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Jahn-Teller effect in tetrahedral d^1 metal complexes

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The role of second-order Jahn-Teller effects in influencing absorption and EPR spectra of d^1 metal ions in tetrahedral symmetry was analyzed. It is shown that the pseudo-Jahn-Teller effect, which mixes the ground and the first excited state, is effective in some tetrahedral d^1 systems, thus providing a plausible explanation for their optical and EPR data.

I. INTRODUCTION

Despite the simple electronic structure of tetrahedral d^1 systems, a clear understanding of their phenomenology is still lacking.¹⁻⁴ The main problem is to explain the strongly reduced anisotropy of the g and A values deduced from the EPR spectra. This reduced anisotropy cannot be explained even considering the $E \otimes \epsilon$ Jahn-Teller (JT) problem on the ground state (greek letters are used to represent vibrational modes).

Indeed, the presence of the JT effect in these systems is widely recognized even though it is not clear how such an effect could explain the observed spectra.

Until a few years ago second-order JT effects, apart from pseudo JT effect,⁵⁻⁸ had been commonly regarded as having little interpretative power. However, the quadratic JT coupling was shown to be essential for the interpretation of both the spectroscopic properties of alkali-halide phosphors, doped with ns^2 impurities,^{9,10} and of transition metal hexafluorides.¹¹ In particular it was demonstrated by an extensive analysis, including JT terms up to the second order in cubic^{9,10} or in lower symmetry systems,¹² that stable distortions of different symmetry can coexist and new kinds of distortions can occur. Such an analysis was first proposed to interpret the fluorescence of Ga^+ , In^+ , and Tl^+ doped phosphors, but the results were also utilized to explain new experimental findings.¹³⁻¹⁶ On the other hand, Stoneham and Lannoo⁵ showed the coexistence of minima of different symmetry due to the pseudo JT effect in tetrahedral and cubic systems.

It is clear that the knowledge of the order of magnitude of the different JT coupling constants represents an essential point in the understanding of the phenomenology of the JT systems. Very recently, a new parametrization method was presented for the calculation of the JT coupling constants in the framework of the angular overlap model (AOM).¹⁷ On these grounds we reexamined different JT systems, which, in spite of their structural simplicity, were not yet fully understood.^{10,18,19}

In this paper we consider tetrahedrally coordinated d^1 metal ions, taking into account first- and second-order JT effects in both ground and excited states with a particular attention to the role of the pseudo JT effect. In Sec. II we

present: (i) the JT problem for the physical system considered, recalling the main concepts of Stoneham and Lannoo's theory⁵; (ii) our theoretical approach based on the AOM,²⁰ and the analysis of the absorption band shape ($E \rightarrow T_2$), making use of a Monte Carlo integration technique first proposed by Cho,²¹ and finally (iii) we show how EPR spectra are affected in the presence of strong pseudo JT mixing. In Sec. III the results we have obtained are discussed and the spectroscopic behavior of tetrahedral d^1 systems is interpreted.

II. THEORY

A. The Jahn-Teller problem

It is useful to consider the Hamiltonian

$$H = H_{LF} + H_{JT} + H_{SO}, \quad (1)$$

where H_{LF} , H_{JT} , and H_{SO} are the ligand field, JT, and spin-orbit coupling Hamiltonians, respectively.

The tetrahedral ligand field splits the 2D term of a d^1 free ion into two levels, 2E (ground state) and 2T_2 , separated by an energy gap Δ . Because both levels are orbitally degenerate, they are JT unstable with respect to the vibrational modes ϵ and τ_2 as it results from the symmetric products²²:

$$[E]_{\text{sym}}^2 = A_1 + E; \quad [T_2]_{\text{sym}}^2 = A_1 + E + T_2. \quad (2)$$

Furthermore, because $E \times T_2 = T_1 + T_2$, the vibrational modes τ_1 and/or τ_2 can couple the ground state with the excited one.

In a tetrahedral system, like ML_4 , there are one ϵ (bending) and two τ_2 (one bending and one stretching) vibrational modes, that have to be considered within the whole JT problem. At this point it should be noted that, throughout the paper, the displacements of the nuclei are expressed in terms of symmetry coordinates, which are *not* normal coordinates in the case of the τ_2 representation. There actually is some mixing between the two τ_2 symmetry coordinates, so that we are not concerned with pure bending or stretching modes. However, for the sake of simplicity, such mixing is ignored and the two coordinates are considered separately. Moreover, due to the greater *softness* of the bending modes, larger JT couplings can be expected for these vibrations, therefore only one τ_2 mode is considered neglecting stretching vibrations in our analysis.

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Choosing $|\theta\rangle, |\epsilon\rangle$ and $|\xi\rangle, |\eta\rangle, |\zeta\rangle$ as the electronic basis functions for the E and T_2 states, respectively, in the harmonic approximation the JT Hamiltonian H_{JT} plus the ligand field Hamiltonian may be written

$$H_{LF} + H_{JT} = \begin{array}{ccccc} & |\theta\rangle & |\epsilon\rangle & |\xi\rangle & |\eta\rangle & |\zeta\rangle \\ \begin{array}{c} w_{11} \\ w_{12} \\ w_{13} \\ w_{14} \\ w_{15} \end{array} & & \begin{array}{c} w_{12} \\ w_{22} \\ w_{23} \\ w_{24} \\ w_{25} \end{array} & \begin{array}{c} w_{13} \\ w_{23} \\ \Delta + w_{33} \\ w_{34} \\ w_{35} \end{array} & \begin{array}{c} w_{14} \\ w_{24} \\ w_{34} \\ \Delta + w_{44} \\ w_{45} \end{array} & \begin{array}{c} w_{15} \\ w_{25} \\ w_{35} \\ w_{45} \\ \Delta + w_{55} \end{array} & + VI, \end{array} \quad (3)$$

where I is the unit matrix, $V = \frac{1}{2}[K_\epsilon(Q_\theta^2 + Q_\epsilon^2) + K_\tau(Q_\xi^2 + Q_\eta^2 + Q_\zeta^2)]$ and the elements w_{ij} of the symmetric 5×5 JT matrix are

$$\begin{aligned} w_{11} &= A_1 Q_\theta + A_2(Q_\theta^2 - Q_\epsilon^2), \\ w_{12} &= -A_1 Q_\epsilon + 2A_2 Q_\epsilon Q_\theta, \\ w_{13} &= -(c_1/2)Q_\xi, \\ w_{14} &= -(c_1/2)Q_\eta, \\ w_{15} &= c_1 Q_\zeta, \\ w_{22} &= -A_1 Q_\theta - A_2(Q_\theta^2 - Q_\epsilon^2), \\ w_{23} &= (\sqrt{3}/2)c_1 Q_\xi, \\ w_{24} &= -(\sqrt{3}/2)c_1 Q_\eta, \\ w_{25} &= 0, \\ w_{33} &= b\left(Q_\epsilon - \frac{Q_\theta}{\sqrt{3}}\right) + b_{\epsilon\epsilon}\left[Q_\epsilon Q_\theta - \frac{(Q_\epsilon^2 - Q_\theta^2)}{2\sqrt{3}}\right] + \frac{b_{\tau\tau}}{3}(2Q_\xi^2 - Q_\eta^2 - Q_\zeta^2), \\ w_{34} &= cQ_\zeta + c_{\tau\tau}Q_\xi Q_\eta, \\ w_{35} &= cQ_\eta + c_{\tau\tau}Q_\xi Q_\zeta, \\ w_{44} &= -b\left(Q_\epsilon + \frac{Q_\theta}{\sqrt{3}}\right) - b_{\epsilon\epsilon}\left[Q_\epsilon Q_\theta + \frac{(Q_\epsilon^2 - Q_\theta^2)}{2\sqrt{3}}\right] + \frac{b_{\tau\tau}}{3}(2Q_\eta^2 - Q_\xi^2 - Q_\zeta^2), \\ w_{45} &= cQ_\xi + c_{\tau\tau}Q_\eta Q_\zeta, \\ w_{55} &= \frac{2b}{\sqrt{3}}Q_\theta + \frac{b_{\epsilon\epsilon}}{\sqrt{3}}(Q_\epsilon^2 - Q_\theta^2) + \frac{b_{\tau\tau}}{3}(2Q_\xi^2 - Q_\eta^2 - Q_\zeta^2). \end{aligned}$$

