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Reduction factors, tunnelling splitting and zero-phonon line intensity in $T \otimes \tau_2$ and $T \otimes (\tau_2 \oplus \epsilon)$ Jahn–Teller systems

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Abstract. First- and second-order reduction factors for the Jahn–Teller systems $T \otimes (\tau_2 \oplus \epsilon)$ and $T \otimes \tau_2$ are calculated using a numerical perturbation method, and checked analytically at strong and weak coupling. Those for $T \otimes \tau_2$ are compared with ones produced analytically by Bates and Dunn, and the general agreement is good. An attempt to find an asymptotic formula for the tunnelling splitting showed its form to be still uncertain with the splitting as small as $10^{-7}\hbar\omega$, but the fit with a WKB calculation is good. The zero-phonon line intensity in $T \otimes \tau$ is calculated numerically and analytically.

1. Introduction

It was originally Ham (1965) who pointed out, when discussing what happened to the spin–orbit coupling when a p state was coupled to a set of ϵ-type vibrations, that the effect within the ground triplet state could be characterised by a set of reduced matrix elements, or reduction factors. These could be divided into those that gave the reduction of operators taken to first order within the ground state, and those allowing for second-order effects when the spin–orbit coupling was small compared to the Jahn–Teller splitting. Obviously the second-order terms become important only when the first-order ones are small, as they may be at strong coupling. Over the years the calculation and measurement of these factors has formed an important part of the characterisation of any Jahn–Teller system under consideration, and a considerable body of information has built up about these factors. The work presented here aims to fill some gaps in the existing calculations with some information that may be useful. The first part is a calculation of the second-order reduction factors in the special case of a triplet state equally coupled to degenerate τ_2 and ϵ vibrations. This system has been studied because the assumed symmetry makes for an elegant way of handling a strongly coupled system numerically, and the results obtained can be usefully compared with results in other regimes. The second is a similar calculation of second-order reduction factors in a triplet state coupled linearly to a set of τ_2 vibrations.

In a recent set of papers, Bates and Dunn (1989), Dunn and Bates (1989) have used transformation methods to calculate some of these reduction factors, and they give numerical results for a range of coupling strengths and a variety of different types of coupling. As their method starts from strongly coupled vibronic wave functions localised in phase space it was not suitable for use with $T \otimes (\tau_2 \oplus \epsilon)$ in equal linear coupling, so the results given here can be used for interpolation but not for comparison.

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On the other hand Bates and Dunn do apply their method to $T \otimes \tau_2$, so this calculation, which is done by a quite different method, should serve as a useful cross-check. We round off this part of the paper by setting out the forms of the reduction factors at large and small k.

Finally we present numerical and analytical calculations of the intensity of the zero-phonon line in $T \otimes \tau$. These results have not been given before, and the numerical results come naturally out of the rest of the work.

2. Form of the effective Hamiltonian

We are looking at a system in which a p state is sufficiently strongly coupled to the vibrations for the spin–orbit coupling to be more or less quenched in the ground state. The coupling is linear and the cluster model is assumed. The ground state is still a T_1 triplet, and the spin–orbit coupling, $\lambda \boldsymbol{l} \cdot \boldsymbol{S}$ in the uncoupled states, is represented up to second order in λ by an effective Hamiltonian. The form of this effective Hamiltonian can be predicted on symmetry grounds, and in particular it can be seen that one constant is needed for the first order terms and four constants for the second-order terms. The first-order terms involve just one reduced matrix element, and will be written as in earlier work as

$$\mathcal{H}_1 = K(T_1)\lambda \boldsymbol{l} \cdot \boldsymbol{S} \tag{1}$$

For the second-order terms we note that within the $l = 1$ basis we can use tensor operators corresponding to $l = 0, 1, 2$ and that within the cubic symmetry the $l = 2$ tensor splits into independent T_2-type and E-type tensors. Accordingly we shall write the second-order terms as

