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Analysis of the T ⊗ (e + 2t_2) Jahn–Teller problem for a tetrahedral cluster

P J Kirk†, C A Bates and J L Dunn
Department of Physics, The University, Nottingham NG7 2RD, UK

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Abstract. The T ⊗ (e + 2t_2) Jahn–Teller (JT) system is studied analytically in strong coupling on a tetrahedral cluster model by transformation methods. Using an energy minimization procedure, the system is shown to be localized in potential-energy minima of tetragonal, trigonal or orthorhombic symmetry depending upon the relative strengths of the e and the two t_2 coupling constants and on the quadratic coupling constants. The addition of an extra t_2 mode to the T⊗(e+t_2) system does not introduce any extra potential-energy minima although their respective depths are increased. Also derived are expressions for symmetry-adapted vibronic states and their energies for the T⊗2t_2 JT system. Projection operator techniques are used starting from the exact vibronic states in the infinite-coupling limit. These results give an insight into the effect of including additional modes from the remainder of the crystal into the JT effect, and hence indicate how a full multimode model can be formulated. The calculation of symmetry-adapted excited states means that it will be possible to undertake analytical calculations of reduction factors. This in turn will provide a new insight into the derivation of improved models for explaining experimental data obtained on specific systems.

1. Introduction

In the last few years, several papers have been published that derive the vibronic ground and excited states for certain Jahn–Teller (JT) vibronic systems in tetrahedral symmetry: Bates and Dunn (1989) and Dunn (1989) for the T⊗e and T⊗t_2 systems respectively; Hallam *et al* (1992) for the T ⊗ (e + t_2) system; and Jamila *et al* (1993) for the E ⊗ e system. These calculations have been based on a tetrahedral cluster model and have been evaluated using a transformation technique developed originally by Bates *et al* (1987). These calculations have been undertaken in order to obtain accurate basis states for the system and for the subsequent modelling of magnetic impurity ions in semiconductor materials. The active modes of this system are one of e and two of t_2 symmetry, and therefore the electrons of the impurity can couple to vibrational modes of these symmetries. However, only one of the t_2 modes has been considered in most previous publications, as the inclusion of both modes is necessarily more complicated.

A much more general problem in JT theory is to consider the coupling of an ion to the whole spectrum of phonon frequencies. This is frequently referred to as the multimode problem, and has been the subject of much theoretical work during the last 25 years or so. Much of this work has concentrated on the E ⊗ e multimode problem in which the concept of a privileged mode was introduced (e.g. Sloncjewski 1963, Fletcher 1972, O'Brien 1972, 1983, Payne and Stedman 1983a, b, c). The multimode corrections to some of the Ham

† Now at: Andersen Consulting, 2 Arundel Street, London WC2R 3LT, UK.

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reduction factors were described, for example, by Evangelou *et al* (1980). O'Brien (1972) also considered the general problem of an electronic T_1 or T_2 triplet interacting with many e and t_2 modes simultaneously provided there was an accidental degeneracy between the e and t_2 modes, but there appears to be virtually no work explicitly involving the $T \otimes t_2$ multimode problem. A method for studying the multimode problem for the $T \otimes e$ JT system was introduced by Ham (1965) and a particular model was devised by Stevens (1969) and developed further by Steggles (1977); this particular approach was summarized in Bates (1978). An analysis and discussion of all multimode models is given in Bersuker and Polinger (1989, sections 3.5, 4.6 and 4.7). In general, it may be possible to reduce the multimode problem to that of a single effective mode for some properties of the system (e.g. the potential energy), but for other properties inaccuracies are introduced. In particular, if wavefunctions (particularly those of the excited states) are required, the kinetic energy must be incorporated, and generally the problem cannot then be reduced to a single-mode problem.

There is clearly a large gap between the simple cluster model used in the publications listed in the first paragraph and the more realistic multimode models. In this paper, we make an improvement in our simple cluster model by including coupling to the e mode and both t_2 modes of the cluster. This represents a first step towards a multimode model, whilst retaining the considerable advantage of the analytical approach. Thus we study an ion having an orbital T_1 triplet state coupled to the e- and two t_2-type cluster vibrations. One of the t_2 modes is radial and the other is transverse (e.g. Bates 1978). It is assumed that the coupling to the vibrations is larger than other perturbations such as spin–orbit coupling. The transformation method presented originally in Bates *et al* (1987) is used. From the analysis, the positions of the potential-energy minima in the eight-dimensional Q-space are found. It will be shown that the addition of an extra t_2 mode does not introduce any extra minima. The analysis gives descriptions of the $T \otimes e$, $T \otimes 2t_2$ and $T \otimes (e + 2t_2)$ JT systems.

Whereas the positions of the minima for these systems could have been predicted from the multimode theories of O'Brien (1972), for example, explicit forms of the excited vibronic states could not be predicted from this source. The main advantage of the transformation method is that accurate analytical expressions for the ground and excited vibronic states can be obtained directly. This is not easy to do with other methods. Thus one of the major aims of this paper is to derive the equivalent sets of vibronic ground and excited states for the $T_1 \otimes 2t_2$ JT system to that for $T \otimes t$. It will then be possible to use these to calculate the various reduction factors that will appear in any effective Hamiltonian for real systems. For example, it is hoped that the addition of the extra t_2 mode may help in overcoming some of the difficulties arising in recent attempts at modelling the experimental results obtained for V^{3+} ions in GaAs (Ulrici *et al* 1985) and in InP (Clerjaud *et al* 1987). Another problem is the interpretation of the optical spectrum observed for the GaP:V^{3+} system; Bates *et al* (1990) described a model for this system in terms of a dominant t_2 mode coupling.

2. Definitions and the unitary transformation method

In the cluster model of the JT effect for a T ($l = 1$) ion coupled linearly to an e (Q_θ, Q_ϵ) and two t_2 (Q_4, Q_5, Q_6; Q_7, Q_8, Q_9) modes of the cluster, the interaction Hamiltonian has the form

$$\mathcal{H}_{\rm int} = V_{\rm E}(Q_\theta E_\theta + Q_\epsilon E_\epsilon) + V_{\rm T}(Q_4 T_{yz} + Q_5 T_{zx} + Q_6 T_{xy}) + V_2(Q_7 T_{yz} + Q_8 T_{zx} + Q_9 T_{xy}) \tag{2.1}$$

where V_E is the e-type coupling constant and V_T and V_2 are the t_2-type coupling constants. The definitions of the orbital operators E_θ, T_{yz}, etc, are given in Bates (1978). The Hamiltonian describing the kinetic and elastic energies of the harmonic lattice is

$$\mathcal{H}_{vib} = \tfrac{1}{2}\sum_j \left(\frac{P_j^2}{\mu_j} + \mu_j \omega_j^2 Q_j^2\right) \tag{2.2}$$

where j is summed over all eight components of the vibrational modes and where P_j is the momentum conjugate to Q_j. This gives a total Hamiltonian $\mathcal{H} = \mathcal{H}_{int} + \mathcal{H}_{vib}$.

A unitary transformation

$$U = \exp\left(i\sum_j \alpha_j P_j\right) \tag{2.3}$$

is then applied to the Hamiltonian and gives the transformed Hamiltonian

$$\tilde{\mathcal{H}} = U^{-1}\mathcal{H}U = \tilde{\mathcal{H}}_1 + \tilde{\mathcal{H}}_2 \tag{2.4}$$

where

$$\begin{aligned}\tilde{\mathcal{H}}_1 = {} & -\tfrac{1}{2}\hbar V_E(\rho_\theta \alpha_\theta - \sqrt{3}\rho_\epsilon \alpha_\epsilon) + \tfrac{1}{2}\sqrt{3}\hbar V_T(\tau_4\alpha_4 + \tau_5\alpha_5 + \tau_6\alpha_6) \\ & + \tfrac{1}{2}\sqrt{3}\hbar V_2(\tau_4\alpha_7 + \tau_5\alpha_8 + \tau_6\alpha_9) + \tfrac{1}{2}\hbar^2\sum_j \mu_j\omega_j^2\alpha_j^2 + \sum_j \tfrac{1}{2}\hbar\omega_j\end{aligned} \tag{2.5}$$

and

$$\begin{aligned}\tilde{\mathcal{H}}_2 = {} & \tfrac{1}{2}V_E(\rho_\theta Q_\theta - \sqrt{3}\rho_\epsilon Q_\epsilon) - \tfrac{1}{2}\sqrt{3}V_T(\tau_4 Q_4 + \tau_5 Q_5 + \tau_6 Q_6) \\ & - \tfrac{1}{2}\sqrt{3}V_2(\tau_4 Q_7 + \tau_5 Q_8 + \tau_6 Q_9) - \sum_j \hbar\mu_j\omega_j^2\alpha_j Q_j + \sum_j \hbar\omega_j(b_j^\dagger b_j).\end{aligned} \tag{2.6}$$

