

Simple Model of the Dynamic Jahn-Teller Effect in Six-Coordinated Copper(II) Complexes

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A model potential is assumed for describing the vibrational degrees of freedom associated with the Jahn-Teller effect in six-coordinated copper (II) complexes. The pseudorotational limit is characterized by a potential that is constant in the region between two concentric cylinders, but becomes infinite elsewhere. The energy spectrum is obtained for both angular and radial excitations. A square-well periodic angular potential is applied as a perturbation, yielding a localization of states. The results are used to describe the temperature dependence of the electron spin resonance spectra of copper (II) complexes with emphasis on the system NaCl:Cu(II) containing the hexachlorocuprate (II) complex.

INTRODUCTION

In 1937, Jahn and Teller proved¹ that a symmetrical nonlinear molecule in a spatially degenerate electronic state can distort in such a way that the electronic degeneracy is removed. Van Vleck (1939) considered² the coupling between the fourfold degenerate 2E_g electronic ground state of an octahedral Cu(II) complex ($3d^9$) and the e_g vibrational mode, and demonstrated that to a first approximation there exists a continuous series of nuclear configurations having the same electronic energy. These configurations are in general of only D_{2h} symmetry, with three different Cu-ligand distances, although the two-dimensional nuclear configuration space includes special directions corresponding to tetragonally elongated or compressed octahedra exhibiting D_{4h} symmetry.³ These higher-symmetry structures (Fig. 1) correspond to extrema in the electronic energy when cubic terms are included in the expansion of the energy as a power series in the nuclear coordinates.⁴ The well-known potential surface (Figs. 2 and 3) in nuclear configuration space is conveniently described in polar coordinates r and ϕ (corresponding to the two components of the e_g stretching mode), as the potential is independent of ϕ if cubic and higher terms are neglected.^{2,3,5,6}

The effects of such Jahn-Teller coupling have been observed in the ESR spectra of Cu(II) in crystals of $ZnSiF_6 \cdot 6H_2O$,^{7,8} $Mg_3La_2(NO_3)_{12} \cdot 24H_2O$,^{7,8} $Mg_3Bi_2(NO_3)_{12} \cdot 24H_2O$,⁷ MgO ,⁹ $AgCl$,¹⁰ $Ca(OH)_2$,¹¹ and $NaCl$.¹² The interpretation of these spectra in terms of the Jahn-Teller effect has been discussed by Abragam and Pryce¹³ (1950) and, more recently, by Ham¹⁴ (1968). In each case, the ESR spectrum at a sufficiently low temperature is characteristic of a six-coordinated Cu(II) ion "frozen" into one of its potential energy minima (X , Y , Z , Fig. 3), while above a certain transition temperature (about 95°K in the case of Cu(II):NaCl¹²) the spectrum becomes "isotropic" and represents an averaging over the possible configurations. One exception is Cu(II):MgO, in which a third type of ESR spectrum, called a "tunneling" spectrum is observed.⁹

The theory of the dynamic Jahn-Teller effect in

octahedrally coordinated d^9 ions has been discussed¹⁵ by O'Brien (1964), who interprets the high-temperature spectrum as a result of the population of a higher vibronic level. The complex may be viewed as "tunneling" from one potential minimum to another.¹² A molecular orbital study³ of the $CuCl_6^{4-}$ complex shows that the Jahn-Teller effect in this system is essentially static in the "radial" coordinate r but, at a sufficiently high temperature, relatively dynamic in the "angular" coordinate ϕ : the isotropic ESR spectrum represents an average over configurations corresponding to the entire range of ϕ but to an essentially fixed value of r (see Fig. 3). In the neighborhood of the radial minimum in the potential energy, the potential energy is found³ to be adequately represented as a function of ϕ by the equation

$$V(\phi) = \frac{1}{2}B[1 - \cos(3\phi)], \quad (1)$$

where B is the "barrier height", equal to the potential energy associated with the tetragonally compressed structures at $\phi = \pi/3$, π , and $5\pi/3$, and the potential energy minimum is $V=0$, associated with the tetragonally elongated structures at $\phi = 0$, $2\pi/3$, and $4\pi/3$. The only symmetry requirement, however, is that V be periodic in (3ϕ) . The ESR spectrum of Cu(II):NaCl has been interpreted³ in terms of a value of B at least several hundred cm^{-1} in magnitude for the $CuCl_6^{4-}$ complex, significantly smaller than the Jahn-Teller stabilization energy of 2380 cm^{-1} (0.295 eV)³ at $r = 0.15 \text{ \AA}$, as indicated in Fig. 3.