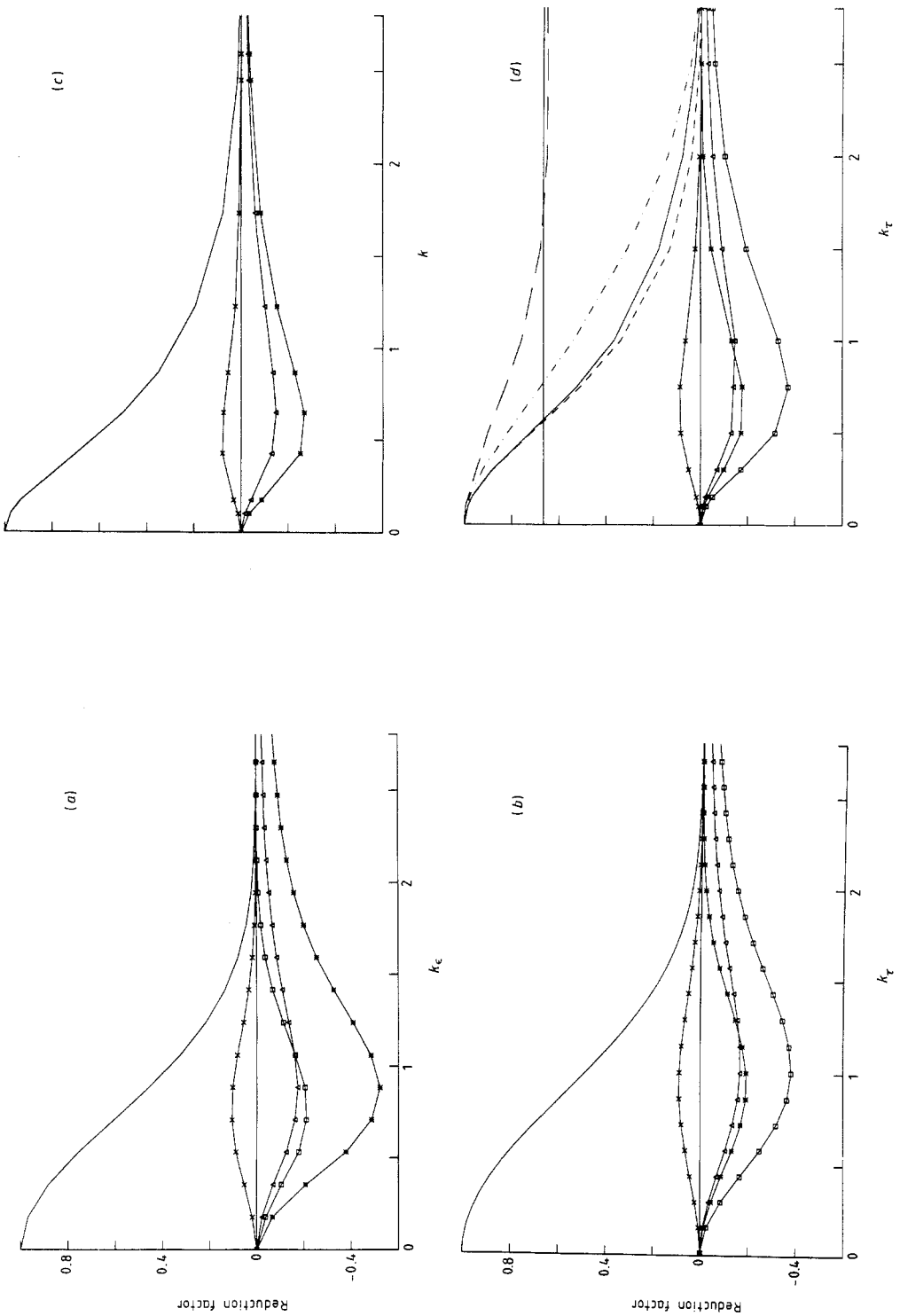
$$\mathcal{H}_2 = \lambda^2[A(\boldsymbol{l} \cdot \boldsymbol{S}) + \tfrac{2}{3}B_E\mathcal{E}(l) \cdot \mathcal{E}(S) + \tfrac{2}{3}B_T\mathcal{T}(l) \cdot \mathcal{T}(S) + Cl(l+1)S(S+1)] \tag{2}$$

where the tensor operators $\mathcal{E}$ and $\mathcal{T}$ are the two parts of the $l = 2$ tensor operator, operating in orbital space and in spin space. The normalisation of these operators is best defined by noting the identity

$$(\boldsymbol{l} \cdot \boldsymbol{S})^2 = -\tfrac{1}{2}(\boldsymbol{l} \cdot \boldsymbol{S}) + \tfrac{2}{3}\mathcal{E}(l) \cdot \mathcal{E}(S) + \tfrac{2}{3}\mathcal{T}(l) \cdot \mathcal{T}(S) + \tfrac{1}{3}l(l+1)S(S+1)\,. \tag{3}$$

