INFLUENCE OF THE Tl^+-ION ELECTRONIC STATE ON THE ISOTROPIC *d*-BOND WITH LIGANDS

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The radial wave functions of an activator Tl^+ ion in the excited electronic state $5d^{10}6s6p$ have been calculated making use of the Hartree-Torrance method. The energy eigenvalues for *d*-, *s*-, and *p*-electrons of the Tl^+ ion introduced into KCl, KBr, and KI crystals have been determined. The energy of the isotropic *d*-bond with ligands has been shown to grow, if the electronic state of the Tl^+ ion becomes excited. This growth is responsible for a substantial reconstruction of thallium complexes within the lifetime of the Tl^+ excited electronic state.

An assumption about the existence of the isotropic d-bond in halogen complexes of Hg-like ions, the outer electron shell of which is of the $nd^{10}(n+1)s^2$ type, was made for the first time in work [1]. According to this assumption, when estimations of the binding energy between the central ion and the ligands are made, the variation of the energy eigenvalue of *d*-electrons of the central ion, which occurs owing to the influence of ligands, has to be taken into account besides the electrostatic ion-ion interaction. This assumption is based, in particular, on the fact that there is rather a strong dependence of the energy eigenvalue of *d*-electrons of a free thallium ion on the configuration of its electron shell. A similar behavior can also manifest itself, if the ion environment changes. The latter assumption correlates with the considerations of E. Wigner and F. Seitz, dated by 1933 [2], concerning the nature of coupling forces between the atoms in metallic sodium.

The essence of the isotropic *d*-bond can be illustratively explained as follows. Let us schematically consider the process of ligand disjoining from the central ion. A gradual increase of the distance between the ligands and the central ion requires that the energy be spent not only to overcome the Coulomb interaction between them, but also to increase the energy eigenvalue of *d*-electrons in the closed electron shell of the central ion. This fact gives rise to the emergence of an additional binding energy; the bond itself was named isotropic *d*-bond, because a closed *d*-shell is spherically symmetric.

In order to test this assumption, the radial wave functions of a thallium ion – a typical representative of Hg-like ions – were calculated in work [3], as well as the dependences of the characteristic energy values of its electrons on the ion environment type. The calculations were made in the framework of several approximations.

According to modern ideas, the electron shell of a thallium ion, which is introduced into a crystal, glass, or an aqueous solution, is considered to preserve its individuality to a great extent. Such a viewpoint is based on experimentally established facts, according to which the characteristics of activator spectra of the indicated media are rather close to one another and are mainly determined by the nearest neighbors of the activator ion [4–6]. In particular, since the absorption spectra of an LiCl—Tl^+ aqueous solution and a KCl—Tl^+ crystallophosphor are practically identical, one may assume that the influence of the environment on the Tl^+ ion is approximately the same in both cases. This circumstance makes it possible, while estimating the coupling forces in thallium complexes, to simplify calculations by considering a Tl^+ ion introduced into a crystal lattice of the KCl type rather than a complex in the aqueous solution. Moreover, this circumstance allows one to use the averaging over the sphere while calculating the radial wave functions, because no violations of the long-range order at the transition from the crystal to the aqueous solution are observed in this case.

In order to take the influence of a crystal lattice on the radial wave functions of a Tl^+ ion into account, the model of the lattice of charged spheres (LCS) [3] was used.

In work [3], it was shown that the absolute energy eigenvalue of energy for *d*-electrons of a Tl^+ ion ($5d^{10}6s^2$) gradually increase in the sequence of lattices of KCl, KBr, and KI, which brings about the corresponding increase of the binding energy between the ion and the ligands. The results of calculations carried out in work [3] agree with experimental ones [7].

In work [8], the characteristic features of the LCS model and its some shortcomings have been analyzed. In order to eliminate the latter, a more perfect model has been proposed, where the distribution of the electron density in ions of the lattice is adopted to be close to the Gaussian one (the Gaussian distribution of electron density, GDED). The calculations, which were executed in work [8] making use of the more perfect GDED model, completely confirmed the main conclusion of work [3] about the existence of the isotropic d-bond between the central Hg-like ion and the ligands.

On the basis of the results of both experimental researches and theoretical calculations, the fact of existence of the isotropic d-bond between the central Hg-like ion, which is in the state with electron configuration $nd^{10}(n+1)s^2$, and the ligands can be considered ascertained.

