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STRONG RESONANCE ABSORPTION OF ULTRASOUND IN OCTAHEDRAL TRANSITION METAL COMPLEXES INVOLVING INVERSION SPLITTING

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It is shown that resonance absorption of ultrasound several orders of magnitude stronger than paramagnetic absorption may occur in octahedral transition metal complexes possessing inversion splitting (previously investigated by the author). This absorption depends on direct transitions between inversion (electron-vibrational) levels and is not related to change of the spin state of the complex. A formula is obtained for the transition probability. The absorption coefficient is calculated for complexes of aqueous Cu^{2+} and Ti^{3+} in a crystalline surrounding and its dependence on the direction of propagation and the polarization is determined. It is shown that the most convenient objects for experimental verification of the effect are hydrated copper salts with trigonal symmetry. The effect of temperature and external magnetic field is determined. The possibility of detecting the effect in liquids is considered.

1. INTRODUCTION

In previous researches, [1,2] we have shown that several equivalent equilibrium configurations are possible in octahedral transition metal complexes for which the electronic term in the configuration of the normal octahedron is degenerate; the interaction between these configurations leads to level splitting (inversion splitting [1])). With the help of a representation of the inversion states, it was possible to explain certain characteristic features of the EPR (electron paramagnetic resonance) spectrum of the Cu^{2+} ion in hydrated salts with trigonal symmetry, in particular, the experimentally observed temperature transition from one form of the spectrum to the other. [3]

The closeness of the inversion levels and their electron-vibrational character suggests the possibility of their successful study by means of ultrasonics. In the known researches of Al'tshuler and co-workers (see [4]) the parametric absorption of ultrasound associated with transitions between magnetic (spin) levels of the system was investigated. Here, in spite of the small absorption coefficient, the use of ultrasonics for the investigation of the paramagnetic properties of crystals has been shown to be fruitful. The inversion levels, in contrast with the magnetic ones, are not associated with the spin states, and transitions between them do not require change of the latter. Taking it into account that the spin levels are only indirectly connected with vibrations of the surroundings while the inversion levels are directly connected, it can be expected that inversion absorption of sound should be significantly greater than the paramagnetic, which makes it possible to use it to solve a number of theoretical and practical problems. Furthermore, it can be assumed that if the absorption coefficient of the complexes is much larger than the absorption coefficient of the liquid, it can be detected not only for the crystalline state but also for solutions. The present communication is devoted to a consideration of this problem.

2. PROBABILITY OF TRANSITION BETWEEN INVERSION LEVELS UNDER THE ACTION OF AN ACOUSTIC PERTURBATION

Let us consider a system consisting of an octahedral transition-metal complex immersed in an elastic medium—a carrier of acoustic vibrations. The interaction of the complex with the medium will be considered to be sufficiently small. By assuming that the frequency of elastic vibrations of the medium is much less than the natural frequencies of the complex, one obtains the result that the interaction only causes the latter to be modulated by

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[1] The name "inversion splitting" is introduced only in analogy with the splitting in ammonia due to inversion. In the octahedral complex, the inversion in the strict sense of the word does not occur, but a transition from one configuration to another can equivalently be graphically represented as a type of "inversion."

the first. If we denote the normal coordinates of the complex by Q_i and the change in these coordinates as the result of modulation by $\widetilde{Q}_i$, then with allowance for the effect of the medium on the complex it is necessary to introduce the following substitution in the Hamiltonian of the latter: $Q_i \rightarrow Q_i + \widetilde{Q}_i$. Here additional terms (perturbations) appear, of which the most significant are the following:

$$H' = \sum_i K_i Q_i \widetilde{Q}_i, \tag{1}$$

where K is the force constant corresponding to the i-th normal vibration of the complex; the summation is carried out over all normal vibrations.

The probability of resonance transition between the inversion levels a and b, with loss of one quantum of vibration of the medium under the action of the perturbation (1), is given by the usual expression

$$P_{a,b} = 2\pi\hbar^{-2}\rho_\omega \,|\langle a, n_\omega \,|\, H' \,|\, b, n_\omega - 1\rangle|^2. \tag{2}$$