These equations have been written in second quantized form (Maier and Sigmund 1984) such that the orbital operators ρ and τ are given by

$$\begin{aligned}&\rho_\theta = c_1^\dagger c_1 + c_2^\dagger c_2 - 2c_3^\dagger c_3 \qquad \rho_\epsilon = c_1^\dagger c_1 - c_2^\dagger c_2 \\ &\tau_4 = c_2^\dagger c_3 + c_3^\dagger c_2 \qquad \tau_5 = c_3^\dagger c_1 + c_1^\dagger c_3 \qquad \tau_6 = c_1^\dagger c_2 + c_2^\dagger c_1\end{aligned} \tag{2.7}$$

where $c_1^\dagger|0\rangle = |x\rangle$, etc, with $|0\rangle$ the orbital vacuum state and $|x\rangle$ the orbital state of the stated symmetry. As in Bates *et al* (1987), $\tilde{\mathcal{H}}_2$ contains terms representing coupling to excited phonon states while $\tilde{\mathcal{H}}_1$ contains only electronic orbital operators (and the zero-point energy). In strong coupling, which implies large α_j, it is only necessary to consider $\tilde{\mathcal{H}}_1$ when calculating the ground states of the system. Thus it is appropriate to use the energy minimization procedure described by Bates *et al* (1987) where the free parameters α_j are chosen to minimize the potential energy of the transformed Hamiltonian $\tilde{\mathcal{H}}_1$. Following on from this analysis, it was found that vibronic ground and excited states of the system could be derived so that physical properties of the system could be deduced.

3. Analysis of $\tilde{\mathcal{H}}_1$ for linear coupling

The Hamiltonian $\tilde{\mathcal{H}}_1$ can be defined with respect to the vibronic basis set $|x;0\rangle$, $|y;0\rangle$ and $|z;0\rangle$, where the second '0' represents the phonon vacuum state. The corresponding matrix can be written in the form:

$$\tilde{\mathcal{H}}_1 = \begin{bmatrix} -A_\theta + \sqrt{3}A_\epsilon + \Delta & \sqrt{3}(A_6 + A_9) & \sqrt{3}(A_5 + A_8) \\ \sqrt{3}(A_6 + A_9) & -A_\theta - \sqrt{3}A_\epsilon + \Delta & \sqrt{3}(A_4 + A_7) \\ \sqrt{3}(A_5 + A_8) & \sqrt{3}(A_4 + A_7) & 2A_\theta + \Delta \end{bmatrix} \tag{3.1}$$

where $A_j = \frac{1}{2}\hbar V_j \alpha_j$ and $\Delta = \frac{1}{2}m\hbar^2 \sum_j \omega_j^2 \alpha_j^2$. Also $V_\theta = V_\epsilon = V_E$, $V_4 = V_5 = V_6 = V_T$ and $V_7 = V_8 = V_9 = V_2$ with the ω_j similarly defined. It should be noted that the zero-point energy

$$\sum_j \tfrac{1}{2}\hbar\omega_j = \tfrac{1}{2}\hbar[2\omega_E + 3(\omega_T + \omega_2)] \tag{3.2}$$

can be ignored throughout the minimization procedure as it is a constant. The eigenvalues E of (3.1) are found by solving the resulting cubic equation following the procedures used in Bates *et al* (1987).

The values of the α_j that minimize the energy may be obtained by differentiating E with respect to the α_j. This gives eight simultaneous equations, which can be solved exactly (Kirk 1992) in terms of the effective coupling constants

$$K_E = -\tfrac{1}{2}(\hbar/2\mu\omega_E)^{1/2}V_E \qquad K_M = \tfrac{1}{2}(3\hbar/2\mu\omega_M)^{1/2}V_M \qquad (M = \text{T or } 2). \tag{3.3}$$

The lowest energy (i.e. possible solutions that are minima) falls into the three categories, I, II and III as follows:

Category I. These are solutions for the case when the ion is coupled to the e-type vibrations only. There are three minima in Q-space having energies

$$E = E_E = -4K_E^2/\hbar\omega_E. \tag{3.4}$$

This case is referred to as the $T \otimes e$ JT problem and the solutions are exactly the same as those obtained in Bates *et al* (1987).

Category II. The ion is coupled to both sets of t_2 modes of vibration. In this case, there are four minima each with an energy given by

$$E = E_{2T} = -4K_T^2/3\hbar\omega_T - 4K_2^2/3\hbar\omega_2. \tag{3.5}$$

This is referred to as the $T \otimes 2t_2$ JT problem. This result could have been predicted from the original work of Öpik and Pryce (1957) and from the formulae in O'Brien (1972). It can be seen that, as far as the positions of the energy minima are concerned, the $T \otimes t_2$ problem is the limiting case of the $T \otimes 2t_2$ JT problem in which one of the coupling constants becomes zero (but see also section 5.3). In general, we note that, in a tetrahedron, as one of the t_2 modes is radial and the other is transverse, it is probable that the two modes couple to the ion with differing strengths. For example, it is expected that radial modes will couple more strongly than transverse modes as this direction is one in which the electric potential changes most rapidly with distance from the central nucleus.

Category III. In this case, the ion is coupled to the e-type and both t_2-type vibrations of the cluster, giving six orthorhombic solutions for the $T \otimes (e + 2t_2)$ JT system with energies

$$E = E_{E2T} = -K_E^2/\hbar\omega_E - K_T^2/\hbar\omega_T - K_2^2/\hbar\omega_2. \tag{3.6}$$

These solutions are only true minima under special conditions involving quadratic coupling (particularly bilinear) terms. Again, this result is consistent with that of O'Brien (1972).

From the expressions (3.4)–(3.6) for the energies, it can be seen that the system will appear to be

(i) *tetragonal* if $E_E < E_{2T}$, i.e. for

$$3K_E^2/\hbar\omega_E > K_T^2/\hbar\omega_T + K_2^2/\hbar\omega_2 \tag{3.7}$$

(ii) *trigonal* if $E_E > E_{2T}$, i.e. for

$$3K_E^2/\hbar\omega_E < K_T^2/\hbar\omega_T + K_2^2/\hbar\omega_2 \tag{3.8}$$

(iii) *orthorhombic* if $E_{E2T} < E_E$ and E_{2T}, which is only possible under certain conditions of quadratic coupling (as discussed, for example, in the case of $T \otimes (e + t_2)$ by Hallam *et al* (1992)).

The energy minimization procedure shows that the number of possible minima is 13, which is exactly the same as that obtained with coupling to only one of the t_2 modes. However, the depths of the minima are increased and the coordinates α_j of the minima are in eight-, rather than five-dimensional Q-space. The α_j for $j = \theta, \epsilon, 4, 5$ and 6 are the same as those given in table 1 of Bates *et al* (1987) while the α_j for $j = 7, 8$ and 9 are obtained from the corresponding values for $j = 4, 5$ and 6 by replacing β_T $(= V_T/\hbar\mu\omega_T^2)$ by β_2 $(= V_2/\hbar\mu\omega_2^2)$. By taking the calculated values of α_j and substituting these into equations (2.5) and (2.6), it can be seen that $\tilde{\mathcal{H}}_1$ is proportional to $K_j^2/\hbar\omega_j$ whereas $\tilde{\mathcal{H}}_2$ is proportional to K_j (where $K_j = K_E$, K_T or K_2 as appropriate). This justifies the approximation that, in the infinite-coupling limit ($K_j \to \infty$), the transformed Hamiltonian $\tilde{\mathcal{H}}_2$ is small and can therefore be ignored.

Although the particular results obtained above are not significant in themselves, they are important in a more general way because they are a first step to the more realistic and complex case of a multimode model for the JT effect involving e- and t_2-type vibrations. In the limiting case of $\omega_T = \omega_2$, it has been found that the positions of the potential-energy minima are in agreement with those of Öpik and Pryce (1957) and subsequent workers (see, for example, Bersuker and Polinger 1989). As stated previously, the states obtained using this method have the advantage over previous approaches in that the states are automatically vibronic in nature owing to the presence of phonon operators in the unitary transformation (2.3).