Here A_1 and A_2 are the linear and quadratic JT constants for the $E \otimes \epsilon$ problem,²³ while b , c and $b_{\epsilon\epsilon}$, $b_{\tau\tau}$, $c_{\tau\tau}$ are the linear and quadratic constants for the $T_2 \otimes (\epsilon + \tau_2)$ problem.⁹ The pseudo JT coupling constant c_1 is defined as

$$c_1 = \langle \xi | \left(\frac{\partial U}{\partial Q_\xi} \right)_0 | \theta \rangle, \quad (4)$$

where the derivative of the electronic potential is computed at the undistorted configuration. The symmetry coordinates are designated (Q_θ, Q_ϵ) for ϵ , and (Q_ξ, Q_η, Q_ζ) for τ_2 vibrational modes; K_ϵ and K_τ are the corresponding force constants, for simplicity assumed to be identical for both electronic states considered.

In the Hamiltonian described above we have included also the pseudo JT terms, which are often disregarded when the linear JT effect is active at a level. However, in the present case there are two reasons for including them: (i) unlike octahedral d^1 or d^9 clusters, the two levels 2E and 2T_2 are quite close to each other, Δ is only on the order of 1 eV; (ii) there is evidence for large interacting terms (see below), which may also appreciably modify the adiabatic potential energy surface (APES) of the ground state. Even in the absence of an $E \otimes \epsilon$ type coupling, the original configuration is unstable when $c_1^2 > (K_\tau \Delta / 2)$ and it will be distorted along the τ_2 coordinate.⁵

On the contrary, the second-order $\epsilon \otimes \tau_2$ terms within the triplet T_2 were omitted, because their inclusion does not qualitatively change the results that are obtained by considering the quadratic JT terms alone.⁹

We also ignored the totally symmetric coordinate, because in the present framework, we were not particularly interested in its effects (broadening of the band shape,²¹ stabilization at different Q_α^0 of different kinds of minima¹⁰).

The inclusion of the spin-orbit coupling leads to a 10×10 matrix, which can be easily factorized into two 5×5 matrices,

when trigonal modes are ignored. One of these matrices written in the basis $|\theta\alpha\rangle, |\theta\beta\rangle, |\epsilon\alpha\rangle \dots |\xi\alpha\rangle, |\xi\beta\rangle$, where α and β stand for the spin up and down, respectively, is reported below:

$$\begin{array}{ccccc}
 & |\theta\beta\rangle & |\epsilon\beta\rangle & |\xi\alpha\rangle & |\eta\alpha\rangle & |\xi\beta\rangle \\
 & \dots & \dots & i\frac{\sqrt{3}}{2}\lambda & \frac{\sqrt{3}}{2}\lambda & \dots \\
 & \dots & \dots & i\frac{\lambda}{2} & -\frac{\lambda}{2} & i\lambda \\
 H_{\text{LF}} + H_{\text{SO}} = & -i\frac{\sqrt{3}}{2}\lambda & -i\frac{\lambda}{2} & \Delta & i\frac{\lambda}{2} & -\frac{\lambda}{2} \\
 & \frac{\sqrt{3}}{2}\lambda & -\frac{\lambda}{2} & -\frac{i\lambda}{2} & \Delta & \frac{i\lambda}{2} \\
 & \dots & -i\lambda & -\frac{\lambda}{2} & -\frac{i\lambda}{2} & \Delta
 \end{array} \quad (5a)$$

From Eqs. (3) and (5a) the complete matrix, including both spin-orbit and JT couplings, can be straightforwardly, although tediously, obtained. However, a better visualization of the role of the spin-orbit coupling may be obtained using the complex basis $(\eta + i\xi)$, $(-\eta + i\xi)$, $i\xi$ for the T_2 state, so that only the off-diagonal terms $\langle {}^2E | H_{\text{SO}} | {}^2T_2 \rangle$ are nonvanishing:

$$\begin{array}{ccccc}
 & |\theta\beta\rangle & |\epsilon\beta\rangle & \Gamma_8(-\frac{1}{2}, T_2) & \Gamma_8(\frac{1}{2}, T_2) & \Gamma_7(-\frac{1}{2}, T_2) \\
 & \dots & \dots & -\sqrt{\frac{3}{2}}\lambda & \dots & \dots \\
 H_{\text{LF}} + H_{\text{SO}} = & \dots & \dots & \dots & -\sqrt{\frac{3}{2}}\lambda & \dots \\
 & -\sqrt{\frac{3}{2}}\lambda & \dots & \Delta - \frac{\lambda}{2} & \dots & \dots \\
 & \dots & -\sqrt{\frac{3}{2}}\lambda & \dots & \Delta - \frac{\lambda}{2} & \dots \\
 & \dots & \dots & \dots & \dots & \Delta + \lambda,
 \end{array} \quad (5b)$$

plus an equivalent 5×5 matrix. Here the normalized spin-orbit wavefunctions Γ_7 and Γ_8 are given by

$$\Gamma_7(-\frac{1}{2}) = -\frac{i}{\sqrt{3}}(\xi\alpha - i\eta\alpha - \xi\beta), \quad (6a)$$

$$\Gamma_7(+\frac{1}{2}) = -\frac{i}{\sqrt{3}}(\xi\beta + i\eta\beta + \xi\alpha), \quad (6b)$$

$$\Gamma_8(-\frac{1}{2}) = \frac{i}{\sqrt{2}}(\xi\alpha + i\eta\alpha), \quad (6c)$$

$$\Gamma_8(+\frac{1}{2}) = -\frac{i}{\sqrt{2}}(\xi\beta - i\eta\beta), \quad (6d)$$

$$\Gamma_8(-\frac{3}{2}) = -\frac{i}{\sqrt{6}}(\xi\beta + i\eta\beta - 2\xi\alpha), \quad (6e)$$

$$\Gamma_8(+\frac{3}{2}) = \frac{i}{\sqrt{6}}(\xi\alpha - i\eta\alpha + 2\xi\beta). \quad (6f)$$

B. The AOM treatment

The AOM can be considered as a simplification of the LCAO-MO in the Wolfsberg–Helmholtz approximation.²⁰ Following this approach the linear JT coupling constants can be expressed as follows¹⁷:

$$\langle \psi_i | \left(\frac{\partial U}{\partial Q_\gamma} \right)_0 | \psi_j \rangle = \sum_{\lambda\omega} \sum_n \frac{\partial}{\partial r_n} [e_{\lambda n} F_{\lambda\omega}(\psi_i, L_n) F_{\lambda\omega}(\psi_j, L_n)] \frac{\partial r_n}{\partial Q_\gamma} \quad (7)$$

if ψ_i and ψ_j belong to the same degenerate state: JT effect. If ψ_i and ψ_j belong to different states: pseudo JT effect.

Here λ indicates the bonding symmetry with respect to the metal–ligand axis (σ, π, δ) and ω specifies the particular orbital (for $\lambda > 0$); $e_{\lambda n}$ is the energy change of a given metal orbital due to the interaction with the suitable orbitals of the n th ligand L ; $F_{\lambda\omega}$, the angular overlap factor, is a fraction of the maximum overlap integral at a given metal–ligand distance and is expressed as a function of the angular coordinates (θ_n, ϕ_n) of the ligands; r_n stands for the generic polar coordinate R_n, θ_n, ϕ_n . The other symbols have their usual significance.

