INVESTIGATION OF THE "JOLTING" OF ELECTRON SHELLS OF ORIENTED MOLECULES CONTAINING P^{32}

É. E. BERLOVICH, L. M. KUTSENTOV, and V. G. FLEĬSHER

A. F. Ioffe Physico-technical Institute, Academy of Sciences, U.S.S.R.

Submitted to JETP editor October 30, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) **48**, 1013-1021 (April, 1965)

The ionization of the outer electron shells of oriented organic molecules containing P^{32} produced as a result of β decay is studied. The slow electrons emitted from a monomolecular source were recorded directly. The "external" ionization effect produced by the β particles in the source can be singled out by investigating the slow electron yield as a function of the angle of emission of the β particles relative to the normal to the surface of the source. The lower limit of yield of ionization electrons from the valence shell of monocetyl phosphate is estimated to be 28% per β decay. By replacing the hydroxyl hydrogen in these molecules by mercury, a correlation was found to exist between the ionization probability and the mean momentum component of the recoil nucleus at an angle of 60° with respect to the molecule axis. Both quantities vary in a similar manner with variation of the β particle energy. The largest ionization contribution depending on the β particle energy is observed when the β particles are emitted perpendicular to the direction of orientation of the molecules and comprises 0.3 ± 0.05 of the total ionization probability for the hard part of the β spectrum. Thus along with "jolting" of the shell due to nonadiabatic change of the nuclear charge on β particle emission which is independent of the particle energy, an ionization is observed which depends on the velocity of the recoil nucleus.

1. INTRODUCTION

THE ionization of electron shells as the result of a sudden change of the nuclear charge, accompanying radioactive transformations, was studied until recently essentially by means of the x-rays produced on filling of vacancies in the shells,[1-4] and by means of the charge spectra of the recoil ions.[5-8] X rays are used principally to investigate the ionization of the inner shells, from which the fluorescence yield is sufficiently large. The charge distribution of the recoil ions is used to determine most accurately the ionization of the outer shells, which leads to formation of low charge states. The ionization of the inner shells is accompanied by nonradiative cascade transitions, which lead to the formation of multiply charged ions. Experimental results for the inner shells agree essentially with the theoretical ones obtained in the nonadiabatic approximation, using hydrogen-like functions.[9-12] For the ionization of the external shells of Ne^{23}, Ar^{41}, Kr^{85}, and Kr^{79}, satisfactory agreement was obtained likewise, in the same approximation, between theory and experiment, by using Hartree wave functions.[7,13] Inasmuch as practically for all cases of radioactive transformations the velocity of the recoil nucleus is much smaller than the velocity of the atomic electron, the perturbation connected with the recoil is adiabatic and the corresponding ionization probability is therefore very small.

An exception is the He^6 nucleus, with a maximum recoil energy of 1418 eV, for which Carlson et al.[6] observed an increase in the ionization with increasing energy. We can expect, however, that under certain special conditions the adiabaticity of the perturbation, connected with the recoil, will become violated. Thus, as a result of a sudden change in the nuclear charge ("jolting") the atomic or the molecular system can be moved to a discrete level of a highly-excited state, located either above the boundary of the energy continuum for the corresponding ion, or below, but near, this boundary. The perturbation connected with the motion of a recoil nucleus, for a system "prepared" in this manner, will be non-adiabatic.

To study the possible contribution of the perturbation connected with the motion of the recoil nucleus, we have investigated the dependence of the ionization of oriented organic molecules, containing P^{32} nuclei, on the angle of emission and energy of the β particles.

2. EXPERIMENTAL SETUP AND PRINCIPAL RESULTS

Acts of ionization of outer shells were registered directly by means of the electrons emitted from the source. Owing to their low energy, the registration of these electrons is connected with several experimental difficulties. So far, only individual investigations were made of the spectra of the "jolt" K-electrons (see, for example, [14,15]). Badenko and two of the authors of the present article[16] apparently succeeded, for the first time, in observing electrons produced upon "jolting" the outer shell. To prepare the source we used the property of surface-active organic compounds to form oriented monomolecular layers on polar liquids.[17] The method of preparing such a source was described by us earlier.[18] Radioactive P^{32} was introduced into the hydrophilic end of the molecule in the synthesis of cetyl alcohol $C_{16}H_{33}OH$ and orthophosphoric acid. The use of orthophosphoric acid with high specific activity in P^{32} (~ 600 mCi/mg) made it possible to synthesize the monocetylphosphate $C_{16}H_{33}OPO(OH)_2$ with large P^{32} content. The specific activity of the monomolecular layer produced on the surface of the water was $\sim 1\ \mu Ci/cm^2$. The monomolecular layer can be readily transferred to the substrate of a source, in the form of an aluminum foil (~ 0.5 mg/cm^2), on which several dozen inactive monomolecular layers were previously deposited, in order to equalize the microirregularities and in order to form a hydrophobic surface. It is easiest to transfer to the substrate a double layer with the hydrophobic ends of the molecules turned inward.

