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Additional information on J. Chem. Phys.

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(Received 2 February 1972)

The effect of more than one pair of degenerate vibrational modes on the energy levels and spectrum of a doubly degenerate electronic state is discussed. The dynamic Jahn–Teller effect for this case is treated by exact numerical methods and by approximation schemes. The effect of quadratic terms in the vibrational coordinates is also treated by these methods. The use of adiabatic surfaces in treating these problems is critically examined.

I. INTRODUCTION

Interest in the dynamical aspects of the Jahn–Teller phenomenon[1] originated in attempts to understand the vibronic structure of degenerate electronic states in molecules. In 1937, Jahn and Teller showed that degenerate electronic states of nonlinear molecules are unstable with respect to certain asymmetric displacements of the nuclei because there can exist a nonzero matrix element between these states which splits the degeneracy *in first order*. If the coupling between the electrons and nuclear displacements is sufficiently strong relative to the zero-point energy of the associated vibration, the molecule undergoes a static distortion to a lower symmetry configuration.[2-4] If the coupling is weaker, or if the zero-point vibrational energy is comparable with the energy barrier separating equivalent configurations, no static distortion occurs and the molecule exhibits a coupled motion of the electrons and vibrational modes.[5-7] This latter situation, the dynamical Jahn–Teller effect, has been the subject of numerous studies[8] wherein a single interaction mode is considered and is shown to give rise to unusual spectral features.

While frequently one vibrational mode dominates the vibronic coupling, most physical systems of experimental interest show comparable or at least nonnegligible coupling through a second vibrational mode. The effect of this is largely unresolved to date and usually interpreted to mean "more or the same" or an enhancement of the features evidenced by coupling through a single mode. Using both numerical methods and a perturbation scheme, we report in this paper investigations on intervibrational interactions using a Jahn–Teller model based on two degenerate electronic states and the harmonic approximation. The spectral pattern predicted by a single vibrational mode is found to be markedly distorted. Both absorption and emission spectra are considered. Similarly, the effect of quadratic coupling which gives rise to Duchinsky effects and frequency shifts is investigated with special interest in its relevance to criteria for stable distortions previously[2] considered to require anharmonic coupling.

Considerable difficulties are encountered in the unambiguous identification of Jahn–Teller interactions; thus, our investigations undertake to determine information on energy "shifts" needed to confirm Jahn–

Teller coupling from spectroscopic data. Three experimental observations of asymmetric progressions are well known. These appear in the Rydberg states of benzene, in CH_3I and in CF_3I.[9]

The appearance of the 0–1 band corresponding to an asymmetric vibration in the second excited states of CH_3I and CF_3I and the splitting of the hot band in the spectrum of CF_3I provide evidence for Jahn–Teller interactions in doubly degenerate states. Moreover, the 1–1 hot band is red shifted by 42 cm^{-1} and is split into two components separated by 7.5 cm^{-1}. This small splitting indicates that the linear coupling parameter must be relatively small. Changes in the force constant are responsible for the red shift of both components. Finally, in benzene the 690 cm^{-1} progression in the Rydberg states might be assigned to a ν_{18} (e_{2g}) progression giving evidence of vibronic interactions.

These systems are characterized by the coupling of doubly degenerate electronic states through doubly degenerate vibrational modes. Consequently our model calculations involve only this symmetry. The energies of practical interest are those of the split first excited vibrational states relative to each other and to the ground vibrational state.

The paper is set out as follows: in Sec. II, the Hamiltonian is presented, in Sec. III, this Hamiltonian is diagonalized for the problem of two sets of degenerate modes interacting with a degenerate pair of electronic states through linear terms, and also for the problem of a degenerate mode interacting with the electronic states through linear and quadratic terms. In Sec. IV, simple approximation schemes for these problems are discussed and compared to the exact results. In Sec. V, a discussion of the results is presented with emphasis on the use of adiabatic surfaces for predicting the spectra of such systems.

II. THE HAMILTONIAN

We wish to describe a system with doubly degenerate excited electronic states (at some symmetric internuclear separation) and doubly degenerate vibrational modes. We will assume the ground electronic state to be nondegenerate. The Hamiltonian will describe interactions between the electronic states through linear and quadratic vibrational coupling. We will use the

TABLE I. First energy spacing in a doubly degenerate electronic state coupled by two degenerate modes.

R^a	K_1^2	K_2^2	Mode one (exact)			Mode two (exact)		
			$E_{0-1}(T)/\omega_1$	E_{0-1}/ω_1	$E_{0-1}(S)/\omega_1$	$E_{0-1}(T)/\omega_2$	E_{0-1}/ω_2	$E_{0-1}(S)/\omega_2$
1.5	0.25	0.25	1.18	1.12	1.17	1.16	1.09	1.17
	0.25	0.50	1.12	1.01	1.17	1.24	1.10	1.24
	0.50	0.25	1.22	1.14	1.24	1.09	1.06	1.17
	0.75	0.25	1.19	1.14	1.26	1.05	1.05	1.17
	1.0	0.25	1.12	1.12	1.26	1.03	1.04	1.17
2.6	0.125	0.22		1.08	1.11		1.13	1.16
	0.25	0.25	1.15	1.13	1.17	1.15	1.15	1.17
	0.56	0.25	1.17	1.16	1.25	1.10	1.08	1.17
1.33	0.125	0.22		1.10	1.16		1.10	1.11
	0.125	0.90		1.05	1.11		1.19	1.26
	0.50	0.22		1.19	1.24		1.05	1.11

^{a} $R=\omega_1/\omega_2$, E_{0-1}/ω_a = energy spacing of ground vibronic state and first vibrational state of mode a in units ω_a. T—transformation method, S—energy spacing for a single coupling mode.

harmonic approximation throughout by expanding all matrix elements about the ground state equilibrium position and keeping terms up to and including those quadratic in nuclear displacement. By this procedure, the Hamiltonian is invariant under the appropriate molecular symmetry group. For convenience, we will express the Hamiltonian in second quantized form (all electronic energies are measured relative to the ground state)

$$\mathcal{H} = \sum_\alpha \epsilon_\alpha C_\alpha^+ C_\alpha + \sum_{l,i} (b_{li}^+ b_{li} + \tfrac{1}{2}) \hbar\omega_i$$
$$+ \sum_{\alpha,l,i} K_{\alpha,l,i} C_{\alpha+l}^+ C_\alpha (b_{l,i} + b_{-l,i}^+)$$
$$+ \sum_{\alpha,l,i} J_{\alpha,l,i} C_\alpha^+ C_\alpha (b_{l,i}^+ + b_{-l,i})(b_{l,i} + b_{-l,i}^+) \hbar\omega_i$$
$$+ \sum_{\alpha,l,i} D_{\alpha,l,i} C_{\alpha+2l}^+ C_\alpha (b_{l,i} + b_{-l,i}^+)(b_{l,i} + b_{-l,i}^+) \hbar\omega_i, \quad (1)$$

where C_α (C_α^+) destroys (creates) an electronic excitation of symmetry α, b_{li} (b_{li}^+) destroys (creates) a vibrational quantum of the component of the ith vibrational species which has symmetry l. By the nature of the symmetry group under consideration, these are the only terms present. $K_{\alpha li}$, the linear coupling parameter, represents the usual Jahn–Teller interaction, here extended to include more than one mode. The term $J_{\alpha li}$ represents the change in vibrational force constant in a given electronic state upon excitation, and $D_{\alpha li}$ represents quadratic interaction between electronic states:

$$K_{\alpha,l,i} = (1/2m_l\omega_l^3\hbar)^{1/2} [\nabla_{l,i} \langle \alpha+l \mid V(q,Q) \mid \alpha \rangle]_{Q_0},$$
$$J_{\alpha,l,i} = (1/2m_l\omega_l^2)$$
$$\times \{\nabla_{l,i}\nabla_{-l,i} [\langle \alpha \mid V(q,Q) \mid \alpha \rangle - V_{gg}(Q)]\}_{Q_0},$$
$$D_{\alpha,l,i} = (1/m_l\omega_l^2)[\nabla_{l,i}\nabla_{l,i} \langle \alpha+2l \mid V(q,Q) \mid \alpha \rangle]_{Q_0}. \quad (2)$$

Quadratic coupling by modes of different frequencies is neglected. The same molecular symmetry labels are appropriate for both nuclear and electronic symmetries. These indices are formulated mod$m$ for molecules having an m-fold axis of rotation.