Because the AOM can take into account covalent effects, its use seems to be more suitable with respect to the crystal field approach in dealing with tetrahedral metal complexes, where a nonnegligible mixing between ligand and metal orbitals is expected.²⁴

Using Eq. (7) it is a simple matter to obtain the linear JT coupling constants for the present JT problem and they are given by the following relationships:

$$A_1 = \frac{4\sqrt{2}}{3R} e_\pi, \quad (8a)$$

$$b = -\frac{2\sqrt{6}}{3R} (e_\sigma - \frac{1}{3} e_\pi), \quad (8b)$$

$$c = -\frac{2\sqrt{2}}{3R} (e_\sigma - \frac{2}{3} e_\pi), \quad (8c)$$

$$c_1 = -\frac{2\sqrt{6}}{3R} (e_\sigma - \frac{2}{3} e_\pi). \quad (8d)$$

Here R is the metal–ligand bond length and can be obtained from structural data, while e_σ, e_π can be evaluated theoretically^{17,20} or estimated from spectroscopic measurement, taking into account for example that the energy gap Δ in the AOM is expressed as

$$\Delta = \frac{4}{3} e_\sigma - \frac{16}{9} e_\pi. \quad (9)$$

Because e_π is always a small fraction of e_σ ,^{25,26} Eqs. (8) show a weak JT effect on the ground state 2E and a strong coupling in the excited one 2T_2 . Moreover, if the linear JT effect is examined within the triplet T_2 alone, *tetragonal* (i.e., ϵ type) distortions should be favored for not too different values of the force constants K_ϵ and K_τ , unless the neglected τ_2 stretching mode is more effective than the τ_2 bending mode considered. It is noticeable that the pseudo JT constant c_1 is comparable with the coupling constant with the ϵ modes, b , so its effect on the ground state cannot be neglected in an accurate treatment.

With a procedure analogous to that used to obtain Eq. (7) the second-order JT coupling constants can also be expressed as a function of the AOM parameters.²⁷ However in this case the values (due to the approximations inherent in the AOM) have only a qualitative meaning.

The resulting expressions are reported here for the sake of completeness:

$$A_2 = \frac{1}{R^2} \left(2e_\sigma - \frac{7}{3} e_\pi \right), \quad (10a)$$

$$b_{\epsilon\epsilon} = \frac{\sqrt{3}}{3R^2} \left(-11e_\sigma + \frac{53}{3} e_\pi \right), \quad (10b)$$

$$b_{\tau\tau} = \frac{2}{9R^2} \left(11e_\sigma - \frac{53}{3} e_\pi \right), \quad (10c)$$

$$c_{\tau\tau} = \frac{4}{3R^2} \left(e_\sigma - \frac{e_\pi}{3} \right). \quad (10d)$$

Some approximate conclusions concerning the *relative* magnitude of the above constants may be drawn: for example $b_{\tau\tau}$ is about one half and opposite in sign to the constant $b_{\epsilon\epsilon}$.

It is remarkable that the second order constant A_2 for the $E \otimes \epsilon$ problem should make a substantial contribution, because it is a function of the σ -bond energy, whereas A_1 is a function of the π -bond energy alone.

C. Absorption band shape

According to the classical Franck–Condon approximation, the normalized line shape function of the optical absorption $E \rightarrow T_2$ may be written as^{21,28}

$$f(E) = \left(\frac{K_\tau}{2\pi kT} \right)^{3/2} \left(\frac{K_\epsilon}{2\pi kT} \right) \sum_{j=1,2} \exp \left[-\frac{(E_j - E_1)}{kT} \right] \times \sum_i^3 \int \cdots \int dQ_\epsilon dQ_\theta dQ_\xi dQ_\eta dQ_\zeta |\langle e_i | \mathbf{M} | g_j \rangle|^2 \times \exp \left[-\frac{K_\epsilon}{2kT} (Q_\epsilon^2 + Q_\theta^2) - \frac{K_\tau}{2kT} (Q_\xi^2 + Q_\eta^2 + Q_\zeta^2) \right] \times \delta[E - X_{ij}(Q_\epsilon, Q_\theta, Q_\xi, Q_\eta, Q_\zeta)], \quad (11)$$

where E is the photon energy, kT is the thermal energy, and $\langle e_i | \mathbf{M} | g_j \rangle$ is the dipole matrix element between each of the different components of the final (e_i) and ground (g_j) electronic states. Note that the factor $\exp[-(E_j - E_1)/kT]$ takes into account the different population on the two sheets arising from the split E level. The transition energies X_{ij} were computed by numerically diagonalizing the Hamiltonian (3). An expression similar to Eq. (11) is obtained when the spin-orbit coupling is included.

The absorption band shape was analyzed making use of a Monte Carlo integration method,²¹ in which the main steps are: (i) generation of random values for the five Q 's, having Gaussian distributions with $\sigma_\epsilon = (kT/K_\epsilon)^{1/2}$ and $\sigma_\tau = (kT/K_\tau)^{1/2}$ for (Q_ϵ, Q_θ) and (Q_ξ, Q_η, Q_ζ) , respectively; (ii) each set of the above five Q 's was substituted in Eq. (3), which was then diagonalized; (iii) the resulting X_{ij} values were accumulated in 80 energy boxes, corresponding to the whole range of optical transitions of our interest. The procedure was repeated 30 000 times. No substantial variation of

the band shape was observed, when the procedure was repeated 60 000 times.

As pointed out by Kapoor and Hensley in a very recent publication,²⁹ the Monte Carlo method is particularly suitable to handle any additional term in the JT Hamiltonian that can be explicitly written down. Moreover such a method does not require the Condon approximation. In fact, the dipole matrix elements were left inside the integral of Eq. (11), still retaining the dependence of the electronic wave function on the nuclear coordinates.³⁰

D. APES of the ground state and vibronic level scheme

The problem of a pure orbital doublet E coupled with ϵ -type vibrational modes has been widely investigated,^{22,23,31-38} so that there is no need to dwell upon this aspect. Here, it is sufficient to remember that linear terms produce the so-called "Mexican hat," characterized by a continuum of minima, whereupon some warping is engendered, when second-order terms are added. For a weak second-order interaction the energy map in the plane Q_ϵ, Q_θ with a threefold symmetry is well known and the three minima and the three saddle points are approximately disposed on a circular path [Fig. 1(a)]. When the constant A_2 increases an appreciable modification of the energy contour occurs, still maintaining the threefold symmetry. When the contribution of the second-order term to the energy becomes greater than the linear one, a "clover" shape is obtained [Fig. 1(b)], and the saddle points move towards the undistorted configuration.

If only metal ions of the first transition series are considered, the spin-orbit coupling values are sufficiently small ($<540 \text{ cm}^{-1}$)³⁹ so that the coupling with the excited state does not cause substantial modifications of the shape of the ground state surface. Of course, there is a mixing of the wave functions of the triplet T_2 into the ground doublet, which is important when the magnetic properties (magnetic susceptibility, paramagnetic resonance spectra) of the system are investigated.