The matrix element in (2) is computed rather easily in our case. For $\widetilde{Q}_i$, it is possible to use an expansion in normal coordinates q_j of the elastic vibrations of the medium excited by the ultrasound:

$$\widetilde{Q}_i = \sum_j a_{ij} q_j. \tag{3}$$

Here (see [5])

$$a_{2j} = R\omega_j v_j^{-1} \sin\delta_j \,(\lambda_{xj}\Phi_{xj} - \lambda_{yj}\Phi_{yj}),$$

$$a_{3j} = \frac{1}{\sqrt{3}} \frac{R\omega_j}{v_j} \sin\delta_j \,(\lambda_{xj}\Phi_{xj} + \lambda_{yj}\Phi_{yj} - 2\lambda_{zj}\Phi_{zj}) \tag{4}$$

etc., where λ_{pj} and Φ_{pj} are the direction cosines of the polarization direction and the velocity v_j, respectively; R is the distance between the central atom and one of the particles forming the octahedral complex, and δ_j is an arbitrary initial phase. For the derivation of (4), it was assumed that the acoustic wavelength is much larger than R.

Further, we have

$$\langle n_\omega \,|\, q \,|\, n_\omega - 1\rangle = [\hbar n_\omega / 2M\omega]^{1/2}, \tag{5}$$

where n_ω is the average number of vibrations of a given type and M is the mass of the medium. Finally, the matrix element $\langle a \,|\, Q_i \,|\, b\rangle$ is computed directly by means of the wave functions of the inversion levels, given in [1]. If we limit ourselves to the case of a tetragonal distortion of the octahedron in the equilibrium configuration, then for transition from the ground state A_1 to a doubly degenerate state E we can get

$$\langle A_1 \,|\, Q_2 \,|\, E\rangle = \langle A_1 \,|\, Q_3 \,|\, E\rangle = Q^0/\sqrt{2},$$

$$\langle A_1 \,|\, Q_i \,|\, E\rangle = 0, \; i \neq 2, 3. \tag{6}$$

Here we neglect the value of the parameter γ (see [1]) in comparison with unity, and also the spin-orbit interaction. Account of the latter in certain cases complicates the form of the wave function of the inversion levels, [6] but changes only slightly the value of the coefficient in front of Q^0 in (6). We note that $KQ^0 = A$, where A is a complex constant calculated by us previously. [5] With account of the relations set forth, we can obtain

$$P_{A_1, E} = J_\omega \pi A^2 R^2 L / 3 d v^3 \hbar^2, \tag{7}$$

where

$$L = \lambda_z^2\Phi_z^2 + \lambda_y^2\Phi_y^2 + \lambda_x^2\Phi_x^2 - \lambda_x\Phi_x\lambda_y\Phi_y - \lambda_x\Phi_x\lambda_z\Phi_z - \lambda_y\Phi_y\lambda_z\Phi_z, \tag{8}$$

and $J_\omega = \rho_\omega n_\omega \hbar\omega v/V$ is the intensity of the ultrasonic vibrations of frequency ω, V is the volume of the medium, d is its density (averaging is carried out over the initial phase δ_j).

In the case of trigonal distortion of the octahedron in equilibrium configurations (which can be realized, for example, for complexes of ions with electronic configuration d^1) the constant A in Eq. (7) is replaced by B (see [1]), and the numerical coefficient and the expression for L characterizing the dependence of the transition probability on the direction of propagation and the polarization of the acoustical vibrations also change.

3. ABSORPTION COEFFICIENT. DEPENDENCE ON DIRECTION OF PROPAGATION AND POLARIZATION

We assume that there are N absorbing complexes per unit volume of the medium. Further, let the incident acoustic wave contain a small spread of frequencies $\Delta\omega$, much smaller than the width of the inversion levels. We denote by $g(\omega)$ the form factor of the absorption line, so that $\int_0^\infty g(\omega)\,d\omega = 1$. Then the energy of acoustical vibrations absorbed per unit volume and per unit time at a temperature T is equal to

$$E = NP_{A_1, E} \frac{\hbar\omega}{kT} \hbar\omega g(\omega)\,\Delta\omega, \tag{9}$$

where, under the assumption that $\hbar\omega \ll kT$, the factor $\hbar\omega/kT$ takes into account the population differences of levels A_1 and E.