This can be compared with the form given by Ham (1965, equation (2.34)), to give for $T \otimes \epsilon$: $B_T = -2A = \mathcal{K}_1$ and $B_E = 3C = (\mathcal{K}_1 + \mathcal{K}_2)$ in terms of his constants. In this case the parameters were calculated analytically, using an exact adiabatic method, and we show the results of that calculation in figure 1(*a*) for comparison with results on other systems. The reduction factors are plotted against the coupling

Figure 1 (*facing page*). (*a*) $T \otimes \epsilon$ reduction factors from Ham (1965). —— = $K(T_1)$, × − × − × = A, * − * − * = B_E, □ − □ − □ = B_T and △ − △ − △ = C. (*b*) $T \otimes \tau_2$ reduction factors from Bates and Dunn (1989) and Dunn *et al* (1990). —— = $K(T_1) = K(E)$, × − × − × = A, * − * − * = B_E, □ − □ − □ = B_T and △ − △ − △ = C. (The difference found between $K(T_1)$ and $K(E)$ is small, and is not shown here.) (*c*) $T \otimes (\tau_2 \oplus \epsilon)$ reduction factors, numerical calculation. —— = $K(T_1)$, × − × − × = A, * − * − * = $B = B_E = B_T$, and △ − △ − △ = C. (*d*) $T \otimes \tau_2$ reduction factors, numerical calculation. —— = $K(T_1)$, — — — = $K(T_2)$, - - - = $K(E)$, × − × − × = A, * − * − * = B_E, □ − □ − □ = B_T, △ − △ − △ = C and — · — = tunnelling splitting.


(a)
(b)
(c)
(d)
Reduction factor
0.8
0.4
0
-0.4
0
1
2
k_ϵ
k_τ
k

strength, k_ϵ where $k_\epsilon^2 = (3/2)E_{\mathrm{JT}}$, and the classical Jahn–Teller energy is $\hbar\omega E_{\mathrm{JT}}$. In the strong-coupling regime where the second-order terms are important they are dominated by the fact that $\mathcal{K}_2 \gg \mathcal{K}_1$, so B_{E} and C are the important parameters, and would determine the pattern of energy levels. In the calculation this inequality corresponds to the larger size of second-order terms that begin and end in the same well over those that connect different wells.

We must also connect our constants with those used by Bates and Dunn (1989, equation (3.8)). The comparison gives, for our constants in terms of theirs, $K(\mathrm{T}_1) = \gamma$, $A = -b/2$, $B_{\mathrm{E}} = b + 3c/2$, $B_{\mathrm{T}} = b + 2d$ and $C = b/3 + e$. (This equivalence assumes the separation of first- and second-order terms implied in their (3.8), and does not correspond to their alternative form (their (4.14)) where some of the second-order terms are included in γ.) These results have now been slightly modified (Dunn *et al* 1990), and they are plotted in a preliminary version in figure 1(*b*), against k_τ, where $k_\tau^2 = (3/2)E_{\mathrm{JT}}$. It is pleasing to see the similarity with $\mathrm{T}\otimes\epsilon$ with the roles of B_{E} and B_{T} interchanged. As these authors use an adiabatic approximation, the inequality can presumably be attributed to a similar geometric effect.

3. $\mathrm{T}\otimes(\tau_2\oplus\epsilon)$

3.1. Theory

The simplicity of working with this equal-coupling or D-mode system comes from the invarience of the Hamiltonian under a complete set of rotations in three dimensions, so all eigenstates can be characterised by angular momentum quantum numbers, and all bilinear operators can be expressed as tensor products. There is also the advantage that the routine of setting up and diagonalising the matrices has often been done and is well understood. The ground state of the Jahn–Teller coupled system is a P state, the same as the uncoupled electronic state, and we assume that there is a spin of multiplicity n that is coupled in by the usual spin–orbit coupling. We use the set of operators defined in the previous section, but with this higher symmetry we must have $B_{\mathrm{E}} = B_{\mathrm{T}} = B$. A convenient way of writing the second-order terms is then

$$\mathcal{H}_2 = \lambda^2\{A(\boldsymbol{l}\cdot\boldsymbol{S}) + B[(\boldsymbol{l}\cdot\boldsymbol{S})^2 + \tfrac{1}{2}(\boldsymbol{l}\cdot\boldsymbol{S}) - \tfrac{1}{3}l(l+1)S(S+1)] + Cl(l+1)S(S+1)\}. \tag{4}$$

As we propose to use the $S = 1/2$ case (two matrices) for our calculations, it being already set up and working, at least one more matrix has to be devised for the order-2 reduction factor. The fact that the reduction factors go with the l operator rather than with $\boldsymbol{l}\cdot\boldsymbol{S}$ is slightly obscured by this form, but it is much easier to handle than the raw tensors. In the special case $S = 1/2$ this reduces to

$$\mathcal{H}_2 = \lambda^2[A(\boldsymbol{l}\cdot\boldsymbol{S}) + \tfrac{3}{2}C]. \tag{5}$$

The B-term has gone because a second-order tensor is zero $S = 1/2$.

