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Transition Probabilities in the $CuCl_4^{2-}$-Complex

By

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Transition probabilities in the $CuCl_4^{2-}$-complex have been calculated using the L.C.A.O.-functions obtained in the preceding paper by P. Ros and G. C. A. SCHUIT. For all transitions the calculated absolute oscillator strenghts turn out to be a factor 2 too large with respect to the experimental values. The calculated transition probabilities are mainly determined by the amount of mixing of the ligand functions in the molecular orbitals. If this mixing is assumed somewhat less the agreement is still better.

Unter Benutzung der L.C.A.O.-Funktionen aus der vorstehenden Arbeit von P. Ros und G. C. A. SCHUIT wurden die Übergangswahrscheinlichkeiten im $CuCl_4^{2-}$-Komplex berechnet. Die absolute Oszillatorstärke, die hauptsächlich vom Gewicht der Ligandenfunktionen abhängt, wird für alle Übergänge um den Faktor 2 zu groß. Verringert man den Beitrag dieser Funktionen, wird die Übereinstimmung mit dem Experiment besser.

A l'aide des fonctions L.C.A.O. du travail précédent de P. Ros et G. C. A. SCHUIT, nous calculons les moments de transition pour l'ion complexe $CuCl_4^{2-}$. Pour toutes les bandes les forces oscillatrices calculées sont deux fois trop grandes devant l'expérience. Elles sont déterminées surtout par le poids des orbitales des ligandes dans les O.M.; l'accord s'améliore par une diminution de ce poids.

Introduction

In the last twenty years many attempts have been made to calculate the stability and the charge distribution of inorganic complexes. In most of these calculations, more or less empirical, the results were checked by comparing them with data obtained from the optical spectra [*2, 3, 4, 6, 7, 9, 10, 14, 15, 20, 21*]. In the present report a calculation of the intensities of the bands in the $CuCl_4^{2-}$-spectrum is described. It is carried out making use of the one electron wave functions and charge distribution arising from a quantitative molecular orbital calculation in which as few as possible empirical parameters are introduced (see preceding paper by P. Ros and G. C. A. SCHUIT and [*19*]). By comparing the calculated intensities with the experimental values the accuracy of the M.O. calculation is checked. By evaluating some terms which up to now have always been approximated or neglected we hope to be able to test and maybe to simplify the usual method of calculating the intensities.

Transition Probability

The probabilities of electric dipole transitions and therefore the intensities of the corresponding absorption bands can be expressed in the oscillator strengths f.

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It is possible to determine f from the optical spectrum, as well as to relate it to the wave functions of the states between which the transition occurs [3, 5, 17].

1. *Theoretical Calculation of f:* The formula for the theoretical calculation of f is given by:

$$f = 1.085 \times 10^{11}\, \bar{\nu}\, P\,, \tag{1}$$

$$P = A\nu_{\mathrm{I}}\, \Sigma_{\mathrm{II}}\, |\langle \Psi_{\mathrm{I}} \,|\, \boldsymbol{r} \,|\, \Psi_{\mathrm{II}} \rangle|^2 \tag{2}$$

$$= \frac{1}{n} \sum_{i=1}^{n} \sum_{j=1}^{m} |\langle \Psi_{\mathrm{I}i} \,|\, \boldsymbol{r} \,|\, \Psi_{\mathrm{II}j} \rangle|^2$$

with $\bar{\nu}$ = mean wave number of the absorption band (cm^{-1}),

P = dipole strength (cm^2),

Ψ_{I} = wave function of the ground state, n-fold degenerate,

Ψ_{II} = wave function of the excited state, m-fold degenerate,

$\boldsymbol{r}$ = position vector, pointing from the origin to the point of integration. It makes no difference for the calculated value of f which point is chosen as origin. We shall take the origin of the main coordinate system, located on the central ion.

To evaluate the transition probabilities in $CuCl_4^{2-}$ we have to calculate $n \times m$ integrals $\langle \Psi_{\mathrm{I}} \,|\, \boldsymbol{r} \,|\, \Psi_{\mathrm{II}} \rangle$ for each allowed transition. Ψ_{I} and Ψ_{II} are wave functions of the whole complex and they may be written as Slater determinantal wave functions, composed from the one electron wave functions of the filled molecular orbitals.

We shall now introduce the following approximations:

a) We assume the $CuCl_4^{2-}$-complex to be perfectly tetrahedral. (The real form of the complex determined by X-ray analysis [13] is a tetragonally distorted tetrahedron; the Cu-Cl distance is equal to 2.22 Å). It can be shown that ignoring the distortion does not affect the f-values much.

b) We suppose that the one electron molecular orbitals are the same before and after the transition. These molecular orbitals are known from the M.O. calculation described in the preceding paper by P. Ros and G. C. A. Schuit. It appears from this calculation that this second assumption is justified.