The total intensity of the incident wave $J = J_\omega \Delta\omega$, so that we obtain the following for the absorption coefficient, with account of (7):

$$\sigma_{A_1, E} = \frac{E}{J} = \frac{\pi}{3} \frac{NA^2R^2}{dv^3kT} \omega^2 g(\omega)\, L. \tag{10}$$

Extremal properties of the directivity and polarization factors

Direction of the extremum	Value of L for	
	transverse oscillations	longitudinal oscillations
I	1	0
II	0	1/2
III (‖)		3/4
III (⊥)		0
Averaged value	2/5	3/10

The factor for the direction of propagation and polarization of the waves L is given by Eq. (8). In the table we have listed its extremal values, and also the value averaged over all possible directions. Here I denotes the direction coinciding with the four-fold axis of the octahedron (there are three such directions altogether and they coincide with the coordinate axes), II is the direction along the trigonal axis (there are four such directions in all), and III is the direction of the two-fold axis that joins two opposite edges of the octahedron (six directions). For the direction III, one distinguishes between two extreme directions of polarization of transverse waves: along the edge intersecting it—III (‖), and perpendicular to this edge—III (⊥). For the direction II, L does not depend on the polarization. Thus the absorption depends very strongly on the propagation direction and the polarization.

Let us estimate the value of the absorption coefficient σ. We consider aqueous complexes of Cu^{2+} ions. In this case, the equilibrium octahedra are tetragonally distrorted and for them (see [1]) $A = 2.5 \times 10^{-4}$ dyne and $R = 2 \times 10^{-8}$ cm. We assume that these complexes are in a crystalline medium that does not take part in the inversion splitting (see below). We can then assume that $N = 10^{19}$ cm^{-3}, $d = 3$ g/cm^3, $v = 3 \times 10^{-5}$ cm/sec, $g(\omega) = 1/\omega_{1/2} = 10^{-8}$ sec^{-1}, and

$$\sigma = 3.5 \cdot 10^{-11} \omega^2 L / 4\pi^2 T. \tag{11}$$

For comparison we point out that for the given case the absorption coefficient corresponding to transitions between spin levels is given by the expression (see [4]) $\sigma = 10^{-40}(\omega^4/16\pi^4 T)$ cm^{-1}. We see that the inversion absorption of ultrasound is many orders of magnitude larger than the paramagnetic absorption. As an example, for $\omega = 10^7$ sec^{-1} and $T = 10°$ K, we get for inversion absorption, $\sigma = 350$ cm^{-1}, which indicates complete absorption in a layer of thickness 10^{-2} cm.

However, in this case it is necessary to require that the intensity of the acoustic wave not be so large that saturation sets in. On the other hand, it is impossible to neglect in Eq. (10) the contribution of the saturation factor $q = 1/(1 + P_{a,b}/W_{a,b})$, where $W_{a,b}$ is the probability of a relaxation transition between the inversion levels. In that connection, a similar coefficient should appear also in formulas for parametric absorption of the ultrasound.

In view of the close coupling of the inversion states with the vibrations of the lattice, the problem of the width of the levels takes on a significant importance. Estimates show that, at least for low temperatures, the lifetimes of the excited states are long enough for a possibility of observing them experimentally for all practically attainable frequencies of ultra- and hyper-sound. Actually, by means of Eq. (7), one can obtain for the probability of relaxation transitions under the effect of the lattice phonons (direct transitions under the condition $\hbar\omega \ll kT$):

$$W_{A_1,E} = 4 \cdot 10^{-13} (\omega^2/4\pi^2) T. \tag{12}$$

Hence, for ultrasound with frequency $\omega = 2\pi \times 10^8$ sec^{-1} and $T = 10°$ K, we have $W = 4 \times 10^4$ sec^{-1}, and for hypersound with $\omega = 2\pi \times 10^{10}$ sec^{-1} we have for the same temperature $W = 4 \times 10^8$ sec^{-1}. We see that although the widths of the inversion levels are relatively large (for similar temperatures), they are much less than the absorbed frequency.

For similar complexes of the Ti^{3+} ion, both tetragonal and trigonal distortions of the octahedron are possible. In the first case, all the qualitative conclusions developed above remain in force, in particular, the extremal properties of L. For an estimate of the numerical value of σ, it is necessary to consider that for the aqueous complex of Ti^{3+} the constant E is one-half the value for Cu^{2+}, and that account of the spin-orbital interaction (see [6]) decreases somewhat the numerical coefficient in Eq. (10). To sum up, it should be expected that the ultrasonic absorption coefficient in aqueous complexes of Ti^{3+} in crystals is an order of magnitude smaller than (11). For trigonal distortions, σ can be shown to be still smaller, since $B < A$.