Since the dynamic behavior of the system under consideration is primarily in the angular coordinate, the adiabatic approximation may be applied,^{3,15} consisting of the assumption that the motion of the nuclei may be characterized by a potential energy corresponding to the energy of the much less massive electrons for fixed nuclear configuration. In the adiabatic approximation, the total electronic-nuclear wavefunction of the system may be expressed as the simple product

$$\psi_{en} = \psi_e(q, Q, n_e) \Psi(Q, n_n), \quad (2)$$

where the electronic part ψ_e depends upon the instantaneous set of nuclear coordinates Q as well as

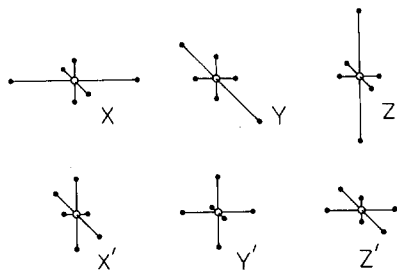


FIG. 1. Schematic drawings of the six special configurations of D_{4h} symmetry, corresponding to special directions in the nuclear configuration space. The three equivalent tetragonally elongated structures X , Y , and Z correspond to potential energy minima, while the three equivalent tetragonally compressed structures X' , Y' , and Z' correspond to potential energy maxima (see Fig. 3).

upon the electronic coordinates q and quantum numbers n_e , but the nuclear part Ψ depends only upon Q and a set of quantum numbers n_n .¹⁶ It may be shown^{3,5} that $\psi_e(\phi)$ is such that $\psi_e(0) = -\psi_e(2\pi)$; therefore, in order that ψ_{en} be single-valued, Ψ must be such that (for fixed r and n_n)

$$\Psi(\phi) = -\Psi(\phi + 2\pi). \quad (3)$$

THEORETICAL MODEL

A simple model will be used, which approximates the above-described system for sufficiently low energies (more specifically, for energies which are small compared to the Jahn-Teller stabilization energy), and which exhibits (qualitatively) those characteristics of that system which give rise to its "dynamic Jahn-Teller" behavior.

The potential surface of Figs. 2-3 is replaced by the potential well of Fig. 4, which, in the case $B=0$, consists of an infinitely deep right circular cylindrical well of outer radius b , with an infinitely high central "post" of circular cross section and radius a . Thus consideration is restricted to the annular region $a \leq r \leq b$ in the nuclear configuration space; this restriction is justified as an approximation for low energies by the observation of relatively static radial Jahn-Teller behavior. Within the region $a \leq r \leq b$, the angular dependence of the potential is introduced by setting $V(r, \phi) = -\frac{1}{2}B$ in the regions $0 \leq \phi < \pi/6$, $\pi/2 \leq \phi < 5\pi/6$, $7\pi/6 \leq \phi < 3\pi/2$, and $11\pi/6 \leq \phi < 2\pi$, and $V(r, \phi) = +\frac{1}{2}B$ in the remaining

FIG. 2. The potential energy surface characteristic of the Jahn-Teller effect, in the two-dimensional nuclear configuration space, in the case of no angular barrier ($B=0$). The potential energy V is dependent on the radial coordinate r but not on the angular coordinate ϕ . See also Fig. 3.

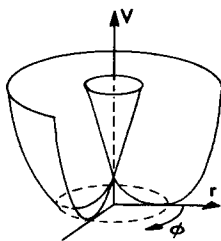
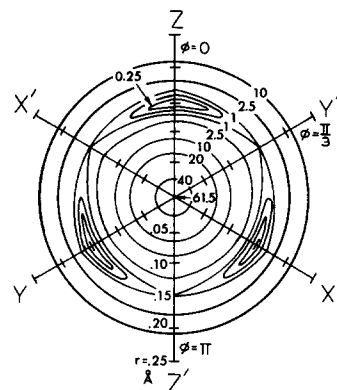


FIG. 3. Energy contours for the electronic ground state in the (r, ϕ) space for the hexachlorocuprate(II) complex in NaCl. Values of the potential energy are indicated in units of the "barrier height" B , with the potential energy taken to be zero at the minima along rays X , Y , and Z . Diagram adapted from Ref. (3), which gives a value of 0.0048 eV for B , implying an energy of $61.5B = +0.295$ eV for the octahedral configuration ($r=0$). Figure 2 is another view of the same surface, neglecting the angular variation of the potential energy.



regions, $\pi/6 \leq \phi < \pi/2$, $5\pi/6 \leq \phi < 7\pi/6$, and $3\pi/2 \leq \phi < 11\pi/6$; thus the angular dependence is analogous to that expressed by Eq. (1) and has the required periodicity in (3ϕ) , but the minimum value of V has been set at $-\frac{1}{2}B$ rather than at 0. The barrier height B must have a positive value if the model is to exhibit the observed low-temperature preference for a tetragonally elongated structure.

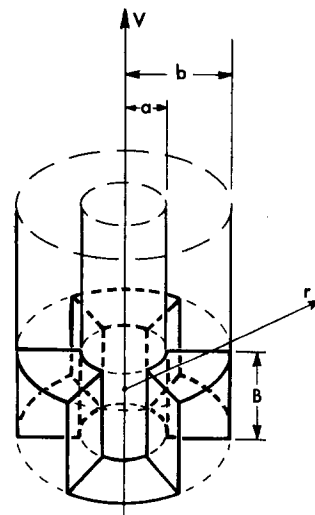
The wave equation for the model system may readily be solved exactly with B set to 0 (no barrier, no angular dependence of V); the angular variation of the potential energy is introduced as a perturbation in order to obtain approximate solutions for the energy levels of the model system for specified barrier heights.