In the ground state Ψ_{I} of $CuCl_4^{2-}$ we have an electron-hole in, say, the molecular orbital ψ_{I}. In the excited state Ψ_{II} we have a hole in ψ_{II}. We can now prove, making use of the orthonormality relations of the molecular orbitals, that $\langle \Psi_{\mathrm{I}} \,|\, \boldsymbol{r} \,|\, \Psi_{\mathrm{II}} \rangle = \langle \psi_{\mathrm{II}} \,|\, \boldsymbol{r} \,|\, \psi_{\mathrm{I}} \rangle = \langle \psi_{\mathrm{I}} \,|\, \boldsymbol{r} \,|\, \psi_{\mathrm{II}} \rangle$. The determinantal wave functions can simply be replaced by the one electron molecular orbitals containing the hole. Another consequence of the assumptions is that we can use the molecular orbitals calculated for the ground state of tetrahedral $CuCl_4^{2-}$. The transitions that are allowed and the component integrals of each "degenerate" transition that are not equal to zero are found by applying the multiplication rules of the group T_d [8, 12]. They are listed in Tab. 1. In the last column of this table the relation between the different components of the same transition is indicated. The integrals $\langle \psi_{\mathrm{I}} \,|\, \boldsymbol{r} \,|\, \psi_{\mathrm{II}} \rangle$ that are not equal to zero because of symmetry have to be calculated. Since a molecular orbital ψ is of the form

$$\psi = C_1\, \varphi_M + C_2\, \chi_L \text{ with } \varphi_M = \text{atomic orbital of the central ion } M$$
$$\text{and } \chi_L = \sum_\alpha C_\alpha\, \varphi_\alpha;\ \varphi_\alpha = \text{atomic orbital of ligand } L_\alpha$$

Table 1. *The dipole vector* $\boldsymbol{r}$ *corresponds to the representation* T_2

Allowed transitions, ground state T_2	Allowed components of these transitions with polarisation	Factor of a_1 in the direct product of the basis vectors. This factor determines the relation between the components of a transition
	$\xi \xrightarrow{x} a_1$	$\xi\, x\, a_1 = \frac{1}{\sqrt{3}} a_1 + \ldots$
$T_2 \to A_1$	$\eta \xrightarrow{y} a_1$	$\eta\, y\, a_1 = \frac{1}{\sqrt{3}} a_1 + \ldots$
	$\zeta \xrightarrow{z} a_1$	$\zeta\, z\, a_1 = \frac{1}{\sqrt{3}} a_1 + \ldots$
	$\xi \xrightarrow{x} \theta$	$\xi\, x\, \theta = -\frac{1}{2\sqrt{3}} a_1 + \ldots$
	$\eta \xrightarrow{y} \theta$	$\eta\, y\, \theta = -\frac{1}{2\sqrt{3}} a_1 + \ldots$
$T_2 \to E$	$\zeta \xrightarrow{z} \theta$	$\zeta\, z\, \theta = \frac{1}{\sqrt{3}} a_1 + \ldots$
	$\xi \xrightarrow{x} \varepsilon$	$\xi\, x\, \varepsilon = \frac{1}{2} a_1 + \ldots$
	$\eta \xrightarrow{y} \varepsilon$	$\eta\, y\, \varepsilon = -\frac{1}{2} a_1 + \ldots$
	$\xi \xrightarrow{y} \gamma$	$\xi\, y\, \gamma = \frac{1}{\sqrt{6}} a_1 + \ldots$
	$\xi \xrightarrow{z} \beta$	$\xi\, z\, \beta = -\frac{1}{\sqrt{6}} a_1 + \ldots$
	$\eta \xrightarrow{x} \gamma$	$\eta\, x\, \gamma = -\frac{1}{\sqrt{6}} a_1 + \ldots$
$T_2 \to T_1$	$\eta \xrightarrow{z} \alpha$	$\eta\, z\, \alpha = \frac{1}{\sqrt{6}} a_1 + \ldots$
	$\zeta \xrightarrow{x} \beta$	$\zeta\, x\, \beta = \frac{1}{\sqrt{6}} a_1 + \ldots$
	$\zeta \xrightarrow{y} \alpha$	$\zeta\, y\, \alpha = -\frac{1}{\sqrt{6}} a_1 + \ldots$
	$\xi \xrightarrow{y} \zeta$	$\xi\, y\, \zeta = -\frac{1}{\sqrt{6}} a_1 + \ldots$
	$\xi \xrightarrow{z} \eta$	$\xi\, z\, \eta = -\frac{1}{\sqrt{6}} a_1 + \ldots$
	$\eta \xrightarrow{x} \zeta$	$\eta\, x\, \zeta = -\frac{1}{\sqrt{6}} a_1 + \ldots$
$aT_2 \to bT_2$	$\eta \xrightarrow{z} \xi$	$\eta\, z\, \xi = -\frac{1}{\sqrt{6}} a_1 + \ldots$
	$\zeta \xrightarrow{x} \eta$	$\zeta\, x\, \eta = -\frac{1}{\sqrt{6}} a_1 + \ldots$
	$\zeta \xrightarrow{y} \xi$	$\zeta\, y\, \xi = -\frac{1}{\sqrt{6}} a_1 + \ldots$

we obtain three types of integrals:

$$a: \langle \varphi_M \mid \boldsymbol{r} \mid \varphi'_M \rangle ,$$
$$b: \langle \varphi_M \mid \boldsymbol{r} \mid \chi_L \rangle ,$$
$$c: \langle \chi_L \mid \boldsymbol{r} \mid \chi'_L \rangle .$$

a: $\langle \varphi_M \mid \boldsymbol{r} \mid \varphi'_M \rangle$ is an integral of functions that belong to the same nucleus. With the assumed atomic orbitals, the radial part of which is given by a linear combination of Slater functions, an analytical form for these integrals is easily derived. Then a computer-program can be written.

