtained from the portion of the field spectrum where one Stark state decays preferentially. By integrating the spectrum in the region of high fields and assuming a statistical population of the Stark states, we can calculate the dependence $W_n(E)$, which allows us to find the quantity ϵ on the basis of the expressions for the decay probability (3) or (4) (depending on the character of the Stark splitting) from the slope of the linear dependence $\ln(W_n/E) = f_1(1/E)$ (or $\ln(W_n/E^2) = f_2(1/E)$). In this way, we obtained preliminary estimates of the binding energy of the states ^4P of the He^- ion and ^2D of the C^- ion.[14,15]

In the present work, we have carried out a more exact treatment of the experimental results, in which the entire field spectrum was used and, in addition, the distribution of the field along the axis of the beam z was taken into account. The D(E) dependence with account of the field distribution along the axis z ($E = E_0 g(z)$) can be written

$$D_p(E_0)=-\frac{1}{v}\sum_{k=1}^{n} f_k \exp\left\{-\int_{-\infty}^{\infty} W_k[E_0 g(z)]\frac{dz}{v}\right\}\int_{-\infty}^{\infty}\frac{dW_k[E_0 g(z)]}{dE_0}dz, \tag{7a}$$

where v is the velocity of the ions and E_0 the maximum field intensity on the z axis.

We have used Eq. (5) in this expression for the decay probability $W_k(E, \epsilon)$. The quantities ϵ, A and f_k enter as parameters in (7a). These quantities were determined with the help of a computer from Eq. (7a) by means of a standard program, the basis of which was the method of least squares. Here the field spectrum corresponding to states of a single term was normalized to unity, i.e.,

$$\sum_k f_k=1.$$

The varied parameters were: the value of the binding energy ϵ, which was taken to be the same for all the "k" states of the term (with the exception of He^-), and the quantity A. The values of A for the probabilities w_{10} and w_{11} (formulas (3), (4)) were assumed to be different, and were denoted by A_{10} and A_{11}, respectively. If the number of Stark states was large, the values of f_k were determined from the statistical weights of these states. Such a method of treatment of the field spectrum made it possible to determine the binding energy with good accuracy and also to obtain an estimate for the quantity A.

2. DESCRIPTION OF THE EXPERIMENT AND BASIC RESULTS

The experimental apparatus for the method of ionization of the atomic particles by an electric field has been described by us earlier.[19,20]

A beam of singly-charged positive ions obtained from a high-frequency ion source was accelerated to an energy of 100 keV and, after passage through a mass-monochromator, was directed through a charge-exchange chamber which was filled with air. The thickness of the charge-exchange target was varied over the range 2×10^{-4}—5×10^{-3} Torr-cm. The negative ions formed as a result of capture of two electrons were then directed into a region with a strong electric field, $E \leq 450$ kV/cm. This field was generated by two parallel electrodes, the gap between which was 0.4 mm in most of the experiments. The beam passed along the direction of the electric field through holes in the electrodes (the field distribution along the beam axis has been studied by us previously[19]). Before entrance into the electrode system, the dimensions of the beam were limited by a diaphragm of diameter 0.2 mm, so that the beam would go through a small paraxial region in which the field distribution was practically the same as on the axis of the system. This diaphragm sharply reduced the intensity of the beam of negative ions, which were therefore registered in an individual-particle counting mode.

The time of flight of the investigated ions through the region of the field was $(1-3)\times10^{-10}$ sec, and the total time of flight of the ions from the place of their production to the place of registration was of the order of 10^{-6}-sec.

In the experiment, we measured the I(E) dependence, which was determined from (1), and the field spectrum D(E). To obtain the field spectrum a periodic rectangular pulse with amplitude ΔE was superposed on the constant field E. The corresponding signal was obtained as the difference of the counts ΔN on two scalers that are switched synchronously with the field pulses. The quantity ΔN was normalized here to the total beam of negative ions at E = 0. At a sufficiently small amplitude ΔE (in comparison with E),

$$\Delta N(E)/\Delta E\approx D(E). \tag{8}$$

In the experiment described, the amplitude of the pulses ΔE amounted to 5 and 10 kV/cm in the case $E \leq 220$ kV/cm and 20 kV/cm for $220 \leq E \leq 450$ kV/cm.