Figure 1a shows a schematic representation of the source. The molecules are aligned perpendicular to the surface of the substrate. The phosphorus atom is surrounded by four oxygen atoms, forming a nearly tetrahedral structure. By immersion in water, on which a monomolecular layer of mercury salt is formed, it is possible to replace to a considerable degree the hydrogen atoms of the hydroxyl group by mercury. Neighboring molecules are in this case more rigidly bound. It is possible to introduce into the molecule in similar fashion various divalent and trivalent cations, forming with the phosphoric acid compounds that are difficult to dissolve. The effect of the mercury on the "jolting" of the electron shell will be seen from what follows. The outer surface of the source, made up of CH_3 radicals, is not only hydrophobic but also oleophobic, thus protecting the source against adsorption of oil vapor. As shown by Langmuir[17], such surfaces have negligible adsorption ability. This ensures stability of the yield of slow electrons over a long time.

The passage of beta particles through the substrate and the source layer is accompanied by "external" ionization, which leads to the formation of slow secondary electrons. These electrons produce a background for the "jolting" electrons. To estimate the contribution of this background, we investigated the dependence of the number of slow electrons on the angle ξ of the emitted beta particles relative to the normal X to the surface of the source. The effect of "external" ionization is inversely proportional to cos ξ, whereas the "jolting" of the electron shell, at least in the nonadiabatic approximation, should not depend on ξ.

The experimental scheme is clear from Fig. 1b. Slow electrons emitted from the source are accelerated by the field between grids C_1 and C_2, and are registered by an electron multiplier (EM) with open input. The beta particles passing through the collimator K are registered by a scintillation spectrometer with anthracene crystal and photomultiplier FÉU-16. The construction of the instrument is such that the photomultiplier can be moved directly in the vacuum over the range of variation of the angle ξ from 0 to 120°. We inves-

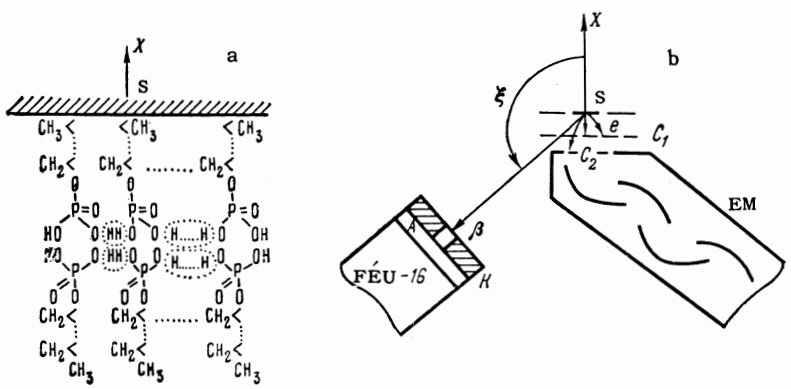

FIG. 1.

tigated the dependence of the number of coincidences $N_{\beta e}$ between the beta particles and the slow electrons on the angle ξ per beta particle ($a = N_{\beta e}/N_{\beta}$).

In the study of the energy dependence of the "jolting" effect with the aid of a multichannel pulse-height analyzer, we registered the spectrum of the beta-particle pulses coinciding in time with the slow-electron pulses. By applying to the grid C_1 a potential which is decelerating with respect to the source S, we can obtain the integral spectrum of the slow electrons. As shown earlier[16], the bulk of the slow electrons have energies less than 8 eV. However, there exists a "tail" of electrons with higher energy, stretching to ~3 keV. The absence of charge on the source was monitored by means of the shift of the curves of the number of coincidences vs. decelerating potential. This shift did not exceed 0.1—0.2 eV.

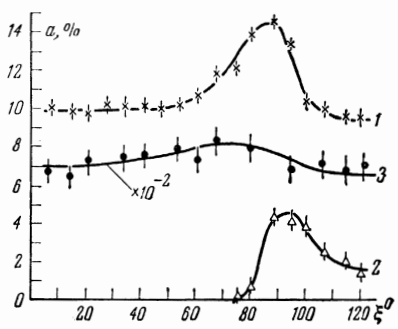

FIG. 2.

