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Coexistence of two kinds of stable Jahn-Teller distortions in molecules with a fourfold symmetry axis

M. Bacci

Istituto di Ricerca sulle onde Elettromagnetiche del Consiglio Nazionale delle Ricerche, Firenze, Italy

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The second-order Jahn-Teller coupling of a doubly degenerate E electronic term with α_1, β_1, and β_2 nondegenerate vibrations has been investigated in molecules with a fourfold symmetry axis. It is shown that rectangular and rhombic distortions can coexist on the adiabatic potential-energy surfaces at different values of the totally symmetric coordinate Q_α. The effect of the spin-orbit coupling for $S = 1/2$ and $S = 1$ is also discussed.

I. INTRODUCTION

In recent works[1-3] we have shown that different kinds of minima (tetragonal, trigonal, orthorhombic) can coexist in O_h symmetry when a triply degenerate state T interacts with ϵ_g and τ_{2g} vibrational modes. This coexistence, which is forbidden in the linear approximation,[4] is possible, for reasonable values of the involved parameters, if quadratic Jahn-Teller (JT) terms and/or anharmonic restoring forces are considered. On this basis we proposed a model for the interpretation of the luminescence of KCl:Tl$^+$-type phosphors; a similar proposal was made by Fukuda *et al.* independently.[5] This model was checked by an elegant experiment of optically detected magnetic resonance[6]; moreover, other experimental results[7,8] were well interpreted on the basis of coexisting minima, thus showing that second-order JT coupling is really effective at least in some physical systems.

Although the JT effect in octahedral symmetry has been extensively investigated, few studies have been reported for lower symmetries.[9] However, with regard to molecules with a fourfold symmetry axis, very recently several experimental results, in particular on porphyrinic systems,[10-13] have been interpreted by considering the JT coupling.

In a molecule of symmetry D_{4h} (see Ref. 14) a doubly degenerate E state (E_g or E_u) couples with the vibrational modes β_{1g} and β_{2g} (Fig. 1).[15-18] In the linear approximation rhombic (Rh) or rectangular (Re) stable distortions are possible according to the relative magnitude of the coupling constants c_1 (β_{1g} modes) and c_2(β_{2g} modes), which are defined as follows:

$$c_1 = -\left\langle E^a \left| \frac{\partial V_E}{\partial Q_1} \right| E^a \right\rangle = \left\langle E^b \left| \frac{\partial V_E}{\partial Q_1} \right| E^b \right\rangle ,$$

$$c_2 = \left\langle E^a \left| \frac{\partial V_E}{\partial Q_2} \right| E^b \right\rangle ,$$

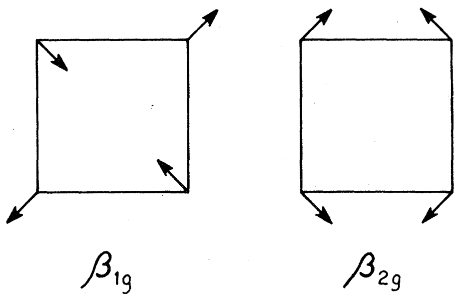

FIG. 1. Jahn-Teller active β_{1g} and β_{2g} vibrations.

where V_E is the electronic potential energy operator and Q_1, Q_2 are the normal coordinates corresponding to the vibrational modes β_{1g} and β_{2g}, respectively. If K_1 and K_2 are the force constants for the harmonic vibrations in Q_1 and Q_2, when $c_1^2/K_1 > c_2^2/K_2$ a pair of Rh minima exists on the adiabatic-potential-energy surface (APES); in the opposite case a pair of Re minima is found. In the special case where $c_1^2/K_1 = c_2^2/K_2$, there is a continuum of minima and the molecule can *rotate* freely between the two configurations.[17]

In the present paper, we intend to show that, as in O_h symmetry, the coexistence of different kinds of minima is possible, if also second-order JT terms are considered.

II. ORBITAL PROBLEM

As it can be seen by simple symmetry arguments (see, for example Appendix IV in Ref. 9) second-order JT coupling for $\beta_{1g} \times \beta_{2g}$ terms is forbidden; however, if the totally symmetric vibrational mode Q_α is considered, nonvanishing terms in $Q_\alpha Q_1$ and $Q_\alpha Q_2$ are found. Therefore, the Hamiltonian to be considered is given by

$$H = VI + W, \tag{1}$$

where I is the unit matrix, $V = \frac{1}{2}(K_\alpha Q_\alpha^2 + K_1 Q_1^2 + K_2 Q_2^2)$

and W is the symmetric 2×2 JT matrix whose elements w_{ij} for an E electronic level in the second-order JT approximation are

$$\begin{aligned} w_{11} &= -(c_1 + c_{\alpha 1}Q_\alpha)Q_1, \\ w_{22} &= (c_1 + c_{\alpha 1}Q_\alpha)Q_1, \\ w_{12} &= (c_2 + c_{\alpha 2}Q_\alpha)Q_2. \end{aligned} \tag{2}$$

Here $c_{\alpha 1}$ and $c_{\alpha 2}$ are the second-order JT coupling parameters and c_1 and c_2, which have been defined previously, are the linear ones.

