

Symmetry-adapted excited states for the $T_{1u} \otimes h_g$ Jahn-Teller system

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Jahn-Teller (JT) systems typically contain a set of equivalent-energy wells in the lowest adiabatic potential-energy surface (APES). Quantum-mechanical tunneling between these wells (the dynamic JT effect) must be allowed for by taking appropriate symmetrized combinations of oscillator-type states associated with the wells. It is important to be able to describe the excited states of such systems for a number of reasons. One particular reason is that they are required for the calculation of second-order vibronic reduction factors, which in turn are useful for modeling experimental data using effective Hamiltonians. In this paper, projection-operator techniques are used to obtain general expressions for the symmetry-adapted excited states of the icosahedral $T_{1u} \otimes h_g$ JT system for the case of D_{5d} minima in the APES. Analytical expressions for the states and their energies for one-phonon excitation are given explicitly. The energies of a selection of states with two-phonon excitations are also obtained and plotted. The results obtained in this paper are applicable to the C_{60}^- molecule.

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I. INTRODUCTION

The electron-phonon interaction plays an important role in unraveling the properties of ionized C_{60} molecules in both the isolated molecular and solid forms. In the past few years, many papers^{1–10} have been published on the effects of this interaction in icosahedral systems in order to provide models for real C_{60} molecules. These and other publications are discussed in the book of Chancey and O'Brien.¹¹ From a theoretical point of view, icosahedral systems are of much interest due to the appearance of threefold, fourfold, and fivefold irreducible representations (irreps.). The lowest unoccupied molecular orbital T_{1u} of the free C_{60} molecule is threefold orbitally degenerate. Therefore, a $T_{1u} \otimes h_g$ Jahn-Teller (JT) interaction with the fivefold degenerate vibrational modes h_g will be dominant in the negatively charged state C_{60}^- . Thus this JT system is the key to the understanding of the electronic structure of this real system.

When a T_{1u} orbital state couples linearly to a vibrational h_g mode, the lowest adiabatic potential-energy surface (APES) is found to consist of a minimum-energy trough, having an accidental symmetry higher than icosahedral. In this case, states of the system must take account of vibrations across the trough and rotations around the trough. All points at the bottom of the trough are equivalent, so the total states must involve an integral over all these points. In real systems, higher-order terms such as quadratic coupling will warp the trough. As long as the higher-order terms are large enough, this will generate wells in the APES. Rather than including the continuum of points at the bottom of the trough, only the points at the bottom of the wells then need be included. For the $T_{1u} \otimes h_g$ problem, there are either ten wells of D_{3d} symmetry or six wells of D_{5d} symmetry, depending upon the strengths of the coupling constants. In infinite coupling, states in these wells could be used as states of the system as a whole. This situation is often referred to as the static JT effect. However, in finite coupling, dynamical tunneling between the wells will take place. Mathematically, this can be accounted for by taking appropriate symmetrized linear combinations of the ground states in each of the

equivalent lowest-energy wells. This restores the icosahedral symmetry of the system, resulting in a T_{1u} ground state. At first sight, the well problem may appear more complicated than the linear case due to the presence of higher-order terms. However, considerable advantages arise from only needing to consider six or ten distinct points and from not having to evaluate multidimensional integrals when determining overlap factors and energy matrix elements.

Dunn and Bates⁶ gave a detailed analytical treatment of the ground state of the $T_{1u} \otimes h_g$ JT system when quadratic coupling terms are included in the vibronic Hamiltonian. Further studies^{12,13} have described the effects of anisotropy in the potential wells and its effect on the ground states. Anisotropy alters the shape of the minima and correspondingly removes some of the degeneracies associated with the phonon frequencies.^{14,15} This is particularly important for systems, such as $T_{1u} \otimes h_g$, in which wells are only introduced by higher-order terms. Not only will the barriers be shallower in the direction(s) around the well, but the frequencies in these directions will be much lower than in the perpendicular directions. The effect of anisotropy in icosahedral systems has been further discussed by Chancey and O'Brien.¹¹

JT effects in molecules and solids are often observed through an analysis of the parameters appearing in effective Hamiltonians.^{16–18} Effective Hamiltonian approaches provide a simple means of modeling experimental data as the effect of the vibronic coupling is “transferred” into simple numerical factors multiplying electronic perturbations. At one level, these factors can be treated simply as fitting parameters. However, this view hides much of the underlying physics as it is not possible then to know whether the values obtained for the parameters have any physical significance. At a deeper level, the numerical factors can be described in terms of vibronic (or Ham) reduction factors (RFs). Calculations can be made relating all of the RFs (and hence all of the fitting parameters) to a smaller set of variables, namely the vibronic coupling strength(s) and vibrational frequencies.

The effect of an electronic perturbation can be included to first or second order in perturbation theory, and the corre-

sponding numerical factors are known as first- and second-order RFs, respectively. If the vibronic coupling is strong, the first-order RFs can be very small and the second-order terms then dominate the effective Hamiltonian.^{16,19} Hence it is important to be able to calculate the magnitudes of the second-order RFs as well as the first-order RFs.^{20,21} First-order RFs are relatively simple to calculate.¹⁶ However, second-order RFs are much more difficult to evaluate as they involve coupling to an infinite set of excited vibronic states. Symmetry-adapted excited vibronic states of the $T_{1u} \otimes h_g$ JT system appropriate to the dynamical JT effect have not yet been investigated. Although it is possible to make an estimate of the values of second-order RFs by simply taking the infinite-coupling well states as the excited states, symmetry-adapted excited states and their energies are needed in order to get more accurate values for the second-order RFs.

The aim of this paper is to derive analytical expressions for the excited states of the $T_{1u} \otimes h_g$ JT system and their corresponding energies, including anisotropic effects. The number of excited states of a given symmetry (irrep.) associated with any number N of phonon excitations is also useful information. These results are derived using group-theoretical methods. Explicit analytical results will be given for states with one-phonon excitation based upon the D_{5d} minima. Some states with two-phonon excitations are also calculated and the results are given graphically. Due to the complicated nature of the results, analytical expressions are not given in this case. The method given can be extended to states with higher numbers of phonon excitations, and also to states associated with the D_{3d} minima.

