JOURNAL OF SOLID STATE CHEMISTRY 44, 343–353 (1982)

# Crystal Field Theory and EPR Parameters in $D_{2d}$ and $C_{2v}$ Distorted Tetrahedral Copper(II) Complexes

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Received November 12, 1981; in revised form May 25, 1982

Calculations of the orbital energy vs tetrahedral ($D_{2d}$ and $C_{2v}$) distortion parameters are reported for copper complexes on the assumption of constant metal–ligand distance. The possible ground states of the complexes are considered and the respective spin Hamiltonian parameters vs distortion parameters dependences are calculated. Comparison with experiment led to good agreement: the relation between the orbital splittings and dihedral distortion angle is found to be linear for symmetry $C_{2v}$ in a wide range of distortion of the regular tetrahedron, and distortion of the $D_{2d}$ crystal field has a compensatory effect lowering the hfs splitting from $4p$-orbital admixture into the ground-state wavefunction.

## 1. Introduction

Tetrahedral coordination of the copper (II) ion is less common than octahedral coordination; moreover, in four-coordinated Cu(II) complexes, square–planar geometry is favored. In spite of this, tetrahedral copper(II) biocomplexes (e.g., $CuN_2S_2$ in blue proteins (*1*)) play an important role in the biological activity of proteins (*2, 3*).

The existing EPR data for Cu(II) ions in tetrahedral coordination point to characteristic differences between the parameters of these spectra and those of copper(II) ions in octahedral and square–planar coordination. The differences are due to the circumstance that the crystalline field splitting in tetrahedral symmetry is usually smaller and has the opposite sign (i.e., the ground-state wavefunction differs) and, moreover, a hybridization of the $3d$ and $4p$ wavefunctions appears.

The regular $T_d$ stereochemistry of the copper(II) complexes is not stable because of the Jahn–Teller effects in triplet state (*4*). Hence, one predominantly deals with pseudotetrahedral complexes, variously distorted with respect to the regular $T_d$ stereochemistry. In the limit, an increase in this distortion leads to planar geometry of the copper complexes (i.e., square–planar $D_{4h}$, rectangular $C_{2v}$, or planar–trigonal $D_{3h}$). Various pseudotetrahedral geometries of copper complexes are shown in Fig. 1.

Trigonal distortion of the four-coordinated Cu(II) complexes is very rare and appears in $ZnO:Cu^{2+}$ (*5*) and is suggested for copper(II) complexes in zeolites (*6*). We shall refrain here from considering this kind of distortion.

Other, more common types of distortion of the tetrahedron consist in tetragonal $D_{2d}$ and rhombic $C_{2v}$ distortion of the complex. Most often, the regular four-coordinated complexes are weakly distorted to slightly flattened tetrahedra or tetrahedrally deformed square–planar geometry. It is very interesting that in deformed tetrahedral

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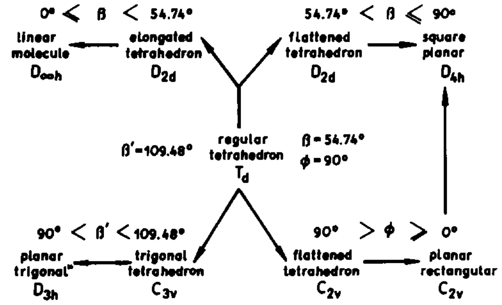

FIG. 1. Symmetry of distorted tetrahedral stereochemistry. Angular distortion parameters $\beta$, $\beta'$, $\phi$ are defined in Fig. 2. (Asterisk indicates that form cannot really exist.)

complexes of the Cu(II) ion, contrary to tetragonal deformation octahedral complexes, each of the $3d$ wavefunctions of the copper ion can be a ground-state wavefunction depending on the symmetry and degree of deformation of the complex. Moreover, a mixing of $d$–$d$ and $d$–$p$ wavefunctions in low-symmetry pseudotetrahedral complexes considerably affects the EPR parameters.

In this paper, we report and discuss crystal field theoretical results for the tetragonally deformed tetrahedron in one-electron formalism of the Cu(II) ion. The deformation of the complex is assumed to occur with the Cu–ligand distance remaining constant. Moreover, we give the accompanying changes in EPR parameters in the crystal field approximation. We omit the additive term representing the destabilization energy $E_0 = 4F_0(R)$ originating in metal–ligand repulsion.

## 2. Crystal Field Theory of Pseudotetrahedral Copper(II) Complexes

In regular $T_d$ symmetry the $^2D$ term of the copper(II) ion splits into a low-lying doublet ($E$) and a high-lying triplet ($T_2$) with splitting equal to

$$\Delta_T = 20qF_4(R)/27, \qquad (1)$$

where $\Delta_T$ is the tetrahedral cubic splitting and $q$ the effective charge of the ligand (in units of elementary charge) distant by $R$ from the central ion, whereas $F_4(R)$ is the fourth-order radial integral of the crystal field (*7*). In a first approximation, on the assumption of small radial extension of the unpaired electron wavefunction, we have

$$F_4(R) = \langle r^4 \rangle / R^5 \qquad (2)$$

with $\langle r^4 \rangle$ the mean-fourth-power radii of the $3d$ orbital. Putting $\langle r^4 \rangle = 0.19555$ Å$^4$ (*8*), we obtain

$$\Delta_T = 16855.488q/R^5, \qquad (3)$$

where $\Delta_T$ is in centimeters$^{-1}$ and $R$ in angstroms. For the typical values $R = 2$ Å and $\Delta_T \approx 3000$ cm$^{-1}$ we get $q \approx 5.7e$. This value of the ligand effective charge leads to good agreement between our calculations and experiment, and we shall apply it henceforth.