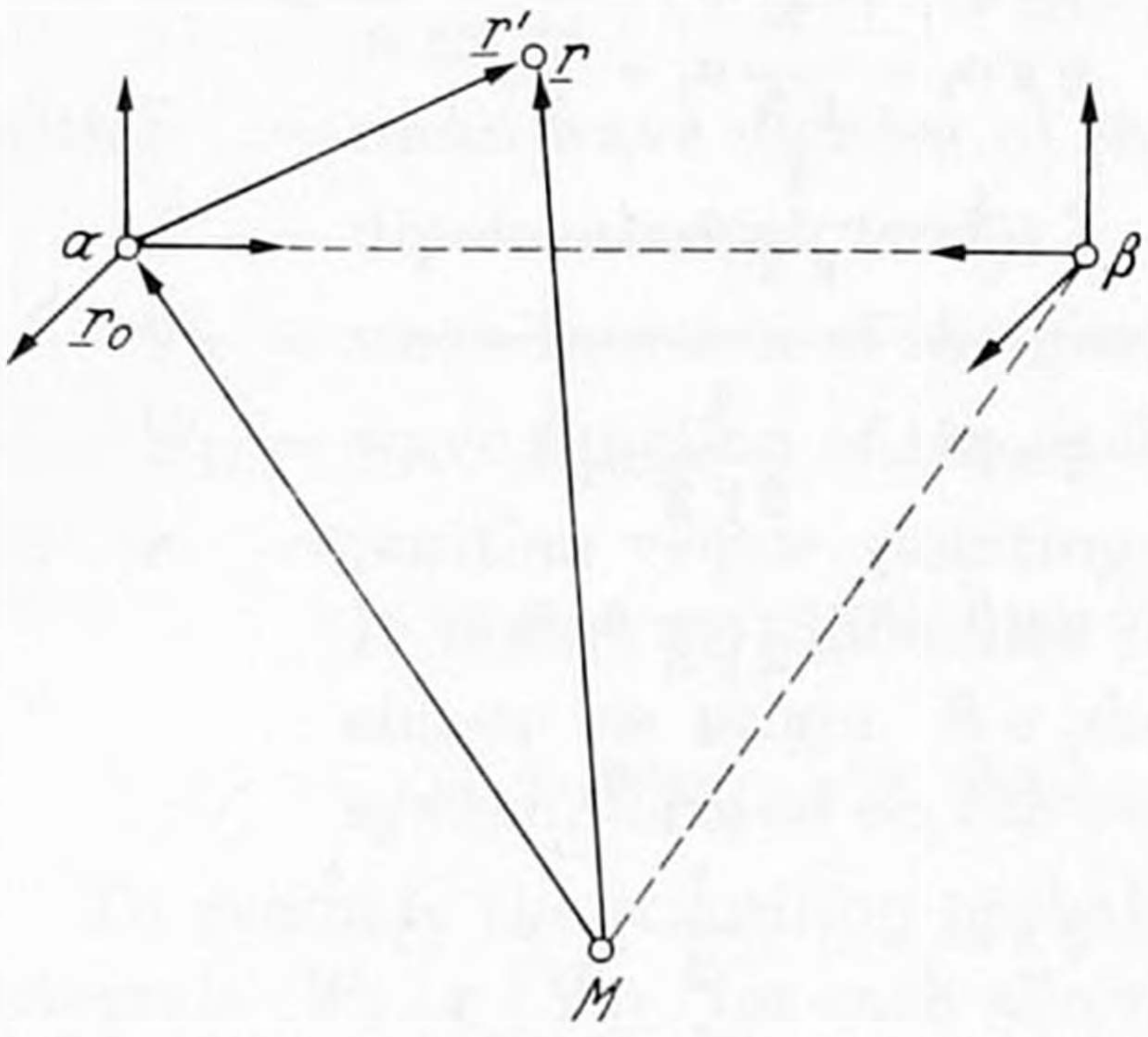

Fig. 1. Coordinate transformation to calculate the integrals $\langle \varphi_\alpha \mid \boldsymbol{r} \mid \varphi'_\beta \rangle$

b: $\langle \varphi_M \mid \boldsymbol{r} \mid \chi_L \rangle$ with $\chi_L = \sum_\alpha C_\alpha \varphi_\alpha$ summation over the ligands L_α. The substitution of χ_L yields: $\sum_\alpha C_\alpha \langle \varphi_M \mid \boldsymbol{r} \mid \varphi_\alpha \rangle$. Now we have integrals of functions that belong to two different nuclei, namely M and L_α. These integrals can be evaluated after a rotation of the main coordinate system and a corresponding transformation operating on φ_M and $\boldsymbol{r}$. By a method given by BALLHAUSEN [5] using elliptical coordinates [18] we can expand them in A_n and B_n integrals that can be computed.

c: $\langle \chi_L \mid \boldsymbol{r} \mid \chi'_L \rangle$ may be written as $\sum_\alpha \sum_\beta C_\alpha C'_\beta \langle \varphi_\alpha \mid \boldsymbol{r} \mid \varphi'_\beta \rangle$. Most of these integrals contain functions that belong to three different nuclei: M, L_α and L_β. We see in Fig. 1 that $\boldsymbol{r}$ can be written as $\boldsymbol{r} = \boldsymbol{r}_0 + \boldsymbol{r}'$, $\boldsymbol{r}'$ belonging to L_α or L_β. This gives:

$$\langle \varphi_\alpha \mid \boldsymbol{r} \mid \varphi'_\beta \rangle = \boldsymbol{r}_0 \langle \varphi_\alpha \mid \varphi'_\beta \rangle + \langle \varphi_\alpha \mid \boldsymbol{r}' \mid \varphi'_\beta \rangle .$$

After rotations of the coordinate systems on the ligands L_α and L_β we are able to calculate $\langle \varphi_\alpha \mid \varphi'_\beta \rangle$ and $\langle \varphi_\alpha \mid \boldsymbol{r}' \mid \varphi'_\beta \rangle$ by a similar method as used in b.

The computer used is the IBM 1620.

All integrals have been computed for different charge distributions and have been obtained as functions of the charge distribution (A, B, C and D, see M.O.