4. The calculation of symmetry-adapted excited states for the $T_1 \otimes 2t_2$ JT system

4.1. Basic ideas

In the transformation method, the Q_j and P_j are written in second quantized form

$$Q_j = (\hbar/2\mu\omega_j)^{1/2}(b_j + b_j^\dagger) \qquad P_j = \mathrm{i}(\hbar\mu\omega_j/2)^{1/2}(b_j - b_j^\dagger) \tag{4.1}$$

where $b_j^\dagger$ and b_j are creation and annihilation operators. Similarly, the unitary transformation in second quantized form is

$$U = \exp\left(\sum_j C_j(b_j - b_j^\dagger)\right) \qquad \text{where} \qquad C_j = -(\tfrac{1}{2}\hbar\mu\omega_j)^{1/2}\alpha_j. \quad (4.2)$$

Also, $\tilde{\mathcal{H}}_1$ becomes

$$\tilde{\mathcal{H}}_1 = -2K_E(\rho_\theta C_\theta - \sqrt{3}\rho C_\epsilon) - 2K_T(\tau_4 C_4 + \tau_5 C_5 + \tau_6 C_6) - 2K_2(\tau_4 C_7 + \tau_5 C_8 + \tau_6 C_9) + \sum_j \hbar\omega_j C_j^2 + \tfrac{1}{2}\sum_j \hbar\omega_j. \quad (4.3)$$

The ground states localized in trigonal wells are $|a;0\rangle$, $|b;0\rangle$, $|c;0\rangle$ and $|d;0\rangle$ where the '0' denotes that all oscillators are in their ground states and where the orbital states take the forms

$$a = \sqrt{\tfrac{1}{3}}(x+y-z) \qquad b = \sqrt{\tfrac{1}{3}}(x-y+z)$$
$$c = \sqrt{\tfrac{1}{3}}(-x+y+z) \qquad d = \sqrt{\tfrac{1}{3}}(-x-y-z). \quad (4.4)$$

These states can then be transformed back to the original space by operating on them with the unitary transformation operator $U = U_k$ appropriate to well k, with the values of α_k appropriate to the well in question. Thus the untransformed state becomes

$$|X_O^{(k)'};0\rangle = U_k|X_O^{(k)};0\rangle \quad (4.5)$$

and where $X_O^{(k)'}$ refers to one of the four potential-energy minima. Although the ground states localized in the wells do not contain phonon excitations, the untransformed states $|X_O^{(k)'};0\rangle$ do, owing to the presence of phonon operators in the unitary transformation. Therefore the untransformed states are automatically vibronic in nature and are often referred to as Glauber states (Judd and Vogel 1975). In the limit of infinite coupling, the system performs small harmonic oscillations around each minimum. In a similar way, a set of localized untransformed excited vibronic states $|X_O^{(k)'};4^l5^m6^n7^\alpha8^\beta9^\gamma\rangle$ can be defined, where 4^l, etc, refer to l t_2-mode Q_4 phonon excitations, etc.

In the finite-coupling regime, these states are not good eigenstates of the system, as they are neither orthogonal to each other nor do they have cubic symmetry. It is therefore necessary to construct linear combinations of the states that have cubic symmetry and are orthonormal. Cubic combinations have been obtained using projection operator techniques, similar to those used for the $E\otimes e$ (Jamila *et al* 1993), $T\otimes t_2$ (Dunn 1989) and $T\otimes(e+t_2)$ (Hallam *et al* 1992) JT systems. A discussion concerning the orthogonality of these states is given in section 5.3.

4.2. Projection operator techniques

Using the appropriate group-theoretical projection operators, it is possible to take a set of non-symmetrized states and produce a set of symmetry-adapted states. (A review of these techniques is given in Hallam *et al* (1992).) To calculate the effect of one of the elements of a particular projection operator, the transformation properties of both the electronic and phonon parts of the states are required. In this connection, we note that, as this paper is

modelling an impurity T_1 ion, the electronic states $|x\rangle$, $|y\rangle$ and $|z\rangle$ transform under the symmetry operations of the T_d group in the same way as the angular momentum operators (l_x, l_y, l_z) and not as the Cartesian operators (x, y, z). Using these transformation properties, we obtain results such as

$$\begin{aligned} JC_2^3|a'; 4^l5^m6^n7^\alpha8^\beta9^\gamma\rangle &= -|a'; (-4)^n5^m(-6)^l(-7)^\gamma8^\beta(-9)^\alpha\rangle \\ &= -(-1)^{l+n+\alpha+\gamma}|a'; 4^n5^m6^l7^\gamma8^\beta9^\alpha\rangle \end{aligned} \tag{4.6}$$

where JC_2^3 is a symmetry operation of the T_d group. Similar results can be generated for each of the other elements of the group.

As shown in appendix A of Hallam *et al* (1992), if a state of arbitrary symmetry is acted upon by a set of projection operators for a specific irreducible representation, then either the resulting states are zero, meaning that there is no state of this particular symmetry, or a basis state for the irreducible representation is generated. Owing to the symmetry properties of the infinite-coupling excited states, it is only necessary to act on the states of one well to produce a complete and distinct set of symmetry-adapted excited states provided all the projection operators for that irreducible representation of the T_d group are used. This approach has been applied to all the irreducible representations of the T_d group in order to derive all the vibronic states $|\phi_i^\Gamma\rangle$ of the system having a symmetry Γ and labelled by the index i (= 1–30); details are given in Kirk (1992). The complete set of 30 states is given in table 1, and restrictions on particular phonon occupation numbers necessary to produce both states of the desired symmetry and each state once only in table 2. The vibronic states are written in terms of the functional states

$$\begin{aligned} |Tx'(l, m, n, \alpha, \beta, \gamma)\rangle = |&c' + (-1)^{m+n+\beta+\gamma}d' - (-1)^{n+l+\alpha+\gamma}a' - (-1)^{l+m+\alpha+\beta}b'; \\ &4^l5^m6^n7^\alpha8^\beta9^\gamma\rangle \end{aligned} \tag{4.7}$$

$$\begin{aligned} |Ty'(l, m, n, \alpha, \beta, \gamma)\rangle = |&b' + (-1)^{l+n+\alpha+\gamma}d' - (-1)^{m+l+\alpha+\beta}c' - (-1)^{n+m+\gamma+\beta}a'; \\ &4^l5^m6^n7^\alpha8^\beta9^\gamma\rangle \end{aligned} \tag{4.8}$$

$$\begin{aligned} |Tz'(l, m, n, \alpha, \beta, \gamma)\rangle = |&a' + (-1)^{l+m+\alpha+\beta}d' - (-1)^{n+l+\alpha+\gamma}c' - (-1)^{n+m+\gamma+\beta}b'; \\ &4^l5^m6^n7^\alpha8^\beta9^\gamma\rangle \end{aligned} \tag{4.9}$$

and

$$\begin{aligned} |E'(l, m, n, \alpha, \beta, \gamma)\rangle = |&a' + (-1)^{m+n+\beta+\gamma}b' + (-1)^{n+l+\alpha+\gamma}c' - (-1)^{l+m+\alpha+\beta}d'; \\ &4^l5^m6^n7^\alpha8^\beta9^\gamma\rangle. \end{aligned} \tag{4.10}$$

Note that the states with $i = 1, 2, 3$ and no phonon excitations give the cubic T_1 triplet ground states of the system and the zero-phonon state with $i = 20$ gives the associated A_2 inversion level.

In order to check that the restrictions on the phonon indices given in table 1 are those which define each state once and once only, the number of vibronic states expected for each representation has been calculated by group-theoretical techniques. The results are given in the appendix and table 3. The number of states predicted in table 2 can then be shown to be consistent with these results.

Table 1. The vibronic states for the $T \otimes 2t_2$ JT system.

Symmetry	i	States $\phi_i^{\Gamma}(l, m, n, \alpha, \beta, \gamma)$
T_1	1,4,7	$\|Tx'(l,m,n,\alpha,\beta,\gamma)\rangle + \|Tx'(l,n,m,\alpha,\gamma,\beta)\rangle$
	2,5,8	$\|Ty'(m,l,n,\beta,\alpha,\gamma)\rangle + \|Ty'(n,l,m,\gamma,\alpha,\beta)\rangle$
	3,6,9	$\|Tz'(n,m,l,\gamma,\beta,\alpha)\rangle + \|Tz'(m,n,l,\beta,\gamma,\alpha)\rangle$
T_2	10,13	$\|Tx'(l,m,n,\alpha,\beta,\gamma)\rangle - \|Tx'(l,n,m,\alpha,\gamma,\beta)\rangle$
	11,14	$\|Ty'(m,l,n,\beta,\alpha,\gamma)\rangle - \|Ty'(n,l,m,\gamma,\alpha,\beta)\rangle$
	12,15	$\|Tz'(n,m,l,\gamma,\beta,\alpha)\rangle - \|Tz'(m,n,l,\beta,\gamma,\alpha)\rangle$
E	16,18	$2\|E'(l,m,n,\alpha,\beta,\gamma)\rangle - 2\|E'(m,l,n,\beta,\alpha,\gamma)\rangle + (-1)^{l+n+\alpha+\gamma}[\|E'(n,m,l,\gamma,\beta,\alpha)\rangle$ $-\|E'(m,n,l,\beta,\gamma,\alpha)\rangle] + (-1)^{m+n+\beta+\gamma}[\|E'(l,n,m,\alpha,\gamma,\beta)\rangle - \|E'(n,l,m,\gamma,\alpha,\beta)\rangle]$
	17,19	$\sqrt{3}\{-(-1)^{l+n+\alpha+\gamma}[E'(n,m,l,\gamma,\beta,\alpha)\rangle + \|E'(m,n,l,\beta,\gamma,\alpha)\rangle]$ $+(-1)^{m+n+\beta+\gamma}[\|E'(l,n,m,\alpha,\gamma,\beta)\rangle + \|E'(n,l,m,\gamma,\alpha,\beta)\rangle]\}$
A_2	20 to 25	$\|E'(l,m,n,\alpha,\beta,\gamma)\rangle + \|E'(m,l,n,\beta,\alpha,\gamma)\rangle + (-1)^{l+n+\alpha+\gamma}[\|E'(m,n,l,\beta,\gamma,\alpha)\rangle$ $+\|E'(m,n,l,\beta,\gamma,\alpha)\rangle] + (-1)^{m+n+\beta+\gamma}[\|E'(n,l,m,\gamma,\alpha,\beta)\rangle + \|E'(l,n,m,\alpha,\gamma,\beta)\rangle]$
A_1	26 to 30	$\|E'(l,m,n,\alpha,\beta,\gamma)\rangle - \|E'(m,l,n,\beta,\alpha,\gamma)\rangle + (-1)^{l+n+\alpha+\gamma}[\|E'(m,n,l,\beta,\gamma,\alpha)\rangle$ $-\|E'(m,n,l,\beta,\gamma,\alpha)\rangle] + (-1)^{m+n+\beta+\gamma}[\|E'(n,l,m,\gamma,\alpha,\beta)\rangle - \|E'(l,n,m,\alpha,\gamma,\beta)\rangle]$