In addition, there exist experimental facts which can be interpreted in such a way that a modification of the electron configuration of the central ion from $nd^{10}(n+1)s^2$ to $nd^{10}(n+1)s(n+1)p$ under the action of light results in the strengthening of the isotropic d-bond. Such a scenario is favored by the experimentally established phenomenon that the structure of the complex becomes substantially reconstructed within the lifetime of the electron shell of the central ion in the excited electronic state [9–11].

In works [9–11], there was also demonstrated that complexes, whose composition depends on the concentration of chlorine ions, are formed in aqueous solutions with available Tl^+ and Cl^- ions. A gradual increase of the chlorine ion concentration is accompanied by the formation of the following complexes of the thallium ion: $\mathrm{Tl(H_2O)}_n\mathrm{Cl}$, $\mathrm{Tl(H_2O)}_n\mathrm{Cl_2}$, $\mathrm{TlCl(H_2O)}_n\mathrm{Cl_2}$, $\mathrm{TlCl_2(H_2O)}_n\mathrm{Cl_2}$, $\mathrm{TlCl_2(H_2O)}_n\mathrm{Cl_3}$, and $\mathrm{TlCl_2(H_2O)}_n\mathrm{Cl_4}$. Attention should be paid to the fact that chlorine ions are contained in both the inner and outer spheres around the central ion. It is also worth noting that, according to the results of researches [12], $n = 4$; moreover, the complex includes an ion of alkaline metal, but the latter circumstance will not be taken into account in this work.

The position of the maximum in the absorption spectrum of the complex is determined by the nearest environment of the thallium ion. Namely, the complexes $\mathrm{Tl(H_2O)}_n\mathrm{Cl}$ and $\mathrm{Tl(H_2O)}_n\mathrm{Cl_2}$ demonstrate the same absorption spectrum as the aqueous solution of thallium, free of chlorine ions, does. This spectrum contains an absorption band at $\lambda_{\max} = 214$ nm in the ultra-violet range. The complex $\mathrm{TlCl(H_2O)}_n\mathrm{Cl_2}$ is characterized by an absorption band at $\lambda_{\max} = 229$ nm, while the complexes $\mathrm{TlCl_2(H_2O)}_n\mathrm{Cl_2}$, $\mathrm{TlCl_2(H_2O)}_n\mathrm{Cl_3}$, and $\mathrm{TlCl_2(H_2O)}_n\mathrm{Cl_4}$ by an absorption band at $\lambda_{\max} = 242$ nm.

In the luminescence spectrum of each complex, the maximum position is also governed by the nearest environment of the thallium ion. However, a very important issue is that the content of the nearest environment can be substantially modified during the lifetime of the thallium ion in the excited electronic state. This process for complexes $\mathrm{Tl(H_2O)}_n\mathrm{Cl}$ can be schematically represented in the following way:

$$\mathrm{Tl(H_2O)}_n\mathrm{Cl} + h\nu_a \rightarrow \mathrm{Tl^*(H_2O)}_n\mathrm{Cl}, \tag{1}$$

$$\mathrm{Tl^*(H_2O)}_n\mathrm{Cl} \rightarrow \mathrm{(TlCl)^*(H_2O)}_n, \tag{2}$$

$$\mathrm{(TlCl)^*(H_2O)}_n \rightarrow \mathrm{(TlCl)(H_2O)}_n + h\nu_l, \tag{3}$$

$$\mathrm{(TlCl)(H_2O)}_n \rightarrow \mathrm{Tl(H_2O)}_n\mathrm{Cl}. \tag{4}$$

The absorption of a quantum of light $h\nu_a$ (1) occurs in the band at $\lambda_{\max} = 214$ nm. During the lifetime of a thallium ion in the excited electronic state, the complex becomes reconstructed: the chlorine ion transits from the outer sphere of the central ion environment into the inner one (2). This process is accompanied by a shift of the energy states of the thallium ion. Radiative deactivation (3) of the excited electronic state of the complex brings about the emergence of the luminescence quantum $h\nu_l$, which is responsible for the luminescence band at $\lambda_{\max} = 395$ nm. At last, the initial structure of the complex becomes restored (4). Note that the luminescence spectrum of the thallium aqueous solution, which is free of chlorine ions, is characterized by a band at $\lambda_{\max} = 367$ nm.