It is clear from the above that by working with the existing matrices for $S = 1/2$ we can expect to be able to find $K(\mathrm{T}_1)$, A and C, but that another piece of information is needed to find B. It turns out that a convenient way to do this is to use the matrices for $^1\mathrm{P}_0$ and $^3\mathrm{P}_1$ which are closely related to those for $^2\mathrm{P}_{1/2}$ and $^2\mathrm{P}_{3/2}$ respectively. As we now have four matrices for the three unknowns A, B and C we can check the correctness of the calculations.

First we look at the related structures of the $^2P_{1/2}$ and $^3P_0$ matrices. After coupling the P state to the vibrations, but before introducing the spin, the coupled states exist in sets corresponding to $L = 1$, $L = 2$ etc (no $L = 0$) (O'Brien 1971, 1976). To couple in a spin of 1/2 to get a resultant $j = 1/2$ only the $L = 1$ states are needed; likewise a spin of 1 can only give $j = 0$ when coupled to the $L = 1$ states. Consequently there is an exact correspondence between these two matrices, with the only difference being in the matrix elements of the operator $\lambda \boldsymbol{l} \cdot \boldsymbol{S}$. As was described previously the basis states of $L = 1$ derive from phonon states of angular momentum 0 or 2 coupled to the original p state, and the matrix elements are found by using appropriate vector coupling formulae. When we do this for $^3P_0$ and compare it with $^2P_{1/2}$ we find that the only difference is that λ is replaced by 2λ, so in fact no new calculations need be done.

The related structures of the $^2P_{3/2}$ and $^3P_1$ matrices are slightly more complicated. To couple a spin of 1/2 to get $j = 3/2$ we need both the $L = 1$ and $L = 2$ states, the $L = 2$ states derive from phonon states of angular momentum 2 and 3, so our matrix will contain two sorts of $L = 2$ states as well as two sorts of $L = 1$ states, and this means there are five different sorts of matrix element of $\lambda \boldsymbol{l} \cdot \boldsymbol{S}$ to be worked out using vector coupling theory. This was done for the calculations described in O'Brien (1976) . To couple a spin of 1 to get $j = 1$ we also need both the $L = 1$ and $L = 2$ states and no more. Consequently the $^3P_1$ matrix only differs from the $^2P_{3/2}$ matrix because matrix elements of $\lambda \boldsymbol{l} \cdot \boldsymbol{S}$ will be different, though they will occur in the same places. It is consequently very easy to convert the one matrix into the other, and this is what has been done.

3.2. Numerical work for $T \otimes (\tau_2 + \epsilon)$

Each of the matrices described above was set up and diagonalised, using the Lanczos routine for sparse matrices as usual. As we only need look for the lowest eigenvalue this routine runs extremely quickly to produce a very accurate eigenvalue. In order to pick out the perturbations to first and second order in λ the eigenvalue was calculated for five or more different small values of λ clustering round zero, and the energy was fitted to a polynomial in λ, and this was done for a variety of different Jahn–Teller coupling strengths.

In order to interpret the results we need the following table of second-order terms

$$\begin{aligned}
&\text{for } ^2P_{1/2} \qquad \mathcal{H}_2 = \lambda^2(-A + \tfrac{3}{2}C) \\
&\text{for } ^2P_{3/2} \qquad \mathcal{H}_2 = \lambda^2(\tfrac{1}{2}A + \tfrac{3}{2}C) \\
&\text{for } ^3P_0 \qquad \mathcal{H}_2 = \lambda^2(-2A + \tfrac{5}{3}B + 4C) \\
&\text{for } ^3P_1 \qquad \mathcal{H}_2 = \lambda^2(-A - \tfrac{5}{6}B + 4C) \\
&\text{for } ^3P_2 \qquad \mathcal{H}_2 = \lambda^2(A + \tfrac{1}{6}B + 4C) .
\end{aligned} \tag{6}$$