Figure 2 shows a plot of $a(\xi)$ (curve 1). The maximum of the curve, at $\xi = \pi/2$, is connected with the "internal" ionization. This can be seen as inactive monomolecular layers of cetyl phosphate are added in succession onto the surface of the source. The yield of the "jolting" electrons then decreased noticeably because of the increase in the thickness of the layer separating the P^{32} from the surface, whereas the number of secondary electrons connected with the "external" ionization and arriving from the layer next to the surface changed little. The yield of slow electrons for small ξ decreased practically exponentially with the increasing number of monomolecular layers. The equivalent mean free path λ, determined from this exponential, was $\sim 2.2\,l$, where l is the length of the molecule, ≈ 23 Å. Curve 2 on Fig. 2 corresponds to a source covered with ten inactive layers. Practically no "jolting" electrons are emitted. We see thus that when $\xi < 70°$ and $\xi > 110°$ the main contribution is made by the "jolting" electrons, while in the region of angles ξ close to $\pi/2$, there is a noticeable additional contribution from "external" ionization.

The energy spectrum of secondary electrons, corresponding to curve 2, is somewhat "softer" than the spectrum of the "jolting" electrons. When a decelerating voltage of 6 V is applied to grid C_1, the "hump" on the coincidence curve decreases noticeably, which also points to its connection with the effect of "external" ionization (see curve 3 on Fig. 2). The background of secondary electrons cannot be determined directly from curve 2, since this curve corresponds to an increased thickness of the zone of "external" ionization for large ξ. At the same time, for small ξ the secondary electrons produced deep inside the source do not pass through the surface. If we assume an exponential dependence of the probability of emission of a secondary electron on the distance between its point of formation to the surface of the source, we can easily determine the correction factors for the conversion to the background curve, corresponding to curve 1. The ordinates of curve 2, decreased by a factor

$$[1 - \exp(-l/\lambda)] / [1 - \exp(-10l/\lambda)],$$

correspond to external ionization in a monomolecular layer of thickness l for $\xi > 100°$. The corresponding ordinates, multiplied by a factor

$$\exp(-l/\lambda) / [1 - \exp(-10l/\lambda)],$$

give the yield of secondary electrons for angles of mirror symmetry about $\pi/2$. The asymmetry of the background curve obtained after introducing the corrections relative to the angle $\xi = \pi/2$ corresponds to the asymmetry of the "hump" on curve 1 (Fig. 2).

For an exact determination of the contribution of the "external" ionization, it is necessary also to take into account multiple scattering and the finite angular resolution of the scintillation detector, which are particularly important for angles close to $\pi/2$. In the region of small ξ, the contribution of "external" ionization Δ can be determined from the end of the curve 2 on Fig. 2, for large ξ, by multiplying the ordinates by the factor indicated above. The value of Δ determined in this fashion amounts to ~1.2% for $\xi = 60°$. The contribution of the "jolting" electrons amounts in this case to ~9.5%. If we use the relation $1/\cos\xi$, then for $\xi = 0$ we obtain $\Delta \approx 0.6\%$. The "external" ionization has a much weaker effect on the energy relationships than on the angular relationships.

At beta-particle energies larger than 200 keV, only a weak relativistic increase of the effective ionization cross section is observed. Conse-

quently the possible influence of the recoil momentum on the ionization of the outer shell is best investigated by studying the correlation of the "jolting" effect with the beta-particle energy. As can be seen from Fig. 3 (curve 1), for monocetyl phosphate molecules there is no appreciable dependence of the ionization on the energy. A different picture is observed, however, when the hydroxyl hydrogen is replaced with mercury. In this case one atom of mercury binds the hydrophilic ends of two monocetyl phosphate molecules. By introducing mercury tagged with the isotope Hg^{203} into a controlled monomolecular layer, it was established that approximately 80% of the hydroxyl hydrogen is replaced. Such a change of the molecular structure leads to the appearance of a clearly pronounced energy correlation, the form of which depends on the angle ξ.