It should be stressed that, when deriving Eq. (3), we assumed the radial integral $F_4$ in the form (2). Strict calculations of $F_4$ applying Ballhausen's "master formula" (*9, 10*) show that $F_4$ from Eq. (2) is underestimated and that, consequently, the value of $q$ in Eq. (3) is slightly overestimated.

### 2.1. $D_{2d}$ Symmetry

The tetragonally $D_{2d}$ distorted four-coordinated complex is presented in Fig. 2a. The perturbation parameter is given by the angle $\beta$ between the $z$ axis of the complex and the Cu–ligand vector. According to the deformation angle, we have a regular tetrahedron ($\beta_T = 54.74°$), an elongated tetrahedron ($\beta < \beta_T$), a flattened tetrahedron ($\beta > \beta_T$), or a square–planar complex for $\beta = 90°$. The $x,y,z$ coordinate system is chosen as for tetrahedral symmetry and, for correlation with the square–planar limit, it should be $\pi/4$ rotated about the $z$ axis when $\beta = 90°$. The matrix elements of the crystal field perturbation in $D_{2d}$ symmetry are

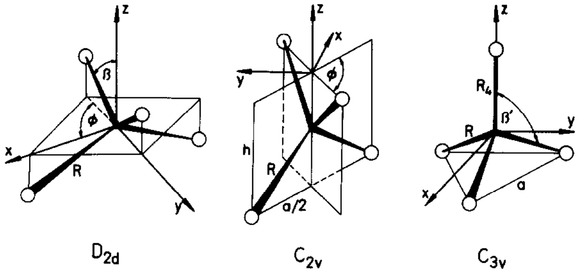

FIG. 2. Tetragonal ($D_{2d}$), rhombic ($C_{2v}$), and trigonal ($C_{3v}$) distortions of a tetrahedron. In $T_d$ symmetry $\beta = 54.74°$, $\beta' = 109.48°$, $\phi = 90°$, $h = 0.707$ a, $R = 0.612$ a.

$$
\begin{aligned}
V_{00} &= eq(4F_2 \cdot A/7 + F_4 \cdot B/7),\\
V_{11} &= V_{-1-1}\\
&= eq(2F_2 \cdot A/7 - 2F_4 \cdot B/21),\\
V_{22} &= V_{-2-2}\\
&= eq(-4F_2 \cdot A/7 + F_4 \cdot B/42),\\
V_{2-2} &= V_{-22} = 5eqF_4 \sin^4\beta/6,
\end{aligned}
\tag{4}
$$

where

$$
\begin{aligned}
A &= 3\cos^2\beta - 1\\
B &= 35\cos^4\beta - 30\cos^2\beta + 3.
\end{aligned}
$$

The other elements of this 5 × 5 matrix vanish. The preceding formulae involve, in addition to $F_4$, the dependence on the second-order radial integral $F_2$. Like $F_4$, the radial function $F_2$ can be approximated by the relation

$$F_2 = \langle r^2 \rangle / R^3, \tag{5}$$

where the mean-second-power radii of the $3d$ orbital is $\langle r^2 \rangle = 0.28786$ Å$^2$ for the copper(II) ion (*8*). The solution of the secular equation reduces to solving an equation of the 2nd degree, and gives, for the energies of the $3d$ orbitals,

$$
\begin{aligned}
\epsilon(z^2) &= 2Ds(3\cos^2\beta - 1)\\
&\quad + \tfrac{27}{140}\Delta_T(35\cos^4\beta\\
&\qquad - 30\cos^2\beta + 3),\\
\epsilon(xy) &= -2Ds(3\cos^2\beta - 1)\\
&\quad + \tfrac{9}{140}\Delta_T(35\cos^4\beta\\
&\qquad - 50\cos^2\beta + 19),
\end{aligned}
\tag{6}
$$

$$
\begin{aligned}
\epsilon(x^2 - y^2) &= -2Ds(3\cos^2\beta - 1)\\
&\quad + \tfrac{9}{35}\Delta_T(5\cos^2\beta - 4),\\
\epsilon(xz,yz) &= Ds(3\cos^2\beta - 1)\\
&\quad - \tfrac{9}{70}\Delta_T(35\cos^4\beta\\
&\qquad - 30\cos^2\beta + 3),
\end{aligned}
$$

where

$$Ds = 2qF_2/7 = 9539.055\ q/R^3 \tag{7}$$

and $Ds$ is in centimeters$^{-1}$ if $R$ is given in angstroms. $Ds$ is a tetragonal crystal field parameter and is related with the tetrahedral cubic splitting parameters $\Delta_T$:

$$Ds(\text{cm}^{-1}) = 0.565932\ R^2\Delta_T. \tag{8}$$

For all known Cu–ligand separations $R$, in tetrahedral complexes, $Ds$ exceeds $\Delta_T$. The parameters $Ds$ and $\Delta_T$ are plotted in Fig. 3 as functions of the Cu–ligand separation.