SOLUTION OF THE UNPERTURBED SYSTEM

The Schrödinger wave equation for the model system is

$$\nabla^2 \Psi + (2\mu/\hbar^2)(E - V)\Psi = 0, \quad (4)$$

FIG. 4. Simple model of potential well approximating that of Fig. 3 (or Fig. 2). The adjustable parameters are a , b , and B . The walls are infinitely high. The floor is composed of flat sections and the potential energy zero is set so that any one of these sections is at a height of either $V = -B/2$ or $V = +B/2$. The discontinuities in the floor of the well are at $\phi = \pi/6$, $\pi/2$, $5\pi/6$, $7\pi/6$, $3\pi/2$, and $11\pi/6$, so that each flat section is bisected by a ray corresponding to one of the six high-symmetry configurations pictured schematically in Fig. 1. As in Fig. 3, the rays in the directions X , Y , and Z pass through minima in the potential energy, while those in the directions X' , Y' , and Z' pass through maxima.



where $\Psi = \Psi(r, \phi)$ describes a state of the system, E is the total energy associated therewith, $V = V(r, \phi)$ is the potential energy, \hbar denotes Planck's constant divided by 2π , and μ is the effective (reduced) mass of the system (equal to three times the mass of one ligand). In the polar coordinates r and ϕ , the Laplacian operator $\nabla^2 = (\partial^2/\partial r^2) + (1/r)(\partial/\partial r) + (1/r^2)(\partial^2/\partial \phi^2)$. For $B=0$, V is independent of ϕ , and in the region $a \leq r \leq b$, $V=0$, independent of r and ϕ ; so in this region, Eq. (4) reduces to

$$(\partial^2 \Psi / \partial r^2) + (1/r)(\partial \Psi / \partial r) + (1/r^2)(\partial^2 \Psi / \partial \phi^2) + k^2 \Psi = 0, \quad (5)$$

where $k^2 \equiv 2\mu E / \hbar^2$. With the expression of Ψ as the product

$$\Psi(r, \phi) = R(r)\Phi(\phi), \quad (6)$$

the wave equation may be reduced to the form

$$(r^2/R)(d^2R/dr^2) + (r/R)(dR/dr) + k^2 r^2 = -(1/\Phi)(d^2\Phi/d\phi^2). \quad (7)$$

With the definition of $m^2 \equiv -(1/\Phi)(d^2\Phi/d\phi^2)$, this equation is separated into angular and radial wave equations,

$$(d^2\Phi/d\phi^2) + m^2\Phi = 0 \quad (8)$$

and

$$r^2(d^2R/dr^2) + r(dR/dr) + (k^2 r^2 - m^2)R = 0. \quad (9)$$

The angular Eq. (8) has the general solution (normalized)

$$\Phi(\phi) = (2\pi)^{-1/2} \exp(im\phi); \quad (10)$$

imposition of the condition of Eq. (3) introduces the restriction of the angular quantum number m to the values $\pm 1/2, \pm 3/2, \pm 5/2$, etc.; i.e., to half-odd-integral values.

The radial Eq. (9) is solved (for the region $a \leq r \leq b$) by defining $\rho \equiv kr$: (9) is transformed into

$$\rho^2(d^2R'/d\rho^2) + \rho(dR'/d\rho) + (\rho^2 - m^2)R' = 0, \quad (11)$$

where $R'(\rho) = R(r)$. Equation (11) is Bessel's equation of order m , and a general solution is

$$R_m'(\rho) = C_1 J_m(\rho) + C_2 Y_m(\rho), \quad (12)$$

where J_m is the (cylindrical) Bessel function of the first kind, of order m , Y_m is the (cylindrical) Bessel function¹⁷ (Neumann function) of the second kind, of order m , and C_1 and C_2 are arbitrary real constants. Since Eq. (9) includes m only in the form of m^2 , $R_m'(\rho)$ may be taken as equal to $R_{-m}'(\rho)$, and it will suffice to solve

$$R_{|m|}(r) = C_1 J_{|m|}(kr) + C_2 Y_{|m|}(kr), \quad (13)$$

imposing the boundary conditions $R(a) = R(b) = 0$, and the normalization condition

$$\int_a^b R^2(r) r dr = 1.$$

The eigenvalues $k_{|m|}$ of k determine the eigenvalues $E_{|m|}$ of E , the total energy, through the relationship

$$E_{|m|} = \hbar^2 k_{|m|}^2 / 2\mu \quad (14)$$

(from the definition of k). In general, the boundary conditions on the radial wavefunction will suffice to determine the corresponding eigenvalues of $k_{|m|}$, and thus the energies $E_{|m|}$ of the states Ψ_m and Ψ_{-m} . Defining $R_{|m|}(a)$ and $R_{|m|}(b)$ by (13) and setting both equal to 0, one obtains the equation

$$J_{|m|}(k_{|m|}a) Y_{|m|}(k_{|m|}b) = J_{|m|}(k_{|m|}b) Y_{|m|}(k_{|m|}a), \quad (15)$$

which may be transformed into the convenient form

$$J_M(K_M) Y_M(\beta K_M) = J_M(\beta K_M) Y_M(K_M), \quad (16)$$

where $M \equiv |m|$, $K \equiv ka$, and $\beta \equiv b/a$. By use of the known identities