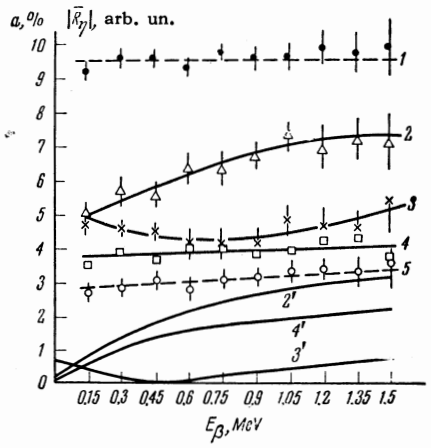

FIG. 3.

Figure 3 shows the corresponding a(E) curves for angles ξ equal respectively to 90° (curves 2, 2', 5), 45° (curves 3, 3'), and 0° (curves 1, 4, 4'). Analogous relations were obtained by introducing Ba in place of Hg. To check on the possible change in the external ionization when atoms with large Z are introduced into the source, a control source was produced, in which the active monomolecular layer was covered by ten inactive monomolecular layers and the mercury was introduced into the last surface layer. In this case only a weak increase in the number of secondary electrons with increasing energy is observed for 90° (curve 5). The increase in the number of "jolting" electrons with increasing beta-particle energy is much more strongly pronounced. Thus, the observed energy dependence of the "jolting" effect is connected with the change in the molecular structure.

3. DISCUSSION OF RESULTS

As can be seen from Fig. 3, the experimental value of the "jolting" effect, for molecules of monocetyl phosphate, amounts to a $\approx 9.5\%$. It must be taken into account that the only "jolting" electrons appearing inside the source that can be registered are those whose momentum is directed towards the surface facing the electron multiplier. If we assume that the momenta of the "jolting" electrons are isotropically distributed in the source, then the measured quantity must be doubled. In addition, inasmuch as the P^{32} atoms are located on the hydrophilic end of the molecule, the electrons must pass through a source layer equal in thickness to the length of the cetyl phosphate molecule. Account of absorption of electrons in this layer is taken by extrapolating to zero thickness the logarithmic plot of the yield of slow electrons vs. the number of inactive monomolecular layers over the active layer. The total magnitude of the "jolting" effect should be increased thereby to ~28%. The existence of a potential barrier on the surface should lead to some additional decrease in the number of registered electrons due to the soft part of their spectrum. Thus, the obtained value of 28% should be regarded as a lower estimate for the "jolting" effect. The magnitude of this effect for the L shell of P^{32}, calculated from the results of several investigations[11,12], is 0.9 and 1%, respectively. For the K-shell the effect is even smaller.

Consequently, the experimentally observed electrons correspond principally to "jolting" of the outer shell. The value of a obtained by us exceeds the probabilities of "jolting" of outer shells of isolated atoms with values of Z that are relatively close to P^{32}, as measured by Carlson[7]. These probabilities amount to 17.5 and 12.5% respectively for Ne^{23} and Ar^{41}. The probability of the $W_{\alpha\alpha'}$ transition of an electron in a polyatomic molecule from a state with wave function φ_α into a state with wave function $\varphi_{\alpha'}$ as a result of β decay of one of the atoms can be obtained from the formula[12]

$$W_{\alpha\alpha'} = \frac{e^2}{E_{\alpha'} - E_\alpha} \int \varphi_{\alpha'}^* \sum_{k=1}^{K} \frac{1}{|\mathbf{r}_k - \mathbf{r}_p|} \varphi_\alpha \, dr_k, \qquad (1)$$

where $E_{\alpha'} - E_\alpha$ is the transition energy, $\mathbf{r}_k$ and $\mathbf{r}_p$ are the radius vectors of the molecular electrons and the radioactive nucleus, respectively, and K is the number of electrons in the state α. This formula was obtained in the Born-Oppenheimer approximation, according to which the

probability $W_{\alpha\alpha'}$ should not depend on the momentum of the recoil nucleus, inasmuch as the vector r_p does not change noticeably during the time of the electronic transition. Thus, the experimentally observed dependence of the yield of slow electrons on the beta-particle energy cannot be explained in this approximation.

A direct interaction between the beta particle and the electrons of a molecule containing decaying P^{32} depends on the beta-particle energy. However, in the energy range considered, from 0.15 to 1.5 MeV, the effective cross section of this interaction is very small and its order of magnitude can at most be $(e^2/\hbar c)^2$.[10] The experimentally observed "external" ionization, arising when beta particles interact with electrons inside the source, increases only very weakly with increasing energy.