To shorten the exposure time, we used a fast-acting apparatus, which preserved the linear counting characteristic to a counting rate of 3×10^5 pulses/sec. The choice of the exposure time and the counting rate was such that the statistical error did not exceed 0.1%. Special control experiments showed that, the errors connected with the operation of the electronic circuit were of the order of 0.01%.

The use of a stabilized source of high voltage and a precision divider for applying the voltage to the set of electrodes made it possible to carry out repeated measurements at fixed values of the field E. The D(E) dependences were measured several times and then averaged.

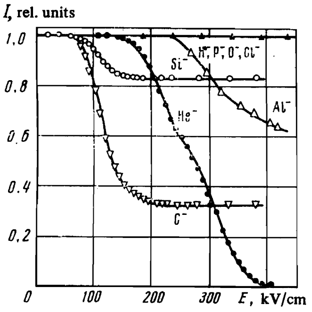

FIG. 1. Attenuation of I(E) of beams of negative ions in an electric field.

Study of the attenuation of a beam of negative ions by the electric field showed that He$^-$, C$^-$, Si$^-$, and Al$^-$ ions were decomposed at fields $E \leq 450$ kV/cm. No attenuation of a beam of P$^-$, O$^-$ or Cl$^-$ ions was observed (with accuracy to within 1%). This is illustrated in Fig. 1, on which are plotted the I(E) dependences. Under the same conditions, we studied the attenuation of a beam of H$^-$ ions, for which it is known that there are no bound excited states.[10] The constant value I = 1 obtained here over the entire range of fields E = 0—430 kV/cm indicated the absence of any effect of the system of electrodes on the measured values of the electron-optical properties.

As is seen from Fig. 1, a beam of He$^-$ ions is completely decomposed by a field $E \approx 400$ kV/cm. This allows us to assume that the He$^-$ beam consists entirely of ions in the $1s2s2p^4P$ state, which is metastable in relation to radiative and auto-ionization transitions. Beams of C$^-$ and Si$^-$ ions are partially attenuated at $E < 200$ kV/cm, and at higher fields further attenuation is not observed. Attenuation of a beam of Al$^-$ ions takes place up to fields $E \approx 430$ kV/cm.

In the identification of states destroyed by the electric field, we have made use both of the calculated values of the binding energy of the excited states (Table II) and our own experimental data on the population of these states in the capture of the electrons by fast atoms and positive ions.[16,21] It has been found that the states destroyed by the field have an electron binding energy that is close to the ${}^2D$ state for C$^-$, to the ${}^2P$ state for Si$^-$ and the ${}^1D$ state for Al$^-$ (see Table II). The relative populations in the destroyed states, defined as the difference in the values of I at the ends of the interval of fields in which attenuation of the beam is observed, are equal to 0.78, 0.22, and 0.33, for C$^-$, Si$^-$ and Al$^-$, respectively, and are close to the statistical populations $(g({}^2D)/[g({}^2D) + g({}^4S)] = 0.715$ for C$^-$, $g({}^2P)/[g({}^2P) + g({}^2D) + g({}^4S)] = 0.3$ for Si$^-$, and $g({}^1D)/[g({}^1D) + g({}^3P)] = 0.25$ for Al$^-$). This allows us to assume that the states ${}^2D$ of the C$^-$ ion, ${}^2P$ of the Si$^-$ ion and ${}^1D$ of the Al$^-$ ion are destroyed by the field. Such an identification of the states destroyed by the field agrees with the experimental data of[23,28]. The state ${}^2D$ of the Si$^-$ ion with binding energy 0.56 eV was observed in[23] by the method of photosplitting. This state could not be destroyed in our experiments. A rough estimate of the binding energy of the C$^-$ ion in the ${}^2D$ state, given in[28], yields the value 0.062 eV, which is also close to the experimental results.