$$J_{1/2}(x) = (2/\pi x)^{1/2}(\sin x), \quad (17)$$

$$J_{-1/2}(x) = (2/\pi x)^{1/2}(\cos x), \quad (18)$$

and

$$Y_m(x) = J_m(x) \cot(m\pi) - J_{-m}(x) \csc(m\pi), \quad (19)$$

and the recursion formula

$$(2m/x)J_m(x) = J_{m-1}(x) + J_{m+1}(x), \quad (20)$$

the Bessel functions may be expressed as

$$J_M(x) = [P_M(x) \sin(x) - Q_M(x) \cos(x)](2/\pi x)^{1/2} \quad (21)$$

and

$$Y_M(x) = [-Q_M(x) \sin(x) - P_M(x) \cos(x)](2/\pi x)^{1/2}, \quad (22)$$

where $P_M(x)$ and $Q_M(x)$ are polynomials in x^{-1} , the coefficients of which may be determined by repeated application of Eqs. (19) and (20) upon (17) and (18).¹⁸ Substitution of (21) and (22) into Eq. (16) leads, after manipulation, to the equation

$$\tan[K_M(\beta - 1)] = F_M(K_M, \beta), \quad (23)$$

where

$$F_M(x, \beta) = \frac{P_M(x) Q_M(\beta x) - P_M(\beta x) Q_M(x)}{P_M(x) P_M(\beta x) + Q_M(x) Q_M(\beta x)}. \quad (24)$$

Thus, with β set, the eigenvalues of K_M for a given M are $K_{M,1}, K_{M,2}, \dots$, the first, second, \dots solutions of Eq. (23). It has been proven¹⁹ that there is an infinite series of such solutions $K_{M,n}$ for each value of M . The numerical solution of Eq. (23) is very tedious for large values of M , but may be performed inexpensively and in a simple manner by means of a digital computer. Approximate solutions for the first several eigenvalues of K_M may be obtained graphically by taking the abscissas of the intersections of the graphs of $\{\tan[K_M(\beta - 1)]\}$ and $F_M(K_M, \beta)$, versus K_M .

The determination of the K eigenvalues completes

the determination of the system's energy spectrum: and

$$E_{M,n} = \hbar^2 K_{M,n}^2 / 2\mu a^2. \quad (25)$$

The number of nodes in the radial wavefunction $R(r)$ is $n-1$.

The solution for the radial wave function $R_{M,n}(r)$ is completed with the evaluation of the constants C_1 and C_2 , through the relation

$$C_1 J_M(K_{M,n}) + C_2 Y_M(K_{M,n}) = 0 \quad (26)$$

and the normalization condition.

NATURE OF THE ENERGY SPECTRUM OF THE UNPERTURBED SYSTEM

The unperturbed system (i.e., the system with $B=0$) is characterized by the three parameters a , β , and μ . With μ and a specified, only $K_{M,n}$ must be evaluated in order to determine [by Eq. (25)] the energy $E_{M,n}$ of the level characterized by the quantum numbers M ($\equiv |m|$) and n . $K_{M,n}$ is evaluated by solution of Eq. (23), which requires specification of M , β , and (implicitly) n ,¹⁸ but does not involve a distinction between the states $\Psi_{m,n}$ and $\Psi_{-m,n}$. Each energy level is therefore doubly degenerate in the unperturbed case: for fixed a , β , and μ , and for a specified value of n (a positive integer), the energy $E_{M,n}$ depends only upon M , the absolute value of m , and thus corresponds to exactly two states, $\Psi_{M,n} = \Phi_M R_{M,n}$ and $\Psi_{-M,n} = \Phi_{-M} R_{M,n}$.

Comparison of Eq. (21) with Eqs. (17) and (18) for $M=1/2$ reveals immediately that $F_{1/2}(x, \beta)$ [in Eq. (24)] is identically zero. The eigenvalues of $K_{1/2}$ are therefore determined by Eq. (23) to be simply

$$K_{1/2,n} = n\pi / (\beta - 1). \quad (27)$$

Application of Eq. (25) shows that the energy of any state with $M=1/2$ is simply that energy associated with the corresponding eigenstate of a system consisting of a single particle of reduced mass μ in an infinitely deep one-dimensional square well of length $(b-a)$:

$$E_{1/2,n} = \hbar^2 \pi^2 n^2 / 2\mu (b-a)^2. \quad (28)$$

An asymptotic expression for $K_{M,n}$, which is a good approximation for large values of n (and thus of K), was presented in 1894 by McMahon²⁰; in terms of the variables defined thus far, his formula for solution of Eq. (16) reads:

$$K_{M,n} = \delta + (p/\delta) + [(q-p^2)/\delta^3] + [(s-4pq+2p^3)/\delta^5] + \dots, \quad (29a)$$

where

$$\delta \equiv K_{1/2,n} = n\pi / (\beta - 1), \quad (29b)$$

$$p \equiv (N-1) / 8\beta, \quad (29c)$$

$$q \equiv 4(N-1)(N-25)(\beta^3-1) / 3(8\beta)^3(\beta-1), \quad (29d)$$

$$s \equiv 32(N-1)(N^2-114N+1073) \times (\beta^5-1) / 5(8\beta)^5(\beta-1), \quad (29e)$$