The vibrational spacings for the vibrations active in the coupling scheme can be estimated from reference state empirical data. $\hbar\omega_i(J_{\alpha,l,i}+1)$ might be approximated by the vibrational energy in an adequate nondegenerate excited state since for large molecules (e.g. benzene), empirical evidence indicates very slight mixing of modes in excited states.

The parameter $K_{\alpha li}$ is easily shown to be the ratio of the static α-electronic distortion energy to a quantum of vibrational energy of the coupling mode (li). In the linear form of this Hamiltonian, the vibronic "angular momentum,"[6,10] with respect to the symmetry axis, $2\lambda = \alpha + l$, is conserved and results in accidental degeneracies which are removed by quadratic interaction terms. In what follows, λ always refers to this pseudoangular momentum and is given by the eigenvalue of the operator[10]

$$\hat{\lambda} = \tfrac{1}{2}[C_\alpha^+ C_\alpha - C_\beta^+ C_\beta] + [\sum_i (b_{li}^+ b_{li} - b_{-li}^+ b_{-li})] \quad (3)$$

III. NUMERICAL CALCULATIONS

A. Linear Coupling of E States Through Two Degenerate Modes

The effect of an additional coupling mode on the energy spacing in the linear Jahn–Teller problem is investigated using an exact numerical calculation for model (1) where $K_{\alpha li} = 0$ ($i \neq i_1, i_2$), $J_{\alpha li} = 0 = D_{\alpha li}$ (all i), and $K_{\alpha li} = K_{\beta li}$. Since the two electronic states

α and β which have different electronic angular momentum, are mixed by the Hamiltonian, the vibronic wavefunctions will be of the form

$$\Psi_{p\lambda}(q, Q) = \psi_\alpha(q)\chi_\alpha{}^{p\lambda}(Q) + \psi_\beta(q)\chi_\beta{}^{p\lambda}(Q). \quad (4)$$

The nuclear functions $X_\alpha(Q)$ are expanded in the (two dimensional) isotropic harmonic oscillator functions $X_{nl}(Q_i)$ $i=1, 2$ where $n=1, 2, \cdots$ the principal quantum number and $l=n-1, n-3, \cdots, -n-1$, (the "angular momentum" or symmetry index).[10]

These are the natural basis for the second quantized Hamiltonian. Thus,

$$\chi_\alpha{}^{p\lambda}(Q) = [a_{1p}{}^{|\lambda|}\chi(Q_1)_{l+1,l} + a_{3p}{}^{|\lambda|}\chi(Q_1)_{l+3,l} + \cdots]$$

$$\times [b_{1p}{}^{|\lambda|}\chi(Q_2)_{l+1,l} + b_{3p}{}^{|\lambda|}\chi(Q_2)_{l+3,l} + \cdots],$$

$$\chi_\beta{}^{p\lambda}(Q) = [a_{2p}{}^{|\lambda|}\chi(Q_1)_{l+2,l+1} + a_{4p}{}^{|\lambda|}\chi(Q_1)_{l+4,l+1} + \cdots]$$

$$\times [b_{2p}{}^{|\lambda|}\chi(Q_2)_{l+2,l+1} + b_{4p}{}^{|\lambda|}\chi(Q_2)_{l+4,l+1} + \cdots]. \quad (5)$$

Vibrational wavefunctions for the uncoupled modes have been factored out. Expansion indices are appropriate for E_1 electronic states coupled by e_2 vibrational modes.

The coefficients a and b were determined by diagonalizing the Hamiltonian operator in a basis of 95 vibronic states designated $|\alpha, n_1l_1, n_2l_2\rangle$ and $|\beta, n_1l_1, n_2l_2\rangle$ which includes all coupled states having $n_1+n_2=2$, $3, \cdots, 10$. The nonzero matrix elements are:

$$\hbar^{-1}\langle x, n_1l_1, n_2l_2 \mid H \mid x, n_1l_1, n_2l_2\rangle$$

$$= n_1\omega_1 + n_2\omega_2 \quad (x=\alpha \text{ or } \beta), \quad (6a)$$

$$\hbar^{-1}\langle \alpha, n_1l_1, n_2l_2 \mid H \mid \beta, n_1'l_1', n_2'l_2'\rangle$$

$$= \sum_{i,j=1}^{2} \delta_{n_i', n_i+1}\delta_{l_i', l_i+1}\delta_{n_j', n_j}\delta_{l_j', l_j}K_i\omega_i[(n_i'+l_i'-1)/2]^{1/2},$$

$$(6b)$$

$$\hbar^{-1}\langle \beta, n_1l_1, n_2l_2 \mid H \mid \alpha, n_1'l_1', n_2'l_2'\rangle$$

$$= \sum_{i,j=1}^{2} \delta_{n_i', n_i+1}\delta_{l_i', l_i-1}\delta_{n_j', n_j}\delta_{l_j', l_j}K_i\omega_i[(n_i'-l_i'-1)/2]^{1/2}.$$

$$(6c)$$

1. Eigenenergies

As expected, the energy levels decrease further in the presence of a second mode giving smaller allowed (0–0) and hot band (1–1) transition energies than predicted from uncoupled Jahn–Teller interactions. However, the increase in the first energy spacing (E_{0-1}) predicted by a single coupling mode is now *decreased* for the vibration of lower energy and also, in most cases, for the vibration of higher energy (see Fig. 1 and Table I).

The splitting of the two components of the first hot band is less than expected from one coupled mode, but as before it increases with stronger coupling. The separation of the 1–1 and 2–2 hot bands decreases for the less energetic vibration and increases for the other in most instances.
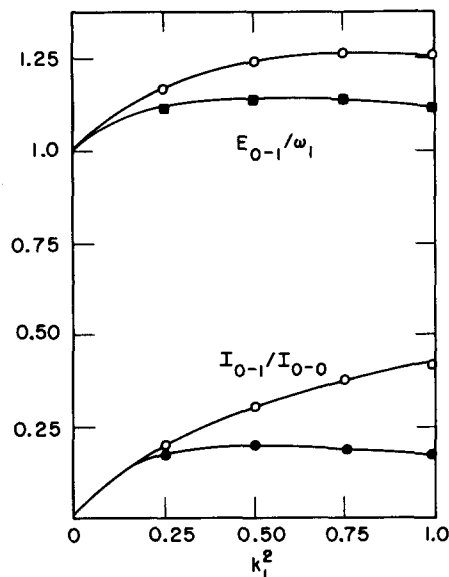

FIG. 1. The energy separation between the 0–1 and 0–0 line in the absorption spectrum at 0 K, and the intensity ratio of those lines for $k_2{}^2=0.25$ and $\omega_1/\omega_2=1.5$. The open circles are for one coupling mode and the shaded circles for two.

These features indicate that the structure of an uncoupled asymmetric progression may be obscured by the irregular spacing of the absorption and emission lines caused by the interference of another active mode. This interference increases as the coupling parameters increase and as the frequency ratio goes to one.

2. Zero Temperature Spectra

By an allowed transition we shall mean that the electronic transition moment is nonzero in the reference configuration of the molecule, Q_0. The intensity with which the $A_{n_1l_1,n_2l_2} \rightarrow E_{p\lambda}$ absorption lines appears is therefore proportional to

$$\mid a_{n_1-l_1, p}{}^{|\lambda|}b_{n_2-l_2, p}{}^{|\lambda|} \mid^2.$$

The most important zero temperature absorption lines are the first three allowed transitions I_{0-0}, I_{0-1} (mode 1), I_{0-1} (mode 2). $\mid a_{n,1}{}^{|1/2|}/a_{1,1}{}^{|1/2|} \mid^2$ describes the relative intensity of emission to the nth vibrational level of mode 1 in the ground electronic state.

I_{0-0} and I_{0-1} for the energetic vibration are decreased slightly with the addition of a less energetic, weakly coupled mode. However, the intensity I_{0-1} for this second mode is very sensitive to the presence of the more energetic mode. When the coupling of both modes is small $(K^2<0.25)$, the vibronic states having an appreciable component of the first vibrational state of the lower energy mode lose intensity to those involving the more energetic mode, so I_{0-1} (mode 2) decreases and I_{0-1} (mode 1) increases relative to the uncoupled value. For larger couplings, I_{0-1} decreases for both modes via borrowing by the higher vibronic states (see Fig. 1 and Table II).