Table 2

Electron transition	$\nu_{max} \simeq \bar{\nu}$ (cm^{-1})	ε_{max} (l mol^{-1} cm^{-1})	Exp. f	Theor. f
crystal field	6,000	shoulder		
$2e \longrightarrow 4t_2$	8,500	122	0.0037	0.0075
first charge transfer				
$t_1 \longrightarrow 4t_2$	24,500	2400	0.040	0.080
second charge transfer				
$3t_2 \longrightarrow 4t_2$	34,000	5700	0.120	0.184
third charge transfer				
$1e \longrightarrow 4t_2$	41,000	$\simeq$ 1800	0.032	0.052
$2t_2 \longrightarrow 4t_2$				0.234
$2a_1 \longrightarrow 4t_2$				0.316

calculation) by means of interpolation formulas. Substitution of the numerical values of A, B, C, D and of the coefficients of the atomic orbitals as found for the ground state of tetrahedral $CuCl_4^{2-}$ produces the integrals $\langle \psi_I \mid \boldsymbol{r} \mid \psi_{II} \rangle$ and the oscillator strengths f. The results are given in Tab. 2. The assumed sequence of the bands is discussed later.

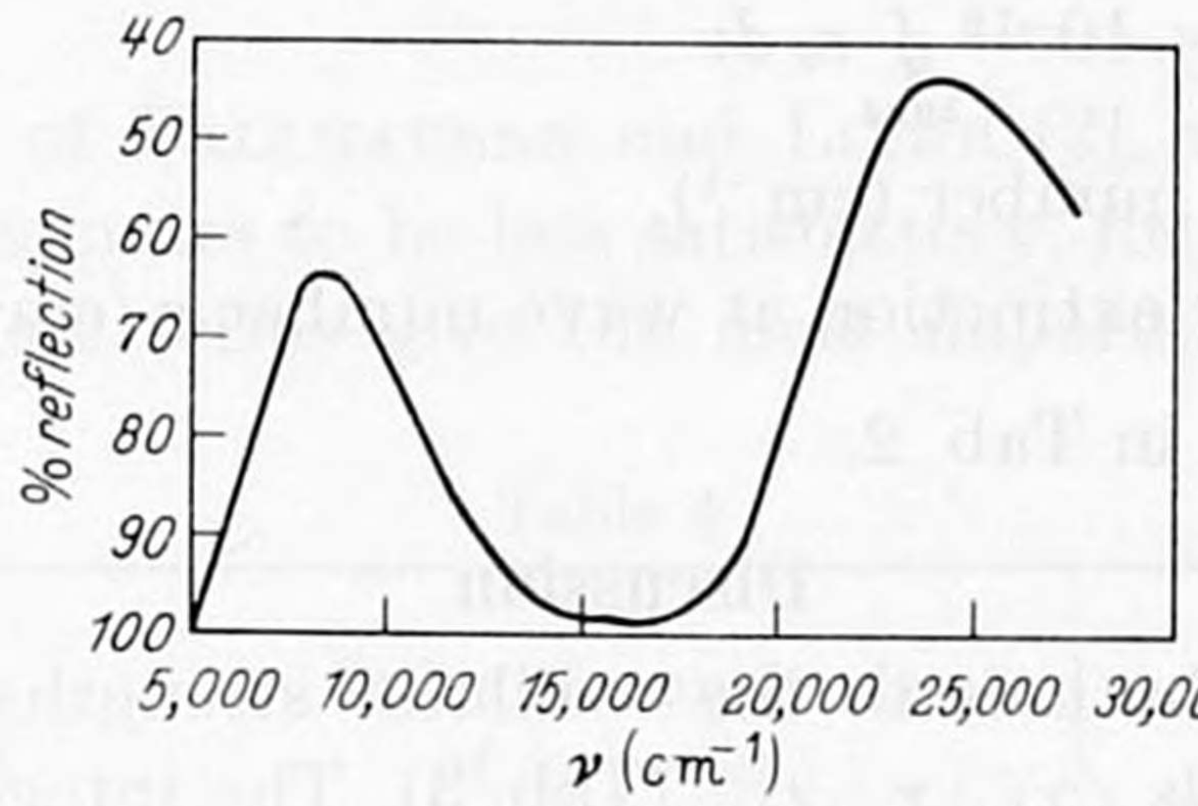

Fig. 2. Reflection spectrum of solid $CuCl_4^{2-}$, 1:200 diluted with KCl

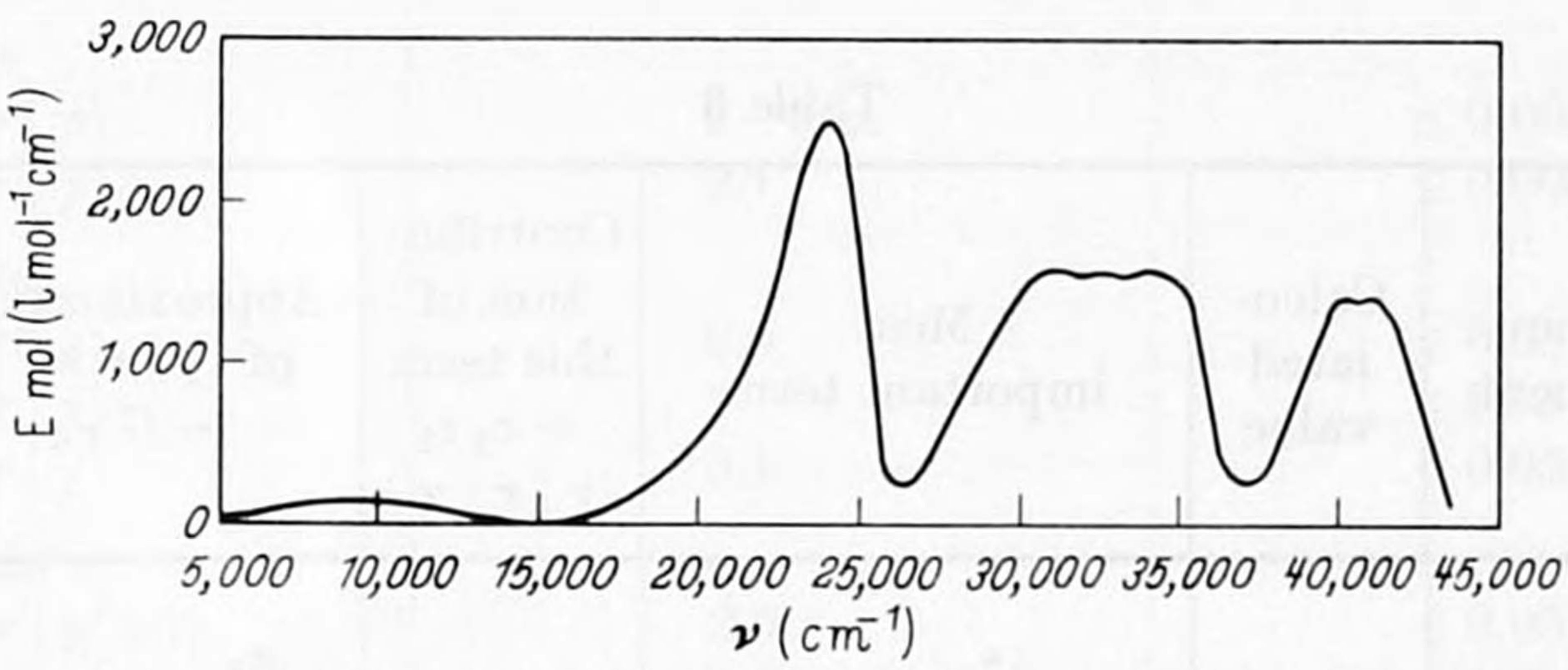

Fig. 3. Absorption spectrum of $CuCl_4^{2-}$ dissolved in KCl-discs. The part of the spectrum $\nu > 25{,}000$ cm^{-1} is disturbed by scattering of the UV radiation due to the opaqueness of the KCl discs. Measuring in KBr discs was impossible because of the Cl^--Br^- exchange

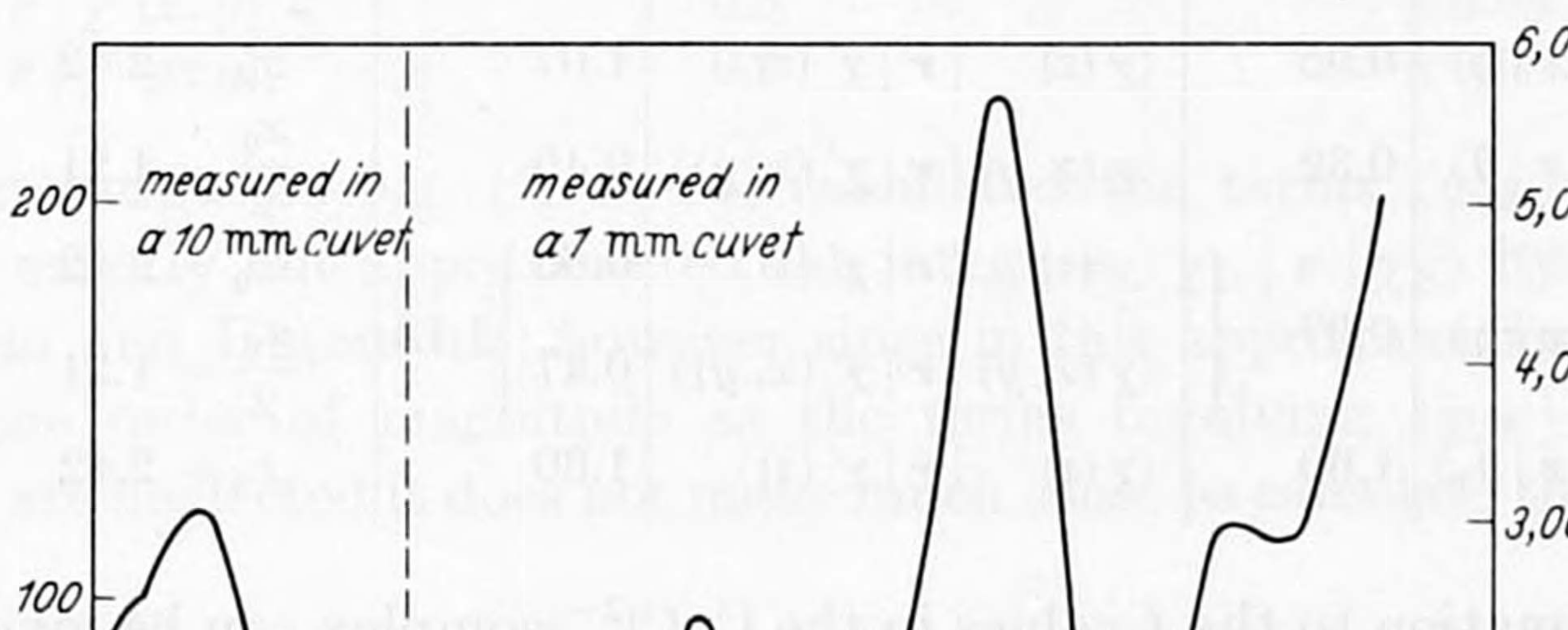

Fig. 4. Absorption spectrum of $CuCl_4^{2-}$ dissolved in acetonitril (conc. 0.001 mol/l, Cl^- conc. larger than 0.1 mol/ obtained by dissolving $(C_2H_5)_4NCl \cdot x\,H_2O$ and drying over $CaCl_2$ and P_2O_5)