II. THE VIBRONIC HAMILTONIAN AND THE INFINITE COUPLING EXCITED STATES

The total Hamiltonian for the $T_{1u} \otimes h_g$ JT system including quadratic terms can be written as⁶

$$\mathcal{H} = \mathcal{H}_{\text{vib}} + \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_3, \quad (1)$$

where the vibrational Hamiltonian \mathcal{H}_{vib} , the linear interaction Hamiltonian \mathcal{H}_1 , and the two quadratic coupling Hamiltonians \mathcal{H}_2 and \mathcal{H}_3 are given by

$$\begin{aligned} \mathcal{H}_{\text{vib}} &= \frac{1}{2} \sum_j \left(\frac{P_j^2}{\mu} + \mu \omega^2 Q_j^2 \right) \hat{L}_{A_1}, \\ \mathcal{H}_1 &= V_1 \sum_j Q_j \hat{L}_{H_j}, \\ \mathcal{H}_2 &= V_2 \sum_j A_j \hat{L}_{H_j}, \\ \mathcal{H}_3 &= V_3 \sum_j B_j \hat{L}_{H_j}, \end{aligned} \quad (2)$$

and where μ is the reduced mass corresponding to vibrational mode Q_j . The index j is taken over all components (θ , ϵ , 4, 5, and 6) of the h_g phonon modes. V_1 is the linear coupling constant and V_2, V_3 are the quadratic coupling con-

stants. \hat{L}_{A_1} is the unit operator and, within the pure electronic basis states x , y , and z of T_{1u} , the \hat{L}_{H_j} are orbital operators that can be expressed in matrix form,

$$\begin{aligned} \hat{L}_{H\theta} &= \frac{1}{2} \sqrt{\frac{3}{5}} \begin{pmatrix} \phi^{-1} & 0 & 0 \\ 0 & -\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}, \\ \hat{L}_{H\epsilon} &= \frac{1}{2} \sqrt{\frac{1}{5}} \begin{pmatrix} \phi^2 & 0 & 0 \\ 0 & -\phi^{-2} & 0 \\ 0 & 0 & -\sqrt{5} \end{pmatrix}, \\ \hat{L}_{H4} &= \sqrt{\frac{3}{10}} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \\ \hat{L}_{H5} &= \sqrt{\frac{3}{10}} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \\ \hat{L}_{H6} &= \sqrt{\frac{3}{10}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \end{aligned} \quad (3)$$

where $\phi = \frac{1}{2}(1 + \sqrt{5})$ is the golden mean. The symmetrized displacement coordinates are

$$\begin{aligned} A_\theta &= \sqrt{\frac{1}{2}} Q_\theta Q_\epsilon + \sqrt{\frac{3}{8}} (Q_4^2 - Q_5^2), \\ A_\epsilon &= \sqrt{\frac{1}{8}} (Q_\theta^2 - Q_\epsilon^2 + Q_4^2 + Q_5^2 - 2Q_6^2), \\ A_4 &= \sqrt{\frac{1}{2}} (\sqrt{3} Q_\theta + Q_\epsilon) Q_4, \\ A_5 &= \sqrt{\frac{1}{2}} (-\sqrt{3} Q_\theta + Q_\epsilon) Q_5, \\ A_6 &= -\sqrt{2} Q_\epsilon Q_6, \end{aligned} \quad (4)$$

and

$$\begin{aligned}
B_\theta &= \sqrt{\frac{3}{8}}(Q_\theta^2 - Q_\epsilon^2) - \sqrt{\frac{1}{24}}(Q_4^2 + Q_5^2 - 2Q_6^2), \\
B_\epsilon &= -\sqrt{\frac{3}{2}}Q_\theta Q_\epsilon + \sqrt{\frac{1}{8}}(Q_4^2 - Q_5^2), \\
B_4 &= -\sqrt{\frac{1}{6}}[(Q_\theta - \sqrt{3}Q_\epsilon)Q_4 + 2\sqrt{2}Q_5Q_6], \\
B_5 &= -\sqrt{\frac{1}{6}}[(Q_\theta + \sqrt{3}Q_\epsilon)Q_5 + 2\sqrt{2}Q_4Q_6], \\
B_6 &= \sqrt{\frac{2}{3}}(Q_\theta Q_6 - \sqrt{2}Q_4Q_5).
\end{aligned} \tag{5}$$

As the A_j and B_j are quadratic in the Q_j 's, they can be written in the form

$$\begin{aligned}
A_j &= \sum_{m,n} a_{mn}^j Q_m Q_n, \\
B_j &= \sum_{m,n} b_{mn}^j Q_m Q_n,
\end{aligned} \tag{6}$$

where the sum is over $\{m,n\} = \{\theta, \epsilon, 4, 5, 6\}$.

Minima of D_{5d} (pentagonal) or D_{3d} (trigonal) symmetry generated by the quadratic coupling terms^{22,23} can be obtained following the unitary transformation and energy-minimization method.^{24,25} The unitary transformation U has the effect of displacing the origin of phonon coordinates from Q_k to $(Q_k - \alpha_k \hbar)$, and the energy minimization fixes the parameters α_k to the well positions. As the symmetry-adapted states are rather complicated, this paper is restricted to the consideration of the D_{5d} minima only, although similar calculations can also readily be undertaken for the D_{3d} minima. The six D_{5d} minima will be labeled A to F . The ground states of the transformed Hamiltonian can be written in the form $|X^{(k)}; 0\rangle$, where $X^{(k)}$ is the electronic state in well k and “0” represents zero-phonon excitations. The corresponding ground state $|X^{(k)'}; 0\rangle$ appropriate to the untransformed Hamiltonian is obtained by multiplying $|X^{(k)}; 0\rangle$ by the shift transformation operator $U = U_k$ for well k , where

$$U_k = \exp \left[\sum_j C_j^{(k)} (b_j - b_j^\dagger) \right], \tag{7}$$

where the $C_j^{(k)}$, which are directly related to the well positions, can be found in Ref. 6. Although there are no phonon excitations contained explicitly in the untransformed ground states, the presence of phonon creation operators in Eq. (7) implicitly includes phonon excitations. This automatically gives the untransformed states their required vibronic nature.

If each well is considered to be isotropic, with each component of the h_g mode having frequency ω , the vibronic excited states associated with each well can be expressed as

$$|\Phi_k(n_\theta n_\epsilon n_4 n_5 n_6)\rangle = |X^{(k)'}; \theta^{n_\theta} \epsilon^{n_\epsilon} 4^{n_4} 5^{n_5} 6^{n_6}\rangle, \tag{8}$$

where θ^{n_θ} , for example, denotes n_θ -phonon excitations of the Q_θ vibrational h_g mode in the well k and $n_\theta + n_\epsilon + n_4 + n_5 + n_6 = N$ is the total number of the phonon excitations in the system. This will be written in the shorthand form $|\Phi_k(\{n_j\})\rangle$, where $\{n_j\}$ is taken to mean dependence upon all phonon excitation numbers n_j for $j = \{\theta, \epsilon, 4, 5, 6\}$.