By a procedure quite analogous to that described in Ref. 2, we have obtained the coordinates (Q_i^0) and the energies (E_i^0) of the stationary points; the cases follow:

(a) rhombic distortions:

$$Q_\alpha^0 = \frac{c_1 c_{\alpha 1}}{K_\alpha K_1 - c_{\alpha 1}^2}, \quad Q_1^0 = \pm\frac{c_1 K_\alpha}{K_\alpha K_1 - c_{\alpha 1}^2},$$

$$Q_2^0 = 0, \quad E^0 = \frac{-c_1^2 K_\alpha}{2(K_\alpha K_1 - c_{\alpha 1}^2)};$$

(b) rectangular distortions:

$$Q_\alpha^0 = \frac{c_2 c_{\alpha 2}}{K_\alpha K_2 - c_{\alpha 2}^2}, \quad Q_1^0 = 0,$$

$$Q_2^0 = \pm\frac{c_2 K_\alpha}{K_\alpha K_2 - c_{\alpha 2}^2}, \quad E^{(0)} = \frac{-c_2^2 K_\alpha}{2(K_\alpha K_2 - c_{\alpha 2}^2)}.$$

If we express the orbital electronic state as $a_1|E^a\rangle + a_2|E^b\rangle$, it can be verified that the solutions for a_1, a_2 in the first-order case are solutions for the second-order problem as well. In particular, for Rh distortions the solutions are: $a_1 = 1$, $a_2 = 0$ and $a_1 = 0$, $a_2 = 1$ [corresponding to the sign (+) or (−) for the coordinate Q_1^0, respectively] and for Re distortions: $a_1 = 1/\sqrt{2}$ and $a_2 = \mp 1/\sqrt{2}$ [corresponding to the sign (+) or (−) for the coordinate Q_2^0, respectively].

The minimum conditions for the above stationary points can be found by the procedure already described[2,4] and the following expressions are obtained:

(c) rhombic distortions:

$$K_1 K_\alpha > c_{\alpha 1}^2, \tag{3}$$

$$\frac{c_1^2}{K_1} > \frac{c_2^2}{K_2}\left(1 + \frac{c_{\alpha 1}(c_1 c_{\alpha 2} - c_2 c_{\alpha 1})}{K_1 K_\alpha c_2}\right)^2; \tag{4}$$

(d) rectangular distortions:

$$K_2 K_\alpha > c_{\alpha 2}^2, \tag{5}$$

$$\frac{c_2^2}{K_2} > \frac{c_1^2}{K_1}\left(1 + \frac{c_{\alpha 2}(c_2 c_{\alpha 1} - c_1 c_{\alpha 2})}{K_2 K_\alpha c_1}\right)^2. \tag{6}$$

When $c_{\alpha 1}$, $c_{\alpha 2} \to 0$, that is, in the linear approximation, the presence of Rh minima excludes Re minima and vice versa ($c_1^2/K_1 \gtrless c_2^2/K_2$, respectively); on the other hand, the introduction of the second-order terms $c_{\alpha 1}$, $c_{\alpha 2}$ allows an overlap between the existence areas of Rh and Re minima. We should like to remark that, if the condition $c_1^2/K_1 \sim c_2^2/K_2$ is matched, little second-order coupling is sufficient to stabilize both kinds of minima (the situation may be visualized in a way quite analogous to that shown in Fig. 2 of Ref. 3). Anyway, also rather different couplings to the β_{1g} and β_{2g} vibrational modes may allow the coexistence: Figure 2 shows Rh and Re coexisting minima when $c_1^2/K_1 = 2(c_2^2/K_2)$. The values we chose to calculate these maps ($c_1 = 3\times 10^3$ cm^{-1}/Å; $c_2 = 10^3$ cm^{-1}/Å; $K_\alpha = 2\times 10^4$ cm^{-1}/Å^2; $K_1 = 1.8\times 10^4$ cm^{-1}/Å^2; $K_2 = 4\times 10^3$ cm^{-1}/Å^2; $c_{\alpha 1} = 10^4$ cm^{-1}/Å^2; $c_{\alpha 2} = -5\times 10^3$ cm^{-1}/Å^2) are arbitrary, but reasonable for common physical systems, except the second-order coupling constants, for which no reliable value is reported; note that the opposite sign of $c_{\alpha 1}$ and $c_{\alpha 2}$ is not a necessary requirement for the coexistence.