2. *Experimental determination of f:* In agreement with the results obtained by several investigators [*6*, *10*, *11*, *16*] we found that it makes no difference to the spectrum of $CuCl_4^{2-}$ whether it is measured in solid state or in solution. The complex seems to have the same structure independent of the surroundings and

of the type of cation. Measuring in solution it is necessary to maintain a large Cl^--concentration to prevent the formation of complexes as $CuCl_{4-x}$ $Solvent_x$ [11]. A Zeiss spectrophotometer PM Q II with monochromator M 4 Q II was used. The obtained spectra are reproduced in Fig. 2, 3, and 4. From the spectrum of Fig. 4 the f-values of the bands have been determined with the formula

$$f = 4.32 \times 10^{-12} \int_{band} \varepsilon_\nu \, d\nu \qquad (3)$$

ν = wave number (cm^{-1}),

ε_ν = molar extinction at wave number ν ($cm^2\ mol^{-1}$).

The results are given in Tab. 2.

Discussion

1. The largest contributions to the oscillator strengths of all transitions are given by certain integrals $\langle \chi_L \mid \boldsymbol{r} \mid \chi_L' \rangle$ (Tab. 3). The integrals that do not occur in this table are at least a factor 10 smaller than the tabulated integrals. A fairly

Table 3

Transition	Component	Calculated value	Most important term	Contribution of this term $= c_2 c_2 \langle \chi \mid \boldsymbol{r} \mid \chi' \rangle$	Approximation of $\langle \chi \mid \boldsymbol{r} \mid \chi' \rangle = G \boldsymbol{r}_0$	Approximation $c_2 c_2' G \boldsymbol{r}_0$
$2e \to 4t_2$	$\langle \xi \mid x \mid \theta \rangle$	0.28 a.u.	$\langle \chi(x,y) \mid \boldsymbol{r} \mid \chi'(x,y) \rangle$	0.30 a.u.	$\frac{x_0}{2} = 1.21$ a.u.	0.29 a.u.
$t_1 \to 4t_2$	$\langle \zeta \mid x \mid \beta \rangle$	0.73	$\langle \chi(x,y) \mid \boldsymbol{r} \mid \chi'(x,y) \rangle$	0.80	$\frac{x_0\sqrt{3}}{2} = 2.10$	0.84
$3t_2 \to 4t_2$	$\langle \zeta \mid x \mid \eta \rangle$	0.95	$\langle \chi(z) \mid \boldsymbol{r} \mid \chi'(z) \rangle$	1.07	$x_0 = 2.42$	1.04
$1e \to 4t_2$	$\langle \xi \mid x \mid \theta \rangle$	0.32	$\langle \chi(x,y) \mid \boldsymbol{r} \mid \chi'(x,y) \rangle$	0.40	$\frac{x_0}{2} = 1.21$	0.39
$2t_2 \to 4t_2$	$\langle \zeta \mid x \mid \eta \rangle$	0.97	$\langle \chi(z) \mid \boldsymbol{r} \mid \chi'(z) \rangle$	0.66 } 1.13	$x_0 = 2.42$	0.63 } 1.07
			$\langle \chi(x,y) \mid \boldsymbol{r} \mid \chi'(x,y) \rangle$	0.47	$\frac{x_0}{2} = 1.21$	0.44
$2a_1 \to 4t_2$	$\langle \xi \mid x \mid a_1 \rangle$	1.60	$\langle \chi(z) \mid \boldsymbol{r} \mid \chi'(z) \rangle$	1.60	$x_0 = 2.42$	1.64

good approximation to the f-values in the $CuCl_4^{2-}$-complex can be given by taking only these $\langle \chi(z) \mid \boldsymbol{r} \mid \chi'(z) \rangle$ and $\langle \chi(x,y) \mid \boldsymbol{r} \mid \chi'(x,y) \rangle$ integrals into account. This is so because in the molecular orbitals used the coefficients of the Cu 4s- and 4p-functions and of the Cl χ (3s)-functions are small (see Tab. 4). The $\langle \chi(z) \mid \boldsymbol{r} \mid \chi'(z) \rangle$ and $\langle \chi(x,y) \mid \boldsymbol{r} \mid \chi'(x,y) \rangle$ integrals can in their turn be approximated by $G \boldsymbol{r}_0$.

$\boldsymbol{r}_0 = x_0, y_0$ or $z_0 = \frac{R_{\text{Cu-Cl}}}{\sqrt{3}}$, the projection of the Cu-Cl distance on an axis of the main coordinate system.

G is a factor 1, $\frac{1}{2}$ or $\frac{1}{2}\sqrt{3}$ depending on the coefficients C_α in

$$\chi_L = \sum_\alpha C_\alpha \varphi_\alpha .$$

The last approximation implies in fact neglecting the overlap between the different ligands.

In this way it is possible to calculate the *f*-values in a fairly good approximation, using only the M.O. coefficients of the ligand orbitals and the distance between the central ion and the ligands (see Tab. 3). This approximation was already used by WOLFSBERG and HELMHOLZ [*20*]. For the $CuCl_4^{2-}$-complex it appears to be a good one. For other complexes it may also be good when certain conditions are fulfilled.