On the contrary, as we have shown, the pseudo JT constant c_1 may be rather so strong as to significantly affect the APES of the ground state. When the coupling with the ϵ modes is vanishing, Stoneham and Lannoo⁵ have demonstrated that, for $c_1^2 > (K_\tau \Delta / 2)$, six orthorhombic (Or) minima are stabilized in the full five-dimensional space $Q_\epsilon \dots Q_\zeta$, whose coordinates are

$$Q_\epsilon^{(0)} = Q_\theta^{(0)} = Q_\zeta^{(0)} = Q_\eta^{(0)} = 0;$$

$$Q_\xi^{(0)} = \pm \frac{1}{2c_1 K_\tau} [4c_1^4 - \Delta^2 K_\tau^2]^{1/2}, \quad (12)$$

plus two equivalent couples of distortions along Q_ξ and Q_η . The energy of the minima is given by the relationship:

$$E^0 = \frac{1}{2} [\Delta - (\Delta^2 + 4c_1^2 Q_\xi^{(0)2})^{1/2} + K_\tau Q_\xi^{(0)2}]$$

$$= \frac{\Delta}{2} - \frac{1}{2} \frac{c_1^2}{K_\tau} - \frac{\Delta^2}{8} \frac{K_\tau}{c_1^2}, \quad (13)$$

and the corresponding electronic eigenfunctions are

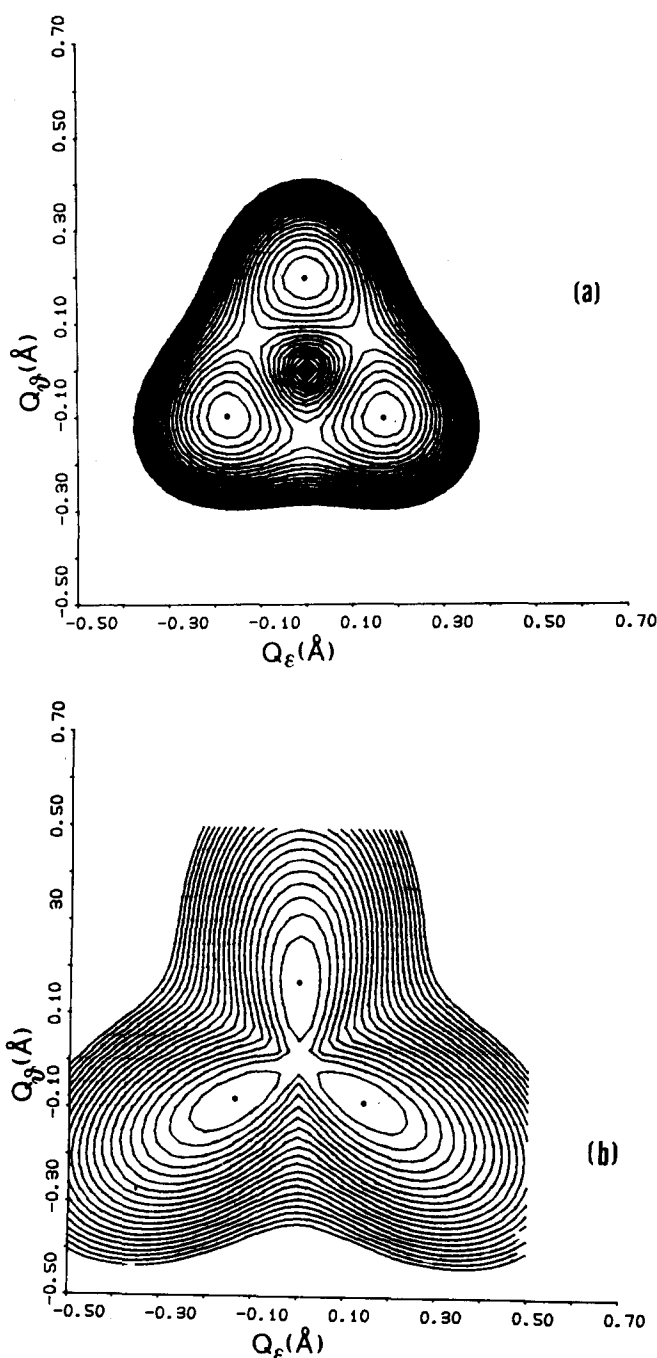


FIG. 1. Energy maps in the Q_θ - Q_ϵ space: (a) $E \otimes \epsilon$ problems, $A_1 = 900 \text{ cm}^{-1}/\text{\AA}$, $A_2 = 500 \text{ cm}^{-1}/\text{\AA}^2$, $E_{\min} = -89 \text{ cm}^{-1}$; (b) $E \otimes \epsilon$ problem, $A_1 = 125 \text{ cm}^{-1}/\text{\AA}$, $A_2 = 2375 \text{ cm}^{-1}/\text{\AA}^2$, $E_{\min} = -10 \text{ cm}^{-1}$. The force constant K_ϵ was taken equal to $5537 \text{ cm}^{-1}/\text{\AA}^2$. Each level line corresponds to an increment of 5 cm^{-1} .

$$|\Psi_\pm\rangle = \sqrt{\frac{1}{2}(1+F)}|\theta\rangle \mp \sqrt{\frac{1}{2}(1-F)}|\xi\rangle \quad (14)$$

with $F = \Delta K_\tau / 2c_1^2$. The other four eigenfunctions are obtained by cyclic permutation $|\xi\rangle \rightarrow |\eta\rangle \rightarrow |\zeta\rangle$ and taking into account the proper combinations of $|\theta\rangle$ and $|\epsilon\rangle$, which behave as $(3z^2 - r^2) \rightarrow (3y^2 - r^2) \rightarrow (3x^2 - r^2)$, respectively.³⁷

Now, let us include also the ϵ vibrational modes. If the two states E and T_2 were considered separately, tetragonal (Te) distortions, which are the only ones allowed for a $E \otimes \epsilon$ problem, will be stabilized on the ground state. On the other

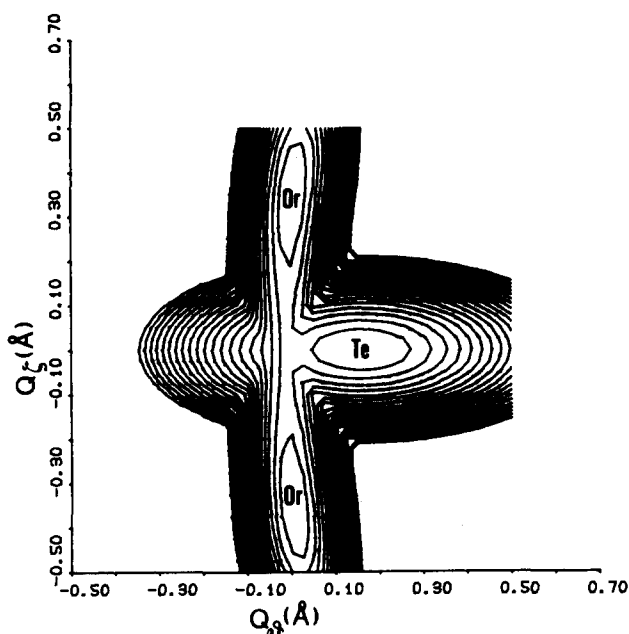


FIG. 2. Energy map of the ground electronic level in the Q_θ - Q_ϵ plane ($Q_\tau = Q_\xi = Q_\eta = 0$), when the pseudo JT effect is considered; $\Delta = 7950 \text{ cm}^{-1}$, $b = -4240 \text{ cm}^{-1}/\text{\AA}$, $A_1 = 125 \text{ cm}^{-1}/\text{\AA}$, $A_2 = 2375 \text{ cm}^{-1}/\text{\AA}^2$, $c = -2500 \text{ cm}^{-1}/\text{\AA}$, $c_1 = -4400 \text{ cm}^{-1}/\text{\AA}$, $K_\epsilon = 5537 \text{ cm}^{-1}/\text{\AA}^2$, $K_\tau = 4545 \text{ cm}^{-1}/\text{\AA}^2$; $E(\text{Te}) = -9.9 \text{ cm}^{-1}$, $E(\text{Or}) = -9.5 \text{ cm}^{-1}$. Increments as in Fig. 1.