The energy levels are plotted vs the distortion angle $\beta$ in Fig. 4a for $R = 2.1$ Å and $q = 5e$. Figure 4 shows that in the compressed tetrahedron $d_{xy}$ is the ground state if $\beta = 54.74$–90°. When the tetrahedron undergoes elongation ($\beta = 0° \div 45°$), the ground-state wavefunction is $d_{z^2}$, and splitting is greater than in the flattened tetrahedron. From $\beta = 45$ to 54.74° the ground state is twice degenerate, with the wavefunction $d_{xz,yz}$. This degeneracy is removed by spin–orbit coupling.

The orbital splitting with respect to the ground state is shown in Fig. 4b for the above-considered cases. Here, the smallest

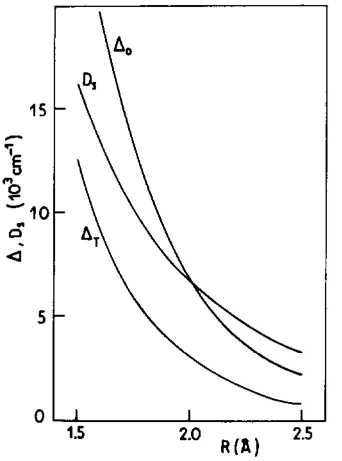

FIG. 3. Influence of the Cu–ligand distance $R$ on the crystal field parameters $\Delta_T$ (cubic splitting in $T_d$ symmetry), $\Delta_0$ (cubic splitting in $O_h$ symmetry), and $Ds$ (tetragonal field parameter in $D_{2d}$ tetrahedral field). Effective charge of a ligand is assumed as $q = 5.7e$.

angle $\beta$ amounts to 30° since no greater elongation of the tetrahedron should be expected to occur because of the steeply increasing ligand–ligand repulsion. In the limit, flattening of the tetrahedron leads to square-planar coordination ($\beta = 90°$), for which the ground state takes the form $d_{x^2-y^2}$ (on rotation of the coordinate system $x,y,z$ by 45°). It is characteristic for this coordination, resulting from Eqs. (6), that the orbital splittings referred to the ground state fulfill the equation

$$3E_{z^2} + 2E_{xy} = 4E_{xz,yz} \tag{9}$$

Most commonly a tetragonally flattened tetrahedron occurs, such as $CuN_2S_2$ with $\beta \approx 60°$ in blue proteins (*1*), $CuN_4$ with $\beta \approx 60°$ in the series of pyrrole-2-carboxaldehyde Schiff base Cu(II) complexes (*11*), and $CuN_4$ with $\beta \approx 70°$ in the series of bis (salicylaldiminato) Cu(II) complexes (*12*). A tetragonally elongated tetrahedron with the ground state $d_{z^2}$ has been proved by EPR to exist in $CaWO_4{:}Cu^{2+}$ (*13*).

A similar analysis of the $d$-orbital energies of $CuCl_4^{2-}$ tetrahedron subject to $D_{2d}$ deformation has been performed by Smith (*24*) assuming the covalency of $\sigma$ and $\pi$ bonding.

### 2.2 $C_{2v}$ Symmetry

The $C_{2v}$-rhombic distorted tetrahedral complex is shown in Fig. 2b. The distortion parameter is given by the angle $\phi$. For $\phi = 90°$, we have the structure of a regular tetrahedron, whereas at $\phi = 0°$ we deal with rectangular-planar geometry. The coordinate system $x,y,z$ is chosen so that the axes $x$ and $y$ shall halve the dihedral angles. The perturbation matrix elements now are

$$\begin{aligned}
V_{00} &= -4eqF_4/9,\\
V_{11} &= V_{-1-1} = 8eqF_4/27,\\
V_{22} &= V_{-2-2} = -2eqF_4/27,\\
V_{1-1} &= V_{-11} = eq(-80F_4\cos\phi/189\\
&\qquad -4F_2\cos\phi/7),\\
V_{2-2} &= V_{-22} = -10eqF_4\cos2\phi/27.
\end{aligned} \tag{10}$$

The other matrix elements vanish and solution of the secular equation, in this case, provides the energies of the orbital levels:

$$\epsilon(z^2) = -3\Delta_T/5,$$

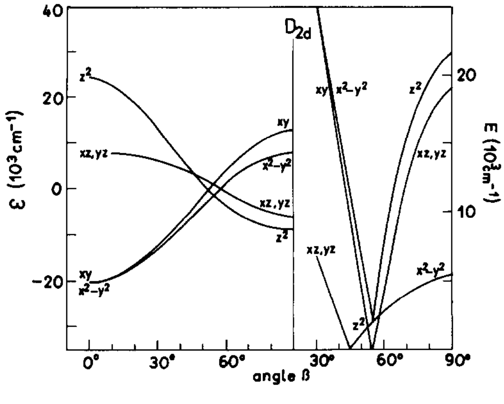

FIG. 4. Influence of the $D_{2d}$ tetragonal distortion of a tetrahedron on $3d$-orbital energies $\epsilon$ and $d$–$d$ transition energies $E$. The angle $\beta$ is defined in Fig. 2. The ground-state wavefunction is $d_{z^2}$ ($A_1$) in the range $\beta$ = 0–45°, $d_{xz,yz}$ ($E$) in the range $\beta$ = 45–54.74°, and $d_{xy}$ ($B_2$) in the range $\beta$ = 54.74–90°. The Cu–ligand separation $R$ = 2.1 Å and $q = 5e$ are assumed.