Consequently, direct interaction of beta particles and molecular electrons can likewise not explain the course of the curves on Fig. 3. Let us consider the possible influence of the momentum of the recoil nucleus on the ionization. The probability $dW_{\alpha\alpha'}$ of transition from the state α into states of the continuous spectrum in the interval from α' to $\alpha' + d\alpha'$, under the influence of a time-dependent perturbation V(t), can be represented in the form [19]

$$dW_{\alpha\alpha'} = \frac{1}{(E_{\alpha'} - E_\alpha)^2} \left| \int_{-\infty}^{\infty} \frac{\partial V_{\alpha\alpha'}}{\partial t} \exp\left\{ \frac{i(E_{\alpha'} - E_\alpha)}{\hbar} t \right\} dt \right|^2 d\alpha' \qquad (2)$$

where $V_{\alpha\alpha'}(t)$ is the matrix element of the perturbation. The value of $dW_{\alpha\alpha'}$ can be appreciable, if V(t) changes noticeably within a time $\sim\hbar(E_{\alpha'} - E_\alpha)$. This condition is the easier to satisfy, the smaller the energy of the transition $E_{\alpha'} - E_\alpha$.

If the atomic shells do not have time to rearrange themselves within the time of emission of the beta particle ($\sim 10^{-18}$ sec for relativistic electrons), then the produced ion is in an excited state. The average excitation energy is $22.85\, Z_p^{2/5}$,[20] where Z_p is the charge of the nucleus, and amounts to ~90 eV for P^{32}. Thus, as a result of beta decay, the molecular system is transferred to an excited level, which can lie much above the boundary of the continuous spectrum for the corresponding ion. The average velocity of the P^{32} recoil nucleus, without account of the binding of the atom in the molecule, is of the order of 10^6 cm/sec at a maximum recoil energy of 78 eV.

If a state of high excitation is maintained within a time on the order of the dissociation time of the molecular ion (10^{-14} sec), then the perturbation connected with the motion of the recoil nucleus will be non-adiabatic, inasmuch as $E_{\alpha'} - E_\alpha$ is small. In this case a noticeable dependence of the ionization on the recoil energy may appear.

As can be seen from a comparison of curves 2, 3, and 4 in Fig. 3, the character of the energy dependence differs for different ξ. The presence of anisotropy points to a probable dependence of the matrix element $V_{\alpha\alpha'}$ not only on the magnitude but also on the direction of the recoil-nucleus momentum.

A quantitative determination of $V_{\alpha\alpha'}$ is impossible, since we do not know the corresponding wave functions. In considering the process qualitatively, we shall assume that there exists a certain direction of initial momentum of the recoil nucleus, making an angle η with the molecule orientation axis, for which the value of $\partial V/\partial t$ is maximal. Let us find the average projection of the recoil momentum on this direction, $\bar{R}_\eta$, and let us compare the dependence of the yield of slow electrons and of the momentum $\bar{R}_\eta$ on the beta-particle energy. With the aid of the distribution $N(E, \theta)$ (E—beta-particle energy, θ—angle between its momentum p and the antineutrino momentum q), we can readily obtain

$$\bar{R}_\eta(\eta, \xi) = B(\eta, \xi) q + C(\eta, \xi) p (1 + bq/3E), \qquad (3)$$

where

$$B(\eta, \xi) = \sin\eta (1 - \cos\xi)/\pi - \sin\xi \cos\eta/2,$$
$$C(\eta, \xi) = 2\sin\xi \sin\eta/\pi - \cos\xi \cos\eta,$$

b is the coefficient of angular $\beta\nu$ correlation, and the angle η is measured from the negative direction of the X axis in Fig. 1.

In calculating expressions (3) we averaged over a cone with apex angle η relative to the X axis, and over all possible directions of the vector q for definite p and θ. Curves 2', 3', and 4' (Fig. 3) for $|\bar{R}_\eta(E)|$, calculated from (3) for an angle $\eta = 60°$, have the same dependence on the beta-particle energy as the experimentally obtained a(E) curves (curves 2, 3, and 4 respectively in Fig. 3).

The value of the coefficient b was chosen equal to $-1/3$ in accordance with the theory of the universal AV interaction, according to which the A variant is realized for the beta decay of P^{32} (transition of the 1—0 type). The minimum on the $|\bar{R}_\eta(E)|$ curve for $\xi = \pi/4$, and the monotonic increase for values of ξ equal to zero and $\pi/2$, can be simultaneously obtained in a comparatively narrow region of angles η from 45 to 70°. The best agreement between the a(E) and $|\bar{R}_\eta(E)|$ relations is obtained for $\eta = 60°$. We note that the angle between the valence band of the phosphorus and the hydroxyl oxygen and the molecule orienta-

tion axis, is ~70° (for a tetrahedral structure formed by the phosphor bonds).