TABLE II. Allowed absorption and emission intensities in a doubly degenerate state coupled by two modes.[a]

R	K_1^2	K_2^2	Mode one		Mode two		Mode one		Mode two	
			I_{0-1}^a/I_{0-0}	$(I_{0-1}/I_{0-0})(S)$	I_{0-1}^a/I_{0-0}	$(I_{0-1}/I_{0-0})(S)$	I_{0-1}^e/I_{0-0}	$(I_{0-1}^e/I_{0-0})(S)$	I_{0-1}^e/I_{0-0}	$(I_{0-1}^e/I_{0-0})(S)$
1.5	0.25	0.25	0.175	0.195	0.084	0.195	0.184	0.205	0.173	0.205
	0.50	0.25	0.191	0.304	0.061	0.195	0.328	0.356	0.153	0.205
	0.75	0.27	0.187	0.371	0.051	0.195	0.449	0.480	0.138	0.205
	1.0	0.25	0.184	0.425	0.045	0.195	0.558	0.588	0.128	0.205
1.33	0.125	0.218	0.161	0.123	0.077	0.182	0.099		0.167	0.201
	0.125	0.89	0.198	0.123	0.215		0.077		0.521	
	0.50	0.218	0.288	0.304	0.039	0.182	0.333		0.138	0.201

[a] I_{0-1}^a/I_{0-0}=ratio of absorption intensities of 0-1 line (mode a) to 0-0 line, I_{0-1}^e/I_{0-0}=ratio of emission intensities, S=single mode coupling.

3. Hot Band Spectra

The splitting of the 1-1 hot band provides an alternative method for the identification of Jahn–Teller coupling.[9] Therefore, we first evaluated the relative absorption intensities in the single coupling mode model. Subsequently, we investigated the modification of our results in the presence of a second coupling mode.

When a single vibration induces the α–β electronic interaction, the lowest vibronic level is not split, but the higher levels are separated. Though only a single 0-1 zero temperature transition appears, two distinct 1-1 hot band transitions are allowed. These are proportional to $|a_{2,2}^{|1/2|}|^2$ and $|a_{1,1}^{|3/2|}|^2$. The intensity ratio of these components denoted $I^{|1/2|}/I^{|3/2|} = I^+/I^-$ is presented in Table III and pictured as a function of K^2 superimposed on a graph of the 1-1 energy splitting $E^\pm$, in Fig. 2. The ratio decreases with increasing K while the energy separation increases. It is the zero temperature 0-1 allowed, upper component whose absorption intensity in the hot band is diminished relative to that of the lower component.

The hot band intensities are further decreased in the presence of a second mode, the lower component being slightly more sensitive to the added coupling (see Figs. 2, 3). The experimental identification of Jahn–Teller coupling in molecules by their hot band spectra will therefore be more difficult for systems characterized by moderate vibronic interactions. In the case of weak coupling, the energy spacings in the hot band will require high resolution.

B. Linear and Quadratic Coupling

Discussions of adiabatic potential surfaces in the literature[2,11,12] give evidence that the modification of
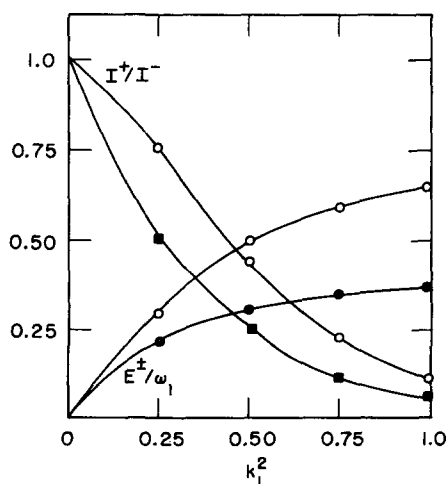

FIG. 2. Energy splittings for the 1-1 hot band (of mode 1) $E^\pm$ and intensity ratios I^+/I^- for $k_2^2=0.25$ and $\omega_1/\omega_2=1.5$. The open circles are for one coupling mode and the shaded circles are for two.

TABLE III. First hot band energy splittings and intensity ratios in a doubly degenerate state coupled by two modes.[a]

$K_1{}^2$	$K_2{}^2$	Mode one			Mode two			Mode one		Mode two
		$E_\pm(T)/\omega_1$	$E_\pm/\omega_1$	$E_\pm(S)/\omega_1$	$E_\pm(T)/\omega_2$	$E_\pm/\omega_2$	$E_\pm(S)/\omega_2$	I^+/I^-	$I^+/I^{(S)}$	I^+/I^-
0.25	0.25	0.303	0.221	0.338	0.303	0.270	0.338	0.507	0.759	0.881
0.50	0.25	0.472	0.308	0.503	0.236	0.265	0.338	0.250	0.443	1.04
0.75	0.25	0.552	0.346	0.592	0.184	0.280	0.338	0.118	0.230	1.25
1.0	0.25	0.573	0.360	0.644	0.143	0.303	0.338	0.052	0.106	1.51

[a] $E_\pm/\omega_a$ = energy splitting of hot band components of mode a in units ω_a. I^+/I^- = intensity ratio of upper hot band component to the lower. T = transformation method, S = single mode coupling.

linear coupling by terms quadratic in the displacement coordinates has definite and sometimes significant observable consequences. Two parameters describe the vibronic coupling in the Hamiltonian attributed to quadratic terms. The isotropic force constants are given by J and the Duchinsky terms by D.

As before, eigenfunctions in the α, β subspace are written as in (4). The Hamiltonian is diagonalized in a basis of 110 complex vibronic states ($n = 1, 2, \cdots, 10$) where the nonzero matrix elements, in units of $\hbar\omega$, are given by:

$$\langle \alpha, nl \mid H \mid \alpha', n'l' \rangle = \delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{l,l'}(J+1)n$$

$$+\delta_{\alpha\alpha'}\delta_{n',n+2}\delta_{l',l}(J/2)[(n'-l'-1)(n'+l'-1)]^{1/2}, \quad (7a)$$

$$\langle \beta, nl \mid H \mid \alpha, n'l' \rangle = \delta_{n',n-2}\delta_{l',l+2}(D/2)$$

$$\times[(n'-l'+3)(n'-l'+1)]^{1/2}+\delta_{n',n+2}\delta_{l',l+2}(D/2)$$

$$\times[(n'+l'-3)(n'+l'-1)]^{1/2}+\delta_{n',n-1}\delta_{l',l-1}K$$

$$\times[(n'+l'+1)/2]^{1/2}+\delta_{n',n+1}\delta_{l',l-1}K[(n'-l'-1)/2]^{1/2}$$

$$+\delta_{n',n}\delta_{l',l+2}D[(n'-l'+1)(n'-l'+1)]^{1/2}. \quad (7b)$$

1. Eigenenergies and Spectral Intensities

The vibronic energies calculated for a range of realistic parameters are displayed in Table IV. The energies increase with increasing J and decreasing D, which correspond to vibrational frequencies ω' in the excited electronic state which are greater than ω, the vibrational frequency in the ground electronic state. This change in the effective frequencies of the coupling modes from ω to $[1+2J+2D]^{1/2}\omega$ and $[1+2J-2D]^{1/2}\omega$ is responsible for a number of differences seen with the addition of quadratic coupling. With $\omega' > \omega$, the effective linear coupling constant is decreased and one expects to find a number of the observables plotted in Figs. 1–3 effectively represented by a smaller K value under quadratic coupling ($J \neq 0$). In many respects, where the $|\lambda| = 3/2$ states are not involved in the observation, this is the case. For example, the E_{0-1} separation for $K = 0.5$, $J = 0.5$ in units ω' is at most 1.08ω (any D), yet for $K = 0.5$, $J = 0$, the separation is 1.17ω. Since the separation decreases with decreasing K, the effective

coupling constant has been lowered. Similarly, the relative absorption and emission intensities, $I_{0-1}{}^a/I_{0-0}$ and $I_{0-1}{}^e/I_{0-0}$ reflect the reduced effective K by decreasing under quadratic ($J > 0$) coupling, (see Table V).