As it is known that the lowest APES contains a trough in the limit of weak quadratic coupling, the wells will be highly anisotropic, with the frequencies of vibration in the directions that correspond to moving around the trough in the linear coupling limit being much lower than those in the perpendicular directions. This anisotropy splits the h_g mode into a singlet a_g and two doublets e_{1g} and e_{2g} . The new modes for well k are a linear combination of the components θ , ϵ , 4, 5, and 6 of the isotropic h_g mode. As the directions around the trough are different for each well k , the components of the e_{1g} and e_{2g} modes are different for each well. They will be labeled $\{\theta_1^k, \epsilon_1^k\}$ and $\{\theta_2^k, \epsilon_2^k\}$, respectively. The appropriate combinations can be generated from the isotropic h_g mode using so-called S matrices that diagonalize the curvature matrix local to each minima. The anisotropic modes for each well can be written down in terms of the components of these matrices, so that

$$\zeta^k = \sum_j S_{\zeta j}^k j, \tag{9}$$

where ζ can be taken as $\{a, \theta_1, \epsilon_1, \theta_2, \epsilon_2\}$ and j is summed over θ , ϵ , 4, 5, and 6. The complete S matrices can be found in Ref. 12 for D_{5d} wells and in Ref. 26 for D_{3d} wells. The localized vibronic excited states for well k equivalent to Eq. (8) but including anisotropy become

$$\begin{aligned}
&|\Phi_k(n_a n_{\theta_1} n_{\epsilon_1} n_{\theta_2} n_{\epsilon_2})\rangle \\
&\equiv |X^{(k)'}; (a^k)^{n_a} (\theta_1^k)^{n_{\theta_1}} (\epsilon_1^k)^{n_{\epsilon_1}} (\theta_2^k)^{n_{\theta_2}} (\epsilon_2^k)^{n_{\epsilon_2}}\rangle,
\end{aligned} \tag{10}$$

which will be written in the shortened form $|\Phi_k(\{n_\zeta\})\rangle$, where the n_ζ refer to the symmetrized phonon excitations n_a , n_θ , etc. It can be seen that the local modes depend upon the well k in a rather complicated manner.

III. SYMMETRY-ADAPTED EXCITED STATES

A. Projection operators

In finite coupling, the vibronic well states (10) are not good eigenstates of the total Hamiltonian of the system as they are neither mutually orthogonal nor do they reflect the actual icosahedral symmetry of the system. To overcome these difficulties, we look for those linear combinations of the untransformed vibronic states that have a specified symmetry within I_h and are such that states of different symmetries are orthogonal. This can be achieved using projection-operator techniques,^{27,28} as used previously for the ground states⁶ of the $T \otimes h$ system. If an arbitrary well state is acted upon by a projection operator of a specific irrep., a symmetry-adapted state will be generated if the chosen well state is a component of the symmetrized state. If it is not, the result will be zero.

TABLE I. The coefficients b^{ki} of the excited state in Eq. (11).

k	$i=1$	$i=2$	$i=3$	$i=4$	$i=5$
A	$2 + \phi m$	$\mu + \phi m$	$\mu(1+m)$	$-\phi - \mu m$	$-\phi - 2m$
B	$\mu(-1+m)$	$-2 - \phi m$	$-\mu - \phi m$	$\phi + \mu m$	$\phi + 2m$
C	1	$\phi(1+m)$	$-\phi - m$	m	$-1 - \phi m$
D	$-\phi - m$	1	$-\phi - m$	m	$\phi(1+m)$
E	$1 + \mu m$	$-\mu m$	$\mu + m$	$-1 - m$	$-\mu$
F	μm	μ	$1 + m$	$-\mu - m$	$-1 - \mu m$

The application of projection operators to the vibronic excited states in an icosahedral system is far more complicated than that in cubic systems where an excitation in one well transforms in a simple manner into an excitation in another well under the symmetry operations of the cubic group, and much tedious work is required. We will illustrate the method by applying projection operators composed of the 60 rotational elements of the I_h group to the state $|\Phi_A(\{n_\zeta\})\rangle$ obtained from Eq. (10) for well $k=A$. We find that when the matrix S_A given in Ref. 29 is used, the resultant states can be written in the form of either $|\Phi_k^i(\{n_\zeta\})\rangle$ or $m|\Phi_k^i(\{n_\zeta\})\rangle$, where $m = (-1)^{n_{\theta_1} + n_{\theta_2}}$ is a phase factor and i is an index arising from the application of the projection operators. i can take values from 1 to 5, reflecting the five-dimensional nature of the vibrations. The phase factor m arises from the symmetry of the matrix S_A . Note that different phase factors may be obtained if an alternative definition of S_A is used, and when the projection operators are applied to different wells.

For the projection operator of T_1 symmetry $\hat{\rho}_{11}^{T_1}$, we can write the excited state generated by application to the state $|\Phi_A(\{n_\zeta\})\rangle$ in the form

$$|\psi^{T_1}(\{n_\zeta\})\rangle = \frac{1}{40} \sum_{k,i} b^{ki} |\Phi_k^i(\{n_\zeta\})\rangle, \quad (11)$$

where the b^{ki} are coefficients. These include a part from the projection operator itself; these coefficients are given in Table I in terms of m and $\mu = \phi^{-1}$. The coefficients also include a geometrical factor that reflects the way the vibronic states are mixed together, which is absorbed through the introduction of the index label i in Eq. (10). For T_1 symmetry, we have nine projection operators that can be classified into three sets corresponding to the three components of the T_1 irrep.

Although it is clear from Eq. (10) and Table I that the excited states are very complicated, nevertheless the normalization and calculation of the energies can still be carried out analytically. In the following and to retain generality, all possible phonon excitations will be considered first. This will make it easier to extend the method to other JT systems at a later date. The specific case of just one-phonon excitation will then be taken as an illustrative example.

For cubic systems, it was possible to apply projection operators to excited well states and determine a complete set of excited states ‘‘by inspection.’’ However, as the results are much more complicated in icosahedral symmetry, a system-

atic method is required for both deriving the excited states and for checking their form. In particular, because the local vibrational modes are defined in a different manner for each well, we need to decompose them into a common basis. The general vibrational mode ζ^k containing n_ζ excitations in well k is expanded as a binomial series in the form

$$(\zeta^k)^{n_\zeta} = \sum_{i_\zeta j_\zeta k_\zeta l_\zeta} \Gamma_{\zeta i}^k [n_\zeta, i_\zeta, j_\zeta, k_\zeta, l_\zeta], \quad (12)$$

where $\Gamma_{\zeta i}^k [n_\zeta, i_\zeta, j_\zeta, k_\zeta, l_\zeta]$ is a function determined from the projection operators. The indices $\{i_\zeta, j_\zeta, k_\zeta, l_\zeta\}$ are summed from 0 to $\{n_\zeta, i_\zeta, j_\zeta, k_\zeta\}$, respectively.