Table 2. Restrictions on the indices.

Symmetry	i	Restrictions
T_1	1, 2, 3	$m=n, \beta=\gamma$
	4, 5, 6	$m=n, \beta>\gamma$
	7, 8, 9	$m>n$
T_2	10, 11, 12	$m=n, \beta>\gamma$
	13, 14, 15	$m>n$
E	16, 17	$l>m, l\geqslant n$
	18, 19	$l=m=n, \alpha>\beta, \alpha\geqslant\gamma$
A_2	20	$l=m=n, \alpha\geqslant\beta\geqslant\gamma$
	21	$l>m, l\geqslant n, \alpha=\beta=\gamma$
	22	$l>m=n, \alpha\neq\beta=\gamma$
	23	$l>m=n, \beta>\gamma$
	24	$l=n>m, \alpha=\beta\neq\gamma$
	25	$l=n>m, \alpha>\gamma$
A_1	26	$l=m=n, \alpha>\beta>\gamma$
	27	$l>m, m=n, \beta>\gamma$
	28	$l>m, m\neq n, l=n, \alpha\neq\gamma, \alpha>\gamma, \beta\neq\gamma$
	29	$l>m, m\neq n, l=n, \alpha=\beta, \alpha\neq\gamma, \beta\neq\gamma$
	30	$l>m>n$

Table 3. Number of vibronic states of each irreducible representation. Row (A) applies if $N_T/3$ and $N_2/3$ are integral; otherwise row (B) applies.

	K even		K odd	
	N_T even N_2 even	N_T odd N_2 odd	N_T even N_2 odd	N_T odd N_2 even
	$R=N_2$ $S=N_T$	$R+2\rightarrow N_2+1$ $R+1\rightarrow N_2+2$ $S+1\rightarrow N_T+2$ $S+2\rightarrow N_T+1$	$R+2\rightarrow N_2+1$ $R+1\rightarrow N_2+2$ $S=N_T$	$R=N_2$ $S+1\rightarrow N_T+2$ $S+2\rightarrow N_T+1$
Symmetry				
T_1	$\frac{3}{8}(R+2)(S+2)[(R+1)(S+1)+1]$			
T_2	$\frac{3}{8}(R+2)(S+2)[(R+1)(S+1)-1]$			
E	(A) $\frac{1}{6}[(R+1)(R+2)(S+1)(S+2)-4]$ (B) $\frac{1}{6}[(R+1)(R+2)(S+1)(S+2)]$			
A_1	(A) $\frac{1}{24}\{(R+2)(S+2)[(R+1)(S+1)-3]+8\}$ (B) $\frac{1}{24}\{(R+2)(S+2)[(R+1)(S+1)-3]\}$			
A_2	(A) $\frac{1}{24}\{(R+2)(S+2)[(R+1)(S+1)+3]+8\}$ (B) $\frac{1}{24}\{(R+2)(S+2)[(R+1)(S+1)+3]\}$			
Total	$(R+1)(R+2)(S+1)(S+2)$			

4.3. The normalization factors

The basis states given in table 1 are not normalized. Normalized symmetry-adapted excited

states can be written in the general form

$$|\psi_i^{\Gamma}(l,m,n,\alpha,\beta,\gamma)\rangle = N_i(l,m,n,\alpha,\beta,\gamma)|\phi_i^{\Gamma}(l,m,n,\alpha,\beta,\gamma)\rangle. \tag{4.11}$$

In order to evaluate N_i, the calculation of the overlaps $\langle\phi_i^{\Gamma}|\phi_i^{\Gamma}\rangle$ is required. This in turn requires the calculation of the overlaps of the excited states in infinite coupling. It is necessary therefore to evaluate the expression

$$\langle X_O^{(k_1)\prime}; X_P^{(k_1)}|X_O^{(k_2)\prime}; X_P^{(k_2)}\rangle = \langle X_O^{(k_1)}|X_O^{(k_2)}\rangle\langle X_P^{(k_1)}|U_{k_1}^{\dagger}U_{k_2}|X_P^{(k_2)}\rangle \tag{4.12}$$

where k_1 and k_2 label states from different potential-energy minima (i.e. 'a', 'b', 'c' or 'd') and $X_P^{(k_1)}$ refers to the phonon state in well k_1, etc. On substitution of the U values and after using the identity

$$\exp[k(b_j^{\dagger} - b_j)] = \exp(-\tfrac{1}{2}k^2)\exp(kb_j^{\dagger})\exp(-kb_j) \tag{4.13}$$

this overlap may be simplified by

$$\langle X_O^{(k_1)\prime}; X_P^{(k_1)}|X_O^{(k_2)\prime}; X_P^{(k_2)}\rangle = \langle X_O^{(k_1)}|X_O^{(k_2)}\rangle S_{2t} \times \left\langle X_P^{(k_1)}\middle|\exp\left(\sum_j D_j^{(k_1k_2)}b_j^{\dagger}\right)\exp\left(\sum_j -D_j^{(k_1k_2)}b_j\right)\middle|X_P^{(k_2)}\right\rangle \tag{4.14}$$

where $D_j^{(k_1k_2)} = C_j^{k_1} - C_j^{k_2}$ and the sum j is over all relevant phonon contributions. The quantity S_{2t} is defined by

$$S_{2t} = \exp\left(-\tfrac{1}{2}\sum_j (D_j^{(k_1k_2)})^2\right) \tag{4.15}$$

and takes the values

$$S_{2t} = \begin{cases} \exp\{-\frac{16}{9}[(K_T/\hbar\omega_T)^2 + (K_2/\hbar\omega_2)^2]\} & \text{when } k_1 \neq k_2 \\ 1 & \text{when } k_1 = k_2 \end{cases} \tag{4.16}$$

when dealing with the $T \otimes 2t_2$ JT system. Thus (4.14) reduces to evaluating the phonon overlap

$$\left\langle 4^l 5^m 6^n 7^{\alpha} 8^{\beta} 9^{\gamma}\middle|\exp\left(\sum_j D_j^{(k_1k_2)}b_j^{\dagger}\right)\exp\left(\sum_j -D_j^{(k_1k_2)}b_j\right)\middle|4^p 5^q 6^r 7^{\lambda} 8^{\sigma} 9^{\tau}\right\rangle. \tag{4.17}$$

As the phonon operators for the different modes commute, it is possible to separate this expression into a product of the overlaps for each of the individual modes. For example, for the Q_6 mode, we have, on expansion of the exponentials,

$$\begin{aligned}\langle 6^n|\exp(D_6^{(k_1k_2)}b_6^{\dagger})\exp(-D_6^{(k_1k_2)}b_6)|6^r\rangle &= \left\langle 6^n\middle|\left(\sum_{i=0}^{\infty}\frac{(D_6^{(k_1k_2)}b_6^{\dagger})^i}{i!}\right)\left(\sum_{h=0}^{\infty}\frac{(-D_6^{(k_1k_2)}b_6)^h}{h!}\right)\middle|6^r\right\rangle \\ &= \sum_{h=\max[0,(r-n)]}^{r}\frac{(D_6^{(k_1k_2)})^{n+h-r}(-D_6^{(k_1k_2)})^h}{(n+h-r)!h!}\frac{(n!r!)^{1/2}}{(r-h)!}.\end{aligned} \tag{4.18}$$

On substitution of the values of the $D_j^{(k_1 k_2)}$ into the latter expression, the phonon overlaps can be defined in terms of the function

$$F_M(m,n) = \begin{cases} \displaystyle\sum_{i=\max[0,(m-n)]}^{m} \frac{(-1)^i (m!n!)^{1/2} X_M^{2i}}{i!(m-i)!(i+n-m)!} & \text{if } m \geqslant 0 \text{ and } n \geqslant 0 \\ 0 & \text{if } m < 0 \text{ or } n < 0 \end{cases} \tag{4.19}$$

where

$$X_M = 4K_M/3\hbar\omega_M \tag{4.20}$$

with $M = \mathrm{T}$ when dealing with overlaps of the modes Q_4, Q_5, Q_6 and $M = 2$ when dealing with overlaps of the modes Q_7, Q_8, Q_9 (this notation will be used throughout the rest of this paper).