$$
\begin{aligned}
\epsilon(xy) &= -\Delta_T(1 + 5\cos 2\phi)/10, \\
\epsilon(x^2 - y^2) &= -\Delta_T(1 - 5\cos 2\phi)/10, \\
\epsilon(yz) &= 2\Delta_T(1 - 10\cos\phi/7)/5 \\
&\qquad -2Ds\cos\phi, \\
\epsilon(xz) &= 2\Delta_T(1 + 10\cos\phi/7)/5 \\
&\qquad + 2Ds\cos\phi,
\end{aligned}
\tag{11}
$$

where $Ds$ and $\Delta_T$ have the same meaning as before. The ground state of the electron $3d^9$ in the $C_{2v}$ perturbated tetrahedron is $d_{xz}$ (Fig. 5). The energy levels are plotted vs the dihedral angle $\phi$ in Fig. 5a, whereas splitting with regard to the ground state is shown in Fig. 5b. In the rectangular-planar limit ($\phi = 0°$) of $C_{2v}$ deformation, the coordination system $x,y,z$ of Fig. 2a is no longer appropriate. In order to achieve good correlation with the square-planar limit, we rotate the coordinate system $x,y,z$ by $\pi/2$ about $x$. We now obtain sequences of orbitals as in the case of square-planar coordination with degenerate orbital level $d_{xz,yz}$. A different degeneracy of the orbitals is found for $\phi = 45°$. Here, the orbitals $d_{xy}$ and $d_{x^2-y^2}$ are degenerate, as for the cubic field. This is so because for $\phi = 45°$ two ligand planes (see Fig. 2a) lie exactly between the lobes of the $d_{x^2-y^2}$ and $d_{xy}$ orbitals. As the angle $\phi$ decreases from the tetrahedral limit to the planar limit, than at $\phi = 45°$ the $|xy\rangle$ wavefunction goes over into $|x^2 - y^2\rangle$ and vice versa.

A discussion concerning the possible ground state in $C_{2v}$ symmetry based on polarized single-crystal electronic spectra of $CuN_4$ complex in Cu(bipyam)$_2$ $(ClO_4)_2$ has already been given in Ref. (*14*). It thus can be presumed that for $\phi > 45°$ we have a $C_{2v}$ distorted, flattened tetrahedron, whereas for $\phi < 45°$ we have tetrahedrally distorted rectangular-planar geometry. It is noteworthy that for the $C_{2v}$ flattened tetrahedron, the orbital splittings referred to the ground-state increase linearly as the dihedral angle decreases. This correlation between the splittings and $\phi$ has been found experimentally as the result of optical spectroscopy studies (*15*). Within the series of pseudotetrahedral $C_{2v}$ copper(II) complexes of 2,2'-dipyridylamine (HDPA) with dihedral angle in the range 55–57°, the $CuN_4$ tetrahedron (*16, 23*) exhibits direct proportionality between the increase in en-

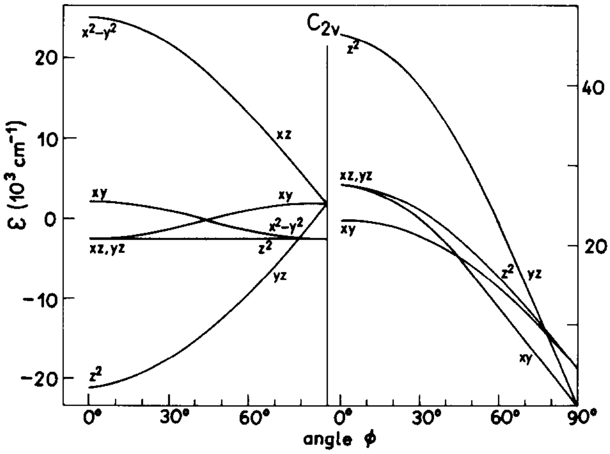

FIG. 5. Influence of the $C_{2v}$ rhombic distortion of a tetrahedron on $3d$-orbital energies and $d$–$d$ transition energies $E$. The dihedral angle $\phi$ is defined in Fig. 2. The ground-state wavefunction is $d_{x^2-y^2}$ $(A_1)$ for small $\phi$ values and $d_{xz}$ $(B_1)$ for large $\phi$ values. The Cu–ligand distance $R = 2.1$ Å and $q = 10e$ are assumed.