Figures 2—5 give the field spectra of the He$^-$, C$^-$, Si$^-$ and Al$^-$ ions, on the basis of which the binding energies of the excited states were determined. It can be seen

TABLE II. Measured and calculated binding energies of metastable excited states of negative ions (in eV)

Ion	State	Data of present paper (exp)	Experiment by photosplitting of electron	Theoretical results			
				from [5]	Clementi [4]	Hunt, Moise-iwitsch [6]	Other authors
He$^-$	$1s2s2p\ {}^4P$	0.075±0.005	0.08±0.002 [22]	—	—	—	0.069 [24]
C$^-$	$2p^3\ {}^2D$	0.037±0.003		−0.05	<0	<0	
Si$^-$	$3p^3\ {}^2P$	0.035±0.004	—	0.02	0.084	0.065	
	$3p^3\ {}^2D$	—	0.56 [23]	0.58	0.582	0.59	
Al$^-$	$3p^2\ {}^1D$	≈0,095		0.13	0.224	0.19	
	$3p^2\ {}^3P$	⩾0.2	—	0.52	0.52	—	0,2 [25] 0,28 [26] 0,27 [27]

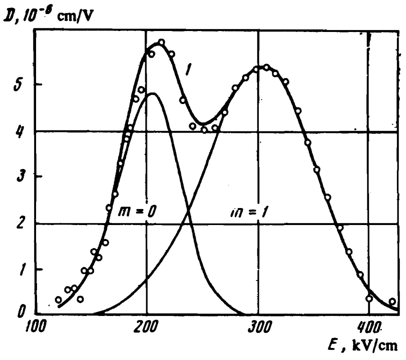

FIG. 2. Field spectrum of the negative He⁻(⁴P) (the dependence D(E) = dI(E)/dE). Circles—experiment. Light lines—calculated lines of the Stark states with projections of orbital angular momenta m = 0 and |m| = 1. Curve 1 (heavy line)—their sum.

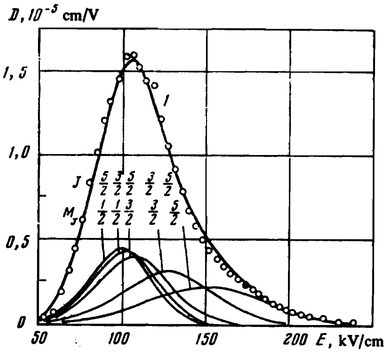

FIG. 3. Field spectrum of the negative ion C⁻ in the state $2p^3\ {}^2D$. Circles—experiment. Light lines—calculated lines of the Stark states corresponding to the various projections of the total angular momentum M_J. The designations of J and M_J for the individual lines are given in the figure. Curve 1 is the total calculated $D_p(E)$ dependence.

that the spectra differ significantly in form. Thus, the He⁻ spectrum represents the overlapping of two lines, the maxima of which are sufficiently well resolved. The spectrum of the Si⁻ ion has an almost symmetric shape, similar to the shape of a single line, while the spectra of C⁻ and Al⁻ are asymmetric.

3. INTERPRETATION OF THE FIELD SPECTRA AND DETERMINATION OF THE BINDING ENERGY OF THE EXCITED TERMS

Treatment of the field spectra and determination of the binding energy present a rather complicated problem. The difficulty lies primarily in the interpretation of the spectra, which have a complicated character, depending to a significant degree on the Stark splitting.