The orbital overlaps are straightforward to calculate and are given by the expression

$$\langle X_O^{(l)} | X_O^{(k)} \rangle = \begin{cases} 1 & \text{if } k_1 = k_2 \\ -\frac{1}{3} & \text{if } k_1 \neq k_2. \end{cases} \tag{4.21}$$

Hence, after much algebra, overlaps for the functional states (4.7) to (4.10) can be determined. In particular,

$$\langle Tx'(l,m,n,\alpha,\beta,\gamma) | Tx'(p,q,r,\lambda,\sigma,\tau) \rangle = 4\delta_{pl}\delta_{qm}\delta_{rn}\delta_{\alpha\lambda}\delta_{\beta\sigma}\delta_{\gamma\tau} - \tfrac{4}{3}S_{2t} \begin{bmatrix} (-1)^{m+n+\beta+\gamma} S'_{\mathrm{T}}(q,r,m,n) S'_2(\sigma,\tau,\beta,\gamma)\delta_{pl}\delta_{\alpha\lambda} \\ -(-1)^{p+n+\lambda+\gamma} S'_{\mathrm{T}}(p,r,l,n) S'_2(\lambda,\tau,\alpha,\gamma)\delta_{qm}\delta_{\beta\sigma} \\ -(-1)^{p+m+\lambda+\beta} S'_{\mathrm{T}}(p,q,l,m) S'_2(\lambda,\sigma,\alpha,\beta)\delta_{rn}\delta_{\gamma,\tau} \end{bmatrix} \tag{4.22}$$

$$\langle E'(l,m,n,\alpha,\beta,\gamma) | E'(p,q,r,\lambda,\sigma,\tau) \rangle = 4\delta_{pl}\delta_{qm}\delta_{rn}\delta_{\alpha\lambda}\delta_{\beta\sigma}\delta_{\gamma\tau} - \tfrac{4}{3}S_{2t} \begin{bmatrix} (-1)^{m+r+\beta+\tau} S'_{\mathrm{T}}(q,r,m,n) S'_2(\sigma,\tau,\beta,\gamma)\delta_{pl}\delta_{\alpha\lambda} \\ +(-1)^{l+r+\alpha+\tau} S'_{\mathrm{T}}(p,r,l,n) S'_2(\lambda,\tau,\alpha,\gamma)\delta_{qm}\delta_{\beta\sigma} \\ +(-1)^{l+m+\alpha+\beta} S'_{\mathrm{T}}(p,q,l,m) S'_2(\lambda,\sigma,\alpha,\beta)\delta_{rn}\delta_{\gamma\tau} \end{bmatrix} \tag{4.23}$$

where

$$S'_M(h,i,j,k) = X_{\mathrm{T}}^{j+k-h-i} F_M(h,j) F_M(i,k). \tag{4.24}$$

It is a simple matter to determine the required normalization factors from these overlap functions.

The functions S'_M are related to the functions S_M that appear in the calculations of the overlaps for the T⊗t JT problem by the relationship $S = -(4/3)S'$. It is possible to see how the results above arise in relation to the single-mode result (Dunn 1989) by tracing the wells from which each term arises. For example, the terms including $\delta_{pl}\delta_{\alpha\lambda}$ come from overlaps between wells '*ab*', '*ba*', '*cd*' and '*dc*'. The single-mode contribution for these wells is $-(4/3)(-1)^{m+n}S'(q,r,m,n)\delta_{pl}$. This must simply be multiplied by a second single-mode overlap function with all labels permuted to the equivalent ones for the second mode, but excluding the extra factor of $-(4/3)$. This is because the one-mode function contribution includes a factor of $-(1/3)$ for the orbital overlaps and a factor of 4 because the term is a sum over four different well combinations. Both considerations should only be included once in a multi-mode problem. Such an analysis is useful, as it clearly indicates how results could be obtained for a full multimode model.

5. Energies of the symmetry-adapted states

5.1. General expressions

To calculate the energies of the symmetry-adapted excited states, it is necessary to evaluate the matrix elements of $\mathcal{H}$ between the functional states (4.7)–(4.10). Consequently we write $\mathcal{H} = \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{vib}}$ in second quantized form where

$$\mathcal{H}_{\text{int}} = K_{\text{T}}[\tau_4(b_4^\dagger + b_4) + \tau_5(b_5^\dagger + b_5) + \tau_6(b_6^\dagger + b_6)] + K_2[\tau_4(b_7^\dagger + b_7) + \tau_5(b_8^\dagger + b_8) + \tau_6(b_9^\dagger + b_9)] \tag{5.1}$$

and

$$\mathcal{H}_{\text{vib}} = \tfrac{1}{2}\sum_j \hbar\omega_M(b_j b_j^\dagger + b_j^\dagger b_j). \tag{5.2}$$

It is necessary to evaluate matrix elements of the form

$$\begin{aligned}\langle X_O^{(k_1)'}; 4^l 5^m 6^n 7^\alpha 8^\beta 9^\gamma | \mathcal{H} | X_O^{(k_2)'}; 4^p 5^q 6^r 7^\lambda 8^\sigma 9^\tau \rangle \\ = \langle X_O^{(k_1)}; 4^l 5^m 6^n 7^\alpha 8^\beta 9^\gamma | U_{k_1}^\dagger \mathcal{H} U_{k_2} | X_O^{(k_2)}; 4^p 5^q 6^r 7^\lambda 8^\sigma 9^\tau \rangle\end{aligned} \tag{5.3}$$

and this requires the use of the commutation relation

$$\mathcal{H}U_k = U_k\left(\mathcal{H} + \sum_{j=4}^{9} C_j^{(k)}\{-2K_j\tau_j + \hbar\omega_j[-(b_j^\dagger + b_j) + C_j^{(k)}]\}\right). \tag{5.4}$$

This relationship can be used, after a great deal of algebra, to evaluate the energies of the functional states. However, many of the details of the calculations follow directly those for the single-mode T ⊗ t JT problem (Dunn 1989). The functional energies are, in effect, the matrix elements for the single-mode problem with $M = \text{T}$ multiplied by the overlaps with $M = 2$ evaluated between the appropriate wells in the appropriate places, plus the same with T and 2 reversed. This greatly simplifies the steps that need to be carried out for the T ⊗ 2t problem, and allows the answers to be written down in a relatively straightforward manner using the functions that appear in the T ⊗ t problem. It also indicates clearly how the multimode problem can be formulated.

The single-mode functions necessary to evaluate the functional energies are:

$$\begin{aligned}H_M(l,h,i,j,k) = -\tfrac{2}{3}X_M^{j+k-h-i}\{2[(l+h+i+\tfrac{3}{2}) - \tfrac{3}{4}X_M^2]F_M(h,j)F_M(i,k) \\ + G_M(h,j)F_2(i,k) + G_M(i,k)F_M(h,j)\}\end{aligned} \tag{5.5}$$

$$G_M(l,m) = X_M^2 l^{1/2}F_M(l-1,m) + (l+1)^{1/2}F_M(l+1,m) \tag{5.6}$$

$$K_M(p,q,r,l,m,n) = J_M(p,q,r,m,n)\delta_{p(l+1)} + J_M(l,q,r,m,n)\delta_{l(p+1)} \tag{5.7}$$

$$J_M(l,h,i,j,k) = -\tfrac{4}{3}X_M^{j+k-h-i+1}l^{1/2}F_M(h,j)F_M(i,k). \tag{5.8}$$

Using these functions we can define the matrix elements of the functional Tx states as

$$\begin{aligned}\langle Tx'(l,m,n,\alpha,\beta,\gamma)|\mathcal{H}|Tx'(p,q,r,\lambda,\sigma,\tau)\rangle \\ = E_{Tx}(\text{T},l,m,n,p,q,r;2,\alpha,\beta,\gamma,\lambda,\sigma,\tau) \\ + E_{Tx}(2,\alpha,\beta,\gamma,\lambda,\sigma,\tau;\text{T},l,m,n,p,q,r)\end{aligned} \tag{5.9}$$

where

$$E_{T\tau}(M, l, m, n, p, q, r; N, \alpha, \beta, \gamma, \lambda, \sigma, \tau)$$
$$= \hbar\omega_M \left\{ 4[(p + q + r + \tfrac{3}{2}) - \tfrac{3}{4}X_M^2]\delta_{lp}\delta_{mq}\delta_{nr}\delta_{\alpha\lambda}\delta_{\beta\sigma}\delta_{\gamma\tau} \right.$$
$$\left. + S_{2t} \begin{bmatrix} (-1)^{m+n+\beta+\gamma}[H_M(l, q, r, m, n)\delta_{pl} + K_M(p, q, r, l, m, n)]S'_N(\sigma, \tau, \beta, \gamma)\delta_{\alpha\lambda} \\ -(-1)^{p+n+\gamma+\lambda}[H_M(m, p, r, l, n)\delta_{qm} - K_M(q, p, r, m, l, n)]S'_N(\lambda, \tau, \alpha, \gamma)\delta_{\beta\sigma} \\ -(-1)^{p+m+\lambda+\beta}[H_M(n, p, q, l, m)\delta_{rn} - K_M(r, p, q, n, l, m)]S'_N(\lambda, \sigma, \alpha, \beta)\delta_{\gamma\tau} \end{bmatrix} \right\}. \tag{5.10}$$

(Note the typographical error in Dunn (1989) in which the terms in $\delta_{\beta\sigma}$ and $\delta_{\gamma\tau}$ were written in terms of the function J, rather than K.)