The lower component of the first vibrational level is altered in a more dramatic manner. The accidental degeneracy of these $|2\lambda| = 3$ states in a D_6- symmetry is resolved by the quadratics. These states are split for small D, both lying below the doublet. However, for greater Duchinsky mixing, one of these nondegenerate levels rises above the doublet, giving an orbital singlet–doublet–singlet set of vibronic states. As expected, after the resolution of the lower doublet, the strongest hot band absorption line of the three belongs to the remaining doublet, whereas this pair represents the weaker line under linear coupling, or small D.

2. Possible Threefold Degeneracy

The maximum barrier to a rotation of the e_2 displacement around the principal symmetry axis arises on the
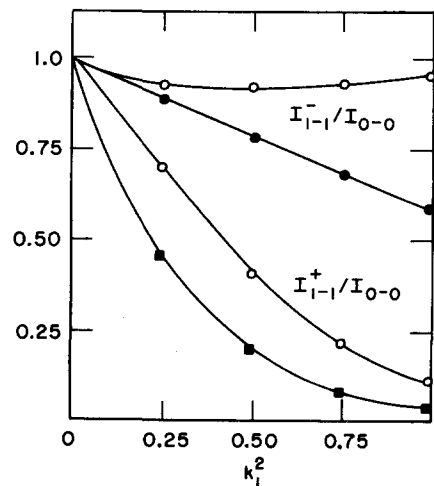

FIG. 3. The intensity of the upper ($+$) and lower ($-$) component of the 1–1 hot band relative to the 0–0 line multiplied by the appropriate Boltzmann factor. $k_2{}^2 = 0.25$, $\omega_1/\omega_2 = 1.5$ and the open and shaded circles have the same meaning as Fig. 2.

TABLE IV. Eigenenergies for a doubly degenerate state coupled by linear and quadratic modes (units ω).[a]

K	J	D	E_0	$E_1{}^S$	$E_1{}^d$
0.5	0.0	0.0	0.774	1.608	1.947
0.5	0.1	0.1	0.891	2.002	2.117
				1.665	
0.5	0.1	0.2	0.853	2.112	1.987
				1.444	
0.5	0.25	0.1	1.060	2.305	2.405
				2.001	
0.5	0.2	0.2	0.980	2.325	2.227
				1.701	
0.5	0.25	0.5	0.793	2.096	1.600
				1.040	
0.5	0.5	0.0	1.294	2.604	2.818
0.5	0.5	0.125	1.287	2.762	2.794
				2.428	
0.5	0.5	0.2	1.276	2.847	2.764
				2.312	
0.5	0.5	0.5	1.116	1.758	2.417
				2.941	
0.5	0.5	0.7	0.971	2.389	1.865
				1.242	
0.5	−0.5	0.0	−1.159	−1.034	−0.809
0.866	0.5	0.0	1.077	2.247	2.744
0.866	0.5	0.2	1.052	1.953	2.652
				2.471	
0.866	0.5	0.5	0.890	1.350	2.092
				2.607	

[a] E_0 = energy of ground vibronic state, $E_1{}^d$ = energy of unresolved doublet with one vibrational excitation; $E_1{}^S$ = energy of resolvable singlets with one vibrational excitation.

adiabatic potential surface when $D = (2J+1)/2$ in the harmonic approximation. This suggests that the lowest vibronic state may be triply degenerate in this limit if

$$[k^2\omega/2(2J+1)]\{1+[2D/(2J+1)]\} \gg \omega. \quad (8)$$

We have investigated this limit numerically and found that a much larger basis is required to describe the ground state. Convergence for the ground state wavefunction and energy was obtained with 110 states

for sets of parameters as follows

$$\begin{pmatrix} K \\ J \\ D \end{pmatrix} = \begin{pmatrix} 0.5 \\ 0.25 \\ 0.5 \end{pmatrix}, \begin{pmatrix} 0.5 \\ 0.1 \\ 0.1 \end{pmatrix}, \begin{pmatrix} 1.0 \\ 1.0 \\ 1.0 \end{pmatrix}, \begin{pmatrix} 1.0 \\ 2.0 \\ 2.0 \end{pmatrix}.$$

All gave a lowest doublet state. However, for the choices:

$$\begin{pmatrix} K \\ J \\ D \end{pmatrix} = \begin{pmatrix} 1.0 \\ 2.0 \\ 2.4 \end{pmatrix}, \begin{pmatrix} 0.5 \\ 1.0 \\ 1.4 \end{pmatrix}, \begin{pmatrix} 0.5 \\ 0.1 \\ 0.55 \end{pmatrix}, \begin{pmatrix} 0.1 \\ 0.25 \\ 0.7 \end{pmatrix},$$

all close to the limit $D = (2J+1)/2$ convergence for neither the lowest state energy nor the wavefunction was obtained with the largest basis (380 states) considered. This indicates a special and substantial recombination of the original basis in the formation of the stationary states, as would be expected in the construction of triplet wavefunctions describing a rigid tetragonal distortion using a basis of the isotropic harmonic oscillator functions having a natural doublet ground state.

More interesting and perhaps more significant is the fact that a near-triplet degeneracy resulted for the ground state regardless of the number of configurations used, and each successive recalculation of the ground state energy was in the direction of a triplet. Surprisingly, the near-triplets occurred even where the limit $[K^2\omega/2(2J+1)]\{1+[2D/(2J+1)]\} > \omega$ was violated. The usefulness of this intuitive requirement for a triplet was further reduced by the fact that the ground state energy calculated for the set of parameters (0.5, 0.1, 0.55) using the 380 basis was *below* the adiabatic well depth.

The information attained in the limit $D \sim (2J+1)/2$ provides a good indication that the adiabatic potential models do not provide a sensitive description of the coupling phenomena. It also suggests strongly that the limit of the harmonic approximation may constitute a mathematical source of the accidental triplet degeneracy.

Thus, criteria for a triply degenerate ground state should be considered using the full quadratic Hamil-

TABLE V. Absorption and emission intensities for linear and quadratic coupling.[a]

K	J	D	$I_{0-1}{}^a/I_{0-0}$	$I_{0-1}{}^e/I_{0-0}$	$I_{1-1}{}^-/I_{0-0}$	$I_{1-1}{}^+/I_{0-0}$	$I_{1-1}{}^d/I_{0-0}$
0.5	0.0	0.0	0.195	0.205	0.920		0.698
0.5	0.5	0.0	0.053	0.080	0.930		0.894
0.5	0.5	0.2	0.057	0.082	0.489	0.434	0.866

[a] $I_{1-1}{}^-/I_{0-0}$ = relative absorption intensity of the lower resolvable singlet in the first hot band to the 0–0 line $\times \exp(\omega/kT)$; $I_{1-1}{}^+/I_{0-0}$ = relative intensity of the upper resolvable singlet hot band; $I_{1-1}{}^d/I_{0-0}$ = relative intensity of the doublet hot band time.

TABLE VI. First vibrational state energies.[a]

$|\lambda|$	K^2	$\Delta E(T)$	(exact) ΔE	$E_{0-1}(T)$	(exact) E_{0-1}	$E_{1-1}(T)$	(exact) E_{1-1}
$\frac{3}{2}$	0.25	−0.409	−0.392			0.389	0.339
$\frac{1}{2}$	0.25	−0.020	−0.053	1.203	1.173		
$\frac{3}{2}$	0.50	−0.720	−0.684			0.606	0.503
$\frac{1}{2}$	0.50	−0.114	−0.181	1.294	1.241		
$\frac{3}{2}$	0.75	−0.986	−0.933			0.709	0.592
$\frac{1}{2}$	0.75	−0.277	−0.341	1.292	1.259		
$\frac{3}{2}$	1.00	−1.12	−1.16			0.645	0.644
$\frac{1}{2}$	1.00	−0.476	−0.512	1.240	1.255		

[a] T=approximate method, ΔE=energy shift under linear coupling, E_{0-1}=energy splitting of lowest allowed states, E_{1-1}=energy splitting of first hot band lines.

tonian with the addition of anharmonicities. Tunneling calculations using adiabatic surfaces are not sufficiently sensitive to the vibronic mixing to give quantitative results. A full quantum mechanical approach without the use of adiabatic models is necessary.

