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Davydov Splitting in the Polarized Absorption Spectra of Single Crystals of some Copper Complexes of α-Amino Acids

By

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This paper presents the absorption spectra observed with polarized light of the single crystals of the copper complexes of *L*-alanine and *DL*-α-aminobutyric acid.

The spectra are interpreted by the crystal-field theory.

Es werden die Absorptionsspektren angegeben, welche mit Hilfe polarisierten Lichts an Einkristallen der Kupferkomplexe von *L*-Alanin und *DL*-α-Aminobuttersäure beobachtet wurden.

Die Spektren wurden an Hand der Kristallfeldtheorie gedeutet.

On donne les spectres d'absorption observés, à l'aide de lumière polarisée, aux cristaux uniques des complexes de cuivre du *L*-alanine et de l'acide *DL*-α-aminobutyrique.

Les spectres sont interprétés suivant la théorie du champ cristallin.

Introduction

The physical properties of transition metal ions can often be described successfully by the crystal-field theory. In the LCAOMO conception the single electron molecular orbitals are represented by wave functions of the type:

$$\Psi_{\text{m.o.}} = c_m \Phi_m + \sum_l c_l \Phi_l$$

where Φ_m is the wave function of the central metal atom or ion and the Φ_l 's are the wave functions of the ligands. The values of the constant c_m and the constants c_l are subject to quantum-mechanical and group-theoretical considerations.

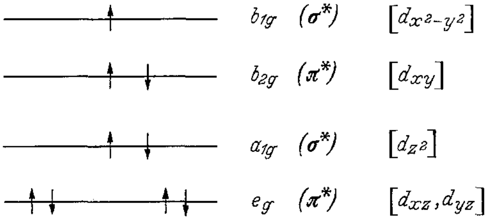

Fig. 1

An extensive molecular-orbital approach to square planar metal complexes of D_{4h} symmetry was recently given by Gray and Ballhausen [4]. The sequence of the molecular-orbital energy levels is reproduced in Fig. 1.

However, the symmetry of the copper complexes of the α-amino acids described in this paper is substantially lower. The copper complex of *L*-alanine was found to have the symmetry C_2 [1], whereas for the copper complex of *DL*-α-aminobutyric acid the point group C_i [5] has been investigated.

In both complex molecules an approximately square planar configuration of the ligands with the nitrogen atoms and the oxygen atoms in trans position has been determined.

As the transitions discussed in this paper are shown to be connected with the highest half-filled level and the next lower filled level, we restrict our attention to these levels.

By correlation it is found that the irreducible representations b_{1g} (σ^*) and b_{2g} (π^*) of the square metal complexes of D_{4h} symmetry will transform under a in the point group C_2 and under a_g in the point group C_i.

Experimental Results

The copper complexes of the α-amino acids were prepared by pouring an excess of basic cupric carbonate into a hot aqueous solution of the α-amino acid, after which the precipitate was removed by filtration.

The single crystals of the copper complex of *L*-alanine were prepared by slow diffusion of alcohol into an aqueous solution of the complex in a tube of about 4 mm in diameter.

The single crystals of the copper complex of *DL*-α-aminobutyric acid were obtained by slowly cooling a saturated aqueous solution of the complex. The thickness of the plate-like crystals of both compounds has not been measured, but the order of magnitude is some tenths of a mm.

The absorption spectra of the aqueous solution of the complexes were run on a Beckmann DK 2 spectrophotometer.

The polarized absorption spectra of the single crystals were observed on a Zeiss PMQ II spectrophotometer in conjunction with a Zeiss polarization microscope.

All measurements were carried out at room temperature.

The Copper Complex of L-Alanine

In an aqueous solution of the complex a *d*-*d* transition is observed at 15,900cm^{-1}. The spectrum is represented in Fig. 2.