Suppose that ν is a sequence number distinguishing different excited states. The most general form for the nonzero symmetry-adapted excited states having symmetry Γ with components γ is then written in terms of nonsymmetrized phonon states as

$$|\psi_\nu^{\Gamma\gamma}(\{n_\zeta\})\rangle = N_\nu^\Gamma(\{n_\zeta\}) \sum_{\{k, n_j^k\}} a_{\{n_j^k\}}^{\nu k} |\Phi_k(\{n_j\})\rangle, \quad (13)$$

where $N_\nu^\Gamma(\{n_\zeta\})$ is a normalization constant (depending upon all five values of n_ζ) and where

$$a_{\{n_j^k\}}^{\nu k} = \sum_{i=1}^5 b_{\{n_j^k\}}^{ki} b_{\{n_j^k\}}^{ki}. \quad (14)$$

k is summed over all six wells, $n_\theta^k = N - \sum_\zeta i_\zeta$, and the values for n_ϵ^k , n_4^k , n_5^k , and n_6^k are given by sums over ζ of i_ζ , ($i_\zeta - j_\zeta$), ($j_\zeta - k_\zeta$), ($k_\zeta - l_\zeta$), and l_ζ , respectively. The constants $b_{\{n_j^k\}}^{ki}$ are a generalized form of the b^{ki} given in Table I for the T_{1x} state, and are determined by the projection operators. $b_{\{n_j^k\}}^{ki}$ is the coefficient for that particular combination of n_j^k phonons in well k , given by

$$b_{\{n_j^k\}}^{ki} = \prod_{\zeta} \sum_{i_\zeta j_\zeta k_\zeta l_\zeta} \Gamma_{\zeta i}^k [n_\zeta, i_\zeta, j_\zeta, k_\zeta, l_\zeta], \quad (15)$$

where the indices n_j^k are each taken from zero to N and are subject to the conditions given above.

The general results obtained are necessarily very complicated. However, they are easier to understand when performed explicitly for given cases. For example, for the case of a single-phonon excitation, there are 60 projection operators of group I to operate on the five nonsymmetric one-phonon excited states located in a given well. These operations give a set of 30 linearly independent symmetry-adapted excited states.³⁰ One result, found after much algebra, is that

$$\begin{aligned} |\psi^{\Gamma\gamma}(01000)\rangle &\equiv |\psi^{\Gamma\gamma}(00100)\rangle, \\ |\psi^{\Gamma\gamma}(00010)\rangle &\equiv |\psi^{\Gamma\gamma}(00001)\rangle. \end{aligned} \quad (16)$$

These equivalences are expected because positions θ_1, ϵ_1 both have e_{1g} symmetry and positions θ_2, ϵ_2 both have e_{2g} symmetry, and hence the members of each pair cannot be distinguished. Nevertheless, this forms a useful check on the calculations. This important result can be extended to N

phonons such that all the independent states must satisfy inequalities such as $n_{\theta_1} < n_{\epsilon_1}$ and $n_{\theta_2} < n_{\epsilon_2}$ to avoid overcounting and specifying states that are not linearly independent.

B. The normalization factors

The normalization constant $N_v^\Gamma(\{n_\xi\})$ for N -phonon excitations can now be evaluated. After much algebra, we find that

$$N_v^\Gamma(\{n_\xi\}) = \left[\sum_{\{k,l,n_j^k,n_j^l\}} a_{\{n_j^k\}}^{\nu k} a_{\{n_j^l\}}^{\nu l} \tau_0^{(kl)} G^{(kl)} \right]^{-1/2}, \quad (17)$$

where $\tau_0^{(kl)} = \langle X^{(k)} | X^{(l)} \rangle$ is the overlap between the electronic states $X^{(k)}$ and $X^{(l)}$, n_j^k and n_j^l are summed over $\theta, \epsilon, 4, 5$, and 6 , while k and l are summed over the six D_{5d} wells,

$$G^{(kl)} = S_I^{(kl)} \prod_j F_j^{(kl)}(n_j^k, n_j^l) \quad (18)$$

is the matrix element between the state $|\theta^{n_\theta} \epsilon^{n_\epsilon} \dots\rangle$ for well k and an equivalent state for a well l of the operator $U_k^\dagger U_l$, and

$$F_j^{(kl)}(a,b) = \sqrt{a!b!} \sum_{p=\max(0,b-a)}^b \frac{(-1)^p (D_j^{(kl)})^{2p+a-b}}{p!(p-b+a)!(b-p)!}. \quad (19)$$

$S_I^{(kl)}$ is the phonon overlap between any two wells, which can be evaluated using techniques described in Ref. 25, with the result

$$S_I^{(kl)} = \langle 0 | U_k^\dagger U_l | 0 \rangle = \exp \left[-\frac{1}{2} \sum_i (D_i^{(kl)})^2 \right], \quad (20)$$

where $D_i^{(kl)} = C_i^{(k)} - C_i^{(l)}$.⁶ Substituting appropriate values gives $S_I^{(kl)} = S_I$ for $k \neq l$ and 1 for $k = l$, where

$$S_I = \exp \left[-2 \left(\frac{\beta' K_1}{\hbar \omega} \right)^2 \right], \quad (21)$$

where $\beta' = \sqrt{6}/(5 - 4\sqrt{2}V_2/\mu\omega^2)$ and $K_1 = -V_1\sqrt{\hbar/2\mu\omega}$.

For one phonon, the excited states and the normalization factors simplify considerably from the general expressions given in Eq. (17), with the normalization factor for the ν th vibronic excited state (with one-phonon excitation) given by

$$N_v^\Gamma(\{n_\xi\}) = \left[\sum_{k,l,m,n} \tau_0^{(kl)} S_I^{(kl)} b_\nu^{km} b_\nu^{ln} (\delta_{mn} - D_m^{(kl)} D_n^{(kl)}) \right]^{-1/2}. \quad (22)$$

Although the notation used here is slightly different, these expressions are found to agree with those given in Ref. 29 once they are evaluated. [Note that in Ref. 29, the $a_i^{(j)} a_n^{(k)}$ in Eq. (4.2) should be replaced by $a_\nu^{(j)} a_\nu^{(k)} a_l^{(\nu j)} a_n^{(\nu k)}$.]

C. The number of excited states

It is relatively simple to determine the total number of excited states with a given number of phonon excitations N

using results from the group theory of the symmetric group, as given in Hammermesh, for example.³¹ A symmetrical tensor of rank N acting on a vector with p components has dimension $(N+p-1)!/N!(p-1)!$. For our problem of h -type phonons, $p=5$. Also, we have six wells and thus an orbital degeneracy of 6. Therefore, the total number of states is

$$\frac{1}{4} (N+1)(N+2)(N+3)(N+4). \quad (23)$$

However, it is also useful to divide these total numbers of states into the number of possible excited states of a given symmetry. This is a much more complicated group-theoretical calculation, involving finding the number of irreps. that are generated from the reducible representations constructed from the infinite coupling excited states. The basic method has been applied previously to T_d symmetry,^{27,32} but the results need to be generalized to apply to the fourfold and fivefold degeneracies that occur in I_h symmetry.