hand, different distortions are possible in the excited state, if the full $T_2 \otimes (\epsilon + \tau_2)$ JT problem is taken into account, however this aspect is not considered here because it has been extensively treated elsewhere.^{9,10} For our purposes, we prefer to stress the possible existence of Or minima even in a E ground state, when pseudo JT terms are considered.⁵ Indeed, for values of $c_1^2 > (K_\tau \Delta / 2)$, besides the three Te minima of the pure $E \otimes \epsilon$ problem, other six Or minima are also stabilized (Fig. 2). Their coordinates have nonvanishing components in the (Q_θ, Q_ϵ) space and can be expressed in the five-dimensional space $(Q_\theta, Q_\epsilon, Q_\xi, Q_\eta, Q_\zeta)$ as: $(\rho, 0, 0, 0, \pm q)$, $(-\frac{1}{2}\rho, -\sqrt{3}/2\rho, 0, \pm q, 0)$, $(-\frac{1}{2}\rho, \sqrt{3}/2\rho, \pm q, 0, 0)$ where now ρ and q are functions of $b, A_1, c_1, K_\epsilon, K_\tau$, and Δ .⁵ The corresponding eigenfunctions are given by expressions quite analogous to those given in Eq. (14), but with modified coefficients.

From a dynamic standpoint, tunneling among Te distortions leads to E and A_1 (or A_2) low lying vibronic levels, depending on flattening (or elongation) of the tetrahedron,^{22,23,37} while tunneling among Or distortions provides A_1 , E , and T_2 vibronic levels (see Fig. 3).

The energies for tunneling levels in the case of Te minima are well known^{22,23} and in our symbolism are given by

$$E(E) = \frac{H_{11}(\text{Te}) + H_{12}(\text{Te})}{1 + (S_{\text{Te}}/2)}, \quad (15a)$$

$$E(A) = \frac{H_{11}(\text{Te}) - 2H_{12}(\text{Te})}{1 - S_{\text{Te}}}, \quad (15b)$$

where H_{ij} ($i, j = 1, 2, 3$) are the full Hamiltonian matrix elements and S_{Te} is the overlap integral for the vibronic wave functions expressed in the adiabatic approximation as a product between the electronic wave function in the minimum

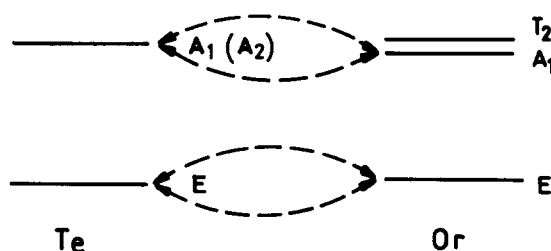


FIG. 3. Low lying vibronic levels arising from tunneling among Te and Or distortions. The first excited level in the Te case belongs to $A_1(A_2)$ irreducible representation, when the JT effect leads to a flattened (elongated) tetrahedron.

and the vibrational wave function of the harmonic oscillator still centered on that minimum.^{23,40} Since the three minima are equivalent it is sufficient to consider only $H_{11}(=H_{22}=H_{33})$, $H_{12}(=H_{13}=H_{23})$, and $S_{\text{Te}}(=S_{12}=S_{13}=S_{23})$.

Analogously, the energies for tunneling levels in the case of Or distortions are given by

$$E(E) = \frac{H_{11}(\text{Or}) + H_{12}(\text{Or}) + H_{13}(\text{Or})}{1 + S_{12} + S_{13}}, \quad (16a)$$

$$E(A_1) = \frac{H_{11}(\text{Or}) + H_{12}(\text{Or}) - 2H_{13}(\text{Or})}{1 + S_{12} - 2S_{13}}, \quad (16b)$$

$$E(T_2) = \frac{H_{11}(\text{Or}) - H_{12}(\text{Or})}{1 - S_{12}}. \quad (16c)$$

Here the subscripts (12) and (13) refer to homologous (equal tetragonal coordinates) or not Or minima, respectively.

When the minima are sufficiently deep the integrals H_{ij} and S_{ij} can be evaluated directly and the following relationships are obtained, if only the ground vibrational state in each well is considered:

$$S_{\text{Te}} = \exp \left[-\frac{3K_\epsilon}{4\hbar\omega_\epsilon} Q_\theta^{(0)2}(\text{Te}) \right], \quad (17a)$$

$$H_{11}(\text{Te}) = \hbar\omega_\epsilon + \frac{3}{2}\hbar\omega_\tau + E_{\text{JT}}(\text{Te}), \quad (17b)$$

$$H_{12}(\text{Te}) = \frac{1}{2}S_{\text{Te}} \left[\hbar\omega_\epsilon + \frac{3}{2}\hbar\omega_\tau + \frac{5}{2}E_{\text{JT}}(\text{Te}) \right], \quad (17c)$$

$$S_{12} = \exp \left[-\frac{K_\tau}{\hbar\omega_\tau} q^2 \right], \quad (17d)$$

$$S_{13} = \exp \left[-\frac{3K_\epsilon}{4\hbar\omega_\epsilon} \rho^2 - \frac{K_\tau}{2\hbar\omega_\tau} q^2 \right], \quad (17e)$$

$$H_{11}(\text{Or}) = \hbar\omega_\epsilon + \frac{3}{2}\hbar\omega_\tau + E_{\text{JT}}(\text{Or}), \quad (17f)$$

$$H_{12}(\text{Or}) = S_{12}(\hbar\omega_\epsilon + \frac{3}{2}\hbar\omega_\tau - \frac{1}{2}K_\tau q^2 + \frac{1}{2}K_\epsilon \rho^2 + A_1\rho + A_2\rho^2), \quad (17g)$$

$$H_{13}(\text{Or}) = S_{13}(\hbar\omega_\epsilon + \frac{3}{2}\hbar\omega_\tau - \frac{1}{4}K_\epsilon \rho^2 + \frac{3}{4}A_1\rho - \frac{3}{8}A_2\rho^2 + a_\zeta c_1 q), \quad (17h)$$

where $Q_\theta^{(0)}(\text{Te})$ is the coordinate of the Te minimum at $Q_\epsilon = 0$ for the $E \otimes \epsilon$ JT problem, and a_ζ is the coefficient of the electronic function $|\zeta\rangle$ in the whole electronic function at the minima $(\rho, 0, 0, 0, \pm q)$. For vanishing $E \otimes \epsilon$ coupling, a_ζ is equal to $[\frac{1}{2}(1-F)]^{1/2}$, as it can be seen from Eq. (14). It is convincing that in both cases the vibronic E level is always the ground state. Furthermore, there is the possibility of a

mixing between the two vibronic E levels, which will be stronger as the levels become closer. Therefore the real vibronic ground state is an admixture of the starting "Te" and "Or" vibronic E states so that large contributions of the excited electronic T_2 level are found into the ground state.

E. Influence of the pseudo JT effect on the EPR spectra

In order to calculate EPR spectra, spin-orbit coupling between the 2E and 2T_2 levels must be included. Spin-orbit coupling tends to cancel the JT effect, giving again undistorted systems for large interactions. However, since spin-orbit constants for the first transition metal series are sufficiently small, a perturbation procedure can be safely followed so that vibronic levels including spin functions are obtained.