TABLE I

THE GROUND-STATES IN TETRAHEDRAL AND PSEUDOTETRAHEDRAL COPPER(II) COMPLEXES (DISTORTION PARAMETERS ARE DEFINED IN FIG. 2)

| | | Ground state | |
|---|---|---|---|
| Symmetry | Distortion parameter value | Symmetry | 3*d* wavefunction |
| $T_d$ | $\beta = 54.74°, \beta' = 109.48°, \phi = 90°$ | $T_2$ | $xy, xz, yz$ |
| $D_{2d}$ | $0 \leq \beta \leq 45°$ | $A_1$ | $z^2$ |
| | $45° < \beta < 54.74°$ | $E$ | $xz, yz$ |
| | $54.74 < \beta \leq 90°$ | $B_2$ | $xy$ |
| $D_{4h}$ | $\beta = 90°$ | $B_1$ | $x^2 - y^2$ |
| $C_{2v}$ | $0 \leq \phi < 45°$ | $A_1$ | $x^2 - y^2$ |
| | $45° < \phi \leq 90°$ | $B_1$ | $xz$ |
| $C_{3v}$ | $90° < \beta' < 109.48°$ | $E'$ | $xz, yz$ |

ergy of the optical transitions (optical band energy) and the decrease in dihedral angle. The same relationship is suggested from studies of halocuprates(II) with dihedral angle in the range of 50° in the $CuCl_4$ pseudotetrahedra (*17*).

Hence, according to the kind and magnitude of deformation of the tetrahedron, the ion Cu(II) exhibits different ground states. The latter are listed in Table I.

## 3. EPR of Pseudotetrahedral Copper(II) Complexes

EPR parameters are affected by various factors, in particular by the ground-state wavefunction.

### *3.1. Ground State $d_{xy}$ ($B_2$)*

The ground-state $d_{xy}$ occurs in $D_{2d}$ flattened tetrahedral Cu(II) complex; the EPR spectrum now possesses the axial symmetry. To this ground state of symmetry $B_2$, the crystal field can admixture the state $4p_z$ of the same symmetry (see Table II). The latter admixture can attain as much as 30% (*18*). Similar effects of hybridization occur for the states $d_{xz}$, $d_{yz}$, and $4p_x$, $4p_y$. Accordingly, the wavefunctions now are

$$
\begin{aligned}
\psi(B_2) &= \alpha d_{xy} + \eta p_z, \\
\psi(B_1) &= d_{x^2-y^2}, \\
\psi(E) &= \gamma d_{xz,yz} + \zeta p_{x,y}, \\
\psi(A_1) &= \delta d_{z^2} + \delta_1 s.
\end{aligned}
\qquad (12)
$$

Hence, neglecting small terms (second-order in $\eta$ and $\zeta$), the spin Hamiltonian parameters become

TABLE II

SYMMETRY OF ORBITALS IN TETRAHEDRAL AND PSEUDOTETRAHEDRAL GEOMETRIES

| | Orbitals | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Symmetry | $z^2$ | $x^2 - y^2$ | $xy$ | $xz$ | $yz$ | $p_z$ | $p_y$ | $p_x$ | $s$ |
| $T_d$ | $E$ | $E$ | $T_2$ | $T_2$ | $T_2$ | $T_2$ | $T_2$ | $T_2$ | $A_1$ |
| $D_{2d}$ | $A_1$ | $B_1$ | $B_2$ | $E$ | $E$ | $B_2$ | $E$ | $E$ | $A_1$ |
| $D_{4h}$ | $A_{1g}$ | $B_{1g}$ | $B_{2g}$ | $E_g$ | $E_g$ | $A_{2u}$ | $E_u$ | $E_u$ | $A_{1g}$ |
| $C_{2v}$ | $A_1$ | $A_1$ | $A_2$ | $B_1$ | $B_2$ | $A_1$ | $B_2$ | $B_1$ | $A_1$ |
| $C_{3v}$ | $A_1$ | $E$ | $E$ | $E$ | $E$ | $A_1$ | $E$ | $E$ | $A_1$ |

$$\begin{aligned} g_{\parallel} &= 2.0023 - 8\alpha^2\lambda_d/E_{x^2-y^2}, \\ g_{\perp} &= 2.0023 - 2(\alpha^2\gamma^2\lambda_d \\ &\qquad -\alpha\gamma\zeta^2\lambda_p)/E_{xz,yz}, \\ A_{\parallel} &= P_d[-\kappa\alpha^2 - \tfrac{4}{7}\alpha^2 + (g_{\parallel} - 2) \\ &\qquad + \tfrac{3}{7}(g_{\perp} - 2)] + P_p\eta^2(-\kappa + \tfrac{4}{5}), \\ A_{\perp} &= P_d[-\kappa\alpha^2 + \tfrac{2}{7}\alpha^2 + \tfrac{11}{14}(g_{\perp} - 2)] \\ &\qquad + P_p\eta^2(-\kappa - \tfrac{2}{5}), \end{aligned} \tag{13}$$