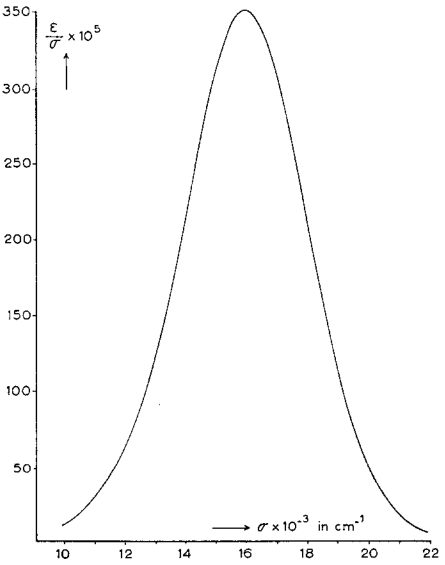

Fig. 2. Absorption spectrum of an aqueous solution of the copper complex of *L*-alanine

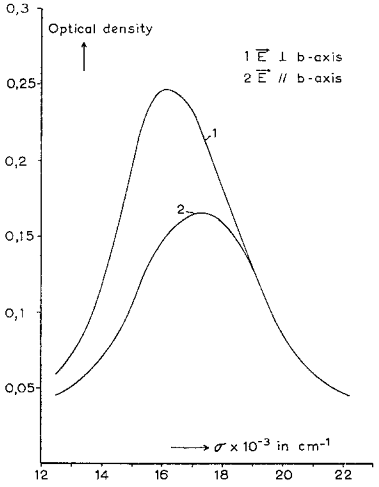

Fig. 3. Absorption spectrum of a single crystal of the copper complex of *L*-alanine

From the Gaussian form of the spectrum we conclude that no overlapping bands are present. Therefore, the absorption will be caused by the transition of one electron.

Dijkstra and Vonk [2] are carrying out an X-ray analysis of the structure of the copper complex of L-alanine. They already found the complex to crystallize in the monoclinic system with two molecules per unit cell. The space group is C_2^2 ($P\,2_1$).

The unit-cell parameters are:

$$a = 9.24\ \text{Å},\quad b = 5.05\ \text{Å},\quad c = 9.59\ \text{Å},\quad \beta = 95.2° \ .$$

In the well developed crystals the 100-face predominated. The crystal spectrum was run with the incident light beam perpendicular to the 100-face. The plane of polarization of the incident light beam was made parallel and perpendicular to the b-axis of the crystal.

The absorption spectrum is given in Fig. 3.

Two absorption bands are observed. The transition moment corresponding to the 16,150 cm^{-1} is polarized perpendicular, and the transition moment corresponding to the 17,250 cm^{-1} absorption band is polarized parallel to the b-axis of the crystal.

The Copper Complex of DL-α-Aminobutyric Acid

The absorption spectrum of an aqueous solution of the copper complex of DL-α-aminobutyric acid is quite analogous to that of the copper complex of L-alanine. The maximum is observed at 16,120 cm^{-1}.

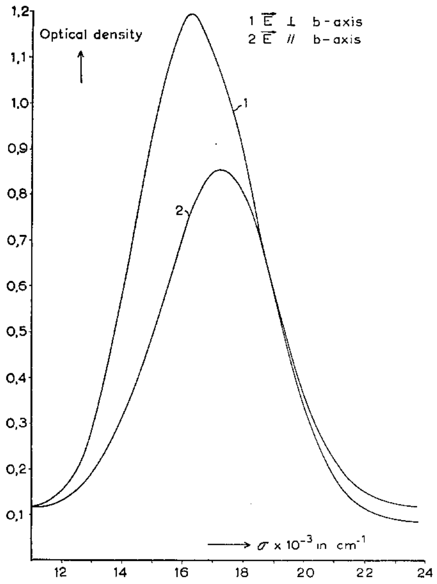

Fig. 4. Absorption spectrum of a single crystal of the copper complex of DL-α-amino-butyric acid

The X-ray analysis of the structure of the copper complex of DL-α-aminobutyric acid was performed by Stosick [5]. According to his results the complex crystallizes in the monoclinic system with two molecules per unit cell. The space group is C_{2h}^5 ($P\,2_1/c$). The unit-cell parameters are:

$$a = 11.09 \pm 0.02\ \text{Å},\quad b = 5.06 \pm 0.01\ \text{Å},$$
$$c = 9.45 \pm 0.02\ \text{Å},\quad \beta' = 87°51' .$$

The crystals obtained by us showed well developed faces and angles. Measurement of the angles revealed that these crystals had the (100) face well developed. The crystal spectrum was run with light polarized parallel and perpendicular to the b-axis, whereas the incident convergent light beam was perpendicular to the (100) face.