As shown by the maps of Fig. 2, the two kinds of distortions are at different values of the totally symmetric coordinate Q_α and Fig. 3 better visualizes the coexistence along the coordinate Q_α; this latter diagram was computed by using the same parameters values of Fig. 2 and it represents the cross section along the projection on the Q_α axis of the path connecting a couple of different minima.

We may observe that, as a rule, the introduction of second-order terms reduces the height of the barrier between the minima, in particular for minima of different symmetry, so that dynamical situations and tunneling between different distortions are favored.

III. SPIN-ORBIT INTERACTION

When the spin-orbit coupling is taken into account, the conditions (3)–(6) for the existence of different minima are modified and mathematical difficulties prevent obtaining analytical expressions. However, useful information can be obtained by an inspection of the formulas, from which the APES's are computed. In the present paper we limit ourselves to considering the terms ^2E and ^3E, but analogous conclusions can be drawn for higher spin multiplicities.

The Hamiltonian to be considered is $H = VI + W + \lambda LS$, where λ is the spin-orbit coupling constant. For a term ^2E two APES's are obtained, which are given by

$$\epsilon_{1,2} = V \pm (w_{11}^2 + w_{12}^2 + \tfrac{1}{4}\lambda^2)^{1/2}, \tag{7}$$

where V, w_{11}, and w_{12} have been defined previously.

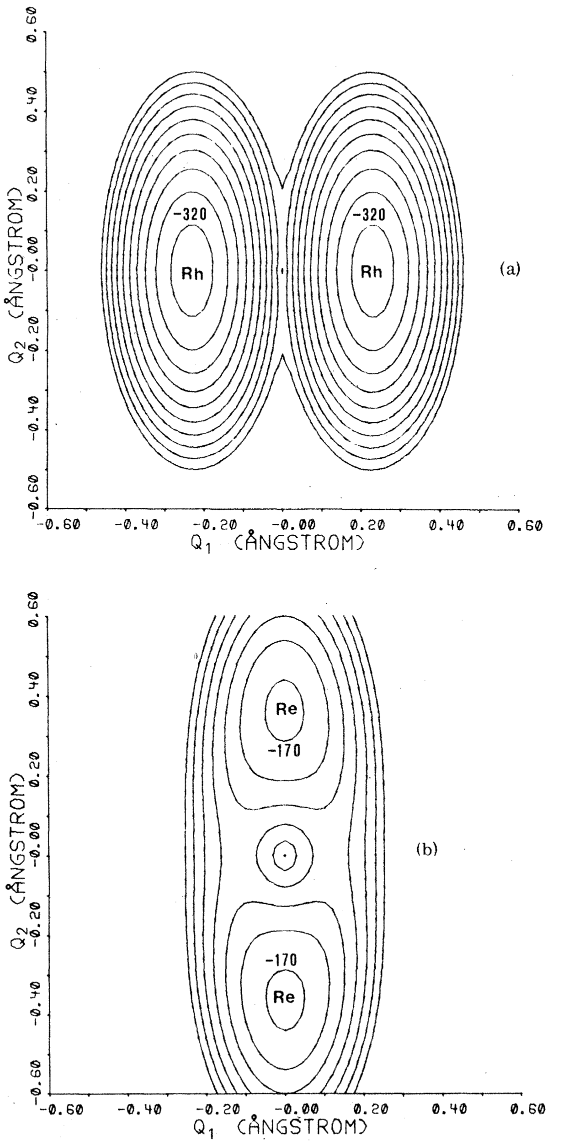

FIG. 2. Coexistence of Rh and Re minima on the $E_{g(u)}$ level. The map in the Q_1Q_2 plane is computed with $c_1 = 3\times 10^3$ cm^{-1}/Å; $c_2 = 10^3$ cm^{-1}/Å; $K_\alpha = 2\times 10^4$ cm^{-1}/Å^2; $K_1 = 1.8\times 10^4$ cm^{-1}/Å^2; $K_2 = 4\times 10^3$ cm^{-1}/Å^2; $c_{\alpha 1} = 10^4$ cm^{-1}/Å^2; $c_{\alpha 2} = -5\times 10^3$ cm^{-1}/Å^2. The energy difference between two successive iso-energetic curves is 50 cm^{-1}. (a) Section for $Q_\alpha^0 = 0.115$ Å, $E_{\rm JT}$ (Rh) $= -346.2$ cm^{-1}. (b) Section for $Q_\alpha^0 = 0.091$ Å, $E_{\rm JT}$ (Re) $= -181.8$ cm^{-1}.