As has already been noted above, each Stark state of a given term of a negative ion, has its own decay probability in the field. The character of the Stark splitting depends on the field intensity and on the value of the L—S interaction. In the case of strong L—S coupling, the splitting of the fine structure $\Delta\epsilon_J$ will be greater than the Stark splitting $\Delta\epsilon_E$. Here the Stark components are determined by the projections of the total angular momentum M_J and their number k will be: k = J + 1 for even J and k = 2J for odd J. But if the interaction between the field E and the orbital momentum L is found to be much greater than the L—S interaction (i.e., $\Delta\epsilon_J \ll \Delta\epsilon_E$), then the Stark components are determined by the projections of M_L and k = L + 1.

To determine the character of the splitting, estimates of the Stark splitting were carried out according to the well-known formula $\Delta\epsilon_E = \frac{1}{2}\alpha E^2$, [29] and the polarizability α of the negative ion was determined from the formula of [13], while we used the values of A obtained in the present work for the amplitude of the wave function. The value of the fine splitting was estimated by extrapolation along the isoelectronic series.

Spectrum of the He⁻ ion. In contrast to the other ions studied, the He⁻ ion is in the auto-ionization $1s2s2p^4P$ state. The fine splitting for this ion was measured in [30], and amounts to 10^{-5} eV, while estimates of $\Delta\epsilon_E$ give 10^{-3} eV. Therefore the splitting in the field, in accord with what has been said above, takes place along the projections M_L, which coincide with the quantum number m of the weakly bound 2p electron, and there are two states in the field: m = 0, |m| = 1 with decay probabilities of the form (3) and (4). Two lines are indeed seen in the He⁻ ion spectrum given in Fig. 2. Therefore, these assumptions on the character of the splitting were used for interpretation of the He⁻ spectrum.

In the treatment of the He⁻ ion spectrum, the following parameters were varied: ϵ_{10} and ϵ_{11} (binding energies for the states m = 0 and |m| = 1, respectively), A_{10}, A_{11} and f. The quantities ε, A, and f obtained as a result of the treatment, are given in Table 3. We note here that the values of ϵ_{10} and ϵ_{11} are in agreement within the limits of error indicated and the values of f obtained for the states m = 0 and |m| = 1 coincide with the relative statistical weights of these states, which are equal to 1/3 and 2/3, respectively. The $D_p(E)$ dependence calculated for the values of the parameters ε, A and f,

TABLE III. Results of treatment of field spectra

Ion	L	M_L	J	M_J	W_k	f_k	A_{10}	A_{11}	$\epsilon\cdot10^3$, eV
He⁻ (⁴P)	1	0			w_{10}	0.33±0.01	0.25±0.06	0.16±0.02	75.2±0.5
	1	1			w_{11}	0.67±0.01			
C⁻ ($^2D_{5/2}$)			5/2	5/2	$\frac{1}{3}w_{11}$	0.205±0.008	0.039±0.008	0.023±0.004	37.3±0.2
				3/2	$\frac{1}{3}(\frac{2}{5}w_{10}+\frac{3}{5}w_{11})$	0.205±0.008			
				1/2	$\frac{1}{3}(\frac{3}{5}w_{10}+\frac{2}{5}w_{11})$	0.205±0.008			
C⁻ ($^2D_{3/2}$)			3/2	3/2	$\frac{1}{3}(\frac{1}{10}w_{10}+\frac{9}{10}w_{11})$	0.205±0.008	0.039±0.008	0.023±0.004	37.3±0.2
				1/2	$\frac{1}{3}(\frac{17}{30}w_{10}+\frac{13}{30}w_{11})$	0.18±0.02			
Si⁻ ($^2P_{3/2}$)			3/2	3/2	$\frac{1}{3}(\frac{1}{2}w_{10}+\frac{1}{2}w_{11})$	0.33	0.023±0.029	0.02±0.023	35±1
				1/2	$\frac{1}{3}(\frac{1}{6}w_{10}+\frac{5}{6}w_{11})$	0.33			
Si⁻ ($^2P_{1/2}$)			1/2	1/2	$\frac{1}{3}(\frac{1}{3}w_{10}+\frac{2}{3}w_{11})$	0.33	0.023±0.029	0.02±0.023	35±1
Al⁻ (¹D)					$\overline{W}=\alpha_1 w_{10}$				≈95
Al⁻ (³P)					$\overline{W}=\alpha_2 w_{11}$				⩾200