$$N \equiv 4M^2 = 4m^2. \quad (29f)$$

It is clear from the form of Eq. (29a) that, for any choice of permissible values of M and β (M must be half of an odd positive integer and β must be greater than 1), n may be chosen sufficiently great so that $K_{M,n}$ approaches $K_{1/2,n}$ with any desired degree of accuracy. This assertion may be verified by examination of the behavior of the function $F_M(x, \beta)$ for any specified values of M and β in the limit as the argument x (corresponding to K) is allowed to increase without bound.⁹ The corresponding approximate expression for the energy $E_{M,n}$ is readily obtained by squaring the sum on the right side of Eq. (29a) (neglecting terms in δ^{-6} , δ^{-8} , etc., which are not completely specified by McMahon's formula), and applying Eq. (25):

$$E_{M,n} = (\hbar^2 / 2\mu a^2) [\delta^2 + 2p\delta^{-2} + 2q\delta^{-4} + \delta^{-4}(2s - 6pq + 2p^3) + \dots], \quad (30)$$

where δ , p , q , and s are defined as in Eq. (29b) through (29e). If the terms in δ^{-2} and δ^{-4} are also regarded as negligible, $E_{M,n}$ may be expressed (approximately) as

$$E_{M,n} \cong (\hbar^2 / 2\mu a^2) (K_{1/2,n}^2 + L_M), \quad (31)$$

where

$$L_M \equiv 2p = (M^2 - \frac{1}{4}) / \beta. \quad (32)$$

Then

$$E_{M,n} = E_{1/2,n} + (\hbar^2 / 2\mu) (M^2 - \frac{1}{4}) / ab; \quad (33)$$

the difference between $E_{1/2,n}$ and $E_{M,n}$ is, in this approximation, simply the energy difference associated with the corresponding excitation of a system satisfying Eq. (10) alone, which system resembles the familiar system consisting of a single particle allowed to move freely on a ring; in this case, the analogous particle would have a reduced mass of μ and would be constrained to move on a ring of radius $(ab)^{1/2}$, the geometric mean of a and b .

Equation (33) becomes, in general, a poorer approximation to the actual value of $E_{M,n}$ as n is decreased (although the equation is obviously exact for any n in the trivial case $M = \frac{1}{2}$). More specifically, for $M \neq \frac{1}{2}$, the validity of the above approximations, based upon Eq. (29a), decreases with decreasing δ ; that is, with decreasing n or increasing β . For a fixed value of n , the validity of the above approximations also decreases with increasing M . The range of usefulness of Eq. (29a) could be increased by the inclusion of terms in δ^{-7} , δ^{-9} , etc.

In order to make obvious, for the purposes of the current study, the orders of magnitude of the energies of the lower levels of the system under consideration, Eq. (25) may be expressed in the following forms:

$$E = (0.0697) (K^2 / \mathfrak{M} a^2) eV; \quad (34)$$

$$E = (1.1165 \times 10^{-13}) (K^2 / \mathfrak{M} a^2) \text{ erg}. \quad (35)$$

In Eqs. (34) and (35), \mathfrak{M} represents the mass of one

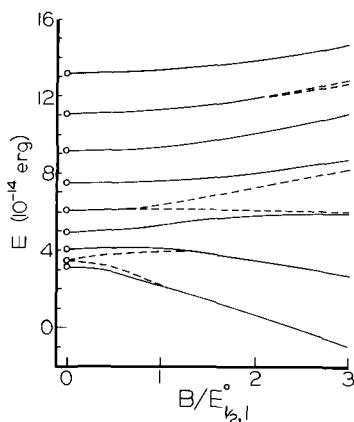


FIG. 5. Lowest energy eigenvalues as functions of barrier height B , for Case I ($\beta=2.0$). Eigenvalues $E_{M,1}^0$ of 'unperturbed' system ($B=0$) indicated by circles: from bottom, $M=1/2, 3/2, 5/2, 7/2, 9/2, 11/2, 13/2, 15/2, 17/2$. Solid lines represent degenerate or nearly degenerate levels; broken lines represent non-degenerate levels.

ligand in atomic mass units (physical system) and \hat{a} represents the dimension a of the potential well, in units of 0.1 \AA . Using the same dimensionless mass and length, the energy $E_{1/2,1}$ of the lowest level may be expressed in a simple fashion:

$$E_{1/2,1} = (0.6878 \text{ eV}) / [\mathfrak{N} \hat{a}^2 (\beta - 1)^2],$$

$$= (1.1019 \times 10^{-12} \text{ erg}) / [\mathfrak{N} \hat{a}^2 (\beta - 1)^2]. \quad (36)$$

Also,

$$E_{1/2,n} = n^2 E_{1/2,1}. \quad (37)$$

At this point, the values of a , β , and μ remain arbitrary. For the numerical calculations, the values initially chosen were $a=0.1 \text{ \AA}$ ($\hat{a}=1.0$), $\mu=104.9 \text{ amu}$ (physical scale), corresponding to six identical Cl^{35} ligands, and $\beta=2.0$. The dimensions a and b were chosen for simplicity and rough conformity to Fig. 3. With these choices of values for the parameters, $\hat{a}^2(\beta-1)^2=1.0$, $\mathfrak{N}=34.98$, and thus, from Eq. (36), energy of the lowest level is $E_{1/2,1}=3.15 \times 10^{-14} \text{ erg}$, $=0.0197 \text{ eV}$.