However, the agreement of the E dependences of curves 2, 3, 4 and 2′, 3′, 4′ (Fig. 3) is only qualitative, since it is impossible to reconcile the curves for all three angles ξ. In particular, when $\eta = 60°$ the value of $|\bar{R}_\eta(E)|$ at $\xi = 0$ increases with increasing energy much more rapidly than the experimentally-observed value of a(E) (compare curves 4 and 4′). Naturally, we cannot expect full correspondence in so simplified an analysis, by singling out only one direction and not taking into account the change in the molecular field with time, brought about both by the motion of the recoil nuclei and by the perturbation of the remaining atoms in the molecule.

Of considerable interest is the role of the heavy atoms Hg or Ba, which are not bound directly with the radioactive P^{32}, but which influence noticeably both the magnitude and the form of the dependence of the slow-electron yield on the beta-particle energy. The decrease in yield upon introduction of these atoms can be related to the drop in the efficiency of registration of slow electrons, due to their additional scattering by the large-Z atoms. A clarification of this circumstance should serve as an object of further investigation. The appearance of an energy dependence can be due to the increased role of the perturbation connected with the recoil when the molecules become heavier. It is known, for example,[21] that the energy necessary to break the bond of a radioactive atom in a polyatomic molecule is smaller in the case of a heavier molecular residue, since for a light residue the greater part of the energy goes to the excitation of the rotational and vibrational degrees of freedom.

Introduction of Hg or Ba makes the molecular residue much heavier, both because of the mass of these atoms, and of the bond between the two molecules of the monocetyl phosphate. The fraction of the energy transferred by the recoil atom to the heavier molecular residue decreases in this case, and the contribution of the effect of ionization of the outer shell, which depends on the recoil, increases. It is likewise not excluded that introduction of Hg and Ba into the molecule gives rise to new states, for which the rearrangement of the shells after the emission of the beta particle turns out to be more "delayed," facilitating the appearance of an energy dependence.

In conclusion, we are grateful to V. M. Lobashov and his co-workers for supplying a compound containing P^{32} with high specific activity.

[1] G. A. Renard, J. phys. rad. **16**, 575 (1952).
[2] F. W. Boehm and C. S. Wu, Phys. Rev. **93**, 518 (1954).
[3] N. Starfelt and J. Sederlund, Phys. Rev. **105**, 241 (1957).
[4] N. L. Lark and M. L. Perlman, Phys. Rev. **120**, 536 (1960).
[5] A. H. Snell and F. Pleasonton, Phys. Rev. **107**, 740 (1957); **111**, 1338 (1958); **116**, 1548 (1959).
[6] Carlson, Pleasonton, and Johnson, Phys. Rev. **129**, 2220 (1963).
[7] T. A. Carlson, Phys. Rev. **130**, 2361 (1963); **131**, 676 (1963).
[8] Snell, Pleasonton, and Need, Phys. Rev. **116**, 1548 (1959).
[9] E. L. Feĭnberg, DAN SSSR **23**, 778 (1939).
[10] A. B. Migdal, JETP **11**, 207 (1941).
[11] I. S. Levinger, J. phys. rad. **16**, 556 (1955).
[12] H. M. Schwartz, J. Chem. Phys. **21**, 45 (1953); **23**, 400 (1955).
[13] A. E. S. Green, Phys. Rev. **107**, 1646 (1957).
[14] Daniel, Schupp, and Jensen, Phys. Rev. **117**, 823 (1960).
[15] Ryde, Person, and Oelsner-Ryde, Nucl. Phys. **47**, 614 (1963).
[16] Badenko, Berlovich, and Fleĭsher, Izv. Akad. Nauk SSSR, ser. fiz. **26**, 197 (1962), Bull. Acad. Sci. Phys. Ser. p. 196.
[17] I. Langmuir, Proc. Roy. Soc. **170**, 1 (1939).
[18] I. I. Badenko and V. G. Fleisher, PTÉ No. 5, 179 (1962).
[19] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Fizmatgiz, 1963.
[20] R. Serber and H. S. Snyder, Phys. Rev. **87**, 152 (1952).
[21] C. Hsiung and A. A. Gordus, J. Chem. Phys. **36**, 947 (1962).

Translated by J. G. Adashko
148