Note. W_k are the decay probabilities of the Stark states as determined by Eqs. (3)-(5): $\overline{W}$ are the probabilities, averated over the states (α_1 and α_2 = const); f_k is the fraction of the kth Stark state at $\sum_k f_k = 1$ for the given term; A_{10} and A_{11} are the amplitudes of the wave functions in Eqs. (3) and (4), respectively.

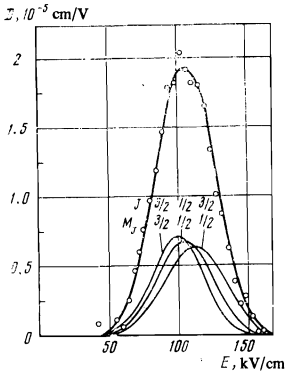

FIG. 4

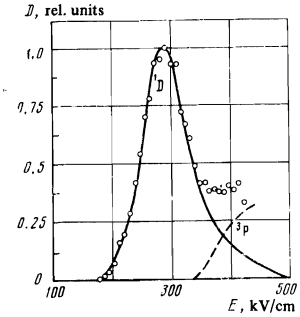

FIG. 5

FIG. 4. Field spectrum of the negative ion Si^- in the state $3p^3\ ^2P$. Notation is the same as in Fig. 3.

FIG. 5. Field spectrum of the negative ion Al^-. Circles—experiment. Solid curve—calculated $D_p(E)$ dependence for the excited state $3p^2\ ^1D$. Dashed curve—$D_p(E)$ dependence for the ground state ^3P.

given in Table 3 provides an excellent description of the experimental spectrum (Fig. 2).

Attempts to apply other interpretations to the spectrum lead to poorer agreement of the calculated $D_p(E)$ dependence with experiment.

Spectra of the C^- and Si^- ions. For the ions $C^-(^2D_{5/2,3/2})$ and $Si^-(^2P_{3/2,1/2})$, the estimates showed that the values of $\Delta\epsilon_J$ (equal to 3×10^{-4} and 10^{-3} eV, respectively) are about an order of magnitude larger than the values of $\Delta\epsilon_E$. In this case, in contrast with the He^- ion, the splitting in the field should take place according to the projections M_J and, consequently, for the C^- ion in the field (at $E \approx 100$ kV/cm) there should be five Stark states and for Si^- three states (see Table III). The decay probabilities of these states are determined by an expression similar to (5), in which the angular momenta L should be replaced by J and l by L. Such an interpretation of the C^- and Si^- spectra was used in their treatment, and the values of f_k for the Stark states were determined from the statistical weights of these states. The results of the treatment of the spectra are contained in Table III. The excellent agreement of the calculated and experimental D(E) dependences is illustrated by Figs. 3 and 4.

For the C^- ion, such a treatment of the spectrum was carried out under the assumptions that the splitting takes place along the projections M_L and that there are three states ($M_L = 0, 1, 2$). Here the same value of the binding energy was obtained within the limits of experimental error, although the quantities A_{10} and A_{11} differed considerably. The agreement between the calculated $D_p(E)$ dependence and the experimental spectrum was poorer in this case (the rms deviation of the calculated from the experimental spectrum was three times as large as in the treatment under the assumption of the presence of M_J states).