Similar processes take place, when $\mathrm{Tl(H_2O)}_n\mathrm{Cl_2}$ complexes absorb light. Schematically, such processes can be presented as follows:

$$\mathrm{Tl(H_2O)}_n\mathrm{Cl_2} + h\nu_a \rightarrow \mathrm{Tl^*(H_2O)}_n\mathrm{Cl_2}, \tag{5}$$

$$\mathrm{Tl^*(H_2O)}_n\mathrm{Cl_2} \rightarrow \mathrm{(TlCl_2)^*(H_2}O)_n, \tag{6}$$

$$\mathrm{(TlCl_2)^*(H_2O)}_n \rightarrow \mathrm{(TlCl_2)(H_2O)}_n + h\nu_l, \tag{7}$$

$$\mathrm{(TlCl_2)(H_2O)}_n \rightarrow \mathrm{Tl(H_2O)}_n\mathrm{Cl_2}. \tag{8}$$

The absorption of light quanta $h\nu_a$ (5) occurs, like in case (1), in the band at $\lambda_{\max} = 214$ nm. Then, the complex becomes reconstructed, and the energy levels become shifted (6). However, since the inner environment sphere of the central ion contains two, rather than one, chlorine ions, the luminescence band is located at another position, namely, at $\lambda_{\max} = 345$ nm.

The following scheme describes the reconstruction processes of the $TlCl(H_2O)_nCl_2$ complexes:

$$TlCl(H_2O)_nCl_2 + h\nu_a \rightarrow (TlCl)^*(H_2O)_nCl_2, \tag{9}$$

$$(TlCl)^*(H_2O)_nCl_2 \rightarrow (TlCl_2)^*(H_2O)_nCl, \tag{10}$$

$$(TlCl_2)^*(H_2O)_nCl \rightarrow (TlCl_2)(H_2O)_nCl + h\nu_l, \tag{11}$$

$$(TlCl_2)(H_2O)_nCl \rightarrow TlCl(H_2O)_nCl_2. \tag{12}$$

In this case, the absorption of light quanta $h\nu_a$ (9) occurs in the band at $\lambda_{\max} = 229$ nm. The luminescence spectrum corresponding to stage (11) looks like that in case (7).

For three other complexes – namely, $TlCl_2(H_2O)_nCl_2$, $TlCl_2(H_2O)_nCl_3$, and $TlCl_2(H_2O)_nCl_4$, – such reconstruction processes are not observed. They are characterized by the absorption band at $\lambda_{\max} = 242$ nm and the luminescence band at $\lambda_{\max} = 435$ nm.

Processes (2), (6), and (10) testify that, when the thallium ion is in the excited electronic state $5d^{10}6s6p$, the increase of the ligand number in the inner environment sphere of the central ion is energetically "beneficial". Returning the thallium ion back into the ground electronic state $5d^{10}6s^2$ is accompanied by a reduction of the ligand number in the inner sphere, which is indicated by processes (4), (8), and (12).

Those facts make it possible to assume that the transition of the thallium ion into the excited electronic state leads to the increase of the isotropic d-bond energy. This means that this transition is to be accompanied by the increase of the absolute value of the eigenvalues of energy of electrons in the closed d-shell.

In order to test this assumption, we calculated the characteristic energy values for d-, s-, and p-electrons of the activator thallium ion in the $5d^{10}6s6p$ state and the corresponding radial wave functions. Since the results of calculations of the eigenvalues of energy of electrons carried out in the framework of the LCS model [3] and the more advanced GDED model [8] have no basic differences, a relatively simple LCS model was used in this work.

To solve the system of equations, which – in atomic units – looks like

$$Z_i' = P_i^2, \tag{13}$$

$$Y' = \left(Y - Z + \sum k_i Z_i - 13\right)\Big/ r, \tag{14}$$

$$Y_i' = (Y_i - Z_i)/r, \tag{15}$$

$$W_i' = [\varepsilon_i + l_i(l_i+1)/r^2 -$$

$$-2(Y + Y_i - St)/r]P_i - 2U_{kr}P_i, \tag{16}$$

$$P_i' = W_i, \tag{17}$$

we used, similarly to what was done in work [3], the Hartree–Torrance method [13]. In the system of equations (13)–(17), the following notations are used: l_i is the orbital quantum number; k_i the number of electrons in the electron shell; ε_i the eigenvalues of energy times two; P_i the radial wave function; Y_i and Z_i are the effective charges of the electron shell for the potential and the field strength, respectively; Y is the effective charge for the potential of the Tl^+ ion; and $Z - 13$ is a quantity, which was calculated according to the results of work [14] in order to take into account the potential created by the nucleus and inner electrons of the thallium ion. The function U_{kr} makes allowance for the influence of the crystal field, and St is a step function [3]. In contrast to work [3], where the subscript i in Eqs. (13)–(17) acquired the values of 1 and 2, now $i = 1, 2, 3$, which corresponds to d-, s-, and p-electrons, respectively.

