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On the Jahn–Teller and PseudoJahn–Teller Effect

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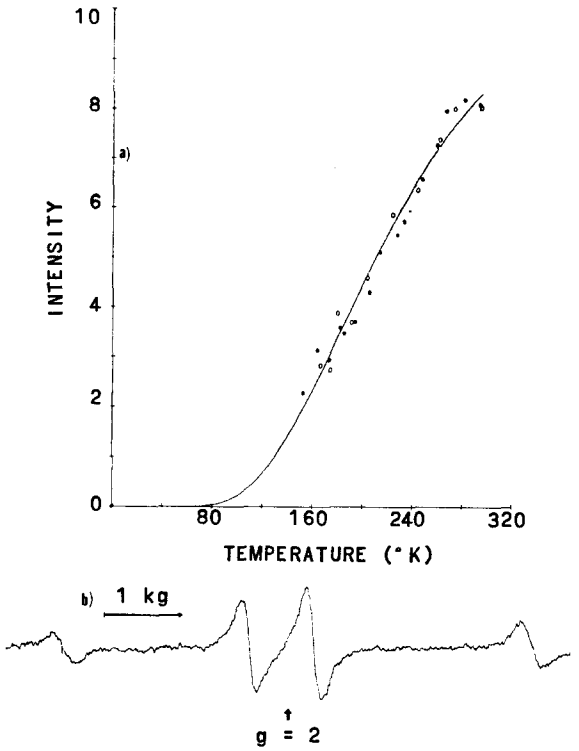

FIG. 1. (a) Variation of X-band signal intensity with temperature. The open and filled circles represent two sets of normalized experimental data and the curve is calculated using Eq. (1) with $J=190.8$ cm^{-1}. (b) A Q-band spectrum of single crystal $enH_2[Fe(III)HEDTA]_2O\cdot 6H_2O$ with the applied magnetic field in the ac plane.

Fe–Fe axis. From the spectrum obtained in this orientation, a value of $|D|=0.15\pm0.01$ cm^{-1} is obtained. A large portion of this value of D may be attributed to a direct dipole–dipole interaction[6];

$$|D_{(\text{dipole-dipole})}{}^{\text{calc}}|=0.12 \text{ cm}^{-1}.$$

If the magnetic field is rotated 180° in a plane roughly perpendicular to the Fe–Fe axis, two maxima and two minima occur for the inner pair of lines, indicating the necessity for terms in the spin Hamiltonian which are quartic with respect to spin operators. In addition, the antisymmetric exchange interaction, $\mathfrak{D}\cdot(\mathbf{S}_1\times\mathbf{S}_2)$, although expected to be small, is allowed by the molecular symmetry.[7]

The resonance lines are not extensively dipolar-broadened since even at room temperature most molecules are in the singlet ($S=0$) ground state. Both the X-band and Q-band linewidths at room temperature are ~150 G and are reduced at 160°K to ~120 G, a reduction consistent with the removal of intermolecular dipolar broadening by depopulation of thermally excited neighbors.

A broader resonance line having a different temperature dependence is observed for certain orientations at 35.5 GHz. This line is more intense and more anisotropic than those due to the quintet transitions and may be due to the triplet ($S=1$) state which is expected to have larger zero-field splittings.[3] However, this assignment is not definitely established.

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[1] (a) H. Schugar, C. Walling, R. B. Jones, and H. B. Gray, J. Am. Chem. Soc. **89**, 3712 (1967). (b) S. J. Lippard, H. Schugar, and C. Walling, Inorg. Chem. **6**, 1825 (1967).

[2] (a) E. B. Fleisher, T. S. Srivastava, J. Am. Chem. Soc. **91**, 2403 (1969). (b) J. Lewis, F. E. Mabbs, and A. Richards, J. Chem. Soc. **A1967**, 1014. (c) W. M. Reif, W. A. Baker, Jr., and N. E. Erickson, J. Am. Chem. Soc. **90**, 4794 (1968).

[3] J. Owen, J. Appl. Phys. Suppl. **32**, 213S (1961).

[4] Using $g=2.00$ and no temperature-independent paramagnetism; see A. Earnshaw and J. Lewis, J. Chem. Soc. **1961**, 396.

[5] Additional lines of lower intensity occur at lower fields. These are presumably due to "forbidden" transitions or arise from states of $S>2$ or from mononuclear impurities.

[6] Assuming that the dipole–dipole contribution to D has the same sign as the crystal-field contribution; see Ref. 3.

[7] T. Moriya, Phys. Rev. **120**, 91 (1960).

On the Jahn–Teller and Pseudo-Jahn–Teller Effect*

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The Jahn–Teller and pseudo-Jahn–Teller effects involving degenerate and nearly degenerate electronic levels, respectively, have been of interest for a number of years.[1–3] The work of Longuet-Higgins *et al.*[1] is the most complete numerical study of this effect for the case of a doubly degenerate vibrational mode interacting with a doubly degenerate electronic level. These authors diagonalized the relevant matrices by computer. Hobey[3] has derived an elegant iterative method to solve the coupled equations. We present a new

TABLE I. Energy lowering in Jahn–Teller effect (in units of ω).

k^2	Ref. (1)	Present work
0.25	−0.226	−0.223
0.5	−0.422	−0.408
1.	−0.767	−0.716
2.	−1.369	−1.245
5.	−2.961	−2.750
20.	−10.493	−10.250

TABLE II. Energy splitting in pseudo-Jahn–Teller effect.