The absorption spectrum is given in Fig. 4. As in the crystal spectrum of L-alanine two absorption bands are observed. The transition moment corresponding to the absorption band at 16,250 cm^{-1} is polarized perpendicular, and the transition moment corresponding to the absorption band at 17,250 cm^{-1} is polarized parallel to the b-axis of the crystal.

Discussion

In a previous publication [*1*] we gave a probable interpretation of the polarized absorption spectra of the copper complex of *L*-alanine. We stated that the description could be given either in terms of a single localized molecule or in terms of an exchange coupling between the molecules in the crystal. We will show now that the number of observed absorption bands, as well as the directions of the corresponding transition moments, can be interpreted satisfactorily by Davydov's crystal-field theory.

Following DAVYDOV's [*3*] notation, we denote the wave function of the ground state of the crystal by:

$$\Psi_0 = \prod_{n\alpha} \varphi^0_{n\alpha} \qquad n = 1, \cdots N; \quad \alpha = 1, \cdots \sigma$$

N denotes the number of unit cells in the crystal, while σ corresponds to the number of molecules in the unit cell.

[DAVYDOV A. S., Theory of molecular excitons p. 33, eq. (3,3)].

If a molecule, $n\alpha$, is excited by absorption of dipole radiation, the following wave function arises:

$$\Psi^f_{n\alpha} = \varphi^f_{n\alpha} \prod_{m\beta \neq n\alpha} \varphi^0_{m\beta} \ .$$

Taking into account the exchange permutation, we obtain:

$$X^f_{n\alpha} = [(S\sigma N)!]^{-\frac{1}{2}} \sum_P (-1)^P P \Psi^f_{n\alpha} \ .$$

(S is the number of participating electrons per molecule).

However, this excitation can spread over the whole crystal. Then, the exciton wave function is:

$$\Phi^f = (\sigma N)^{-\frac{1}{2}} \sum_{n\alpha} a_{n\alpha} X^f_{n\alpha} \ .$$

For two molecules per unit cell, the crystal wave functions are restricted to:

$$\Phi^f_1 = (2N)^{-\frac{1}{2}} \sum_n [X^f_{n1} + X^f_{n2}] \ ,$$

$$\Phi^f_2 = (2N)^{-\frac{1}{2}} \sum_n [X^f_{n1} - X^f_{n2}] \ .$$

The Crystal Spectrum of the Copper Complex of L-Alanine

The character table of the point group C_2 of the copper complex of *L*-alanine, and the character table of the space group C^2_2 ($P\,2_1$) of the crystal, are analogous and can easily be found in text-books of group theory. It follows that the wave function representing the ground state of the crystal will transform like the A representation of the space group. The wave functions of the excited states of the crystal which interest us are represented by:

$$\Phi^A_1 = (2N)^{-\frac{1}{2}} \sum_n [X^A_{n1} + X^A_{n2}] \ ,$$

$$\Phi^A_2 = (2N)^{-\frac{1}{2}} \sum_n [X^A_{n1} - X^A_{n2}] \ .$$

From symmetry considerations we now deduce the irreducible representations to which the excited states of the crystal belong. It appears that the wave function Φ_1^A transforms as the A representation and the wave function Φ_2^A transforms as the B representation of the space group under discussion. Transitions from the ground state of the crystal to the excited states discussed are allowed by absorption of electric dipole radiation. The $A \rightarrow A$ transition will be polarized parallel to the b-axis, whereas the $A \rightarrow B$ transition will be polarized perpendicular to the b-axis.