The approximation of BALLHAUSEN and LIEHR [*2*], who neglected all terms involving $\langle \chi_L \mid \boldsymbol{r} \mid \chi_L' \rangle$ appears to be less satisfactory, for from the exact calculation it follows that these terms give the most important contributions to the transition probabilities.

Table 4

Type of integral $\langle \varphi \mid \boldsymbol{r} \mid \varphi' \rangle$	Order of magnitude of $\langle \varphi \mid \boldsymbol{r} \mid \varphi' \rangle$	Order of magnitude of $c\,c'\,\langle \varphi \mid \boldsymbol{r} \mid \varphi' \rangle$ (c, c' are M.O. coefficients)
copper – copper		
$\langle s \mid \boldsymbol{r} \mid p \rangle$	2 a.u.	≤ 0.005 a.u.
$\langle d \mid \boldsymbol{r} \mid p \rangle$	0.1	≤ 0.005
copper – ligands		
$\langle s \mid \boldsymbol{r} \mid \chi \rangle$	0.5	≤ 0.05
$\langle p \mid \boldsymbol{r} \mid \chi \rangle$	1	≤ 0.05
$\langle d \mid \boldsymbol{r} \mid \chi \rangle$	0.1	≤ 0.05
ligands – ligands		
$\langle \chi(s) \mid \boldsymbol{r} \mid \chi'(s) \rangle$	2.5	≤ 0.05
$\langle \chi(z) \mid \boldsymbol{r} \mid \chi'(z) \rangle$	2.5	≤ 1.5
$\langle \chi(x,y) \mid \boldsymbol{r} \mid \chi'(x,y) \rangle$	1.5	≤ 1.0
$\langle \chi(s) \mid \boldsymbol{r} \mid \chi'(z) \rangle$	0.5	≤ 0.05
$\langle \chi(s) \mid \boldsymbol{r} \mid \chi'(x,y) \rangle$	0.5	≤ 0.05
$\langle \chi(z) \mid \boldsymbol{r} \mid \chi'(x,y) \rangle$	0.1	≤ 0.05

Several investigators e.g. [*7*, *9*, *15*] calculated the terms $\langle \varphi_M \mid \boldsymbol{r} \mid \varphi_M' \rangle$ and $\langle \varphi_M \mid \boldsymbol{r} \mid \chi_L \rangle$ exactly but approximated the integrals $\langle \chi_L \mid \boldsymbol{r} \mid \chi_L' \rangle$ by the method of WOLFSBERG and HELMHOLZ; however since in this approximation terms that have the same order of magnitude as the terms involving $\langle \varphi_M \mid \boldsymbol{r} \mid \varphi_M' \rangle$ and $\langle \varphi_M \mid \boldsymbol{r} \mid \chi_L \rangle$ are neglected it does not make much sense to calculate these integrals exactly.

2. To obtain the positions of the optical bands we must take the difference between the total energies of the excited and ground states. In the M.O. description we saw, however, that it is too difficult to calculate the total energies from the one electron energies and the electron repulsions. Therefore the best we can do is to estimate the positions of the absorption bands from the one electron energies of the ground state. A qualitative scheme for this is given in Fig. 5 for the tetrahedral (T_d) and for the real, distorted tetrahedral, (D_{2d}) form of the $CuCl_4^{2-}$-complex. The distortion causes a splitting of the degenerate energy levels:

$$\begin{array}{lcl} T_d & & D_{2d} \\ A_1 & \longrightarrow & A_1 \\ E & \longrightarrow & A_1 + B_2 \\ T_1 & \longrightarrow & E + A_2 \\ T_2 & \longrightarrow & E + B_2 . \end{array}$$

In T_d-symmetry the ground state has a symmetry T_2, in D_{2d} a symmetry B_2. The allowed transitions are (see Tab. 1):

T_d		D_{2d}
$T_2 \longrightarrow A_1$	corresponding to	$B_2 \longrightarrow aA_1$
$T_2 \longrightarrow E$	,, ,,	$B_2 \longrightarrow bA_1$
$T_2 \longrightarrow T_1$	,, ,,	$B_2 \longrightarrow aE$
$aT_2 \longrightarrow bT_2$	,, ,,	$B_2 \longrightarrow bE$

(The prefixes a and b are added to distinguish states with the same symmetry.)