Spectrum of the Al^- ion. A feature of the spectrum of Al^- ions (Fig. 5) is the presence of a break at $E \approx 350$ kV/cm. The Al^- ion can have three low-lying energy terms ^1S, ^1D, and ^3P. From the data of the calculations in[4,6] the very highest term ^1S lies above the boundary of the continuum (the level $2P_{1/2}$ of the Al atom) and therefore is not bound. The measurements of the fraction of Al^- ions that are destroyed in the field (which is equal to 0.33 and is close to the ratio of the statistical weight of the ^1D term to the sum of the statistical weights of the ^1D and ^3P terms) are in agreement with this. Therefore, the break in the spectrum at high fields is probably explained by the onset of destruction of the ground state ^3P of the Al^- ion. Incomplete resolution of the lines, which evidently belong to different terms, and the low accuracy of the measurements of the spectrum at $E \gtrsim 400$ kV/cm have permitted us to make only rough determinations of the value of ϵ. The estimates are also given in Table III.

The P^-, O^- and Cl^- ions. The beams of these ions were not attenuated in fields $E \leq 450$ kV/cm, which suggests that they lack states with binding energy $\epsilon < 0.2$ eV or have a very small population of such states.

4. ANALYSIS OF ERRORS IN THE DETERMINATION OF THE BINDING ENERGY, AND COMPARISON OF THE DATA OBTAINED WITH THE RESULTS OF OTHER PAPERS

The accidental errors in the measurements of the field spectrum were composed of errors determined by the counting statistics and of errors in the determination of the total beam current. The statistical errors in finding ΔN are decisive, inasmuch as the latter is determined as the difference of two nearly equal quantities.

The program used to determine ϵ and A allowed us to obtain the rms errors of determination of ϵ and A from the given rms errors of measurement of the D(E) dependence. These errors, obtained in the treatment of the field spectra, are given in Table III (in the last four columns).

Along with these accidental errors connected with measurement of the quantity D(E) itself, there is the error in the determination of the field intensity E, which is mainly due to inaccuracy in the measurement of the gap between the electrodes and the departure of the shape of the hole edges in the electrodes from its computed value. This error for E amounts to about 10%, which leads to an error of 7% for the value of ϵ. The total rms error of determination of the binding energy is given in Table II (in the column "data of present paper").

We regard as systematic errors those connected with the approximate character of expressions (3), (4). In these expressions, in particular, no account is taken of the change in the binding energy in the field, while the binding energy of the Stark states existing in the field is obtained from treatment of the field spectra. However, estimates show that this change does not exceed 5% of the value of ϵ.

More rigorous solution of the problem of the detachment of an electron by an electric field might allow us to obtain exact expressions for the probability of this process. This would allow us to obtain more accurate values of ϵ. However, it can be hoped that these corrections will not be very large, inasmuch as the character of the exponential dependence should be preserved in the expression for the decay probability.

As was pointed out above, measurement of binding energies $\epsilon \leq 0.1$ eV is quite difficult by other methods. The results of certain studies carried out by the methods of photosplitting and photoelectron spectroscopy, are given along with our results in Table II. There is excellent agreement with the results obtained by Brehm, Gusinow and Hall[22] for He^-. Table II also gives data from some theoretical studies on the binding energy of low-lying excited terms of negative ions. It follows from the Table that the data of[5] are in better agreement with the experimental results than are the other calculations. Our estimate of the binding energy for the ground state ^3P of the Al^- ion (electron affinity) agrees with the calculation of Zollweg[25] and is close to the affinity values in[26,27].

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[1] H. S. W. Massey, Negative Ions, London and New York, 1950.

[2] L. M. Branscomb, Adv. Electronics and Electron Phys. **9**, 43 (1957),

[3] H. Hotop, W. C. Lineberger, and T. A. Patterson, Electronic and Atomic Collisions (Abstracts of papers VIII ICPEAC), Belgrade, 1973, p. 598.

[4] E. Clementi, A. D. McLean, D. L. Raimondi and M. Yoshimine, Phys. Rev. **133A**, 1274 (1964).

[5] B. L. Moiseiwitsch, Advances Atom Molec. Phys. **1**, 61 (1965).

[6] J. Hunt and B. L. Moiseiwitsch, Atom Molec. Phys. **3**, 892 (1970).