The relationship between $^2P_{1/2}$ and $^3P_0$ gives the simple equation

$$-2A + \tfrac{5}{3}B + 4C = 4(-A + \tfrac{3}{2}C) . \tag{7}$$

Using this to eliminate B gives the second-order terms for the triplet states as

$$\begin{aligned}
&\text{for } ^3P_0 \qquad \mathcal{H}_2 = \lambda^2(-4A + 6C) \\
&\text{for } ^3P_1 \qquad \mathcal{H}_2 = \lambda^2(C) \\
&\text{for } ^3P_2 \qquad \mathcal{H}_2 = \lambda^2(\tfrac{4}{5}A + \tfrac{21}{5}C) .
\end{aligned} \tag{8}$$

The procedure used was to run the doublet matrices to get values of A and C, and then to run the $^3P_1$ matrix to check that the same value of C was obtained. The results are plotted in figure 1(*c*). against k, where $k^2 = (3/2)E_{JT}$ and the classical Jahn–Teller energy is $\hbar\omega E_{JT}$. (This scale is chosen for k so as to be easily compared with the other results.) As can be seen, we agree with Dunn and Bates (1989) in finding the second-order terms smaller than at unequal coupling, though we do not find such a marked effect. We do find B and C dominate A and $K(T_1)$ at large coupling, so as with the other two cases there is a pattern of energy levels that only depends on the coupling being strong enough.

4. Theory and numerical work for $T \otimes \tau_2$

Although this system only involves threefold degeneracy of the vibrations as compared with the fivefold degeneracy in the previous case, it is actually more difficult to handle because of the lack of an extra, accidental symmetry. The first numerical work over the range of coupling strengths by Caner and Englman (1966) was not improved on for a long time because, in order to produce symmetry-adapted wave functions, it used a tabulation of spherical harmonics that could not be generalised. Sakamoto and Muramatsu (1978) devised and used a method of setting up the matrices without using symmetry-adapted wave functions, at the expense of having much larger matrices. Sakamoto (1980) extended this calculation to include angular momentum operators, and his method is the one that will be followed here. This method produces large, real matrices which are diagonalised using the Lanczos process, and computing times remain reasonable in this study, because we are only interested in the energies of the lowest states.

The Sakamoto method uses a set of basis states which can be written

$$|\mathrm{p}, n_1, n_2, n_3, s_z, \pm 1\rangle \tag{9}$$

where p is one member of the T triplet, (x, y, z), and these p states are real; n_1, n_2 and n_3 are the number of excitations in each of the three components of the τ_2 vibrational state, and s_z is the spin component ($s = 1/2$ is assumed). The final parameter, ± 1, is an index that doubles the number of bases so as to change a complex Hermitian matrix into a real symmetric one. If the actual matrix is $\mathcal{A} = \mathcal{B} + \mathrm{i}\mathcal{C}$, in terms of real matrices, then we look for the eigenvalues of the real symmetric matrix

$$\mathcal{D} = \begin{pmatrix} \mathcal{B} & -\mathcal{C} \\ \mathcal{C} & \mathcal{B} \end{pmatrix}. \tag{10}$$

This matrix has the same eigenvalues as $\mathcal{A}$, but each appears twice (Sakamoto 1980). The Lanczos method automatically picks out one of a set of degenerate eigenvalues.

As before, the matrix was set up and diagonalised for a variety of different Jahn–Teller coupling strengths and the operator $\lambda \boldsymbol{l} \cdot \boldsymbol{S}$ was included for several small values of λ. The two lowest energies were then fitted to polynomials in λ, and from the coefficients in the polynomials the quantities $K(T_1)$, A and C could be deduced. The starting vector of the Lanczos process was chosen so that both of the two lowest levels appeared in the result. Since $S = 1/2$ these matrices will not give us B_E or B_T. The large size of this matrix, even for a moderate phonon excitation number, made it difficult to run reliably at the higher coupling strengths. It was necessary to check

for truncation errors by cautiously increasing the number of phonon excitations and seeing whether the results changed.