The normalization constants for the wave functions and the characteristic energy values were determined following the same algorithm as was applied in work [3]. The radial wave functions of d-electrons turned out the most "sensitive" to small variations of the characteristic energy values. For instance, in the case of optimal values for the normalization constants and the characteristic energy values for d-, s-, and p-electrons, the amplitude of the radial wave function for d-electrons at a point $r = 0.001$ is of the order of 10^{-6}. At the same time, if any of the found characteristic energy values for d-, s- or p-electrons varies by ± 0.001, the absolute value of the radial wave function for d-electrons at the same point $r = 0.001$ becomes larger by about 5 orders of magnitude.

We have calculated the radial wave functions for an activator thallium ion in the KCl, KBr, and KI crystal lattices. The results of calculations for d-, s-, and p-electrons of a Tl^+ ion ($5d^{10}6s6p$) introduced into the KCl crystal lattice are depicted in Fig. 1. The

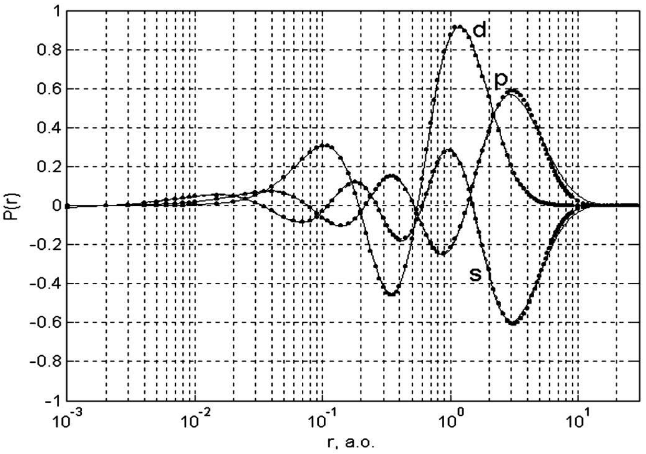

Fig. 1. Radial wave functions for d-, s-, and p-electrons of a Tl^+ ion ($5d^{10}6s6p$) in vacuum (points) and in the KCl crystal (solid curves)

corresponding radial wave functions in the case of KBr and KI crystals have similar profiles.

Figure 1 demonstrates that the values of the radial wave functions of a p-electron in vacuum and in the KCl crystal differ by approximately a factor of two at a point $r = 10$ a.u. This difference decreases, if one approaches the nucleus, and increases, if r grows; however, such an increase cannot be detected in the figure due to the selected scale. Such a behavior of the analyzed wave functions is caused by the fact that, in comparison with the field created by the nucleus and the inner electrons of the Tl^+ ion, the "relative contribution" of the averaged crystal field (the summand U_{kr} in Eq. (16)) is small at small r and increases with r. Therefore, the differences between the radial wave functions also increase as the distance r grows. Similar regularities are observed for other radial functions as well. Note that the radial wave functions were calculated, as in work [3], starting from $r = 30$ a.u.

The binding energy in the complex was evaluated, like in work [3], by the formula

$$V = \frac{1}{2}\sum_i k_i \varepsilon_i + U_{m0}, \qquad (18)$$

where U_{m0} is the Madelung potential.

The eigenvalues of energy for d-, s-, and p-electrons of the activator Tl^+ ion ($5d^{10}6s6p$) in KCl, KBr, and KI crystals are quoted in Table 1. The prelast row contains the values of the quantity V determined by relation (18). For the sake of comparison, the values of the analogous quantity V_0 for the thallium ion in the ground state, which were calculated in work [3], are given in the last row.

By confronting the tabulated values of V and V_0, one can see that the transition of a thallium ion into the excited electronic state, provided that all other conditions remain constant, gives rise to the growth of the binding energy in the complex. This increase is induced by the change of the characteristic energy of d-electrons, when the thallium ion transits into the excited electronic state.

For the sake of comparison, Table 2 quotes the characteristic energy values for d-electrons of the activator Tl^+ ion in the ground electronic state $5d^{10}6s^2$, which were obtained in work [3].