The eigenvalues $K_{M,n}$ were evaluated for this case ($\beta=2.0$) for all permissible values of M from $\frac{1}{2}$ through $19/2$ and for all permissible values of n from 1 through 10. Some eigenvalues of $K_{M,1}$ were also evaluated for the case $\beta=3.0$, using the same values of a and μ . The values calculated for the two cases are listed in Appendix B and Appendix C, respectively. The corresponding energy eigenvalues for $n=1$ are listed in Appendix D and presented graphically at $B=0$ in Fig. 5 (Case I) and Fig. 6 (Case II).

INTRODUCTION OF THE ANGULAR BARRIER

Since the eigenvectors Ψ_j^0 of the 'unperturbed' problem form a complete orthonormal set, the eigen-

vectors Ψ of the 'perturbed' system may be expressed as linear combinations of the Ψ_j^0 . In theory, the entire infinite set of basis vectors Ψ_j^0 must be used for exactness; it will be assumed, however, that a small set of basic vectors corresponding to low energy levels will suffice for an approximate solution, at least for sufficiently small values of the angular barrier B .

The diagonal elements of the matrix $\langle i | (\hat{H}^0 + V) | j \rangle$, where \hat{H}^0 is the Hamiltonian for the unperturbed system, are simply the energy eigenvalues E_i^0 , since, with the potential energy zero set so that the potential energy assumes values of $B/2$ and $-B/2$, the integral $\langle j | V | j \rangle = 0$. The basis vectors were $\Psi_{m,1}^0$, where m was allowed to range over all half-odd-integral values from $-17/2$ to $+17/2$, inclusive. These are the eigenvectors corresponding to the lowest energies, in general, for values of β in the neighborhood of the values used, 2.0 and 3.0. Although $\Psi_{m,2}^0$ attains comparably low energies if m is quite small, the matrix elements involving interactions between these states and those for which $n=1$ are quite small compared with those matrix elements involving two states of the same value of n .

The general off-diagonal matrix element in the matrix to be diagonalized is $\langle m | V | m' \rangle$, which is the product, since $V=V(\phi)$, of the integral

$$\int_0^{2\pi} (\Phi_m^0)^* V \Phi_{m'}^0 d\phi$$

and the overlap integral

$$\int_a^b R_m^0 R_{m'}^0 r dr.$$

The integral involving the angular wavefunctions Φ_m^0 and $\Phi_{m'}^0$ is zero unless $m=m' \pm 3$, since the function

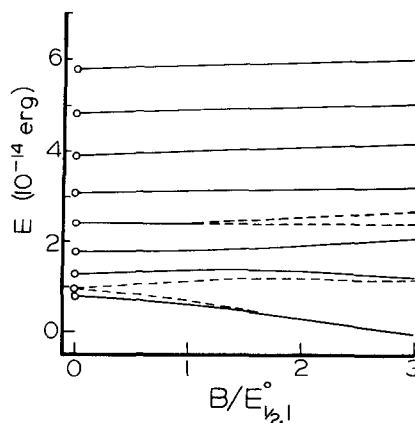


FIG. 6. Lowest energy eigenvalues as functions of barrier height for Case II ($\beta=3.0$). Eigenvalues $E_{M,1}^0$ of 'unperturbed' system ($B=0$) indicated by circles: from bottom, $M=1/2, 3/2, 5/2, 7/2, 9/2, 11/2, 13/2, 15/2, 17/2$. Solid lines represent degenerate or nearly degenerate levels; broken lines represent non-degenerate levels.

$V = V(\phi)$ is periodic in (3ϕ) ; when $m = m' \pm 3$,

$$\int_0^{2\pi} (\Phi_m^0)^* V \Phi_{m'}^0 d\phi = \frac{B}{\pi},$$

regardless of the values of m and m' . The overlap integral

$$\int_a^b R_m^0 R_{m'}^0 r dr$$

was evaluated numerically and found to be very nearly 1.0 in all cases involved in the matrix elements required. The matrix elements were therefore taken to be

$$\begin{aligned} \langle m | (\hat{H}^0 + V) | m' \rangle &= E_M^0 && \text{if } m = m'; \\ &= B/\pi && \text{if } m = m' \pm 3; \\ &= 0 && \text{otherwise.} \end{aligned} \quad (38)$$

The resulting matrix was diagonalized numerically by digital computer, using values of a and μ as above (0.1 Å and 104.9 amu, respectively). Values of the energy eigenvalues of the perturbed system were obtained for $\beta = 2.0$ (see Fig. 5) and for $\beta = 3.0$ (see Fig. 6). B was varied, in each of these two cases, from zero to $3E_{1/2,1}^0$. Note that if the scales of Figs. 5 and 6 were equalized, both being given in absolute energy values (ergs), the graphs would appear nearly identical. These graphs present a strong qualitative similarity to the corresponding graph (appropriately transformed) given¹⁵ by O'Brien's more complex model.

As the barrier height B is increased, those energy levels characterized by quantum numbers M such that $2M/3$ is not an integer remain degenerate; those energy levels having values of M such that $2M/3$ is an integer are split, and the twofold degeneracy of the 'unperturbed' system changes to threefold degeneracy as a limiting case for very large values of B . If B is allowed to increase without bound, threefold degeneracy must be approached as the potential well comes to resemble three identical and noninteracting 'boxes.'