Because of the problem of matrix size it did not seem sensible to work with $S = 1$, as was done for $T \otimes (\tau_2 \oplus \epsilon)$, but instead the orbital operator, l, was introduced without the spin. For this new calculation the basis states were

$$|p, n_1, n_2, n_3, \pm 1\rangle \tag{11}$$

so for a given level of phonon excitation the matrix was half the size. Two different operators were used: l_z and $l_x + l_y + l_z$. Using the same sort of polynomial analysis as before, the first operator gives us $K(T_1)$, B_E and C, and the second one gives us $K(T_1)$, B_T and C, and clearly the duplication of the parameters calculated gives an extra check on the results, which are plotted in figure 1(*d*).

A final layer of the calculation was undertaken in order to calculate the other first-order reduction factors as well as the tunnelling splitting. For these the operators are real, so the Sakamoto duplication device could be abandoned, and the basis states were just

$$|p, n_1, n_2, n_3\rangle . \tag{12}$$

Two different operators were used, one E-type and one T_2-type, and the starting vector was chosen so that the first excited singlet state appeared as well as the ground triplet. For the calculation of $K(E)$ and $K(T_2)$ the polynomial fit method was again used, but with these smaller matrices it was easier to push up the coupling strength, and the results are also shown in figure 1(*d*).

The second-order reduction factors become important at moderately strong coupling where they outweigh the effect of $K(T_1)$. Here the important result is that $|B_T| \gg |B_E|$, which agrees with Bates and Dunn (1989), and enables the pattern of zero-phonon line splittings to be predicted unambiguously. The quantity C which is also large has no effect on the splittings. Our results differ somewhat from Bates and Dunn (1989) and Dunn *et al* (1990), though the overall pattern is still remarkably similar. A comparison of the different results for B_T, $K(T_1)$ and $K(E)$ is shown in figure 2.

Our values for the first-order reduction factors confirm the results of Caner and Englman (1966) in particular showing $K(T_2)$ approaching 2/3 from below, and showing $K(E)/K(T_1) > 1$ with the ratio increasing with increasing coupling strength. This latter inequality was shown by Ham (1990) to be associated with the different effects of the adiabatic approximation on these two factors, and it was not so large in the approximation used by Dunn and Bates.

One reason for finding better numerical values of the first-order reduction factors was to look at the prediction of Leung and Kleiner (1974). These authors showed that the quantity

$$3f(T_1) = 1 - \tfrac{3}{2}(K(T_2) - K(T_1)) - K(E) \tag{13}$$

was either very small and positive or zero over the whole range of coupling strengths. $3f(T_1)$ was previously calculated by Sakamoto and Muramatsu (1978), and we agree closely with them in finding it small and rising up to a maximum at about $k_\tau = 3$, after which we find it starts to fall again (see table 1).

The value of $K(T_2)$ in strong coupling can also be compared with the prediction by Ham (1990) that $\frac{2}{3} - K(T_2) \rightarrow \text{constant}/k_\tau^2$. Using Ham's calculation and allowing

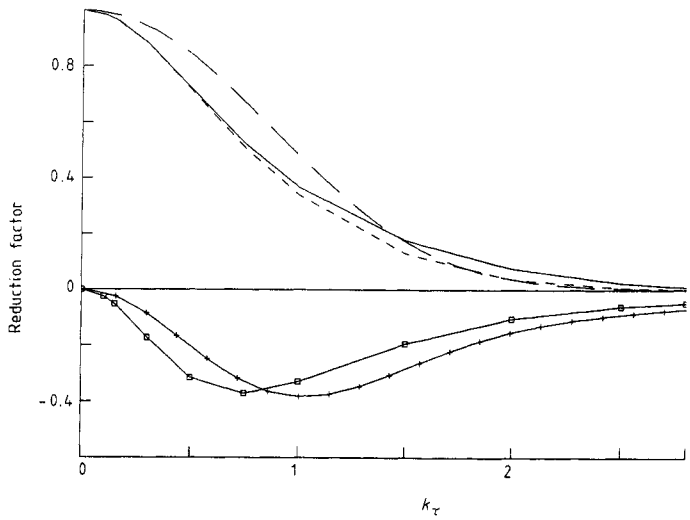


Figure 2. A comparison of Bates and Dunn (1989) and Dunn *et al* (1990) and this work. — — — = $K(T_1) = K(E)$ from Bates and Dunn. + − + − + = B_T from Dunn *et al*. —— = $K(T_1)$, − − − = $K(E)$, and □–□–□ = B_T from this work.