The absorption band observed at 15,900 cm^{-1} in a solution of the copper complex of L-alanine will split into two transitions. This is actually observed in the crystal. The transitions are at 16,150 cm^{-1} and at 17,250 cm^{-1}.

The Crystal Spectrum of the Copper Complex of DL-α-Aminobutyric Acid

As stated above, the symmetry of the molecule of the copper complex of DL-α-aminobutyric acid will be C_i.

For the isolated molecule of the copper complex of DL-α-aminobutyric acid the electric dipole transition $A_g \rightarrow A_g$ is forbidden. However, vibronic interaction with α_u vibrations causes a slight mixing of ungerade character into the gerade electronic wave function. Consequently, the transition now becomes allowed.

As shown by STOSICK [5], the space group of the crystals of the copper complex of DL-α-aminobutyric acid is C_{2h}^5 ($P\,2_1/c$).

According to the vibronic mechanism a vibration of α_u symmetry will be active. This vibration and the resulting electronic transition moment transform under the A_u representation of the point group of the molecule, i. e. transform like the translation vector (T_x, T_y, T_z). A change of the plane of polarization of the light—as carried out in the crystal measurements—will not lead therefore to a quenching of the active vibration in the vibronic mechanism. The same vibration progression can be expected for all polarization directions of the incident light beam.

As the ungerade part of the wave function is responsible for the optical phenomena discussed, we shall only pay attention to the A_u character of the wave function.

The ground state wave function of the single molecule has A_g symmetry. As a consequence, the wave function representing the ground state of the crystal transforms under the A_g representation of the space group C_{2h}^5 ($P\,2_1/c$). The first excited states of the crystal are:

$$\Phi_1^{A_u} = (2N)^{-\frac{1}{2}} \sum_n [X_{n1}^{A_u} + X_{n2}^{A_u}] \; ,$$

$$\Phi_2^{A_u} = (2N)^{-\frac{1}{2}} \sum_n [X_{n1}^{A_u} - X_{n2}^{A_u}] \; .$$

The nature of the symmetry properties of these excited states can be found out with the aid of group theory.

It follows that the wave function $\Phi_1^{A_u}$ transforms as the A_u representation, and the wave function $\Phi_2^{A_u}$ transforms as the B_u representation of the space group.

From these considerations we conclude that through the action of electric dipole radiation two transitions can be expected. The transition $A_g \rightarrow A_u$ will be polarized parallel to the b-axis, whereas the transition $A_g \rightarrow B_u$ will be polarized perpendicular to the b-axis.

The absorption band observed at 16,120 cm^{-1} in a solution of the copper complex of DL-α-aminobutyric acid will split into two transitions.

This is actually observed in the crystal. The transitions are at 16,250 cm^{-1} and at 17,250 cm^{-1}.

Final Remarks

The interpretation of the crystal spectra of the copper complexes of L-alanine and DL-α-aminobutyric acid can be given by Davydov's crystal field theory. The theory accounts for the right number of bands observed and the predicted directions of the transition-moments agree with the experimental data.

It should be possible to calculate the magnitude of the DAVYDOV splitting if the position of the molecules and the potential energy between the molecules in the crystal are known.

At the moment, the difficulty encountered in such a calculation seems to be the potential energy, as not only exchange forces but also ionic forces between the molecules will operate.

In a previous paper [*1*] we made some suggestions with regard to the phenomenon of the anomalous rotatory dispersion of the optically active copper complexes of α-amino acids. We think that some remarks may be stated more definitely now. A description of the crystal absorption spectra was made by taking into account the highest half-filled level and the next lower filled level. Therefore it is in line with these considerations that the Cotton effect observed on an aqueous solution of the copper complex of L-alanine is connected with a $^2A \rightarrow {}^2A$ transition. This transition is allowed for absorption of electric dipole radiation and for absorption of magnetic dipole radiation, the corresponding transition moments both lying along the z-axis.

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