Similarly, the energies of the functional E states are

$$\langle E'(l, m, n, \alpha, \beta, \gamma)|\mathcal{H}|E'(p, q, r, \lambda, \sigma, \tau)\rangle$$
$$= E_E(\mathrm{T}, l, m, n, p, q, r; 2, \alpha, \beta, \gamma, \lambda, \sigma, \tau)$$
$$+ E_E(2, \alpha, \beta, \gamma, \lambda, \sigma, \tau; \mathrm{T}, l, m, n, p, q, r) \tag{5.11}$$

where

$$E_E(M, l, m, n, p, q, r; N, \alpha, \beta, \gamma, \lambda, \sigma, \tau)$$
$$= \hbar\omega_M \left\{ 4[(p + q + r + \tfrac{3}{2}) - \tfrac{3}{4}X_M^2]\delta_{lp}\delta_{mq}\delta_{nr}\delta_{\alpha\lambda}\delta_{\beta\sigma}\delta_{\gamma\tau} \right.$$
$$\left. + S_{2t} \begin{bmatrix} (-1)^{m+r+\beta+\tau}[H_M(l, q, r, m, n)\delta_{pl} - K_M(p, q, r, l, m, n)]S'_N(\sigma, \tau, \beta, \gamma)\delta_{\alpha\lambda} \\ +(-1)^{l+r+\alpha+\tau}[H_M(m, p, r, l, n)\delta_{qm} - K_M(q, p, r, m, l, n)]S'_N(\lambda, \tau, \alpha, \gamma)\delta_{\beta\sigma} \\ +(-1)^{l+m+\alpha+\beta}[H_M(n, p, q, l, m)\delta_{rn} + K_M(r, p, q, n, l, m)]S'_N(\lambda, \sigma, \alpha, \beta)\delta_{\gamma\tau} \end{bmatrix} \right\}. \tag{5.12}$$

From these, the state definitions in table 1 and the normalization factors derived from the functional overlaps (4.22) and (4.23), it is a relatively straightforward procedure to calculate the energies of all of the vibronic states.

5.2. *Energies of the ground states*

It is possible to write down much simpler expressions for the energies of the T_1 vibronic ground state and its associated inversion level, as neither contain any phonon excitations. After substitution of the normalization factors and relevant functions, the results are found to be

$$E_G^{T_1} = \tfrac{3}{2}(\hbar\omega_T + \hbar\omega_2) - \frac{4}{9}\left(\frac{K_T^2}{\hbar\omega_T} + \frac{K_2^2}{\hbar\omega_2}\right)\left(\frac{9 + 7S_{2t}}{3 + S_{2t}}\right) \tag{5.13}$$

and

$$E_G^{A_2} = \tfrac{3}{2}(\hbar\omega_T + \hbar\omega_2) - \frac{4}{9}\left(\frac{K_T^2}{\hbar\omega_T} + \frac{K_2^2}{\hbar\omega_2}\right)\left(\frac{3 - 7S_{2t}}{1 - S_{2t}}\right) \tag{5.14}$$

respectively. These results have an identical form to those of $T \otimes t$ (Dunn and Bates 1989) provided $K_T^2/\hbar\omega_T$ is replaced by $(K_T^2/\hbar\omega_T + K_2^2/\hbar\omega_2)$ and S_t by S_{2t}. However, it must be stressed that these equivalences are not true in general.

5.3. Results for the excited states

The energies of all vibronic states can be evaluated directly from the formulae quoted in the tables, for any given input parameters. We present here the results for some specific choices of parameters. For simplicity, only states with zero and one phonon excitation will be considered, although the results are valid for any number of phonon excitations. It is also useful to define a ratio of coupling strengths

$$\eta = V_2/V_T = (K_2/K_T)(\omega_2/\omega_T)^{1/2}. \tag{5.15}$$

5.3.1. Case of equal frequencies. The simplest choices of parameters are when the frequencies of the two modes are equal ($\omega_T = \omega_2 = \omega$). Figures 1, 2 and 3 show the calculated energies, relative to the T_1 ground state, with the parameter η taking values 0.1, 0.6 and 0.9 respectively.

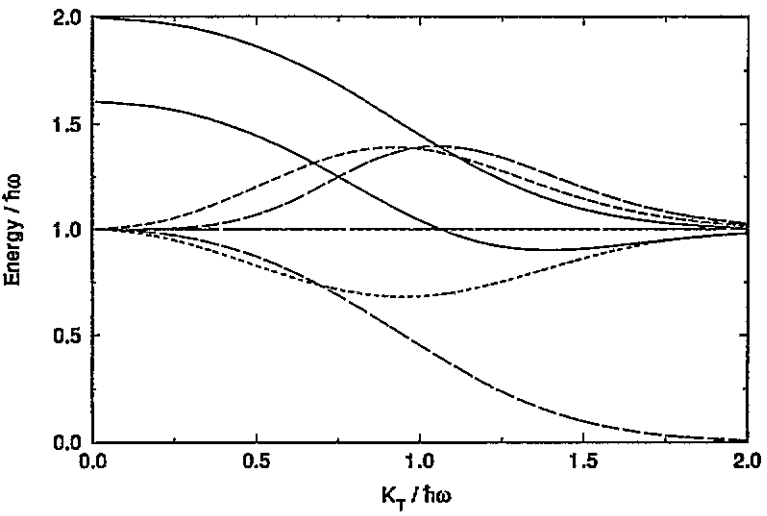

Figure 1. Energies relative to the T_1 ground state for $\eta = 0.1$ and $\omega_T = \omega_2 = \omega$ with the key: T_1, full curves; T_2, short dashed curves; E states and their accidentally degenerate T_1 states, medium dashed curves; A_2, long dashed curves.

When considering the special cases for which the frequencies of the two modes are equal, it is useful to make an orthogonal transformation in Q-space

$$q_i = (Q_i + \eta Q_{i+3})/(1+\eta^2)^{1/2} \qquad q_{i+3} = (\eta Q_i - Q_{i+3})/(1+\eta^2)^{1/2} \tag{5.16}$$

for $i = 4, 5, 6$ such that, when the coupling to the e modes is neglected, the Hamiltonian $\mathcal{H} = \mathcal{H}_{int} + \mathcal{H}_{vib}$ given by (2.1) and (2.2) becomes (O'Brien 1994)

$$\mathcal{H} = V_T(1+\eta^2)^{1/2}(q_4 T_{yz} + q_5 T_{zx} + q_6 T_{xy}) + \tfrac{1}{2}\sum_j (p_j^2/\mu_j + \mu_j \omega_j^2 q_j^2) \tag{5.17}$$

where p_j is the momentum conjugate to q_j. This indicates that the results obtained should be identical to those of the single-mode $T \otimes t_2$ problem with an effective coupling constant

$$V_T' = V_T(1+\eta^2)^{1/2} \tag{5.18}$$

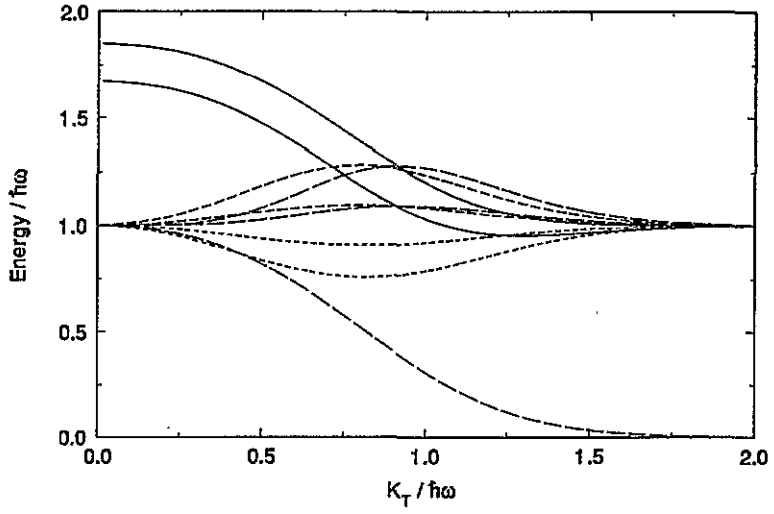

Figure 2. Energies as in figure 1 but with $\eta = 0.6$.