The infinite coupling vibronic excited states form a reducible representation that can be written as the direct product of the orbital and phonon representations,

$$\Lambda_{\text{reducible}}^{(N)} = \Lambda_{\text{orbit}} \otimes \Lambda_H^{(N)}, \quad (24)$$

where $\Lambda_H^{(N)} = \Lambda_h \otimes \Lambda_h \otimes \dots$ to N factors is the symmetrical product³³ and the subscript (H or h) denotes the type of modes. Explicitly, $\Lambda_{\text{reducible}}^{(N)}$ can be written as the direct addition of the irreps. Γ_μ in the form

$$\Lambda_{\text{reducible}}^{(N)} = n_{\Gamma_1}^{(N)} \Gamma_1 \oplus n_{\Gamma_2}^{(N)} \Gamma_2 \oplus \dots \oplus n_{\Gamma_\gamma}^{(N)} \Gamma_\gamma, \quad (25)$$

where $n_{\Gamma_\mu}^{(N)}$ is an integer expressing the number of times the irrep. Γ_μ appears in $\Lambda_{\text{reducible}}^{(N)}$, which is equivalent to the number of multiplets of symmetry Γ_μ that occur for N -phonon excitations. According to group theory, $n_{\Gamma_\mu}^{(N)}$ can be calculated using the reduction formula

$$n_{\Gamma_\mu}^{(N)} = \frac{1}{h} \sum_{R \in I_h} \chi_{\Gamma_\mu}^*(R) \chi_{\text{reducible}}^{(N)}(R), \quad (26)$$

where h ($= 60$) is the order of the group I_h , R is the rotational operator of I_h , $\chi_{\Gamma_\mu}(R)$ is the character of the group element R , and $\chi_{\text{reducible}}^{(N)}(R)$ is the character of $\Lambda_{\text{reducible}}^{(N)}$. The latter can be calculated using the relation

$$\chi_{\text{reducible}}^{(N)}(R) = \chi_{\text{orbit}}(R) \chi_H^{(N)}(R), \quad (27)$$

where $\chi_H^{(N)}(R)$ is the character of the symmetrical product $\Lambda_H^{(N)}$ and $\chi_{\text{orbit}}(R)$ is the character of Λ_{orbit} . As the orbital electronic states localized in the D_{5d} wells form reducible representations of T_1 and T_2 symmetries, Λ_{orbit} should be the direct addition of T_1 and T_2 . Thus the characters $\chi_{\text{orbit}}(R)$ for the rotational operations $R = C_1, C_2, C_3, C_5$, and C_5^2 , respectively, of the I_h group are easily found from the charac-

TABLE II. The number of multiplets $n_{\Gamma_\mu}^{(N)}$ of a given symmetry Γ and number of phonon excitations N .

Γ	$n_{\Gamma_\mu}^{(N)}$	Validity range
A_u	$(N-1)(N+1)(N+3)(N+7)/240$	N odd
	$(N-1)(N+2)(N+4)(N+6)/240$	N even
	$(N+5)(N^3+5N^2-5N+15)/240$	$N/5$ odd
	$N(N^3+10N^2+20N-40)/240$	$N/5$ even
$T_{1u}=T_{2u}$	$(N+1)(N+3)(N^2+6N+13)/80$	N odd
	$(N+2)(N+4)(N^2+4N+8)/80$	N even
	$(N+5)(N^3+5N^2+15N-5)/80+1$	$N/5$ odd
	$N(N^3+10N^2+40N+80)/80+1$	$N/5$ even
G_u	$N(N+5)(N^2+5N+10)/60$	$N/5$ integer
	$(N+1)(N+2)(N+3)(N+4)/60$	All other N
H_u	$(N+1)^2(N+3)(N+5)/48$	N odd
	$N(N+2)(N+4)^2/48$	N even

ter table of the I_h group, giving $\chi_{\text{orbit}}(R) = 6, -2, 0, 1$, and 1 , respectively. After much algebra and by carefully studying the irreps. of H symmetry, a general expression for the character $\chi_H^{(N)}(R)$ has been obtained in terms of the recurrence formula,

$$\chi_H^{(N)}(R) = \frac{1}{N} \sum_{m=1}^N \chi_H(R^m) \chi_H^{(N-m)}(R), \quad (28)$$

where $\chi_H^{(0)}(R) = 1$ has been presumed. It should be noted that this formula is valid not only for the irreps. of H symmetry, but for all degenerate vibronic systems. This includes the representation G of the I_h group and the E and T_2 representations of the T_d group. It is a more general form of the recursion formulas given in Ref. 33 for the characters of the symmetrical product representations for twofold- and threefold-degenerate cases.

Having found the number of multiplets transforming as a given irrep. Γ_μ , the total number of states (of any symmetry) with N -phonon excitations can be calculated by summing the expressions for the numbers of states $n_{\Gamma_\mu}^{(N)}$ with each symmetry Γ_μ given in Table II, after multiplying by the appropriate dimensionalities of the irreps. After much algebra, it is found that the total number of states agrees with that given in Eq. (23).

IV. ENERGIES OF THE SYMMETRY-ADAPTED STATES

In order to evaluate the energies of the symmetry-adapted excited states, we must calculate the expectation values of the total Hamiltonian \mathcal{H} in Eq. (1) between the excited vibronic states $|\psi_\nu^\Gamma(\{n_\xi\})\rangle$. The calculation is most conveniently carried out by writing the Hamiltonian in second quantized form.¹³ It is also helpful to use the commutation relation

$$[\mathcal{H}, U_k] = U_k \sum_j \left(\hbar \omega C_j^{(k)} [C_j^{(k)} - (b_j^\dagger + b_j)] - 2K_1 \hat{L}_{Hj} C_j^{(k)} + 2 \sum_{m,n} \hat{L}_{Hj} (K_2 a_{mn}^j + K_3 b_{mn}^j) \{2C_m^{(k)} C_n^{(k)} - [C_n^{(k)} (b_m^\dagger + b_m) + C_m^{(k)} (b_n^\dagger + b_n)]\} \right), \quad (29)$$

where $K_s = \hbar V_s / 2\mu\omega$ ($s=2,3$) and $\{j,m,n\}$ are all summed over $\{\theta, \epsilon, 4, 5, 6\}$. Finally, after much algebraic work, the general expression for the energy of the vibronic symmetry-adapted states for N -phonon excitations is found to be