[7] E. McDaniel, Collision Phenomena in Ionized Gases, Wiley, 1964 (Russian translation: Mir, 1967, p. 421).

[8] J. F. Paulson, J. Chem. Phys. **52**, 5491 (1970).

[9] H. Hotop and W. C. Lineberger, ibid. **58**, 2379 (1973).

[10] B. M. Smirnov, Atomnye stolknoveniya i élementarnye protsessy v plazme (Atomic Collisions and Elementary Processes in Plasma), Atomizdat, 1968.

[11] A. C. Riviere and D. R. Sweetman, Proc. VI Intern. Conf. on Ionization Phenomena in Gases, Vol. 1, Paris, 1963, p. 105.

[12] A. C. Riviere and D. R. Sweetman, Phys. Rev. Lett. **5**, 560 (1960); Proc. V. Intern. Conf. on Ionization Phenomena in Gases (Munich, 1961), Amsterdam, Vol. 2, 1962, p. 1236.

[13] Yu. N. Demkov and G. F. Drukarev, Zh. Eksp. Teor. Fiz. **47**, 918 (1964) [Sov. Phys.-JETP **20**, 614 (1965)].

[14] V. A. Oparin, R. N. Il'in, I. T. Serenkov, E. S. Solov'ev and N. V. Fedorenko, ZhETF Pis. Red. **12**, 237 (1970) [JETP Lett. **12**, 162 (1970)].

[15] V. A. Oparin, R. N. Il'in, I. T. Serenkov, E. S. Solov'ev and N. V. Fedorenko, ibid. **13**, 351 (1971) [**13**, 249 (1971)].

[16] V. A. Oparin, R. N. Il'in, I. T. Serenkov, E. S. Solov'ev, and N. V. Fedorenko, Electronic and Atomic Collisions (Abstracts of Papers, VII ICPEAC) Amsterdam, 1971, p. 796.

[17] B. M. Smirnov and M. I. Chibisov, Zh. Eksp. Teor. Fiz. **49**, 841 (1965) [Sov. Phys.-JETP **22**, 585 (1966)].

[18] B. M. Smirnov and M. I. Chibisov, Abstracts of Papers, V All-Union Conf. on Physics of Electronic and Atomic Collisions, Uzhgorod, 1972, p. 79.

[19] R. N. Il'in, B. I. Kikiani, V. A. Oparin, E. S. Solov'ev and N. V. Fedorenko, Zh. Eksp. Teor. Fiz. **47**, 1235 (1964) [Sov. Phys.-JETP **20**, 835 (1965)].

[20] R. N. Il'in, V. A. Oparin, I. T. Serenkov, E. S. Solov'ev and N. V. Fedorenko, ibid. **59**, 103 (1970) [**32**, 59 (1971)].

[21] I. T. Serenkov, R. N. Il'in, V. A. Oparin and E. S. Solov'ev, Electronic and Atomic Collisions (Abstracts of Papers) VIII ICPEAC, Belgrade, 1973, p. 830.

[22] B. Brehm, M. A. Gusinow, and J. L. Hall, Phys. Rev. Lett. **19**, 739 (1967).

[23] D. Feldmann, Z. Naturforsch. **26a**, 1100 (1971).

[24] E. Holien and S. Geltman, Phys. Rev. Lett. **153**, 81 (1967).

[25] R. J. Zollweg, J. Chem. Phys. **50**, 4251 (1969).

[26] R. J. S. Grossley, Proc. Phys. Soc. Lond. **83**, 375 (1964).

[27] J. W. Edic and F. Rohrlich, J. Chem. Phys. **37**, 1151 (1962).

[28] J. L. Hall and M. W. Siegel, ibid. **48**, 943 (1968).

[29] I. I. Sobel'man, Vvednie v teoriyu atomnykh spektrov (Introduction to the Theory of Atomic Spectra), Fizmatgiz, 1963.

[30] D. R. Mader and R. Novick, Atomic Physics III, Plenum Press, 1973, p. 169.

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