Table 1. Values of first-order reduction factors.

k_τ	$K(T_2)$	$K(T_1)$	$K(E)$	$3f(T_1)$
0.5	0.90209	0.71600	0.72085	$<10^{-4}$
0.75	0.82596	0.50863	0.54200	$<10^{-4}$
1	0.76097	0.33977	0.36817	$<10^{-4}$
1.5	0.67867	0.13040	0.17695	6.46×10^{-4}
2	0.65020	0.03797	0.07713	4.53×10^{-3}
2.5	0.6492	0.00729	0.01448	1.27×10^{-2}
2.8	0.6517	0.00219	0.00970	1.60×10^{-2}
3	0.6532	0.0001	0.0048	1.69×10^{-2}
3.4	0.6562		0.00095	$<1.62 \times 10^{-2}$
3.8	0.6580			$<1.30 \times 10^{-2}$

in addition for the spheroidal symmetry of the trigonal wells we find the constant in this expression to be $(1/4)/(6)^{1/2}$, and this is consistent with the numerical results. On the other hand $K(E)$ approaches zero by something like a $1/k_\tau^6$ law.

5. Approximate values of the second-order reduction factors

5.1. Small k

The values of the second-order reduction factors at small coupling strengths are calculated using perturbation theory. It turns out that to get these factors to order k^2 it is only necessary to include corrections to the states to first order in k. To this order the admixtures of excitations of different normal modes are independent, so the reduction factors for $T \otimes \tau$ and $T \otimes \epsilon$ add up to give those for $T \otimes (\tau \oplus \epsilon)$. They are shown in table 2. These results are of no importance experimentally as the effect of the spin–orbit coupling at second order is swamped by the first-order term at weak

coupling, but they provide a useful check of results found by other methods. In particular they are fitted by the numerical results. The results for $T \otimes \tau$ have been given by Polinger (1989), and those for $T \otimes \epsilon$ can be derived from Ham's formulae (1965).

Table 2. Second-order reduction factors at weak coupling.

	A	B_E	B_T	C
$T \otimes \tau$	$\frac{3}{4}k^2$	$-\frac{3}{2}k^2$	$-\frac{5}{2}k^2$	$-k^2$
$T \otimes \epsilon$	$\frac{1}{2}k^2$	$-2k^2$	$-k^2$	$-\frac{2}{3}k^2$
$T \otimes (\tau \oplus \epsilon)$	$\frac{5}{4}k^2$	$-\frac{7}{2}k^2$	$-\frac{7}{2}k^2$	$-\frac{5}{3}k^2$

5.2. Large k

To find the asymptotic forms of the reduction factors for large k we start by writing the basis for the lowest adiabatic potential energy surface as

$$(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta) \tag{14}$$

and finding the expectation values of the various operators in this state, as was done for $K(E)$ and $K(T_2)$ in O'Brien (1969). For the second-order reduction factors there is no diagonal expectation value, but there is a contribution in second-order perturbation from the coupling between the different APES. In this approximation the energy difference between the APES is $2k^2$ at the relevant point in phase space, while the θ, ϕ form of the operator is closely related to the operators for $K(E)$ and $K(T_2)$. The result is the set of asymptotic values shown in table 3, which are well fitted by the numerical values at large k. The results for $T \otimes \tau$ agree with Polinger (1989), and those for $T \otimes \epsilon$ with Ham (1965). Values of the asymptotic reduction factors arising from other mixtures of coupling strengths can be deduced from the values of $K(T_2)$ and $K(E)$ in O'Brien (1969).

Table 3. Second-order reduction factors at strong coupling.

	A	B_E	B_T	C	$B_T^{A,T}$
	0	$K(E)/2k^2$	$K(T_2)/2k^2$	$1/6k^2$	$\langle A\|\|T_2\|\|T\rangle/2k^2$
$T \otimes \tau$		$K(E) = 0$	$K(T_2) = 2/3$		$\langle A\|\|T_2\|\|T\rangle = 1/\sqrt{3}$
$T \otimes \epsilon$		$K(E) = 1$	$K(T_2) = 0$		
$T \otimes (\tau \oplus \epsilon)$		$K(E) = 2/5$	$K(T_2) = 2/5$		

Another effect that comes in at strong coupling is the coupling of the singlet, A, state to the ground triplet. This must be included when the tunnelling splitting becomes comparable to the second-order spin–orbit coupling. The asymptotic value of the cross-term can be calculated in exactly the same way as the other asymptotic values, and is shown in the last column of the table. It is mainly relevant for $T \otimes \tau$. The value of $B_T^{A,T}$ can be extracted from our numerical work, with some difficulty. Where k is large the result agrees with the asymptotic formula, and its value at smaller k is unimportant.