IV. APPROXIMATION SCHEME

Numerical calculations are of necessity long and involved and require an entirely new calculation for each molecule, i.e., for each set of values for the coupling constants. These features are shared by approximate schemes which have been suggested.[13] Recently, in a new approach Alper and Silbey[14] (AS) overcame these difficulties by performing a canonical transformation and subsequent second-order perturbation calculation. They found the ground state energy "shift" as a function of K in good agreement with exact values for the linear model of doubly degenerate electronic states coupled through one degenerate vibrational mode. We extend this approach to deal with two modes and in conjunction with another transformation to deal with linear and quadratic interactions. The results of the previous calculations will be used to evaluate results of our approximate methods.

A. First Vibrational State–One Mode

Before proceeding to more difficult cases, the ability of the (AS) method to predict energy levels of excited vibrational states is assessed. The energy "shifts" of the first vibrational levels obtained are listed in Table VI. They are in reasonable agreement with the exact calculations.

B. Linear Coupling Through Two Degenerate Modes

Again consider the model Hamiltonian where $K_{al}=0$ $(l\neq l_1, l_2)$, $J_{al}=0=D_{al}$ (all l). We rewrite the Hamiltonian in terms of the real orbitals and modes $c_1=(c_\alpha+c_\beta)/\sqrt{2}$, $c_2=(c_\alpha-c_\beta)/i\sqrt{2}$, $b_{1i}=(b_{li}+b_{-li})/\sqrt{2}$ and $b_{2i}=(b_{li}-b_{-li})/\sqrt{2}i$:

$$H = \epsilon(c_1^+c_1+c_2^+c_2) + \hbar\omega_i(b_{1i}^+b_{1i}+b_{2i}^+b_{2i}+1) + \hbar\omega_j(b_{1j}^+b_{1j}+b_{2j}^+b_{2j}+1) + \hbar\omega_i(K_i/\sqrt{2})$$

$$\times\{(b_{1i}^++b_{1i})(c_1^+c_1-c_2^+c_2)-(b_{2i}^++b_{2i})(c_1^+c_2+c_2^+c_1)\}+\hbar\omega_j(K_j/\sqrt{2})$$

$$\times\{(b_{1j}^++b_{1j})(c_1^+c_1-c_2^+c_2)-(b_{2j}^++b_{2j})(c_1^+c_2+c_2^+c_1)\}. \quad (9)$$

The intraorbital coupling is removed by the unitary transformation $\mathcal{H} = \exp(-S')H\exp(+S')$ where $S' = (K_i/\sqrt{2})(b_{1i}-b_{1i}^+)(c_1^+c_1-c_2^+c_2)+(K_j/\sqrt{2})(b_{1j}-b_{1j}^+)(c_1^+c_1-c_2^+c_2)$

$$\mathcal{H} = \epsilon(c_1^+c_1+c_2^+c_2)+\hbar\omega_i(b_{1i}^+b_{1i}+b_{2i}^+b_{2i}+1)+\hbar\omega_j(b_{2j}^+b_{2j}+b_{1j}^+b_{1j}+1)-\frac{1}{2}\{\hbar\omega_iK_i^2+\hbar\omega_jK_j^2\}\{c_1^+c_1+c_2^+c_2\}$$

$$-\{(\hbar\omega_iK_i/\sqrt{2})(b_{2i}+b_{2i}^+)\exp[-(K_i^2+K_j^2)]\exp(-\sqrt{2}K_ib_{1i}^+)\exp(\sqrt{2}K_ib_{1i})\exp(-\sqrt{2}K_jb_{1j}^+)$$

$$\times\exp(\sqrt{2}K_jb_{1j})c_2^+c_1+(\hbar\omega_jK_j/\sqrt{2})(b_{2j}+b_{2j}^+)\exp-(K_i^2+K_j^2)\exp(-\sqrt{2}K_ib_{1i}^+)\exp(\sqrt{2}K_ib_{1i})\exp(-\sqrt{2}K_jb_{1j}^+)$$

$$\times\exp(\sqrt{2}K_jb_{1j})c_2^+c_1\}-\text{c.c.} \quad (10)$$

For real values of the coupling constants (as occur for benzene), the smallness parameter $K^2\exp(-K^2)$ is generally appropriate for a perturbation calculation.

To second order, the energy of the ground states is given by

$$E_0 = \epsilon + \hbar\omega_i + \hbar\omega_j + (\hbar/2)[\omega_i K_i^2 + \omega_j K_j^2] - \exp[-2(K_i^2 + K_j^2)][\hbar\omega_i K_i/2]^2 \sum_{n,m=0}^{\infty} (2K_i^2)^n (2K_j^2)^m$$

$$\times \{n!m![m\hbar\omega_j + (n+1)\hbar\omega_i]\}^{-1} - \exp[-2(K_i^2 + K_j^2)][\hbar\omega_j K_j/2]^2 \sum_{n,m=0}^{\infty} \frac{(2K_i^2)^n (2K_j^2) g}{n!m![(n+1)\hbar\omega_j + n\hbar\omega_i]} . \quad (11)$$

These summations converge rapidly, often giving three significant figures if only *three* terms in each double sum are considered. Table VII gives ΔE_0 as a function of K_i, K_j, and $R = \omega_i/\omega_j$; exact values are included for comparison. Energies of the first excited vibrational levels of each mode characterized by $|\lambda| = 3/2$ and $1/2$ were calculated in the same manner and are again expressed in terms of simple sums. These results are included in Table VII; exact energies are added for comparison.

The salient features of the energy "shifts" and spacings are correctly described by the transformation–perturbation scheme. The energies decrease with the addition of another coupling mode and the energy spacing E_{0-1} is less than described by a single coupling mode, especially for the most energetic vibration. The hot band splittings are also shown to be decreased. However, this approximate method consistently underestimates the absolute energy "shifts" and overestimates the energy spacings. Both methods show the interaction between the two vibrations increases as their coupling parameters increase and as the frequency ratio goes to one.

C. Linear and Quadratic Coupling by a Degenerate Vibration

The appropriate electron–phonon Hamiltonian written in real coordinates is:

$$H = \epsilon(c_1^+ c_1 + c_2^+ c_2) + \hbar\omega(b_1^+ b_1 + b_2^+ b_2 + 1) + (\hbar K\omega/\sqrt{2})[(c_1^+ c_1 - c_2^+ c_2)(b_1 + b_1^+) - (c_1^+ c_2 - c_2^+ c_1)(b_2 + b_2^+)]$$

$$+ (J+D/2)\hbar\omega[(b_1 + b_1^+)^2 c_1^+ c_1 + (b_2 + b_2^+)^2 c_2^+ c_2] + (J-D/2)\hbar\omega[(b_1 + b_1^+)^2 c_2^+ c_2 + (b_2 + b_2^+)^2 c_1^+ c_1]$$

$$+ D\hbar\omega(b_1 + b_1^+)(b_2 + b_2^+)[c_1^+ c_2 + c_2^+ c_1] \quad (12)$$

in the subspace of two electronic states and a degenerate vibrational mode.