$$E_\nu^\Gamma(\{n_\xi\}) = N_\nu^\Gamma(\{n_\xi\})^2 \sum_{\{k,l,n_j^k,n_j^l\}} a_{\{n_j^k\}}^{vk} a_{\{n_j^l\}}^{vl} \times \sum_i \left\{ G^{(kl)} \left[\hbar \omega \tau_0^{(kl)} \left(\frac{1}{2} + n_i^l + C_i^{(l)2} \right) - 2K_1 C_i^{(l)} \tau_i^{(kl)} \right] + G_i^{(kl)} (K_1 \tau_i^{(kl)} - \hbar \omega \tau_0^{(kl)} C_i^{(l)}) + \sum_{mn} \tau_i^{(kl)} (K_2 a_{mn}^i + K_3 b_{mn}^i) [R_{mn}^{(kl)} + 4G^{(kl)} C_m^{(l)} C_n^{(l)} - 2(C_n^{(l)} G_m^{(kl)} + C_m^{(l)} G_n^{(kl)})] \right\}, \quad (30)$$

with $\tau_i^{(kl)} = \langle X^{(k)} | \hat{L}_{Hi} | X^{(l)} \rangle$. The sum indices are as for the normalization factors. $G_m^{(kl)}$ and $R_{mn}^{(kl)}$ are matrix elements between the state $|\theta^n \epsilon^n \epsilon^n \dots\rangle$ for well k and an equivalent state for a well l of the operators $U_k^\dagger U_l (b_m^\dagger + b_m)$ and $U_k^\dagger U_l (b_m^\dagger + b_m)(b_n^\dagger + b_n)$, respectively. When these expressions are evaluated, we find that

$$G_m^{(kl)} = R_m^{(kl)} \left[\sqrt{(n_m^l + 1)} F_m^{(kl)}(n_m^k, n_m^l + 1) + \sqrt{n_m^l} F_m^{(kl)}(n_m^k, n_m^l - 1) \right] \quad (31)$$

and

$$R_{mm}^{(kl)} = R_m^{(kl)} \left[\sqrt{(n_m^l + 1)(n_m^l + 2)} F_m^{(kl)}(n_m^k, n_m^l + 2) + (2n_m^l + 1) F_m^{(kl)}(n_m^k, n_m^l) + \sqrt{n_m^l(n_m^l + 1)} F_m^{(kl)}(n_m^k, n_m^l - 2) \right] \quad (32)$$

for $m=n$ and

$$R_{mn}^{(kl)} = P_{mn}^{(kl)} \left[\sqrt{n_m^l n_n^l} F_m^{(kl)}(n_m^k, n_m^l - 1) F_n^{(kl)}(n_n^k, n_n^l - 1) + \sqrt{(n_m^l + 1)(n_n^l + 1)} F_m^{(kl)}(n_m^k, n_m^l + 1) F_n^{(kl)}(n_n^k, n_n^l + 1) + \sqrt{n_m^l(n_n^l + 1)} F_m^{(kl)}(n_m^k, n_m^l - 1) F_n^{(kl)}(n_n^k, n_n^l + 1) + \sqrt{n_n^l(n_m^l + 1)} F_m^{(kl)}(n_m^k, n_m^l + 1) F_n^{(kl)}(n_n^k, n_n^l - 1) \right] \quad (33)$$

for $m \neq n$, where

$$R_m^{(kl)} = S_I^{(kl)} \prod_{n \neq m} F_n^{(kl)}(n_n^k, n_n^l), \quad (34)$$

$$P_{mn}^{(kl)} = S_I^{(kl)} \prod_{s \neq m, n} F_s^{(kl)}(n_s^k, n_s^l).$$

The energies of all excited symmetry-adapted states can be evaluated directly from Eq. (30). This procedure includes setting up projection operators, finding out the excited states and their normalization factors, calculating the various overlaps, and finally the matrix elements. Due to their complexity, the analytical results will only be given here for the one-phonon case, although in principle the formula can be used to obtain all excited states. The one-phonon energies can be expressed as

$$\begin{aligned} E_i^{T_1} &= \frac{H_{11}^{i1} + H_{12}^{i1}}{1 + S_I^{i1}}, \\ E_i^{T_2} &= \frac{H_{11}^{i1} - H_{12}^{i1}}{1 - S_I^{i1}}, \\ E_i^G &= \frac{H_{11}^G - (-1)^i H_{12}^G}{1 - (-1)^i S_I^g}, \\ E_i^H &= \frac{H_{11}^H - (-1)^i H_{12}^H}{1 - (-1)^i S_I^h}, \end{aligned} \quad (35)$$

where the label $i = 1$ or 2 distinguishes different sets of states of the same symmetry. The required overlaps are

$$\begin{aligned} S_I^{1i} &= \frac{1}{5} S_I (12w^2 - 1), \\ S_I^{2i} &= \frac{1}{5} S_I (1 - 2w^2), \\ S_I^g &= \frac{1}{5} S_I (3 + 4w^2), \\ S_I^h &= -\frac{1}{5} S_I (3 + 2w^2), \end{aligned} \quad (36)$$

with $w = K_1 \beta' / \hbar \omega$. The $H_{11}^{i\Gamma}$ are ‘‘diagonal’’ matrix elements given by

$$H_{11}^{1i} = a - \frac{4\sqrt{2}}{5} K_2, \quad (37)$$

$$H_{11}^{2i} = H_{11}^{2i} = H_{11}^G = H_{11}^H = a + \frac{\sqrt{2}}{5} K_2 + \sqrt{\frac{2}{5}} K_3,$$

with $a = \frac{7}{2} \hbar \omega + K_1 w (-f + \frac{5}{3} \beta') - (8\sqrt{2}/3) K_2 w^2$ and where $f = 2\sqrt{\frac{2}{3}}$. The $H_{12}^{i\Gamma}$ are ‘‘off-diagonal’’ matrix elements of the form

$$H_{12}^{i\Gamma} = \frac{b^{i\Gamma}}{5} S_I \left(\frac{7}{2} \hbar \omega + K_1 w c^{i\Gamma} + d^{i\Gamma} \right), \quad (38)$$

where

$$b^{1i} = -b^{2i} = b^{1i_2} = -b^{2i_2} = -\frac{b^{ig}}{3} = \frac{b^{ih}}{3} = -1,$$

$$c^{1i} + 7f = 12fw^2 + \frac{1}{3} \beta' (12w^2 - 103),$$

$$c^{2i} - 2f = c^{2i_2} + f = 2fw^2 + \frac{2}{3} \beta' (w^2 - 14), \quad (39)$$