Compound	ΔE	ΔW (Present work)	ΔW (Previous)
Toluene⁻	708 cm⁻¹ [a]	483 cm⁻¹	470 cm⁻¹ [a]
Toluene⁻	548[b]	390 cm⁻¹	370[b]
Toluene⁻	365[b]	267 cm⁻¹	284[b]

[a] Reference 3.
[b] Reference 4.

method which requires relatively little computation and which gives excellent agreement with the work of Ref. 1. We have also applied the method to the pseudo-Jahn–Teller effect.[3,4]

The Hamiltonian for this problem may be written in second quantized form as

$$H=\epsilon(c_\alpha^\dagger c_\alpha+c_\beta^\dagger c_\beta)+\omega(b_l^\dagger b_l+b_{-l}^\dagger b_{-l})+k\omega[c_\alpha^\dagger c_\beta(b_l^\dagger+b_{-l})+c_\beta^\dagger c_\alpha(b_l+b_{-l}^\dagger)], \quad (1)$$

where the c_α and c_β are the annihilation operators for an electron in the degenerate α and β orbitals of energy ϵ; the b_l and b_{-l} are the annihilation operators for quanta of vibrations l and $-l$, respectively, each of energy ω. The coupling has been taken to be linear in the coordinate. We have used the complex orbitals α and β, and the complex vibrational coordinates l and $-l$ in accord with previous work. However, it is more convenient to use the real orbitals and coordinates defined by the transformations

$$b_1=\sqrt{2}^{-1}(b_l+b_{-l}); \qquad b_2=(\sqrt{2}i)^{-1}(b_l-b_{-l}),$$
$$c_1=\sqrt{2}^{-1}(c_\alpha+c_\beta); \qquad c_2=(\sqrt{2}i)^{-1}(c_\alpha-c_\beta). \quad (2)$$

Using these we find

$$H=\epsilon(c_1^\dagger c_1+c_2^\dagger c_2)+\omega(b_1^\dagger b_1+b_2^\dagger b_2)+(k\omega/\sqrt{2})\times[(c_1^\dagger c_1-c_2^\dagger c_2)(b_1+b_1^\dagger)-(c_1^\dagger c_2+c_2^\dagger c_1)(b_2+b_2^\dagger)]. \quad (3)$$

We may remove the first coupling term by performing a unitary transformation on H. The transformed Hamiltonian is given by $\hat{H}=U^\dagger HU$, with

$$U=\exp[(k/\sqrt{2})(c_1^\dagger c_1-c_2^\dagger c_2)(b_1-b_1^\dagger)]. \quad (4)$$

Thus

$$\hat{H}=\epsilon(c_1^\dagger c_1+c_2^\dagger c_2)+\omega(b_1^\dagger b_1+b_2^\dagger b_2)-\tfrac{1}{2}k^2\omega(c_1^\dagger c_1-c_2^\dagger c_2)^2-(k\omega/\sqrt{2})(b_2+b_2^\dagger)\times\{c_1^\dagger c_2\exp[-\sqrt{2}k(b_1-b_1^\dagger)]+c_2^\dagger c_1\exp[\sqrt{2}k(b_1-b_1^\dagger)]\}. \quad (5)$$

Notice that the third term in $\hat{H}$ is already diagonal. We now calculate the energy of the ground state, $c_1^\dagger|0\rangle$, (where $|0\rangle$ is the vacuum state) to second order in the nondiagonal term of $\hat{H}$. We find

$$E^{(2)}=\epsilon-\omega\{\tfrac{1}{2}k^2+\tfrac{1}{4}[1-\exp(-2k^2)]\}. \quad (6)$$

In Table I we compare this energy lowering to the energy of the lowest state of Ref. 1 for a large range of k. The agreement is excellent.

We have also calculated the electronic energy splitting for the pseudo-Jahn–Teller effect by the same method. We first add a term $\frac{1}{2}\Delta E(c_1^\dagger c_1-c_2^\dagger c_2)$ to $\hat{H}$. The initial energy splitting ΔE is changed to ΔW due to the vibronic interaction. Using the values of ΔE and k given by Hobey[3] or Purins and Karplus[4] we have calculated ΔW (again to second order). The results are given in Table II. The agreement is again excellent.

A more detailed discussion of this work will be published at a later date.

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[1] H. C. Longuet-Higgins, U. Öpik, M. H. L. Pryce, and R. A. Sack, Proc. Roy. Soc. (London) **A244**, 1 (1958).
[2] W. Moffitt and W. R. Thorson, in *Calcul des fonctions d'onde moleculaire* (Recherche Memoire Centre National de la Recherche Scientifique, Paris, 1958).
[3] W. Hobey, J. Chem. Phys. **43**, 2187 (1965).
[4] D. Purins and M. Karplus, J. Chem. Phys. **50**, 214 (1969).

Fluorescence Decay Times of Photoexcited Benzene and Toluene in the Gas Phase*

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Fluorescence decay times in the nanosecond region have been measured through a pulse sampling or a phase-shift technique in recent years.[1] Most measurements have been made in condensed media,[1,2] avoiding problems with low intensity in the gas phase. Since gas-phase data are needed in the assessment of the competition between radiative and radiationless processes, we wish to report preliminary results obtained on the decay times of the first excited singlets of benzene and toluene in the gas phase.

A pulsed deuterium discharge lamp (TRW nanosecond spectral source 31A, 4–7-nsec pulse at half-peak width) with saturated $CoSO_4/NiSO_4$ and "D_3P" solution filters[3] (transmission between 230 and 280 nm, 58% at 252 nm) was used for excitation most frequently. Fluorescence intensity from the sample in a T-shaped "Suprasil" fluorescence cell at room temperature was monitored by a photomultiplier tube (RCA 1P28 or 8575 V1) whose output was sampled and displayed on an oscilloscope (Tektronix 556 with 1S1 plug-in). The displays were photographed and averaged over 10 or more displays to improve the signal-to-noise