As shown by Ham^{32,37} a Zeeman interaction in such a vibronic 2E ground state leads, in the absence of strain, to two spin transitions corresponding to the anisotropic g factors

$$g_{\pm} = g_1 \pm qg_2[1 - 3(l^2m^2 + l^2n^2 + m^2n^2)]^{1/2}, \quad (18)$$

where l , m , and n are the direction cosines of the magnetic field; for a d^1 (or d^9) electronic configuration $g_1 = 2.0023 - (4\lambda/\Delta)$ and $g_2 = -(4\lambda/\Delta)$. The parameter q is a reduction factor, which must lie between 1 (no coupling) and $\frac{1}{2}$ (strong JT effect) for a dynamic JT effect with only linear coupling and no warping. On the other hand, in the presence of strong linear plus nonlinear couplings the lower bound for q is 0.484.^{22,37,41}

When a small axial static distortion is introduced (let us say along the S_4 axis of the tetrahedron) the quartet spin-orbit ground level Γ_8 splits into two Kramers doublets and the resultant g values are now³⁷

$$g_{\parallel} = g_1 + qg_2, \quad (19a)$$

$$g_{\perp} = g_1 - \frac{1}{2}qg_2 \quad (19b)$$

for elongated tetrahedra and

$$g_{\parallel} = g_1 - qg_2, \quad (20a)$$

$$g_{\perp} = g_1 + \frac{1}{2}qg_2 \quad (20b)$$

for flattened tetrahedra. Quite analogous expressions can be obtained for the hyperfine parameters A_{\parallel} and A_{\perp} , putting A_{\parallel} , A_{\perp} , A_1 , and A_2 in place of g_{\parallel} , g_{\perp} , g_1 , and g_2 , respectively, in Eqs. (19) and (20). In such a case, for a d^1 (or d^9) electronic configuration, A_1 and A_2 are given by

$$A_1 = -P \left(\frac{4\lambda}{\Delta} + \kappa \right), \quad (21)$$

$$A_2 = -P \left(\frac{4}{7} + \frac{34}{7} \frac{\lambda}{\Delta} \right), \quad (22)$$

where $P = 2\gamma\beta\beta_N\langle r^{-3} \rangle$, γ is the nuclear g factor, β_N the nuclear magneton, $\langle r^{-3} \rangle$ the one-electron average of r^{-3} , and κ the parameter characterizing the Fermi contact term.

Equations (19) and (20) are valid also in the case of Te and Or coexistence, but a new reduction factor q' has to be introduced, which is given by

$$q' = a^2q(\text{Or}) + b^2q(\text{Te}), \quad (23)$$

a and b being the mixing coefficients of the two "Te" and "Or" vibronic levels E ; $q(\text{Or})$ and $q(\text{Te})$ are, respectively, the

reduction factors when only Or (no $E \otimes \epsilon$ coupling) or Te (no pseudo JT coupling) distortions occur.

Under the assumption of a nuclear motion localized in the neighborhood of the bottom of the minima and retaining only linear terms the following expressions are obtained:

$$q(\text{Te}) = \frac{1 + 2S_{\text{Te}}}{2 + S_{\text{Te}}}, \quad (24)$$

$$q(\text{Or}) = \frac{1 + S_{12} + 4S_{13}}{2(1 + S_{12} + S_{13})}, \quad (25)$$

The $E \otimes \epsilon$ JT problem by itself generally provides only small stabilization energies in tetrahedral d^1 systems and therefore $q(\text{Te})$ values are close to 1. On the contrary strong JT interactions can give $q(\text{Or})$ values as small as 1/2. As a consequence, looking at relationship (23), it can be deduced that the quenching resulting from the whole JT interaction is much larger than one would obtain if only the $E \otimes \epsilon$ JT problem were considered.

III. RESULTS AND DISCUSSION

Let us consider first the absorption band shape for the transition $^2E \rightarrow ^2T_2$ (Fig. 4). As long as the coupling with the ϵ modes alone is taken into account, no splitting of the absorption band is observed for vanishing values of the spin-orbit coupling. The situation is quite similar to that widely described by Toyozawa and Inoue⁴² for $A \rightarrow T$ transitions, because the intersections (at $Q_i = 0$) of the APES's arising from the T_2 state are crossing and not branching points. Still in the framework of the coupling with the ϵ vibrational modes alone, a splitting is obtained by introducing the spin-orbit coupling, but it is only of the order of $(3/2)\lambda$, which is the energy gap between the two spin-orbit levels (Γ_8, Γ_7) of the 2T_2 state. However much larger splittings may be found by introducing the coupling constant c , with the trigonal modes in the excited level: the characteristic spreadeagle shape shown in Fig. 4(a) is obtained, which is again analogous to that computed for the $A \rightarrow T$ case. The second order constant A_2 simply smooths the curve [Fig. 4(b)], whereas drastic changes are induced by the pseudo JT effect [Figs. 4(c)–4(e)]. This latter produces a two wings band, where two out of three subbands are collapsed into the higher energy wing; moreover a reduction of the total splitting is observed. It is important to keep well in mind that these modifications of the band shape, which could mimic a lowering of symmetry, are actually simply due to the JT effect in a quite dynamic limit. The role of the quadratic coupling constants b_{ee} , $b_{\tau\tau}$, and $c_{\tau\tau}$ is far less evident even for sufficiently high values. They at most provide an asymmetrical intensity for the three subbands [Figs. 4(f)–4(h)]. The splitting is mainly governed by the constants c and c_1 . If the shape of $d-d$ absorption spectra of the V(IV) compounds is examined,^{4,43} for which experimental data are not clear, pseudo JT (and also quadratic) effect could be inferred from our analysis.

Now let us dwell a little upon the supposed anomalies observed in some tetrahedral d^1 systems.

In order to explain the optical spectra of zircon-type crystals doped with V^{4+} and EPR spectra of YPO_4 and YVO_4 doped with Cr^{5+} , Greenblatt *et al.*^{3,4} invoked motion-