$$c^{1g} + 3f = c^{2g} + f = -\frac{4}{3} fw^2 - \frac{1}{3} \beta' \left(\frac{4}{3} w^2 - 17 \right),$$

$$c^{1h} + 2f = c^{2h} + f = -\frac{2}{3} fw^2 - \frac{1}{3} \beta' \left(\frac{2}{3} w^2 - 8 \right),$$

and

$$\begin{aligned} d^{1i} &= -6K_2'(3 + 13w^2 - 12w^4) + 6K_3'(3 - 13w^2 + 12w^4), \\ d^{2i} &= -6K_2'(6 + w^2 - 2w^4) + 6K_3'(2 - 7w^2 - 2w^4), \\ d^{2i_2} &= 3K_2'(15 + 10w^2 + 4w^4) - 3K_3'(1 - 6w^2 + 4w^4), \\ d^{1g} &= K_2'(9 - 6w^2 - 8w^4) - K_3'(7 + 38w^2 + 8w^4), \\ d^{2g} &= -2K_2'w^2(15 + 4w^2) + K_3'(8 + 2w^2 - 8w^4), \\ d^{1h} &= -2K_2'w^2(3 + 2w^2) + K_3'(8 - 22w^2 - 4w^4), \\ d^{2h} &= K_2'(9 - 18w^2 - 4w^4) + K_3'(7 - 4w^4), \end{aligned} \quad (40)$$

where $K_2' = (\sqrt{2}/9)K_2$ and $K_3' = \frac{1}{3}\sqrt{\frac{2}{3}}K_3$. These results agree with the preliminary results given in Ref. 29.

To understand either the general analytical results or the specific results of Eq. (35), it is necessary to plot the energies obtained as a function of the linear and quadratic coupling strengths. However, the quadratic coupling parameters K_2 and K_3 are not free; they must obey the additional restrictions¹² $-15\sqrt{2}\hbar\omega/16 < \sqrt{5}K_3 < 3K_2 < 15\sqrt{2}\hbar\omega/16$ to ensure that the D_{5d} extrema are the lowest-energy wells in the APES. We will choose the values $K_2 = -K_3 = 0.05\hbar\omega$, which satisfy the above inequalities, although results can be obtained for any values. Results will also be given for zero quadratic coupling ($K_2 = K_3 = 0$). Although the D_{5d} extrema will not be wells in this case, it is useful to illustrate the effect of the quadratic coupling.

The energies of the symmetry-adapted excited states T_1 relative to the ground state are plotted in Fig. 1 as a function of the linear coupling K_1 for all of the states with $N=1$ and for a selection of states with $N=2$. Figures 2–4 give the equivalent results for the T_2 , G , and H states, respectively. The tunneling level $E_g^{T_2}$ is also included in Fig. 2 in order to show the effect of K_2 and K_3 , as this was not given in Ref. 6.

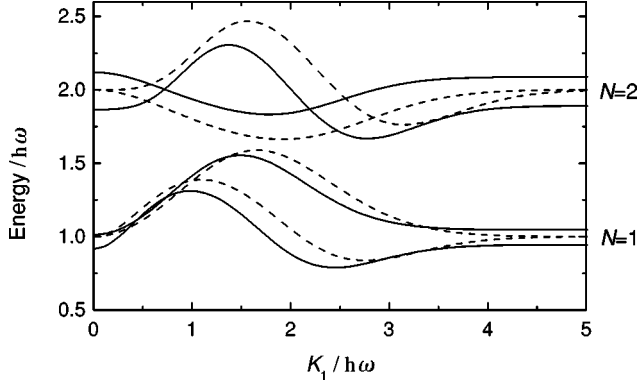


FIG. 1. Energy relative to the T_{1u} ground state of the symmetry-adapted excited states of T_{1u} symmetry with $N=1$ and a selection of states with $N=2$, as a function of the coupling strength K_1 . The dotted lines are for $K_2=K_3=0$ and the solid lines for $K_2=-K_3=0.05\hbar\omega$.

It is found that the energy gaps between the excited and ground states increase as the absolute values of the parameters K_2 and K_3 increase. This is especially the case in the weak and intermediate ranges of the coupling strength.

Figures 1–4 show that there are significant deviations from $\hbar\omega$ of the energies of the one-phonon states relative to the ground state in strong coupling due to the inclusion of quadratic coupling. There are also some deviations in weak coupling. The deviations depend directly upon the values of the quadratic coupling parameters K_2 and K_3 . It is possible to calculate these deviations analytically by taking appropriate limits of the formula given in the preceding section. It is found that, relative to the T_{1u} ground state, the T_{1u} and T_{2u} states labeled by $i=1$ attain the limit $[1 - (4\sqrt{2}/5)K_2]\hbar\omega$ in strong coupling. All other states attain the limit $[1 + (\sqrt{2}/5)K_2 + \sqrt{3}/5K_3]\hbar\omega$. In weak coupling,

$$\begin{aligned}
 E_g^{T_2}, E_1^{T_2} &\rightarrow \left(1 - \sqrt{2}K_2 + \sqrt{\frac{2}{5}}K_3\right)\hbar\omega, \\
 E_i^{T_1} &\rightarrow \left(1 - \frac{1}{\sqrt{2}}K_2 + (-1)^i \frac{3}{\sqrt{10}}K_3\right)\hbar\omega, \\
 E_2^{T_2} &\rightarrow \left(1 - \sqrt{2}K_2 + \frac{3}{\sqrt{10}}K_3\right)\hbar\omega, \\
 E_1^G &\rightarrow \left(1 + \frac{1}{\sqrt{2}}K_2 - \frac{1}{2\sqrt{10}}K_3\right)\hbar\omega, \\
 E_2^G &\rightarrow \left(1 + \frac{1}{\sqrt{2}}K_2 - \frac{3}{\sqrt{10}}K_3\right)\hbar\omega, \\
 E_i^H &\rightarrow \left(1 + \frac{1}{\sqrt{2}}K_2 + (-1)^i \frac{3}{\sqrt{10}}K_3\right)\hbar\omega,
 \end{aligned} \tag{41}$$