where $\lambda_d = -829$ cm$^{-1}$ and $\lambda_p = -925$ cm$^{-1}$ are free-ion spin–orbit coupling constants for 3*d* and 4*p* orbitals, respectively. $E_{ij}$ are the energy separations between the ground state ($B_2$) and the $d_{ij}$ orbital. $P_d = 0.0360$ cm$^{-1}$ and $P_p = 0.0402$ are the copper-ion dipolar hfs parameters for 3*d* and 4*p* orbitals, and $\kappa$ is the Fermi contact parameter ($\kappa_0 = 0.43$ in free Cu(II) ion). An admixture of states $B_2$ and $E$ does not affect $g_{\parallel}$ but slightly lowers $g_{\perp}$ and $A_{\perp}$. The hfs splitting value $A_{\parallel}$ is the most strongly affected by $4p_z$ mixing. Since the first term of (*13*) is negative, whereas the second term—that due to the 4*p* admixture—is but slightly smaller and positive, it lowers $|A_{\parallel}|$ very considerably. If the *p*-state admixture is negligible ($\eta = \zeta = 0$), i.e., when dealing with a purely $d_{xy}$ ground state, the dependence of $g$ and $A$ on the deformation angle of the flattened tetrahedron is easy to obtain. Assuming the splitting values of Eqs. (6) for $R = 2.1$ Å and $q = 5e$ and taking $P_d = 0.0360$ cm$^{-1}$ and $\kappa = 0.25$ (as in aqua-copper(II) complexes), we obtain the plot of $g$ and $A$ values vs angle $\beta$ shown in Fig. 6. One notes that when the tetrahedron is compressed (involving an increase in $\beta$ from 54.74 to 90°), $g_{\parallel}$, $g_{\perp}$, and $A_{\perp}$ decrease, whereas $|A_{\parallel}|$ strongly increases. In the square-planar limit ($\beta = 90°$) the changes in $g_{\parallel}$, $g_{\perp}$, and $A_{\perp}$ are negligible. Obviously, the $D_{2d}$ deformation of the tetrahedron leads to a change in $|A_{\parallel}|$ opposite to that caused by an admixture of 4*p* orbital; however, this effect can only partly compensate for the decrease in $|A_{\parallel}|$ caused by the admixture in question.

The influence of such a tetragonal deformation on the EPR parameters can be evaluated by comparing the latter for square-planar ($D_{4h}$) and pseudotetrahedral ($D_{2d}$) $[CuCl_4]^{-2}$ complexes in $K_2PdCl_4$:$Cu^{2+}$ (*19*) and $CsZnCl_4$:$Cu^{2+}$ (*20*), respectively,

$$g_{\parallel} = 2.233, \quad g_{\perp} = 2.049,$$
$$A_{\parallel} = 164, \quad A_{\perp} = 34.5,$$
$$g_{\parallel} = 2.446, \quad g_{\perp} = 2.090,$$
$$A_{\parallel} = 25, \quad A_{\perp} = 48,$$

where the $A$ values are in $10^{-4}$ cm$^{-1}$. The above comparison shows that the tetrahedral deformation of the $[CuCl_4]^{2-}$ complex

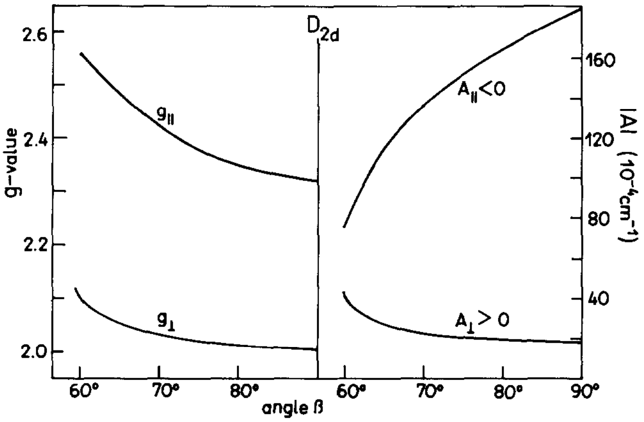

FIG. 6. Dependence of the spin Hamitonian parameters $g$ and $A$ on angular distortion of the $D_{2d}$ flattened tetrahedron with $d_{xy}$ ground-state wavefunction; $R = 2.1$ Å, $q = 5e$, $\kappa = 0.25$, $P = 0.036$ cm$^{-1}$.

is in good agreement with the predictions of crystal field theory (Fig. 6).

### *3.2. Ground State $d_{z^2}$ $(A_1)$*

This ground state of the Cu(II) ion occurs in the tetragonally elongated $D_{2d}$ tetrahedron. For this ground state, an "inverted" axial EPR spectrum is expected with the spin Hamiltonian parameters (with accuracy to the second-order of perturbation calculus)

$$
\begin{aligned}
g_{\|} &= 2.0023 - 3(\lambda/E_{xz,yz})^2,\\
g_{\perp} &= 2.0023 - 6\lambda/E_{xz,yz}\\
&\qquad - 6(\lambda/E_{xz,yz})^2,\\
\frac{A_{\|}}{P} &= -\kappa\left(1 - 3\,\frac{\lambda^2}{E^2_{xz,yz}}\right) + \frac{4}{7}\\
&\qquad + \frac{6}{7}\frac{\lambda}{E_{xz,yz}} + \frac{15}{7}\frac{\lambda^2}{E^2_{xz,yz}}, \qquad (14)\\
\frac{A_{\perp}}{P} &\ -\kappa\left(1 - \frac{3\lambda^2}{2E^2_{xz,yz}}\right) - \frac{2}{7}\\
&\qquad - \frac{45}{7}\frac{\lambda}{E_{xz,yz}} - \frac{57}{14}\frac{\lambda^2}{E^2_{xz,yz}},
\end{aligned}
$$