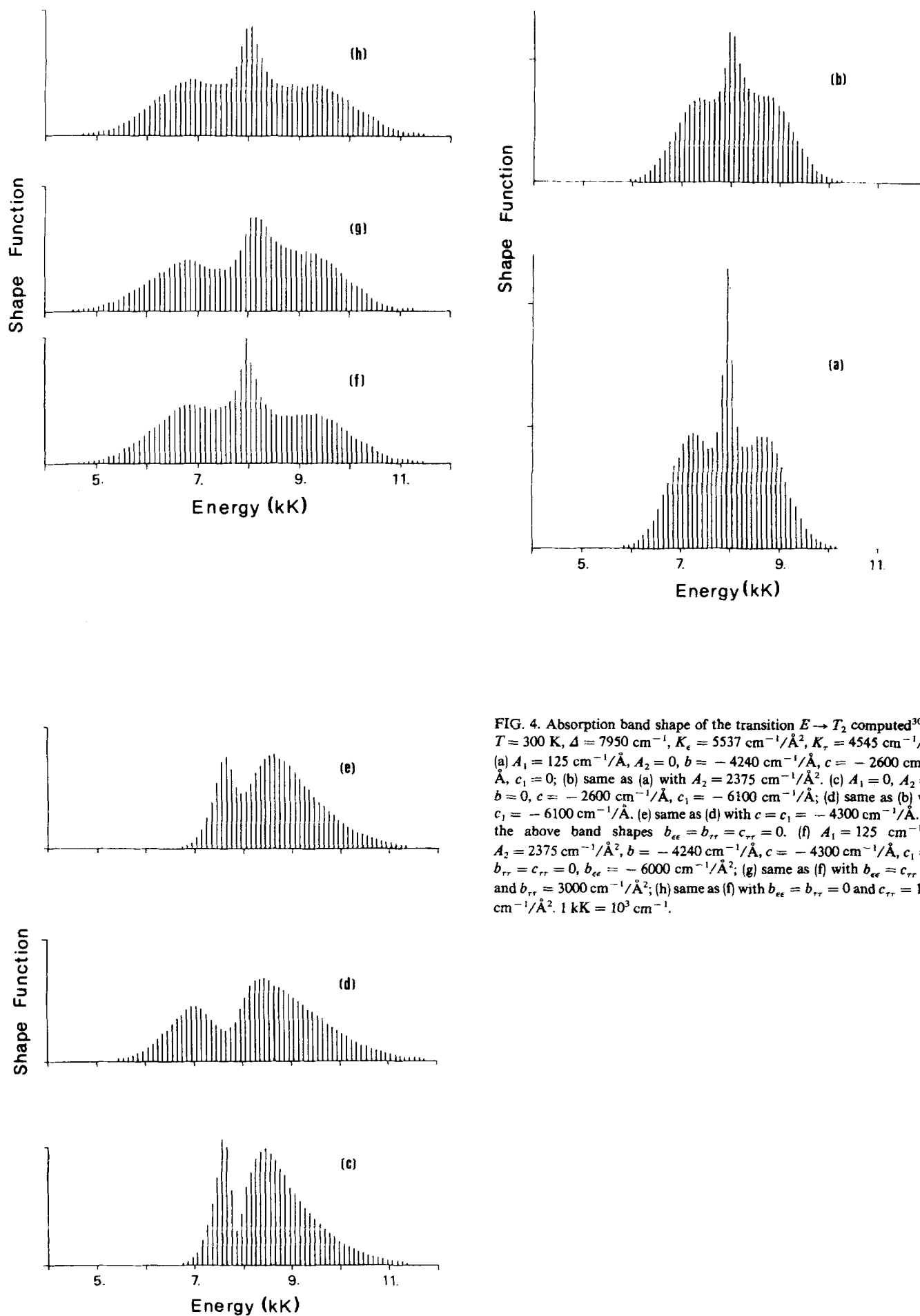


FIG. 4. Absorption band shape of the transition $E \rightarrow T_2$ computed³⁰ for $T = 300$ K, $\Delta = 7950$ cm^{-1} , $K_e = 5537$ $\text{cm}^{-1}/\text{\AA}^2$, $K_r = 4545$ $\text{cm}^{-1}/\text{\AA}^2$. (a) $A_1 = 125$ $\text{cm}^{-1}/\text{\AA}$, $A_2 = 0$, $b = -4240$ $\text{cm}^{-1}/\text{\AA}$, $c = -2600$ $\text{cm}^{-1}/\text{\AA}$, $c_1 = 0$; (b) same as (a) with $A_2 = 2375$ $\text{cm}^{-1}/\text{\AA}^2$. (c) $A_1 = 0$, $A_2 = 0$, $b = 0$, $c = -2600$ $\text{cm}^{-1}/\text{\AA}$, $c_1 = -6100$ $\text{cm}^{-1}/\text{\AA}$; (d) same as (b) with $c_1 = -6100$ $\text{cm}^{-1}/\text{\AA}$. (e) same as (d) with $c = c_1 = -4300$ $\text{cm}^{-1}/\text{\AA}$. For the above band shapes $b_{ee} = b_{rr} = c_{rr} = 0$. (f) $A_1 = 125$ $\text{cm}^{-1}/\text{\AA}$, $A_2 = 2375$ $\text{cm}^{-1}/\text{\AA}^2$, $b = -4240$ $\text{cm}^{-1}/\text{\AA}$, $c = -4300$ $\text{cm}^{-1}/\text{\AA}$, $c_1 = 0$, $b_{rr} = c_{rr} = 0$, $b_{ee} = -6000$ $\text{cm}^{-1}/\text{\AA}^2$; (g) same as (f) with $b_{ee} = c_{rr} = 0$ and $b_{rr} = 3000$ $\text{cm}^{-1}/\text{\AA}^2$; (h) same as (f) with $b_{ee} = b_{rr} = 0$ and $c_{rr} = 1500$ $\text{cm}^{-1}/\text{\AA}^2$. 1 kK = 10^3 cm^{-1} .

al effects among local distortions of unknown origin. Furthermore, the 4 K spectra of VCl_4 in a large variety of host systems (CCl_4 , CBr_4 , TiCl_4 , cyclohexane, toluene, and others) showing resolved vanadium hyperfine structure, are all very similar and can be fitted with an almost axial spin Hamiltonian, whereby $g_{\parallel} = 1.95 \pm 0.01$, $g_{\perp} = 1.91 \pm 0.01$, $A_{\parallel} < 50$ and $A_{\perp} = 105 \pm 10 \times 10^{-4} \text{ cm}^{-1}$. The data can be interpreted in terms of a vibronic ground state of the general form^{1,44}

$$|\Psi\rangle = \sin \alpha |\theta\rangle \chi_I + \cos \alpha |\epsilon\rangle \chi_{II} \quad (26)$$

with $\langle \chi_I | \chi_{II} \rangle = 0$ and α within the narrow range of 57 ± 3 deg in all cases.^{1,2} Here χ_I and χ_{II} are arbitrary vibrational wave functions. In an interpretation within an ideal single mode $E \otimes \epsilon$ type coupling model χ_I and χ_{II} depend only on Q_θ and Q_ϵ and can be described e.g., numerically,⁴⁵ or by linear combinations of harmonic oscillator functions centered at the undistorted configuration.⁴⁶ For an $E \otimes \epsilon$ case in a weak perturbing tetragonal matrix field it has been pointed out by several authors^{22,31,32} that α values between 30° and 60° should be "forbidden." In fact, model calculations of the type performed by Feiner⁴⁷ and by us^{1,2,44,48} produce, for any reasonable choice of $E \otimes \epsilon$ JT potential parameters (A_1, A_2) and tetragonal or rhombic matrix potentials, α values significantly below 30° (if the elongated tetrahedron is favored) or above 60° (if the flattened geometry is preferred). Such conditions are closely related to the bounds within which the reduction factor q must lie.^{22,37} Indeed the EPR results for VCl_4 (α invariably close to 60° , but sometimes significantly below) correspond to a q value smaller than $1/2$ and, in the present case, such a reduction could hardly be explained by multimode coupling effects⁴⁹ or by referring to states of the type encountered in Slonewski's resonances.^{22,41}

On the contrary it seems that pseudo JT effect may be effective in all these systems. In fact, following the AOM parametrization method, we may estimate the different JT coupling constants starting from the experimental data. We chose the values of 7950 cm^{-1} and 0.16 \AA for Δ ($d-d$ absorption spectrum⁴³) and for the JT radius R_{JT} (electron diffraction analysis⁵⁰), respectively.

Since R_{JT} is given by

$$R_{JT} = \frac{A_1}{K_\epsilon - 2A_2}, \quad (27)$$

using for K_ϵ the value obtained by the general valence force field ($0.11 \text{ mdyn/\AA} \equiv 5537 \text{ cm}^{-1}/\text{\AA}^2$)⁵¹ we have obtained e_σ and e_π from Eqs. (9) and (27)⁵² and then the different coupling constants. The most significant constants are reported in Table I. At this point it should be remarked that the sign of A_2 provides an elongated tetrahedron, unlike what has been found experimentally. However anharmonic terms, which were not considered here, can reverse the direction of the distortion.¹⁷ Moreover it has to be considered that ligand-ligand repulsion, which is neglected in the AOM, could play a fundamental role in stabilizing flattened tetrahedra.