The isotropic contributions to the force constants simply shift the frequency of the active mode in the excited states from the ground electronic state value. These uninteresting couplings are diagonalized to expose the Duchinsky and Jahn–Teller interactions. This is accomplished by the transformation: $\tilde{H} = \exp(S) H \exp(-S)$ where $S = f_1 c_1^+ c_1 (b_1 b_1 - b_1^+ b_1^+) + f_2 c_2^+ c_2 (b_1 b_1 - b_1^+ b_1^+) + f_2 c_1^+ c_1 (b_2 b_2 - b_2^+ b_2^+) + f_1 c_2^+ c_2 (b_2 b_2 - b_2^+ b_2^+)$ where $f_1 = -\frac{1}{8} \ln(1 + 2J + 2D)$ and $f_2 = -\frac{1}{8} \ln(1 + 2J - 2D)$, a Bogoliubov u–v transformation in phonon space. The limit $|D| < J + 1/2$ adds no restriction to the calculation; it corresponds to the limit of validity of the harmonic approximation. Writing $\tilde{H} = \tilde{H}_0 + \tilde{H}_1 + \tilde{H}_2$, we find

$$\tilde{H}_0 = \epsilon(c_1^+ c_1 + c_2^+ c_2) + \omega(b_1^+ b_1 + b_2^+ b_2 + 1) + c_1^+ c_1 (b_1^+ b_1 + \tfrac{1}{2})[\omega_1 - \omega] + c_2^+ c_2 (b_2^+ b_2 + \tfrac{1}{2})[\omega_1 - \omega]$$

$$+ c_1^+ c_1 (b_2^+ b_2 + \tfrac{1}{2})[\omega_2 - \omega] + c_2^+ c_2 (b_1^+ b_1 + \tfrac{1}{2})[\omega_2 - \omega],$$

$$\tilde{H}_1 = (K\omega/\sqrt{2}) \exp(2f_1)(b_1 + b_1^+) c_1^+ c_1 - (K\omega/\sqrt{2}) \exp(2f_2)(b_1 + b_1^+) c_2^+ c_2,$$

$$\tilde{H}_2 = -(K\omega/\sqrt{2}) \exp(2f_1)(b_2 + b_2^+) c_2^+ c_1 \exp[-P(1,2)] - (K\omega/\sqrt{2}) \exp(2f_2)(b_2 + b_2^+) c_1^+ c_2 \exp[-P(1,2)]$$

$$+ D\omega \exp[2(f_1 + f_2)](b_1 + b_1^+)(b_2 + b_2^+)\{c_2^+ c_1 \exp[-P(1,2)] + c_1^+ c_2 \exp[P(1,2)]\}, \quad (13)$$

where

$$P(1,2) = (f_1 - f_2)(b_1 b_1 - b_1^+ b_1^+) - (f_1 - f_1)(b_2 b_2 - b_2^+ b_2^+),$$

$$\omega_1 = [1 + 2J + 2D]^{1/2}\omega,$$

and

$$\omega_2 = [1 + 2J - 2D]^{1/2}\omega.$$

The frequency of mode 1 in the potential of electronic state I is given by $\tilde{H}_0$ as ω_1.

As in the past, the linear terms severely limit the utility of perturbation expansion since often $K \sim 1$. In the spirit of the Alper and Silbey method, the intraorbital coupling is diagonalized and the interorbital coefficient substantially reduced by the transformation: $H' = \exp(S) \tilde{H} \exp(-S)$ where $S = -g_a c_1^+ c_1 (b_1 - b_1^+) + g_b c_2^+ c_2 (b_1 - b_1^+)$ with the result

$$H' = \epsilon(c_1^+ c_1 + c_2^+ c_2) + \omega(b_1^+ b_1 + b_2^+ b_2 + 1) + c_1^+ c_1 (b_1^+ b_1 + \tfrac{1}{2})[\omega_1 - \omega] + c_2^+ c_2 (b_2^+ b_2 + \tfrac{1}{2})[\omega_1 - \omega]'$$

$$+ c_1^+ c_1 (b_2^+ b_2 + \tfrac{1}{2})[\omega_2 - \omega] + c_2^+ c_2 (b_1^+ b_1 + \tfrac{1}{2})[\omega_2 - \omega] + g_a^2 c_1^+ c_1 \omega + g_b^2 c_2^+ c_2 \omega - 2K\omega g_a \exp(2f_1) c_1^+ c_1 - 2K\omega g_b$$

$$\times \exp(2f_2) c_2^+ c_2 - g_a \omega_1 c_1^+ c_1 (b_1 + b_1^+) + g_b \omega_2 c_2^+ c_2 (b_1 + b_1^+)$$

$$+ (K\omega/\sqrt{2}) \exp(2f_1) c_1^+ c_1 (b_1 + b_1^+) - (K\omega/\sqrt{2}) \exp(2f_2)(b_1 + b_1^+) c_2^+ c_2 + \tilde{\mathcal{K}}_2'. \quad (14)$$

The choice of g_a and g_b deserves some discussion. Linear coupling terms vanish for the choice:

$$g_a = (K/\sqrt{2}) \exp(6f_1) \quad \text{and} \quad g_b = (K/\sqrt{2}) \exp(6f_2). \tag{15}$$

However, the resultant Hamiltonian is no longer invariant under the appropriate point group term by term. H_0' predicts a lower symmetry than the true vibronic symmetry, so the perturbation will have to restore the proper degeneracies. A different transformation which retains at least the molecular symmetry in H_0', leaving the perturbation expansion to break any accidental zeroth order degeneracies is given by:

$$g_a = \sqrt{2}K \exp(6f_1) \quad \text{and} \quad g_b = (K/\sqrt{2}) \exp(6f_2). \tag{16}$$

This choice, however, voids the purpose of a second transformation since linear coupling remains. A compromise in which the intraorbital coupling of at least one electronic state disappears and the molecular symmetry is retained in H_0' suggests itself. Then, we would require

$$g_a = (K/\sqrt{2}) \exp(6f_1) \quad \text{and} \quad g_b = (K/\sqrt{2}) \exp(6f_2)[1+2D \exp 4f_1]. \tag{17}$$

This leaves linear coupling in $c_2^+c_2$ space having a smallness parameter $K\sqrt{2}D \exp(4f_1+2f_2)$. A second-order perturbation expansion will be useful only if $\sqrt{2}D \exp(4f_1+2f_2) \ll 1$. Realistically, $\frac{1}{2} < \omega'/\omega < 2$, ω' being the frequency of a normal vibration in an excited state, and $D^{1/2} \sim 0.3$. Therefore, at worst, the coefficient is $1.2K$ and, at best, $0.15K$. Most commonly, $(\omega'/\omega) \sim 1$ and the coefficient becomes $\sim 0.4K$. Proceeding with this transformation, however, the symmetry is again totally destroyed by the first order correction. Therefore, with a second-order perturbation expansion in mind, choice (15) is employed as the best of the alternatives. With this choice,

$$H' = \epsilon(c_1^+c_1+c_2^+c_2) + \omega(b_1^+b_1+b_2^+b_2+1) - (K^2\omega/2)[(c_1^+c_1/1+2J+2D)+(c_2^+c_2/1+2J-2D)]$$

$$+ c_1^+c_1[(b_1^+b_1+\tfrac{1}{2})(\omega_1-\omega)+(b_2^+b_2+\tfrac{1}{2})(\omega_2-\omega)] + c_2^+c_2[(b_1^+b_1+\tfrac{1}{2})(\omega_2-\omega)+(b_2^+b_2+\tfrac{1}{2})(\omega_1-\omega)]$$

$$+ \omega\{c_1^+c_2(K/\sqrt{2}) \exp(2f_1)[2D \exp(8f_2)-1] \exp(-R^2/2)(b_2+b_2^+) \exp(Rb_1^+) \exp(-Rb_1) \exp[-P(1,2)]+\text{c.c.}\}$$

$$+ \omega\{c_2^+c_1D \exp[2(f_1+f_2)] \exp(-R^2/2)(b_1+b_1^+)(b_2+b_2^+) \exp(Rb_1^+) \exp(-Rb_1) \exp[-P(1,2)]+\text{c.c.}\}, \tag{18}$$

where

$$R = -\{[1+(2\Delta/d)](K/2) \exp(6f_1)+(K/2) \exp(6f_2)\},$$

$$\Delta = (f_1-f_2),$$

$$d = 1-\Delta+(\Delta^2/3)+(\Delta^3/6). \tag{19}$$

The factorization of the exponential operators and evaluation of the matrix elements of $H'-H_0'$ are presented in the appendix. These matrix elements are written: $\langle II, ms \mid H'-H_0' \mid I, pt \rangle$ where m and s are the quantum numbers of components 1 and 2 of the coupling mode, I and II refer to the electronic states such that

$$\langle II, ms \mid H'-H_0 \mid I, pt \rangle = \sum_{n=0} \mathcal{Q}_n \mathcal{R}_n \mathcal{S}_n, \tag{20}$$

where

$$\mathcal{Q}_n = \sum_{q=0}^{n} \frac{R^{2q+m-n}(-)^q m! n!}{q!(m-n+q)!(n-q)!} \left[A + B\frac{m-n+q}{R} + B\frac{R(m+1)}{(m-n+q+1)} \right], \tag{21a}$$