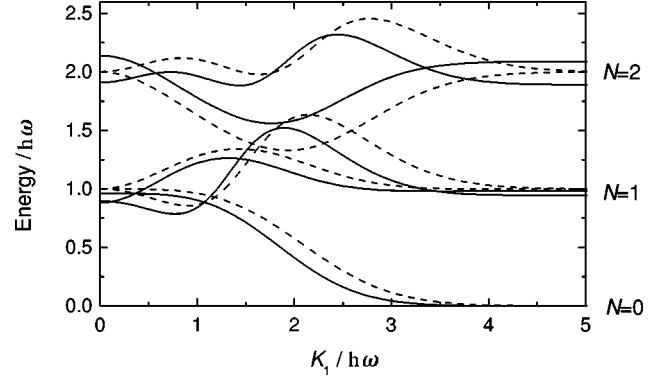


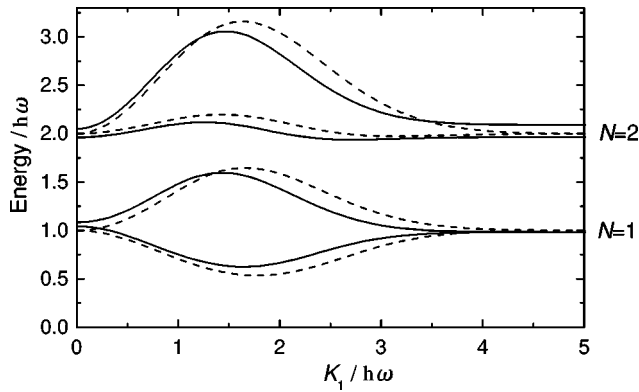
FIG. 2. As Fig. 1 but for the T_{2u} excited states. The T_{2u} tunneling levels ($N=0$) are also shown.

where $E_g^{T_2}$ is the energy of the zero-phonon tunneling level. Although these limits explain the results shown in the figures, it should be noted that when the linear coupling parameter is very small, the quadratic coupling parameters would be expected to be even smaller, approaching zero as K_1 approaches zero. In this case, the one-phonon states all attain the limit $\hbar\omega$, as expected. Similarly, the energies converge rapidly to the expected value of $N\hbar\omega$ in the strong-coupling limit when K_2 and K_3 approach zero.

At first sight, it would seem that the two quadratic coupling coefficients are almost independent of each other. The positions and energies of the D_{5d} wells only depend upon V_2 while the D_{3d} wells only depend upon V_3 . However, the strong- and weak-coupling limits for the D_{5d} wells are affected as much by V_3 as they are by V_2 . This shows that both types of quadratic coupling must be included in the vibronic problem.

V. DISCUSSION

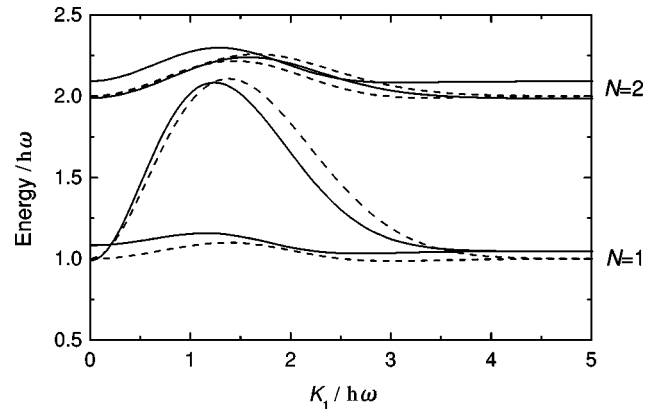
The results given in the preceding section provide a reasonable approximation to the true excited states and energies of the dynamical $T_{1u} \otimes h_g$ JT system in the presence of quadratic coupling. However, some inaccuracies have inevitably been introduced in our desire to produce analytical results of use for further calculations. Although excited states belonging to different symmetries are orthogonal to each other, states having the same symmetries may not be mutually orthogonal. For example, the 30 excited states containing one-phonon excitation belong to four symmetries, namely T_1 , T_2 , G , and H . Each symmetry contains two different sets of states. There is nothing in our procedure to ensure that the pairs of states of the same symmetry are orthogonal. In fact, it can be deduced that only the two sets of states pertaining to T_1 symmetry are orthogonal to each other. If this lack of nonorthogonality is a problem, it will increase rapidly as N increases. Nevertheless, Figs. 1–4 do not show any noticeable differences between the T_1 states and the remaining states. Therefore, we do not believe that the nonorthogonality introduces significant errors. The properties of symmetry-adapted excited states of like symmetries in cubic symmetry were discussed previously in Refs. 27 and 34. Also, anisotropy in the potential-energy minima in the APES has been

FIG. 3. As Fig. 1 but for the G excited states.

included via the effect upon the frequencies but, due to the complications of icosahedral symmetry, the effect of anisotropy in the phonon overlaps has been neglected, as have second-order anisotropic corrections to the well states.¹⁹

It would be possible to obtain more accurate analytical results, for example by orthogonalizing symmetry-adapted states of the same symmetry and/or by including anisotropy to second-order in perturbation theory. However, despite the details of the calculations presented here being complicated due to the icosahedral symmetry, the results obtained have an analytical form that can be written down and computed relatively easily. They also apply across the full range of coupling strengths. The results can be used in further calculations, such as of second-order RFs or in determining the effects of additional perturbations, without it being necessary to repeat any derivations. Further enhancements to the model presented would result in even more cumbersome states. If more accurate results are required, then alternative numerical approaches should be sought. However, it would be much more difficult to cover all coupling strengths in one model. Also, the results would be harder to extend and use in further calculations, as well as showing much less clearly the effects of anisotropy and tunneling between potential wells.

Another approach to the dynamical $T_{1u} \otimes h_g$ JT system would be to consider linear coupling only, in which the lowest APES consists of a two-dimensional trough.¹¹ The trough can be mapped onto the surface of a sphere, with each point fixed by angles θ , ϕ , and γ . Appropriate states can be constructed taking into account vibrations across the trough and rotations around the trough, including all points at the bottom of the trough via an integral over θ , ϕ , and γ . However, the disadvantage of this method is that, in order to evaluate the energies of the resultant states, it is necessary to evaluate

FIG. 4. As Fig. 1 but for the H excited states.

six-dimensional integrals. This will not be considered further here.

VI. CONCLUSIONS

The calculations described in this paper are based on the framework that in the strong-coupling limit, vibronic states confined within minima in the APES are good eigenstates of the system so that the JT system is essentially static. When the coupling is not so strong, the barriers between the minima are not high enough to prevent tunneling between the minima and the JT system becomes dynamic. This leads to the idea of symmetry-adapted vibronic states. The calculations have shown that, despite the heavy algebraic details involved, analytical expressions for the excited symmetry-adapted vibronic states and their energies can be obtained covering the whole range of coupling strengths. The results show the expected behavior in both the weak- and strong-coupling limits. In this paper, results have only been given for the case when the D_{5d} points are absolute minima in the APES. However, the methods presented can easily be extended to D_{3d} wells in the $T_{1u} \otimes h_g$ system, or indeed to JT systems of other symmetries. We have also shown that previous work in cubic symmetry cannot be applied directly to icosahedral symmetry.

The importance of the symmetry-adapted excited states, from which it is possible to obtain more reliable values for the second-order RFs, will form the basis of future work.

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