where $\lambda = \lambda_d$ and $P = P_d$ as in formula (13). The $g$ and $A$ values vs $\beta$ (the angle of the $D_{2d}$ deformation) are plotted in Fig. 7 for $q = 10e$, $R = 2.1$ Å (Eqs. (6)), $\kappa = 0.25$, and $P = 0.0252\ cm^{-1}$ (i.e., on the assumption of the orbital reduction factor $k = 0.7$). Such an inverted EPR spectrum (with $g_{\|} < g_{\perp}$) is observed for copper(II)-doped $CaWO_4$ (*13*) with $g_{\|} = 2.072$, $g_{\perp} = 2.286$, $|A_{\|}| = 38.5 \times 10^{-4}$ cm$^{-1}$, $|A_{\perp}| = 55.6 \times 10^{-4}$ cm$^{-1}$. Thus the ordering of the $g$ and $A$ parameters is in conformity with crystal field theory (Fig. 7), but the experimental values of the hfs parameters $A$ are much lower. This is so because of the quite uncommonly low value of $P = 10 \times 10^{-4}$ cm$^{-1}$ (Eqs. (14)), postulated on the basis of EPR measurements (*13*) (i.e., with $k \approx 0.03$) for the case under consideration. Taking $P = 0.0072$ cm$^{-1}$ (i.e., the orbital reduction coefficient $k = 0.2$), one gets for $\beta = 35°$ (Fig. 7), $g_{\|} = 2.0$, $g_{\perp} = 2.29$, $A_{\|} = 44 \times 10^{-4}$ cm$^{-1}$, and $A_{\perp} = -53 \times 10^{-4}$ cm$^{-1}$, in good agreement with the experimental results.

### *3.3. Ground State $d_{x^2-y^2}$ $(A_1)$*

This ground state appears in $C_{2v}$ tetrahedrally distorted rectangular geometry of copper(II) complexes. With regard to the doublet $d_{xz}$ $(B_1)$ and $d_{yz}$ $(B_2)$ splitting, one should expect a nonaxial EPR spectrum for the above type of symmetry.

On inspection of Table II one notes that the wavefunctions are mixed in the ground and in other states, i.e., that

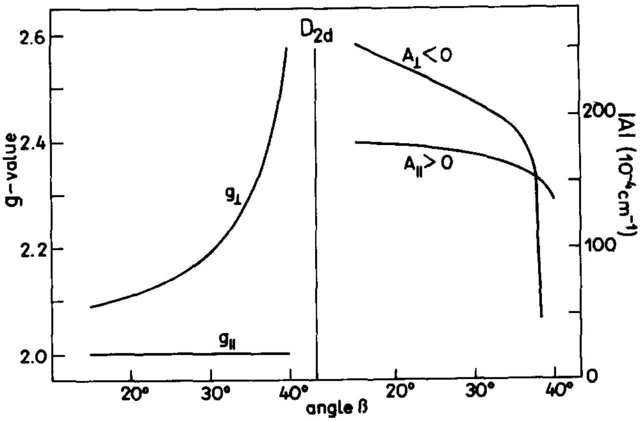

FIG. 7. Dependence of the parameters $g$ and $A$ on angular distortion of the $D_{2d}$ elongated tetrahedron with $d_{z^2}$ ground-state wavefunction; $R = 2.1$ Å, $q = 10e$, $\kappa = 0.25$, $P = 0.0252$ cm$^{-1}$.

$$\begin{aligned} \psi(A_1) &= \alpha d_{x^2-y^2} + \delta d_{z^2} + \eta p_z + \delta_1 s, \\ \psi(A_2) &= d_{xy}, \\ \psi(B_1) &= \beta_1 d_{xz} + \zeta_1 P_x, \\ \psi(B_2) &= \beta_2 d_{yz} + \zeta_2 P_y. \end{aligned} \qquad (15)$$

With the wavefunctions in the preceding form the formulae for $g$ and $A$ become highly complicated. They are to be found in Ref. (*21*) with omission of admixtures from $p$ and $s$ orbitals ($\eta = \delta = \zeta = 0$). On neglecting the $d_{z^2}$ admixture to the ground state, one obtains formulae for $g$ and $A$ identical with Eqs. (13) with $E_{x^2-y^2}$ replaced by $E_{xy}$ for the case of an axially symmetric spectrum. A plot of $g$ and $A$ vs the dihedral angle $\phi$ in symmetry $C_{2v}$ (with nonaxial EPR spectrum) is shown in Fig. 8 on omission of the $p$-orbital admixture (at $R$ = 2.1 Å, $q$ = 10$e$, $P$ = 0.360 cm$^{-1}$, $\kappa$ = 0.25). Thus, for the above deformation of the complex, the spin Hamiltonian parameters remain essentially unaffected, and the unaxiality of the EPR spectrum (i.e., $g_y - g_x$) is very small and practically negligible.