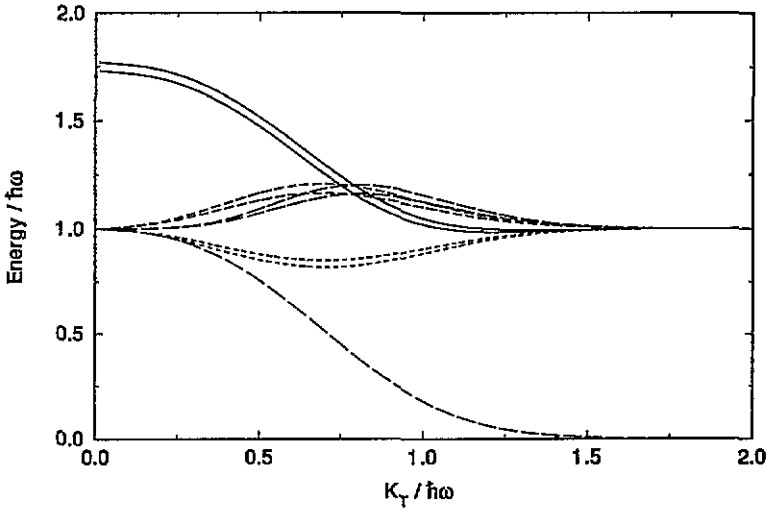

Figure 3. Energies as in figure 1 but with $\eta = 0.9$.

rather than V_T, and with the addition of a set of energy levels due to an uncoupled t_2 mode. The levels due to the uncoupled mode should include a set of levels at energy $\hbar\omega$ relative to the ground state, plus a T_1 (i.e. $A_2 \otimes T_2$) level that varies in energy from $2\hbar\omega$ in weak coupling to $\hbar\omega$ in strong coupling, such that it remains $\hbar\omega$ above the A_2 inversion level.

Figure 1 ($\eta = 0.1$) does show both a pattern of levels for the $M = T$ modes that is very similar to that for the single-mode $T \otimes t_2$ problem (figure 2 of Dunn 1989), plus a set of levels due to the uncoupled mode as required. However, the levels that should be at $\hbar\omega$ show noticeable deviations from this value when the coupling to the second mode is larger (figures 2 and 3). This can be attributed to the fact that states of a given symmetry are not necessarily orthogonal to each other (although they are orthogonal to the states of other

symmetries). For example, consider the two T_2 states with one phonon excitation:

$$\begin{aligned} |\phi_{Q_5}\rangle &= |\phi_{13}^{T2}(0,1,0,0,0,0)\rangle = |t\rangle - |u\rangle \\ |\phi_{Q_8}\rangle &= |\phi_{10}^{T2}(0,0,0,0,1,0)\rangle = |v\rangle - |w\rangle \end{aligned} \tag{5.19}$$

where

$$\begin{aligned} |t\rangle &= |Tx'(0,1,0,0,0,0)\rangle \qquad |u\rangle = |Tx'(0,0,1,0,0,0)\rangle \\ |v\rangle &= |Tx'(0,0,0,0,1,0)\rangle \qquad |w\rangle = |Tx'(0,0,0,0,0,1)\rangle. \end{aligned}$$

These states have an overlap $\langle\phi_{Q_5}|\phi_{Q_8}\rangle = (8/3)S_{2t}X_TX_2$, which is only zero in the limits of very strong coupling (to either mode) or weak coupling to one of the modes. Therefore, orthogonal combinations of these two states should be taken. The transformation (5.16) suggests that the correct states to use should (in un-normalized form) be

$$\begin{aligned} |\phi_{q_5}\rangle &= (|t\rangle + \eta|v\rangle) - (|u\rangle + \eta|w\rangle) \\ |\phi_{q_8}\rangle &= (\eta|t\rangle - |v\rangle) - (\eta|u\rangle - |w\rangle). \end{aligned} \tag{5.20}$$

It can be verified that these combinations are indeed orthogonal when $X_2 = \eta X_T$, which occurs when the two frequencies are equal. It is also possible to show (by substitution into expression (5.9)) that the state $|\phi_{q_8}\rangle$ has energy $\hbar\omega$ relative to the ground state. The state $|\phi_{q_5}\rangle$ has (absolute) energy

$$E_{q_5} = \hbar\omega[4(3 + S_t) - \tfrac{9}{4}X_T'^2 + S_tX_T'^2(\tfrac{1}{4} - \tfrac{7}{4}X_T'^2)]/[3 + S_t(1 + X_T'^2)]. \tag{5.21}$$

This is identical to that predicted in Dunn (1989) for the single-mode $T \otimes t_2$ JT problem for an effective coupling given by $X_T' = X_T(1 + \eta^2)^{1/2}$, with the addition of an extra $(3/2)\hbar\omega$ to allow for the zero-point energy of the additional mode. This is consistent with the predictions of (5.18). The results for this energy level for the case $\eta = 0.6$ using both the original and orthogonalized states are presented in figure 4. These results suggest that it would have been better to work the whole problem in terms of the transformed Q-space, even for cases of unequal coupling. However, although possible, this would greatly complicate the required calculations. Hence this has not been attempted in this paper. It is interesting to note that in figure 3 ($\eta = 0.9$), where the magnitudes of the two couplings are almost the same, all of the levels apart from the ground and inversion levels form pairs. The overall pattern is very similar to that of the single-mode case.

It can be seen that in all three figures, there are some T_1 states that do not attain the correct values of integral units of $\hbar\omega$ in the limit of weak coupling to both modes ($K_T \to 0$). This is again because of non-orthogonality of states of a given symmetry. In fact, for equal frequencies, the T_1 states with $l = 1$ and $\alpha = 1$ respectively approach the limits

$$2\hbar\omega(4 + 3\eta^2)/(5 + 3\eta^2) \qquad \text{and} \qquad 2\hbar\omega(3 + 4\eta^2)/(3 + 5\eta^2). \tag{5.22}$$

These produce the values of $1.6\hbar\omega$ and $2\hbar\omega$ respectively when $\eta = 0$. The same effects of non-orthogonality also arose in the single-mode problem, in which the value of $1.6\hbar\omega$ was also obtained for the T_1 state with $l = 1$ (figure 1 of Dunn 1989). In that paper, new orthogonalized combinations of states were taken for the cases that did not attain the correct weak-coupling limit. The new combinations did exhibit the correct behaviour (figure 2 of Dunn 1989). Again, this has not been attempted in this paper as the main advantages in obtaining an analytical method would be lost.

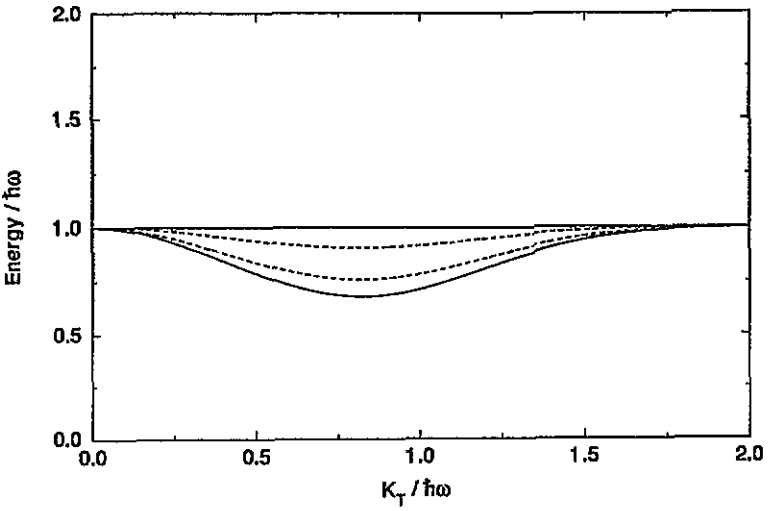

Figure 4. Energies of the T_2 one-phonon states with $\eta = 0.6$ for non-orthogonalized (short dashed curves) and orthogonalized (full curves) states.

5.3.2. General results. More general results for $\eta = 0.6$ are shown in figures 5 and 6 when the oscillator frequencies are not equal (which is the situation that is more likely to occur in real $T \otimes 2t_2$ JT systems). Figure 5 shows results for $\omega_T = \omega$ and $\omega_2 = 0.8\omega$, and figure 6 shows $\omega_T = 0.8\omega$ and $\omega_2 = \omega$. Both sets of results are plotted in units of $\hbar\omega$ (rather than $\hbar\omega_T$ or $\hbar\omega_2$) to keep the overall scaling of the two problems the same. The results are similar to the case of equal frequencies, but where the states separate into two sets that tend to the two different values of $\hbar\omega_M$ in strong coupling.