APPLICATION TO ESR SPECTRA

As previously mentioned, the ESR spectra of six-coordinated copper(II) complexes are associated at low temperatures with "localized", or statically distorted, complexes, with a transition at higher temperatures to "delocalized" complexes. The latter are characterized by their pseudorotation along the angular coordinate ϕ . We earlier showed⁸ that the angular barrier must be at least several hundred cm^{-1} in magnitude for the CuCl_6^{-4} complex in Cu(II):NaCl in order that the ground-state splitting be not more than about 0.03 cm^{-1} , a quantity proportional to the anisotropy in the g tensor multiplied by the magnetic field strength used in the ESR experiment. This is the condition that must be satisfied in order to observe "localized" complexes at low temperatures.

The transition to "delocalized" complexes can be interpreted in terms of the results of the previous

section. For Case I, defined by radii of $a = 0.1 \text{ Å}$ and $b = 0.2 \text{ Å}$, a barrier of 321 cm^{-1} yields a ground-state splitting of only 0.03 cm^{-1} , with the doubly degenerate level lying low. This result is comparable with our previous value of B , obtained⁸ with a localized harmonic oscillator basis. For this barrier height, the next two levels occur at 144.9 cm^{-1} (nondegenerate) and 147.0 cm^{-1} (doubly degenerate) above the ground state. Thus, relative to a completely localized initial description, in which all levels would be triply degenerate, this level displays an "inversion" splitting of 2.1 cm^{-1} , which is 70 times the ground-state splitting and considerably larger than the anisotropy in the Zeeman interaction. The population of these states should then lead to the appearance of a "delocalized" spectrum. If for simplicity we ignore all higher states and consider only the lowest six, it is simple to show that the nondegenerate state at 144.9 cm^{-1} achieves a 5% Boltzmann population at 103°K . and a 10% population at 243°K . Since the population of each of the two states at 147.0 cm^{-1} is not much less than this, the population of each of the nearly triply degenerate ground-state levels is about 28.3% and 23.3%, respectively, at these two temperatures. The populations of 5% and 10% were selected somewhat arbitrarily, but do indicate that a barrier of 300 cm^{-1} does not preclude having a sizeable population of excited, delocalized states at temperatures of about 100°K . The key assumption made in this analysis that the high-temperature ESR spectrum is associated in part with the thermal population of excited vibrational states of the complex, rather than being described by a thermally activated "hopping" process that basically involves ground-state complexes.²¹ The latter process might well, of course, involve the same excited states, located at an energy of roughly half the barrier height.

SUMMARY

In summary the Jahn-Teller effect for doubly degenerate electronic states coupled to doubly degenerate vibrational modes is described in terms of a model potential which is constant in the region between two concentric cylinders but is infinite elsewhere. Although applicable to any system of this type in which the Jahn-Teller stabilization energy is sufficiently great that the "upper-branch" of the potential energy surface can be ignored, the specific case considered is an octahedral complex of Cu(II) ions with Cl^- ligands. Since the Jahn-Teller mode in this case is the Raman active e_g stretching mode, the spectrum of states corresponding to the radial excitations is experimentally accessible. Although the actual spacings are probably closer to those of a harmonic oscillator than to our cylindrical square well, the latter offers an appealingly simple picture of both the radial and angular aspects of the Jahn-Teller effect.²²

The threefold angular perturbation, necessary for

interpreting ESR spectra of Cu(II) complexes, is also introduced as a square-well potential rather than the more familiar $\cos(3\phi)$ form. Ground-state "inversion" splittings calculated using the angular square well potential are similar to those calculated using harmonic oscillator basis functions together with a $\cos(3\phi)$ potential.^{3,15} For example, the present result of 0.03 cm^{-1} for radii of $a=0.1 \text{ \AA}$ and $b=0.2 \text{ \AA}$, and a barrier at 321 cm^{-1} , compares with a value of 0.05 cm^{-1} obtained using our harmonic oscillator energy expressions³ with a fixed radius of $(ab)^{1/2}=0.1414 \text{ \AA}$ and the same barrier and reduced mass as in the square-well case. A possible application of the square-well angular potential is to systems perturbed by an external applied stress^{3,12} or by random internal crystal strains. Although the equivalence of the minima is destroyed in such cases, the form of the angular potential remains sufficiently simple that matrix elements are trivial to calculate.

for $M=3/2$:

$$P=x^{-1},$$

$$Q=1;$$

for $M=5/2$:

$$P=3x^{-2}-1,$$

$$Q=3x^{-1};$$

for $M=7/2$:

$$P=15x^{-3}-6x^{-1},$$

$$Q=15x^{-2}-1;$$

for $M=9/2$:

$$P=105x^{-4}-45x^{-2}+1,$$

$$Q=105x^{-3}-10x^{-1}.$$

APPENDIX A: REMARKS ON THE SOLUTION OF EQ. (23)

Examples of P_M and Q_M [$P=P_M(x)$, $Q=Q_M(x)$]:

For $M=1/2$:

$$P=1,$$

$$Q=0;$$

In general, P always contains a highest term in x^{-1} which is of a higher degree by one than the highest term in x^{-1} in Q . Thus if the function $F_M(x, \beta)$ [see Eq. (24)] is multiplied in both numerator and denominator by x^{2M-1} , the numerator becomes a polynomial in x of degree $2M-2$, while the denominator becomes a polynomial in x of degree $2M$; thus, as x increases without bound, $F_M(x, \beta)$ approaches zero for any value of β .