An EPR spectrum corresponding to such $C_{2v}$ deformation has been observed by us in dehydrated copper(II)-doped NaY-zeolites. On dehydration of the zeolite at 400°C, we observed a powder EPR spectrum with well-separated hfs lines at both $g_\parallel$ and $g_\perp$, with the parameters obtained by computer simulation of the spectrum $g_\parallel$ = 2.336, $g_\perp$ = 2.055, $|A_\parallel| = 167 \times 10^{-4}$ cm$^{-1}$, and $|A_\perp| = 24 \times 10^{-4}$ cm$^{-1}$, i.e., the spectrum was axial within a high degree of accuracy (error in $A$ values amounted to ±1). The four-coordinated low-symmetrical complex $CuO_4$ is postulated on the basis of structural and physicochemical studies (one water molecule and three oxygen atoms of the host lattice of the zeolite). A low symmetry of the complex and an axially symmetric EPR spectrum are possible only in the case of a $C_{2v}$ deformed four-coordination complex, as is indicated by the above-discussed results of crystal field theory.

### *3.4. Ground State $d_{xz}$ ($B_1$)*

This ground state exists in $C_{2v}$ symmetry at large dihedral angles, i.e., for slight deformations of the tetrahedron, as well as in a narrow range of angles $\beta$ for $D_{2d}$ deformation (see Table I), and at $C_{3v}$ trigonal deformation of the tetrahedron (*6*). The EPR spectra of Cu(II) complexes with this ground state are characterized by spin Hamiltonian parameters atypical for Cu(II).

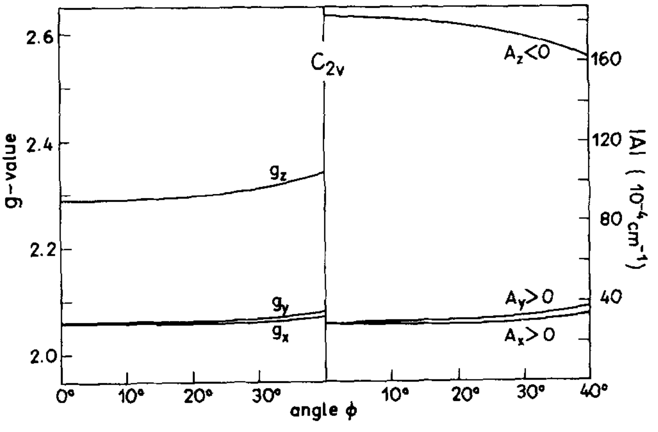

FIG. 8. Dependence of the parameters $g$ and $A$ on angular distortion of the $C_{2v}$ rhombic distorted rectangular complex with $d_{x^2-y^2}$ ground-state wavefunction; $R$ = 2.1 Å, $q$ = 10$e$, $\kappa$ = 0.25, $P$ = 0.036 cm$^{-1}$.

For the pure $d_{xz}$ state we have

$$g_{\parallel} = 0,$$

$$g_{\perp} = 6\lambda\left(\frac{1}{E_{xy}} - \frac{1}{E_{x^2-y^2}}\right),$$

whereas orbital mixing (see Table II) leads to very essential changes in the parameters and highly complicated formulae (*22*). Depending on the degree of deformation of the complex and the magnitude of the admixture of other orbitals to the ground state, the values of $g_{\parallel}$ and $g_{\perp}$ can be positive or negative and range from −2 to +4 (*1, 22*). The EPR experiment, of course, measures only the magnitude of the $g$ factors.

## 4. Conclusions

On the basis of crystal field theory, we analyzed the changes in orbital energies and EPR parameters due to deformation of the regular tetrahedral complex of the Cu(II) ion. We assumed the Cu–ligand distance as unaffected by deformation, and neglected ligand–ligand repulsion. Moreover, when considering the EPR parameters, we assumed that all the ionic parameters (the spin–orbit coupling constant $\lambda$, orbital reduction parameters $k$, and Fermi contact contribution $\kappa$ to hfs) remain constant during the deformation. In spite of these simplifying assumptions, the theory led to good results. We succeeded in confirming the experimentally found linear dependence of the orbital splittings and the dihedral angle in $C_{2v}$ of the perturbated tetrahedron. We found that in the $D_{2d}$ flattened tetrahedron the effect of $4p_z$ orbital mixing into the $d_{xy}$ ground state is partly compensated by the effect of the crystal field.

The results of Figs. 6 and 8 show that the effect of tetrahedron deformation for the ground states $d_{xy}$ and $d_{x^2-y^2}$ is similar to that of tetragonal octahedron deformation, i.e., an increase in $g_{\parallel}$ entails a decrease in $|A_{\parallel}|$, and vice versa.

A modification of the results should be expected if spin–orbit coupling is taken into account in the crystal field theory and if a closer analysis is performed of the influence of $4p$-orbital admixture in conjunction with MO theory.

## Acknowledgment

The authors wish to thank Prof. Dr. J. Stankowski for his interest and encouragement.

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