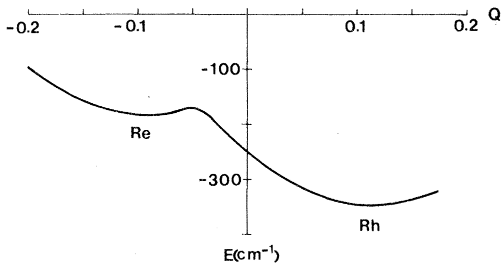

FIG. 3. Cross section along the projection on the Q_α axis of one of the possible paths connecting Rh and Re minima. The parameter values are the same as in Fig. 2.

Each APES is twofold degenerate, because Kramer's degeneracy is not removed by the JT effect.

The expression (7) is quite analogous to that given in Ref. 17, save that in w_{11} and w_{12} also second-order JT terms are included. As a general rule, the spin-orbit interaction tends to cancel the JT effect and for sufficiently high $\lambda(|\frac{1}{2}\lambda| > |w_{11}|$ and $|w_{12}|)$ the different kinds of minima coalesce at $Q_i = 0$ $(i = \alpha, 1, 2)$. On the other hand, if the conditions for the coexistence of Rh and Re minima are matched, the introduction of a small spin-orbit coupling still allows this coexistence, but the coordinates of the minima approach to zero. Note that, as in the orbital problem, the Rh and Re minima have Q_2^0 and $Q_1^0 = 0$, respectively. The coexistence is possible, if $|\frac{1}{2}\lambda|$ is smaller than both $|w_{11}|$ and $|w_{12}|$. When the value of $|\frac{1}{2}\lambda|$ is comprised between $|w_{11}|$ and $|w_{12}|$ only one kind of minima is possible that is Rh minima if $|w_{11}| > |w_{12}|$ and Re minima vice versa.

In the case of a term ^3E we have four APES's two of which are accidentally doubly degenerate. The expressions for the energy are

$$\epsilon_{1,2} = V \pm (w_{11}^2 + w_{12}^2 + \lambda^2)^{1/2}, \tag{8}$$

$$\epsilon_{3,4} = V \pm (w_{11}^2 + w_{12}^2)^{1/2}. \tag{9}$$

Equation (8) corresponds to the two doubly degenerate surfaces and it is very similar to Eq. (7), save that λ^2 substitutes $\frac{1}{4}\lambda^2$; therefore analogous considerations can be drawn and are summarized as follows:

$\lvert\lambda\rvert < \lvert w_{11}\rvert, \lvert w_{12}\rvert$,	possibility of Rh and Re coexistence
$\lvert w_{12}\rvert < \lvert\lambda\rvert < \lvert w_{11}\rvert$,	Rh minima
$\lvert w_{11}\rvert < \lvert\lambda\rvert < \lvert w_{12}\rvert$,	Re minima
$\lvert\lambda\rvert > \lvert w_{11}\rvert, \lvert w_{12}\rvert$,	no JT distortions.

However, if one looks at Eq. (9), the term ^3E behaves in a different way from the term ^2E. In fact if any coupling with other terms is neglected, the intermediate APES's given by Eq. (9) are unaffected by the spin-orbit coupling; as a consequence, when Rh and Re minima coexist on the lower potential surface given by Eq. (9), this coexistence persists independently of the spin-orbit coupling value.

IV. CONCLUSIONS

Besides a purely theoretical interest, does some physical system exist, for which such a coexistence is possible? Indeed there is experimental evidence for the coexistence of different JT distortions (tetragonal and trigonal) in O_h symmetry,[6,8] and therefore it is likely that this latter does not constitute an isolated case: porphyrinic systems are, in our opinion, probable candidates. However, at this point, a question is necessary: if there is the coexistence, how can we reveal it? When minima coexist on excited states, measurements of the polarization degree of the luminescence bands[8] or optical detection of magnetic resonance[6] are very effective. When coexisting distortions are on the APES of the ground state, only one distortion is stabilized at low temperature and/or for high-energy barriers between the minima, unless the stabilization energies are comparable; otherwise a dynamical situation is found and the molecule appears undistorted. At present it is our intention to determine what experiments are the most proper in order to reveal the coexistence on the ground state.

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[18] We should like to remark that in literature the two vibrations β_{1g} and β_{2g} were often exchanged with each other, depending on the orientation of the reference axes; in the present paper we adopt the notation of Ref. 17 (see Fig. 1), so that the square, which symbolizes the molecule in the symmetrical configuration, is distorted into a diamond by the vibrations β_{1g} and into a rectangle by the vibrations β_{2g}.