$$\mathcal{R}_n = \sum_{j=0 \text{ or } 1}^{n \text{ or } p \text{ (lower)}} a_{2j}b_{n-j}c_{p-j} \left[\frac{n!p!}{2^{n+p}}\frac{2\alpha}{1+\alpha^2} \right]^{1/2}, \tag{21b}$$

$$\mathcal{S}_n = \sum_{j=0 \text{ or } 1}^{(s-1) \text{ or } t \text{ (lower)}} a_{2j}'b_{s-1-j}'c_{t-j} \left[\frac{(s-1)!t!}{2^{s-1+t}}\frac{2\alpha}{1+\alpha^2} \right]^{1/2} (s)^{1/2}$$

$$+ \sum_{j=0 \text{ or } 1}^{(s+1) \text{ or } t \text{ (lower)}} a_{2j}'b_{s+1-j}'c_{t-j}' \left[\frac{(s+1)!t!}{2^{s+1+t}}\frac{2\alpha}{1+\alpha^2} \right]^{1/2} (s+1)^{1/2}, \tag{21c}$$

a_{2j}, b_{n-j}, c_{p-j} are Hutchisson's[15] functions for $\alpha = [(1+2J+2D)/(1+2J-2D)]^{1/2}$ (see Appendix for A and B). Primed functions are defined for α^{-1}.

The energy "shifts" of the ground and first vibrational states are presented as functions of K, J, and D in Table VIII. Notice that the proper symmetry is not restored to either vibrational level. In general, the improper splitting in the ground vibrational state is negligible and the energies are reasonably increased by the positive changes in the potential slopes considered.

TABLE VII. Absolute energy shifts. Jahn–Teller coupling through two modes.[a]

			$\|\lambda\|=\frac{1}{2}$						$\|\lambda\|=\frac{3}{2}$				$\|\lambda\|=\frac{1}{2}$	$\|\lambda\|=\frac{3}{2}$
K_1^2	K_2^2	$\Delta E_0(T)$	ΔE_0 (exact)	$\Delta E_1^1(T)$	$\Delta E_1^2(T)$	ΔE_1^1 (exact)	ΔE_1^2	$\Delta E_1^1(T)$	$\Delta E_1^2(T)$	ΔE_1^1 (exact)	ΔE_1^2	$\Delta E_0(s)$	$\Delta E_1^1(s)$	$\Delta E_1^1(s)$
0.25	0.25	−0.341	−0.353	−0.166	−0.233	−0.233	−0.292	−0.469	−0.536			−0.226	−0.053	−0.391
0.50	0.25	−0.508	−0.535	−0.287	−0.449	−0.392	−0.493	−0.759	−0.685	−0.454	−0.472	−0.422	−0.181	−0.684
0.75	0.25	−0.659	−0.704	−0.468	−0.627	−0.566	−0.672	−1.02	−0.811	−0.700	−0.670	−0.600	−0.341	−0.933
1.0	0.25	−0.800	−0.866	−0.675	−0.783	−0.742	−0.839	−1.25	−0.926	−0.912	−0.859	−0.767	−0.512	−1.16

[a] ΔE_0—energy shift of lowest vibronic state, ΔE_1^2—energy shift of first vibrational state of mode 2; all energies are in units ω_1. T=transformation method, s=single mode coupling.

The negative Jahn–Teller energy shifts are diminished $(D>J)$ and become positive $(J>D)$ with decreasing D and increasing J, as the sum of the frequencies ω_1 and ω_2 increases, thereby diminishing or offsetting the linear effect. The first vibrational levels appear to be greatly distorted by the misleading symmetry of the low order Hamiltonian. The energy shifts predicted for small nonzero values of D are unrealistically large. Where $D=0$, degenerate perturbation theory gives reasonable energy shifts having the proper degeneracies.

V. DISCUSSION

Jahn–Teller behavior within a doubly degenerate electronic state has been ascribed to a number of observations where the "characteristic" double peaked absorption pattern occurs. However, unambiguous identification of this interaction is difficult because the "characteristic" spectrum has not been observed in gas phase molecules where $K^2 \leq 1$. In solids, where stronger coupling occurs, other contributing effects such as crystal stress and imperfections cannot be eliminated.

In gas phase studies, criteria for the Jahn–Teller phenomena must include energy spacings in a progression attributed to an asymmetric vibration, as well as the hot band splittings and relative intensities. Our investigations show that in the majority of systems, those which exhibit comparable or at least non-negligible coupling through a second vibration, the structure of the progression of the dominant active mode may be obscured by irregular energy spacings and lessened intensity due to the interference of a less energetic vibration. The hot band splitting and intensities are also reduced, thereby necessitating higher resolution experimental study.

When two degenerate vibrations both interact weakly $(K^2<0.25)$ with the electronic motion, intensity borrowing by the more energetic progression occurs, however, this detailed interaction between the two vibrations is masked when the coupling of either increases and both lose intensity to higher vibrational states.

In these investigations, the linear coupling constants K were taken as parameters because a quantitative evaluation is generally approximate. In considering the benzene anion where the degenerate electronic states are labeled Ω_-, Ω_+, and the symmetry coordinates S_m are related to the normal modes of symmetry m defined as eigenfunctions of C_6 by $S_m = \sum_g S_g^{m'} Q_g^{m'}$, we found

$$\langle \Omega_- \,|\, H_{elec} \,|\, \Omega_+ \rangle = (\tfrac{1}{3})^{1/2}\beta' \sum_g S_g^{(-2)'} Q_g^{(-2)}$$
$$+ \tfrac{1}{4}(\tfrac{1}{6})^{1/2}\beta'' \sum_{\substack{n,m,f,g \\ m+n=2,4}} S_f^{m'} S_g^{n'} Q_f^m Q_g^n, \quad (22)$$

where β is the resonance integral and derivatives are taken with respect to internuclear separation. The S_g^m are numerically equivalent to Whiffen's[16] $S^{m'}$, consistent

TABLE VIII. Absolute energy shifts (units ω) for linear and quadratic coupling.[a]

K	J	D	$\Delta E_0(T)$	(exact) ΔE_0	$\Delta E_1(S)$	$\Delta E_1(T)$	(exact) ΔE_1	$\Delta E_1(S)$
0.50	0	0	−0.223	−0.226	−0.226	−0.385	−0.392	−0.391
			−0.233			−0.385		
						−0.004	−0.053	−0.053
						−0.004		
0.50	0.2	0.0	+0.017	+0.15	−0.226	+0.078	+0.64	
			+0.017			+0.078		
						+0.385	+0.306	
						+0.385		
0.50	0.2	0.2	−0.036	−0.020	−0.226	−1.41	−0.299	
			−0.031			+1.31	+0.227	
						+2.19	+0.227	
						+3.26	+0.325	
0.50	0.5	0	+0.294	+0.294	−0.226	+0.620	+0.604	
			+0.294			+0.620		
						+0.849	+0.819	
						+0.849		
0.50	0.5	0.2	+0.267	+0.276	−0.226	−1.53	+0.312	
			+0.268			+1.01	+0.764	
						+2.59	+0.764	
						+5.81	+0.847	
0.50	0.5	0.7	−0.009	−0.029	−0.226	−0.827	−0.758	
			−0.086			−0.982	−0.135	
						+0.148	−0.135	
						+1.95	+0.389	

[a] ΔE_0 = energy shift of ground vibronic state, ΔE_1 = energy shift of first vibrational state, T = transformation method, S = linear coupling.

with the normalization of the Q's and the constants in K. We find $K_1{}^2 = 0.384$ for the 1595 cm^{-1} vibration and $K_2{}^2 = 0.449$ for the 606 cm^{-1} mode.

Hobey[13] has simplified this calculation by using the vibrational F and G matrices[17] to approximate the transformation from symmetry coordinates to normal modes. His approximations diagonalizing the F and G matrices are not valid for the C–C–C bending mode (606 cm^{-1}), however. Off-diagonal terms in the F matrix are not negligible in the bending modes; the magnitude of these terms is 30% of the diagonal term compared with 3% for stretch modes. The high–low frequency separation for the G matrix[18] is much less accurate for bending modes and yields $G^{1/2} = 4.69 \times 10^{11}$ g$^{1/2}$, while the value obtained from (F) and Whiffen's data is 0.84×10^{11} g$^{1/2}$. Hobey's procedure for evaluating K is adequate for the C–C stretch, but inadequate for the C–C–C bending mode.