It should be noted that, in this work, while calculating the radial wave functions of the Tl^+ ion in the excited electronic state, we used an approximation, according to which the arrangement of the nearest chlorine ions with respect to the Tl^+ one remains the same as it is for the Tl^+ ion in the ground electronic state. However, according to the results of calculations obtained in work [15], which are widely used in monographies [2, 16], the equilibrium distance between the thallium ion and the nearest chlorine ions decreases, when the former transits into the excited electronic state. Making allowance for this circumstance in our calculations would result, in our opinion, to even larger growth of the ε_d value with the transition of the thallium ion from the ground into the excited electronic state. Therefore, the applied approximation is entirely eligible, so that the conclusion about the strengthening of the isotropic d-bond in the excited electronic state of thallium ion remains valid.

This feature of the isotropic d-bond allows not only the thallium-complex reconstruction, when the thallium

Table 1. Eigenvalues of energy ε_i, the Madelung potential U_{m0}, and the binding energies V and V_0 of the complex for the Tl^+ ion in the $5d^{10}6s6p$ and $5d^{10}6s^2$ state, respectively

Parameter	KCl	KBr	KI
ε_d	1.469	1.457	1.449
ε_s	0.291	0.265	0.246
ε_p	0.176	0.149	0.129
U_{m0}	0,295	0.281	0.265
V	7.873	7.771	7.699
V_0	6.935	6.954	6.977

Table 2. Eigenvalues of energy ε_d for the Tl^+ ion ($5d^{10}6s^2$) in the KCl, KBr, and KI crystals

KCl	KBr	KI
1.226	1.234	1.260

is in the excited electronic state, but also a number of additional experimental facts to be explained.

The luminescence spectrum of the crystallophosphor KCl–Tl$^+$ is characterized by a large enough Stokes shift. Really, the maximum of the absorption band is located at $\lambda_{\max} = 249$ nm, whereas the maximum of the luminescence band at $\lambda_{\max} = 305$ nm. Such a large Stokes shift results in the practically total absence of reabsorption. However, for a concentrated aqueous solution of LiCl–Tl$^+$, the Stokes shift is much greater at room temperature. The absorption-band maximum is located at $\lambda_{\max} = 242$ nm, while the luminescence-band one at $\lambda_{\max} = 435$ nm. A considerable growth of the Stokes shift for the aqueous solution in comparison with the crystal may be associated, in our opinion, with the fact that the liquid phase of the LiCl–Tl$^+$ solution does not interfere with a reduction of the distance between the thallium ion and the chlorine ions nearest to it, which occurs owing to the strengthening of the isotropic d-bond. As a result, the relative variation of the equilibrium distance between Tl$^+$ and Cl$^-$ ions in the solution and in the crystal, which accompanies the transition of the thallium ion into the excited state, will be larger in the former case; in its turn, this circumstance corresponds to the increase of the Stokes shift in this case.

On the basis of the proposed explanation for a large Stokes shift of the luminescence spectrum of a LiCl–Tl$^+$ solution, one can draw a conclusion that the Stokes shift should be smaller, if the solution turns into the solid state. Really, the fast cooling of a concentrated LiCl–Tl$^+$ aqueous solution down to a temperature of about 100 K transforms it into a vitreous specimen. The position of the maximum in the absorption spectrum remains intact, whereas the luminescence spectrum becomes shifted to $\lambda_{\max} \approx 400$ nm, i.e. a substantial reduction of Stokes losses is observed.

Thus, the results of our calculations of the radial wave functions of the activator Tl$^+$ ion in the excited electronic state $5d^{10}6s6p$ and the obtained eigenvalues of energy for d-, s-, and p-electrons evidence for an increase of the isotropic d-bond energy in the complexes concerned. This circumstance explains the origins of the experimentally found considerable reconstruction of the complexes within the thallium-ion lifetime in the excited electronic state. The increase of the energy of the isotropic d-bond between the thallium ion in the excited electronic state and the ligands can explain the anomalously large Stokes shift of the luminescence spectrum in LiCl–Tl$^+$ solutions.

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ВПЛИВ ЕЛЕКТРОННОГО СТАНУ ІОНА ТАЛІЮ НА ІЗОТРОПНИЙ d-ЗВ'ЯЗОК З ЛІГАНДАМИ

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Резюме

Методом Хартрі–Торранса виконано розрахунки радіальних хвильових функцій активаторного іона Tl$^+$ в збудженому електронному стані $5d^{10}6s6p$. Визначено власні значення енергії d-, s- та p-електронів іона Tl$^+$, який введено в кристали KCl, KBr та KI. Показано, що енергія ізотропного d-зв'язку з лігандами зростає при переході іона Tl$^+$ в збуджений електронний стан. Цим зростанням зумовлена суттєва перебудова комплексів талію за час існування збудженого електронного стану.