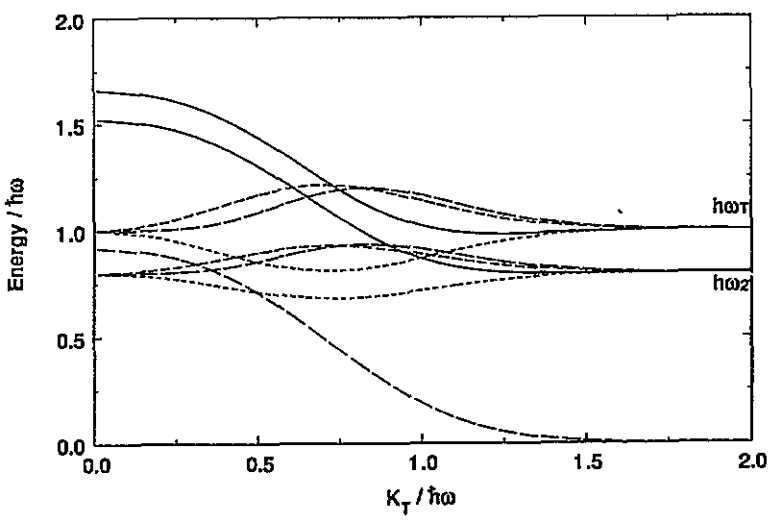

Figure 5. Energies as in figure 1 but with $\eta = 0.6$, $\omega_T = \omega$ and $\omega_2 = 0.8\omega$.

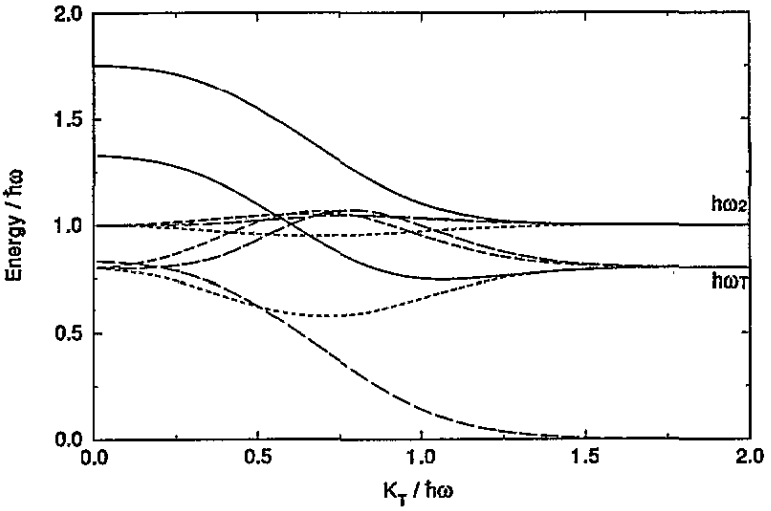

Figure 6. Energies as in figure 1 but with $\eta = 0.6$, $\omega_T = 0.8\omega$ and $\omega_2 = \omega$.

It must be noted that the results presented in these figures will exhibit non-orthogonality effects in a similar way to the equal-coupling results, and again should be corrected accordingly. However, these results are still useful in predicting the behaviour in cases of non-equal coupling. In particular, the inversion level is predicted to tend to the energy

$$\delta = \hbar\omega_T(1 + \eta^2/\nu^2)/(1 + \eta^2/\nu^3) \tag{5.23}$$

where $\nu = \omega_2/\omega_T$ in the weak-coupling limit, which is intermediate between the two values of $\hbar\omega$ when $\nu \neq 1$.

Calculations (O'Brien 1994) based on the method of Öpik and Pryce (1957) suggest that, when the frequencies of the two modes are not equal, four states should tend to the energy $\hbar\omega_T$ and, four to the energy $\hbar\omega_2$, but that the remaining 16 one-phonon states should attain an energy that is a combination of these two values. The reason why this is not seen here is probably because the $\tilde{\mathcal{H}}_2$ part of the transformed Hamiltonian (2.6) has been neglected in the calculations. In the single-mode problem, anisotropic effects mean that one-third of the states should have a frequency ω and the remaining two-thirds a frequency $\sqrt{(2/3)}\omega$. Although our basic method predicts all states to have the frequency $\hbar\omega$, when $\tilde{\mathcal{H}}_2$ is included via perturbation theory (Dunn and Bates 1989), two-thirds of the modes are predicted to have an effective frequency that is a Taylor expansion of $\sqrt{(1 - 1/3)}\omega$. This suggests that the single-mode results would be correct to infinite order in perturbation theory. The effect of the inclusion of $\tilde{\mathcal{H}}_2$ has not been investigated for the two-mode problem.

For all parameter values, there is an accidental degeneracy between the states $|\psi_7^{T1}(0, 1, 0, 0, 0, 0)\rangle$ and $|\psi_{16}^{E}(1, 0, 0, 0, 0, 0)\rangle$. These states are directly equivalent to the states $|\psi_4^{T1}(0, 1, 0)\rangle$ and $|\psi_{10}^{E}(1, 0, 0)\rangle$ respectively of the single-mode problem (Dunn 1989), which also exhibit an accidental degeneracy. The corresponding pair of states $|\psi_4^{T1}(0, 0, 0, 0, 1, 0)\rangle$ and $|\psi_{18}^{E}(0, 0, 0, 1, 0, 0)\rangle$ for equivalent excitations of the second ($M = 2$) mode are also accidentally degenerate.

6. Summary

This paper has presented the derivation of a set of symmetry-adapted excited states for the

T⊗2t₂ JT system by forming symmetry-adapted combinations of the infinite-coupling states in the potential-energy surface minima in Q-space. This set has been shown to be complete using group theory techniques. Analytical expressions for the normalization factors and energies of these states have been obtained. Although the results are not exact due to non-orthogonality of states of a given symmetry to other states of the same symmetry, they form a useful basis for further calculations. In particular, first- and second-order reduction factors, which are of interest in the T ⊗ 2t₂ JT system, can be evaluated. The results have also been written in a form that indicates how the T ⊗ 2t₂ JT problem can be extended to a full multimode problem.

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Appendix. Calculation of the number of states

The excited states in the infinite coupling limit are used as basis sets for this calculation. A state localized in the kth potential energy minima can be written in a general form as

$$|X_O^{(k)'}; X_{t_2}^{(k)}, Y_{t_2}^{(k)}\rangle \tag{A1}$$

where $|X_O^{(k)'}\rangle$ represents the electronic part of the state and $|X_{t_2}^{(i)}\rangle$ and $|Y_{t_2}^{(i)}\rangle$ the two t_2-type phonon components of the state. The reducible representation of the vibronic states can therefore be defined as the direct product of the representations for each part of the state

$$\Gamma_{\text{vib}} = \Gamma_O \otimes \Gamma_{t_2'}^{(N)} \otimes \Gamma_{t_2''}^{(M)} \tag{A2}$$

where

$$\Gamma_{t_2'}^{(K)} = \Gamma_{t_2'} \otimes \Gamma_{t_2'} \ldots \text{to } K \text{ factors} \tag{A3}$$

where $K = N_T + N_2$. $N_T = l + m + n$ is the number of phonon excitations for the $M = T$ mode, and $N_2 = \alpha + \beta + \gamma$ is the number of phonon excitations for the other ($M = 2$) mode. To calculate this direct product we require the characters of each representation. These are given in Appendix 1 of Dunn (1989) for the orbital and t_2 phonon representations. Using these results, the character of the total reducible representation of the vibronic states, Γ_{red}, is then given by

$$\chi_{\text{red}}(R) = \chi_{\text{orbit}}(R)\chi_{t_2}(R)\chi'_{t_2}(R) \tag{A4}$$

and hence the character table of Γ_{red} for the T_d point group is

	E	$^3C_2$	$^6JC_4$	$^6JC_2$	$^8C_3$
Γ_{red}	$4\chi_{t_2}(E)\chi'_{t_2}(E)$	0	0	$2\chi_{t_2}(JC_2)\chi'_{t_2}(JC_2)$	$\chi_{t_2}(C_3)\chi'_{t_2}(C_3)$

The number of vibronic states corresponding to each irreducible representation has been calculated from the table above and from the reduction formula:

$$a_j = \frac{1}{g}\sum_{R=1}^{g} \chi^j(R)^* \chi_{\mathrm{red}}(R) \tag{A5}$$

where a_j represents the number of times the irreducible representation Γ_j appears in the reduction of Γ_{red}, g is the order of the group and $\chi^j(R)^*$ are the characters of the irreducible representations of the T_d group. The number of states calculated using group theory is given in table 3; the results agree with the number of states generated by the phonon restrictions presented for each set of states.

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