When quadratic coupling is added, the spectral pattern predicted by a simple vibration is altered in two ways. The vibrational frequency change reduces the effective linear interaction. Secondly, accidental vibronic degeneracies in the hot band are resolved if Duchinsky mixing is nonzero. The position of the hot band doublet relative to the resolved orbital singlets depends on the magnitude of this mixing, as do the relative spectral intensities.

Transformation–perturbation schemes have been suggested as alternatives to numerical calculations for linear coupling through two degenerate vibrations and for the linear and quadratic couplings of a single mode. Using the first, the modification of the energy spacing seen with the addition of a second vibration were reasonably predicted by the transformation scheme: the E_{0-1} energy spacing is decreased as are the hot band splittings and all absolute energies. However, this perturbation method overestimates the energy spacings.

The second transformation scheme which dealt with linear and quadratic interactions, provides a useful qualitative description of energy separations in the absence of Duchinsky mixing. However, when this mixing is nonzero the zeroth-order Hamiltonian has lower symmetry than the full Hamiltonian, and the proper degeneracies must be restored by the perturbation expansion; a second-order treatment is inadequate. In fact, for small D, a perturbation approach is not warranted because of the near-degeneracy of the initial states.

A final comment is in order concerning the frequent use[2,11,12] of the adiabatic potential surfaces to predict spectral patterns and criteria for stable and semistable nuclear distortions. The degeneracy of the lowest vibronic states is a function of the Duchinsky parameter, D, for the triple degeneracy can be described on the adiabatic surface using the Hamiltonian complete in linear and quadratic terms and without the anharmonics previously[2,11,12] required to destroy the adiabatic potential's cylindrical symmetry under linear coupling. Our criterion for a triply degenerate state, $D \approx (2J+1)/2$, is supported by our exact quantum mechanical calculations. Since this criterion corresponds to the harmonic limit, a full and proper treatment should include all anharmonicities as well. Previous workers neglected the Duchinsky quadratics and the anharmonic interaction in the complex representation.

We also conclude that studies of the adiabatic surfaces do not yield quantitative vibronic results. The exact wavefunctions are not accurately described by either conic surface nor by a superposition of the wavefunctions on each surface at the appropriate energy level, except for the lowest states for large K. For example, when $K^2 = 10$, the wavefunction at the second "characteristic" Jahn–Teller absorption peak is very localized, supporting the notion of a superposition of the ground state nuclear function on the upper surface and appropriate functions for the lower surface. However, the corresponding eigenvalue is $\sim 5\omega$ above the cusp, a fact in contradiction to the adiabatic prediction. In addition, the energy separation of the absorption peaks is less than that explained by adiabatic models, in fact, for $K^2 < 5$ the adiabatic model still predicts an absorption peak separation.

This brief discussion suggests strongly that the use of adiabatic surfaces to construct wave functions and thereby describe optical spectra is not valid in the energy region where the characteristic Jahn–Teller structure occurs.

ACKNOWLEDGMENTS

APPENDIX

Using Hamiltonian (18) where V is the nondiagonal part, matrix elements of the form

$$\langle m \mid \exp(Rb_1^+) \exp(-Rb_1) \exp[\Delta(b_1b_1 - b_1^+b_1^+)] \mid p \rangle \tag{A1}$$

and

$$\langle s \mid (b_2 + b_2^+) \exp[-\Delta(b_2b_2 - b_2^+b_2^+)] \mid t \rangle \tag{A2}$$

need to be evaluated. Suppressing subscripts, we have

$$\langle m \mid \exp(Rb^+) \exp(-Rb) \exp[\Delta(bb - b^+b^+)] \mid p \rangle = \sum_{n=0} \langle m \mid \exp(Rb^+) \exp(-Rb) \mid n \rangle \langle n \mid \exp\Delta(bb - b^+b^+) \mid p \rangle$$

$$= \sum_{n=0} \sum_{q=0} [R^{2q+m-n}(-)^q(m!n!)^{1/2}/q(m-n+q)!(n-q)!]$$

$$\times \langle n \mid \exp[\Delta(bb - b^+b^+)] \mid p \rangle.$$

We can use the calculations of Hutchisson[15] to calculate $\langle n \mid p' \rangle = \langle n \mid \exp[\Delta(bb - b^+b^+)] \mid p \rangle$ because $\mid p' \rangle$ differs from $\mid p \rangle$ in a frequency shift only. Hutchisson's parameters d_x and e_y are zero here, so

$$\langle n \mid \exp[\Delta(bb - b^+b^+)] \mid p \rangle = 0, \quad n + p \text{ odd},$$

$$\neq 0, \quad n + p \text{ even}.$$

Hutchisson's C_3 can be evaluated using McCoy's theorem[18]

$$\exp Z = \exp[\Delta(bb - b^+b^+)] = N[\exp W],$$

where N is the "normal ordering" operator which moves all creation operators to the left of annihilation operators and where

$$W = Abb + Bb^+b^+ + Gb^+b + F$$

and

$$A = [\tanh 2\Delta]/2 = -B,$$

$$F = -[\ln \cosh 2\Delta]/2,$$

$$G = [\cosh 2\Delta]^{-1} - 1,$$

therefore,

$$\exp Z = \exp F \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \frac{A^{n-l-m} B^m G^l}{(n-l-m)!\,m!\,l!} (b^+)^{2m+l} (b)^{2n-2m-l}.$$

Now consider the diagonal elements

$$\langle t \mid \exp Z \mid t \rangle = \langle t \mid\mid t \rangle,$$

where we must require $n \le t$ and $l = n - 2m$. Using the expression for $\exp Z$ above, one finds:

$$\langle t \mid \exp Z \mid t \rangle = [\cosh 2\Delta]^{-1/2} \sum_{n=0}^{t} \sum_{m=0}^{n/2 \text{ or } (n-1)/2} \frac{t! [-\tfrac{1}{2} \tanh^2 2\Delta]^m [\cosh^{-1} 2\Delta - 1]^{n-2m}}{(t-n)!\,m!\,m!\,(n-2m)!}.$$

Thus

$$\langle 0 \mid\mid 0 \rangle = [2/\alpha(\alpha^2+1)]^{1/2} \alpha, \qquad \alpha = (\omega'/\omega)^{1/2}$$

$$\langle 1 \mid\mid 1 \rangle = [2\alpha/(\alpha^2+1)]^{3/2},$$

$$\langle 2 \mid\mid 2 \rangle = [2\alpha/(\alpha^2+1)]^{1/2} \{ [2\alpha/(1+\alpha^2)]^2 - \tfrac{1}{2} \tanh^2(-\tfrac{1}{4} \ln\alpha^4) \}.$$

Comparison with Hutchisson's results shows his parameter C_3 is given by

$$C_3 = [2\alpha/(\alpha^2+1)]^{1/2}.$$

Therefore,

$$\langle n \mid \exp\Delta(bb - b^+b^+) \mid p \rangle = \sum_{l=x}^{n \text{ or } p \text{ (lower)}} a_{2l} b_{n-l} c_{p-l} [n!\,p!/2^{n+p}]^{1/2} [2\alpha/(1+\alpha^2)]^{1/2},$$

where for: n and p odd, $x=1$ and l is odd only;

n and p even, $x=0$ and l is even only;

and where,

$$a_{2l} = (1/l!)(4\alpha/1+\alpha^2),$$

$$b_{n-l} = \{1/[\tfrac{1}{2}(n-l)]!\}[(1-\alpha^2)/(1+\alpha^2)]^{(n-l)/2},$$

$$c_{p-l} = \{1/[\tfrac{1}{2}(p-l)]!\}[-(1-\alpha^2)/(1+\alpha^2)]^{(p-l)/2}.$$

Insertion of these results into

$$\sum_{n=0}^{\infty} \langle m \mid \exp(Rb^+) \exp(-Rb) \mid n \rangle \langle n \mid \exp[\Delta(bb - b^+b^+)] \mid p \rangle$$

and the use of the same techniques to evaluate Expression (A2) leads to the result (18).

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