APPENDIX B: SOME EIGENVALUES OF K FOR $\beta=2.0$

The following are solutions $K_{M,n}$ of Eq. (16), with $\beta=2.0$, for half-odd-integral values of M from 1/2 through 19/2, and for integral values of n from 1 through 10, correct to five places after the decimal point. See also Fig. 7.

$n \setminus M$	1/2	3/2	5/2	7/2	9/2
1	3.14159	3.28601	3.55579	3.92252	4.35840
2	6.28319	6.36068	6.51307	6.73556	7.02183
3	9.42478	9.47720	9.58127	9.73553	9.93792
4	12.56637	12.60589	12.68461	12.80190	12.95687
5	15.70796	15.73966	15.80288	15.89731	16.02248
6	18.84956	18.87600	18.92880	19.00766	19.11261
7	21.99115	22.01383	22.05915	22.12697	22.21713
8	25.13274	25.15260	25.19228	25.25171	25.33076
9	28.27433	28.29199	28.32729	28.38016	28.45052
10	31.41593	31.43182	31.46360	31.51121	31.57461
$n \setminus M$	11/2	13/2	15/2	17/2	19/2
1	4.84100	5.35385	5.88541	6.42787	6.97604
2	7.36468	7.75663	8.19030	8.65866	9.15513
3	10.18591	10.47664	10.80707	11.17405	11.57441
4	13.14838	13.37508	13.63550	13.92804	14.25106
5	16.17779	16.36251	16.57582	16.81682	17.08455
6	19.24300	19.39850	19.57860	19.78275	20.01034
7	22.32939	22.46349	22.61910	22.79585	22.99334
8	25.42928	25.54708	25.68395	25.83963	26.01385
9	28.53827	28.64327	28.76537	28.90439	29.06012
10	31.65369	31.74838	31.85856	31.98409	32.12482

APPENDIX C: SOME EIGENVALUES OF K FOR $\beta=3.0$

The following are the first sixteen solutions (in order of magnitude) $K_{M,n}$ of Eq. (16), with $\beta=3.0$, for half-odd-integral values of M . Column e gives maximum uncertainties; an asterisk (*) indicates that the value is correct to five places after the decimal point.

M	n	K	e
1/2	1	1.57080	*
3/2	1	1.73717	*
5/2	1	2.02066	*
7/2	1	2.36711	*
9/2	1	2.74070	*
11/2	1	3.12287	*
1/2	2	3.14159	*
3/2	2	3.24	± 0.02
5/2	2	3.43	± 0.02
13/2	1	3.50557	*
7/2	2	3.69	± 0.01
15/2	1	3.88605	*
9/2	2	4.02	± 0.02
17/2	1	4.26370	*
11/2	2	4.38	± 0.02
19/2	1	4.64	± 0.01

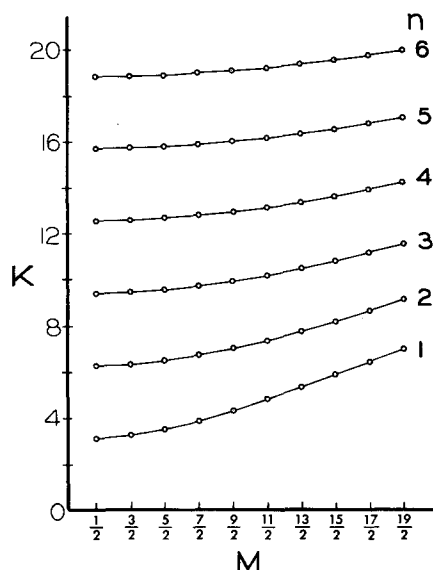


FIG. 7. Solutions $K_{M,n}$ of Eq. (16), with $\beta=2.0$, for the lowest ten values of M ($M=1/2, 3/2, \dots, 19/2$) and the lowest six values of n ($n=1, 2, \dots, 6$). Each open circle represents an eigenvalue of $K_{M,n}$ and thus a doubly degenerate energy level, the energy of which is given by Eq. (25). To a first approximation, for β differing slightly from 2.0, the graph will remain accurate if the ordinate be taken as $(\beta-1)K_{M,n}$.

APPENDIX D: LOW ENERGY EIGENVALUES ($n=1$) FOR $\beta=2.0$ AND $\beta=3.0$

The following are energy eigenvalues $E_{M,1}^0$ of the 'unperturbed' system ($B=0$), for $a=0.1 \text{ \AA}$, $\mu=104.9 \text{ amu (phys.)}$, for values of β of 2.0 and 3.0, and for half-odd-integral values of M from 1/2 to 17/2 inclusive. See also Figs. 5 and 6.

M	$E^0(\beta=2.0)$	$E^0(\beta=3.0)$
1/2	$3.15 \times 10^{-14} \text{ erg}$	$0.79 \times 10^{-14} \text{ erg}$
3/2	3.45	0.96
5/2	4.04	1.30
7/2	4.91	1.79
9/2	6.06	2.40
11/2	7.48	3.11
13/2	9.15	3.92
15/2	11.06	4.82
17/2	13.19	5.80

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