4. POSSIBILITIES OF EXPERIMENTAL INVESTIGATION

The large values of σ allows one to hope that inversion absorption of ultrasound can be observed by direct measurement of the absorption coefficient. The best objects for experimental study are crystals of hydrated copper salts with trigonal symmetry. In these crystals, the effect of the surroundings does not remove the inversion splitting of the aqueous copper complex, and from a comparison of the theoretically expected EPR spectrum (more precisely, its temperature or frequency dependence) with the experimentally measured spectrum, one can determine the approximate values of the amounts of inversion splitting at different temperatures.[3]

Thus, for example, for the crystal $CuSiF_6 \cdot 6H_2O$ diluted with zinc, at $T = 12°$ K, the inversion splitting is $\delta \sim 10^7$ sec^{-1} and increases strongly with increase in temperature. For the diluted crystal $Cu(BrO_3)_2 \cdot 6H_2O$, this same frequency is reached at $T < 7°$ K, while for $Cu_3La_2(NO_3)_{12} \cdot 24H_2O$, diluted with magnesium, at $T \sim 30°$ K, while for the same crystal, but undiluted, such an inversion splitting is possible only for $T \gtrsim 170°$ K (see[3]).

It is convenient in practice to carry out research on resonant absorption at a constant frequency of ultrasound by means of a slow variation of temperature. For the example given above of the $CuSiF_6 \cdot 6H_2O$ crystal diluted by zinc, it is evidently suitable to use ultrasound at a frequency $\omega = 2\pi \times 10^8$ sec^{-1} [the higher the frequency, the larger the ultrasonic absorption coefficient; see Eq. (11)] and measure the temperature dependence of the absorption coefficient, beginning with $T \sim 7°$ K. By taking into account the strong temperature dependence of the inversion splitting δ, it is possible to choose a very narrow range of measurements. Here, of course, it is also necessary to be guided by the foregoing table of extremal values of the absorption coefficient as a function of the direction of propagation and polarization. For example, in accord with this table, for longitudinal waves, the largest absorption coefficient corresponds to a direction of the velocity of the wave along one of the four-fold axes of the octahedron of the water molecules around the Cu^{2+} ion.

One can get additional possibilities of varying the resonant frequency by the effect of an external static magnetic field. It follows from a previously [3] obtained dependence of the energy of the inversion levels on the intensity of the magnetic field H, directed along a four-fold axis of the octahedron, that identical spin states, for example 1^- and 2^-, approach to within 4/9 of the initial splitting with increase in H (for $\beta H \approx 2\delta$) and then diverge again. The transition probability changes only slightly in this case. Such magnetic tuning of the frequency can be effective, especially in those cases in which the temperature tuning is too coarse.

The large probability of transition between inversion levels under the action of acoustical vibrations suggests the possibility that the ultrasonic absorption considered can also be observed in octahedral complexes in solutions (electrolytes). Obviously, it is necessary in this case that the absorption of the complexes be much larger than the absorption of the solvent. This condition is satisfactorily fulfilled for inversion absorption in most cases. Actually, for water for example, the absorption coefficient of ultrasound at room temperature amounts to $10^{-16}(\omega^2/4\pi^2)$ cm^{-1}, while for absorption of aqueous complexes of copper in solutions we easily obtain from (10) that $\sigma \approx 3 \times 10^{-13}(\omega^2/4\pi^2)$ cm^{-1} (in contrast to a crystal, one can set $N = 10^{18}$ cm^{-3}, $v = 1.5 \times 10^5$ cm/sec; $d = 1$ g/cm^3, $T = 300°$ K). Probably the case of the Cu^{2+} ion in aqueous solutions is the most suitable object of investigation of absorption of ultrasound in solutions.

In the case of a liquid surrounding, the complex can be considered as free, so that the value of the inversion splitting is determined only by the internal barrier between the equivalent configurations. To each vibrational state there corresponds in this case an inversion splitting, and for room temperatures, in principle, several values of δ_K should be observed, an idea concerning which can be obtained from the approximate calculation given earlier.[1] Of these, only those corresponding to the ground and first-excited vibrational states fall in the range of practically obtainable ultrasonic frequencies. Unfortunately, it is not yet possible to point to an experiment from which the presence of inversion splitting in liquids and the frequencies corresponding to them would follow directly, as in the case of crystals of hydrated copper salts with trigonal symmetry.

The strong absorption of ultrasound by single crystals of copper salts, together with its anisotropy, also makes it possible to propose (see[7]) the principle of construction of a polarizer and analyzer of ultrasonic oscillations (the analog of the Nicol prism for light waves), realization of which would make it possible to disclose new methods of investigation of molecular systems, in particular, by determining the rotation of the plane of polarization of the acoustic vibrations.

It would be interesting to obtain experimental verification of the results reported in this communication.

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