The small value found for the $E \otimes \epsilon$ JT stabilization energy is particularly significant because it accounts for the

TABLE I. Jahn-Teller coupling constants evaluated for VCl_4 in the framework of the AOM.^a

I	II
$e_\sigma = 6040 \text{ cm}^{-1}$	$e_\sigma = 7300 \text{ cm}^{-1}$
$e_\pi = 58 \text{ cm}^{-1}$	$e_\pi = 1000 \text{ cm}^{-1}$
$A_1 = 51 \text{ cm}^{-1}/\text{\AA}$	$A_1 = 880 \text{ cm}^{-1}/\text{\AA}$
$A_2 = 2608 \text{ cm}^{-1}/\text{\AA}^2$	
$E_{JT} = 4 \text{ cm}^{-1b}$	$E_{JT} = 70 \text{ cm}^{-1b}$
$b = -4594 \text{ cm}^{-1}/\text{\AA}$	$b = -5315 \text{ cm}^{-1}/\text{\AA}$
$c = -2601 \text{ cm}^{-1}/\text{\AA}$	$c = -2188 \text{ cm}^{-1}/\text{\AA}$
$c_1 = -4580 \text{ cm}^{-1}/\text{\AA}$	$c_1 = -5062 \text{ cm}^{-1}/\text{\AA}$

^a $R(\text{V-Cl}) = 2.14 \text{ \AA}$ (Ref. 50); the values of column I have been calculated from Eq. (27), whereas in column II are reported the values calculated assuming $A_2 = 0$.

^b Jahn-Teller stabilization energy for the $E \otimes \epsilon$ problem.

quite dynamical behavior even at very low temperatures.¹ At the opposite side, the large value of c we have obtained can actually account for the splitting of the absorption band. Finally the pseudo JT constant c_1 is just a little larger than $(K_\pi \Delta/2)^{1/2} = 4250 \text{ cm}^{-1}$, for a K_π value of $4545 \text{ cm}^{-1}/\text{\AA}^2$ ⁵¹; therefore in such a case Or minima can be stabilized besides the Te ones.

Actually the weak JT stabilization energy for the pure $E \otimes \epsilon$ problem should provide a reduction factor $q(\text{Te})$ close to 1. On the contrary a sufficiently high pseudo JT effect leads to much more reduced $q(\text{Or})$ values [see Eq. (25)]. Therefore, if the ground vibronic level is mainly described by the pure "Or" vibronic level E , the effective reduction factor q' will be approximately equal to $q(\text{Or})$ [see Eq. (23)]. In the presence of a strong interaction the three low lying vibronic levels E , A_1 , and T_2 are very close to each other so that even small static perturbations may allow large mixing between E and A_1 levels (in D_{2d} symmetry A_1 representations of the T_d point group behave again as A_1 , while E splits into $A_1 + B_1$). Because the Kramers doublet 2A_1 provide an isotropic g value equal to g_1 , the new g values (and analogously the A values), which are obtained for the flattened situation when the mixing E , A_1 is considered, are

$$g_{\parallel} = g_1 - q'' g_2, \quad (28a)$$

$$g_{\perp} = g_1 + \frac{1}{2} q'' g_2. \quad (28b)$$

Here $q'' = m^2 q'$, and m is the mixing coefficient of the vibronic level A_1 arising from the unperturbed doublet $E(|\Psi\rangle_{g.s.} = m|A_1(E)\rangle + m|A_1(A_1)\rangle$, where in round brackets are indicated the irreducible representations for the T_d point group). It can be seen that the new reduction factor q'' can go well below $1/2$, depending only on the magnitude of the interaction between the two vibronic levels.

As a matter of fact we believe that the phenomenology of VCl_4 in different host lattices is mainly governed by a strong pseudo JT effect, which is probably accompanied by a small static crystal field and, eventually, by a strong nonlinear coupling, as it can be deduced from the e_σ dependence of the second order coupling constant A_2 [see Eq. (10a)].

The approximations involved in order to estimate the relevant potential parameters prevent reliable predictions of the shape of the ground state APES. In addition to the ap-

proximations inherent in the AOM treatment, we have assumed identical force constants in the two electronic states and have ignored the contributions of the τ_2 stretching mode. Therefore a detailed analysis in terms of vibronic wavefunctions consistent with the derived APES does not seem appropriate at present, without additional experimental information on the spacings of the lowest vibronic levels. However, in the case considered, pseudo JT effects might easily dominate first order JT couplings without any unreasonable parameter choices.

As for V^{4+} and Cr^{5+} in zircon-type lattices, a very rough estimation in the framework of the AOM, by using the data reported in Ref. 4, shows that the conditions for the stabilization of Or distortions by means of pseudo JT effect are again likely matched. In fact putting $\Delta \sim 11\,000\text{ cm}^{-1}$,⁴ and considering that, as a rule, e_π is 0.10–0.30 times e_σ ,^{25,26} from Eqs. (8) and (9) the ratio $2c_1^2/\Delta$ should be in the range $15\,900\text{--}19\,500\text{ cm}^{-1}/\text{\AA}^2$. We have previously seen that for values of the bending force constant K_r smaller than $2c_1^2/\Delta$ Or minima occur in the APES of the ground state: actually the values of $15\,900\text{--}19\,500\text{ cm}^{-1}/\text{\AA}^2$ (or smaller) are the expected ones for bending modes in a tetrahedral cluster like MO_4 , even if the “cluster” model could appear a too crude approximation for such doped crystals. However it was not our intention here to perform an accurate interpretation of the experiments of Refs. 3 and 4, but simply to point out some systems, where our theoretical results could help in the interpretation of unclear experimental results.

In conclusion, we have presented evidence that in the case of tetrahedral d^1 systems the usual simple $E \otimes e$ coupling model (to first or second order) is likely to break down because of strong off-diagonal τ_2 coupling effects to the nearby excited T_2 electronic state. Consequently, it is suggested that absorption and EPR spectra of such systems have to be reexamined, in the light of the present considerations.

ACKNOWLEDGMENTS

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³⁰At this point it has to be remarked that the dipole matrix element vanishes for pure d orbitals, while it will be nonzero when the $3d\text{--}4p$ metal orbital mixing and/or covalency effects are considered. Indeed in tetrahedral complexes, $d\text{--}d$ transitions gain intensity mainly by the above mechanisms (see, i.e., Ref. 24, Chap. 7), which have to be taken into account in the analysis of the absorption spectrum of a transition metal compound. Let us describe the one-electron orbitals as:

$$\Psi_{\xi(\eta,\zeta)} = \alpha_1 |\xi\rangle_{(\eta,\zeta)} + \alpha_1^{(r)} p_{x(y,z)} + \alpha_1^{(n)} \chi_{x(y,z)},$$

$$\Psi_{e(\theta)} = \alpha_2 |\epsilon\rangle_{(\theta)} + \alpha_2^{(n)} \Pi_{e(\theta)},$$

where p_x , p_y , p_z stand for the $4p$ metal orbitals, while $\chi_x \dots \Pi_\theta$ stand for the suitable linear combinations of the ligand orbitals. It is easily to verify the following relationships:

$$\langle \Psi_\xi | \mathbf{M} | \Psi_e \rangle = A \mathbf{i}; \quad \langle \Psi_\eta | \mathbf{M} | \Psi_e \rangle = A \mathbf{j};$$

$$\langle \Psi_\xi | \mathbf{M} | \Psi_\theta \rangle = (A/\sqrt{3}) \mathbf{i}; \quad \langle \Psi_\eta | \mathbf{M} | \Psi_\theta \rangle = (A/\sqrt{3}) \mathbf{j};$$

$$\langle \Psi_\zeta | \mathbf{M} | \Psi_\theta \rangle = (2/\sqrt{3}) A \mathbf{k}.$$

If ligand contributions are neglected A is given by

$$A = \frac{\alpha_1^{(r)} \alpha_2^{(n)} \langle r \rangle}{\sqrt{5}}, \quad \text{where } \langle r \rangle = \langle R_{3d} | r | R_{4p} \rangle.$$

Since we were interested in relative intensities only, we evaluated the dipole matrix element $\langle e_i | \mathbf{M} | g_j \rangle$ in units of A without calculating explicitly the values of the α coefficients and of the radial integral. Also A was assumed to be constant for any nuclear configuration within the potential well considered.

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