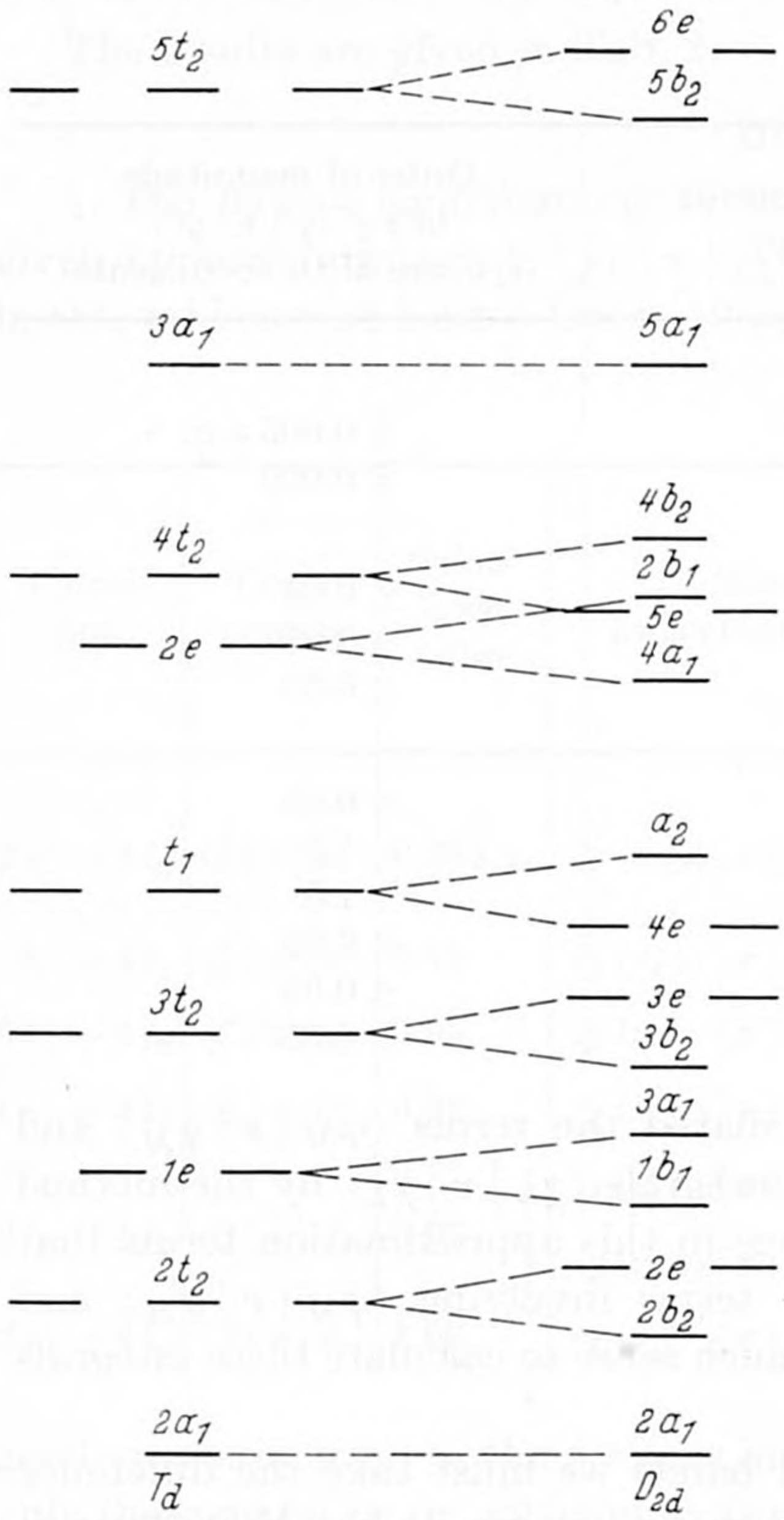

Fig. 5. Qualitative scheme of the one electron energies

The observed bands in the spectrum are:

a) The crystal field band that has a maximum extinction at 8,500 cm^{-1} and a small shoulder at 6,000 cm^{-1}.

In T_d symmetry the only crystal field transition is $T_2 \longrightarrow E$; in terms of one electron transitions: $2e \longrightarrow 4t_2$.

In D_{2d} three crystal field transitions are possible:

$$B_2 \longrightarrow E \quad \text{or} \quad 5\,e \longrightarrow 4\,b_2$$
$$B_2 \longrightarrow A_1 \quad \text{or} \quad 4\,a_1 \longrightarrow 4\,b_2$$
$$B_2 \longrightarrow B_1 \quad \text{or} \quad 2\,b_1 \longrightarrow 4\,b_2$$

of which the last one is symmetry-forbidden.

The transition $4\,a_1 \longrightarrow 4\,b_2$ corresponds to the large band. The shoulder is caused by the transition $5\,e \longrightarrow 4\,b_2$ ($5\,e$ and $4\,b_2$ are the states resulting from the split $4\,t_2$ state) or by the forbidden transition $2\,b_1 \longrightarrow 4\,b_2$.

b) Three charge transfer bands with maxima at 24,500, 34,000 and 41,000 cm^{-1}. We cannot predict the positions of these bands quantitatively from the one electron energies, we can only say something about the sequence in which they appear. So we expect the first charge transfer band to be caused by the transition:

	in T_d	in D_{2d}
	$t_1 \longrightarrow 4\,t_2$	$4\,e \longrightarrow 4\,b_2$
	in T_d	in D_{2d}
the second by:	$3\,t_2 \longrightarrow 4\,t_2$	$3\,e \longrightarrow 4\,b_2$
and the third by:	in T_d	in D_{2d}
	$1\,e \longrightarrow 4\,t_2$	$3\,a_1 \longrightarrow 4\,b_2$
or by:	$2\,t_2 \longrightarrow 4\,t_2$	$2\,e \longrightarrow 4\,b_2$
or less likely by:	$2\,a_1 \longrightarrow 4\,t_2$	$2\,a_1 \longrightarrow 4\,b_2$.

This sequence of the absorption bands is affirmed by the comparison of the calculated oscillator strengths with the observed values (see Tab. 2). The third charge transfer band can now be ascribed to the transition $1\,e \longrightarrow 4\,t_2$ since the other two possibilities require much higher f-values.

Conclusions

1. For all transitions the calculated f-values are about a factor 2 too high with respect to the experimental values. This may partly be ascribed to the fact that eq. (3) is only valid for ideal gases, whereas our absorption spectrum has been measured in solution.

2. The agreement of the calculated and observed relative f-values is still better.

3. The above agreement is good enough to distinguish different transitions from their f-values.

4. The transition probabilities, also that of the crystal field transition, are mainly determined by the amount of mixing of the ligand functions in the molecular orbitals. The mixing of the copper $4p$-function affects the intensities of the bands hardly at all.

5. The agreement of the calculated f-values with the observed values is still better if one assumes that the mixing of the ligand functions in the molecular orbitals is somewhat less.

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