As the coupling strength moves from being purely $T\otimes\tau$ to $T\otimes(\tau\oplus\epsilon)$ the asymptotic tunnelling splitting becomes greater, until at equal (strong) coupling the level splittings go as $1/k^2$ (O'Brien 1969), but there are many more of them, and consequently more second order reduction factors to be considered. They could be found by vector coupling methods, but seem too unlikely to be needed to be worth tabulating here.

6. Tunnelling splitting in $T\otimes\tau$

One quantity looked at was the tunnelling splitting, the energy difference between the lowest triplet state and the first excited singlet state, and in particular we tried to find an asymptotic form for this splitting at strong coupling. For this purpose the calculation was pushed to the point where this splitting, Δ, was $\sim 10^{-7}$, at which point the matrix size needed for convergence was $\sim 70\,000 \times 70\,000$ and the computation became difficult. We tried to find the best values of a, b and c to fit the splitting to the relation

$$\log(\Delta) \approx a + b\log(k_\tau) + ck_\tau^2 \tag{15}$$

where k_τ is the coupling strength, which is related to the Jahn–Teller energy by $E_{JT} = \frac{2}{3}k_\tau^2$. As a, b and c may themselves vary with k_τ, this was done by a simple linear fitting of this formula to three successive values of Δ and k_τ. The results are shown in table 4.

Table 4. Tunnelling splitting and fitting parameters.

k_τ	Δ	a	b	c
1.5	3.11×10^{-1}			
2	1.386×10^{-1}	−0.167	1.049	−0.634
2.5	4.206×10^{-2}	−0.425	1.920	−0.721
2.8	1.663×10^{-2}	−0.517	2.116	−0.735
3	8.207×10^{-3}	−0.468	2.029	−0.729
3.4	1.635×10^{-3}	−0.385	1.903	−0.723
3.6	6.625×10^{-4}	−0.280	1.763	−0.717
3.8	2.520×10^{-4}	−0.199	1.664	−0.714
4	9.014×10^{-5}	−0.102	1.549	−0.710
4.4	9.614×10^{-6}	−0.027	1.470	−0.708
4.7	1.534×10^{-6}	+0.126	1.319	−0.704
5	2.145×10^{-7}			

As can be seen we seem to have a fit with a $\Delta \sim 0.7E_{JT}\exp(-1.1E_{JT})$ law in the neighbourhood of $k_\tau = 3$, but there is a shift to a lower power of k_τ in the prefactor as the coupling gets stronger, and a more sophisticated computation is needed to get a true asymptotic form.

A discussion of methods of calculating this quantity analytically is given by Bersuker and Polinger (1989), and by O'Brien (1989). A simple overlap method gives

$$\Delta \propto E_{JT}\exp(-1.24E_{JT}) \tag{16}$$

which is clearly too small, while a calculation by Polinger (1974), which includes the calculation of a tunnelling integral, gives

$$\Delta \approx \frac{4}{2\pi}(\tfrac{2}{3})^{1/2}\exp(-0.73E_{JT}) \tag{17}$$

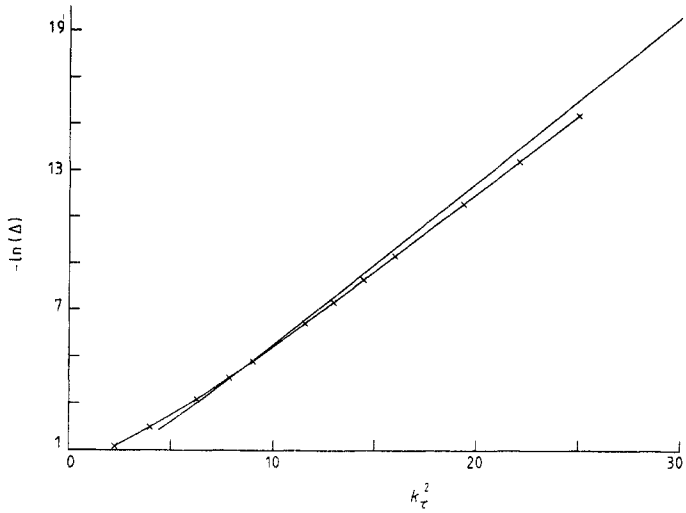


Figure 3. Log of tunnelling splitting plotted against k_τ^2: —— = Polinger (1990), x – x – x = numerical.

which looks like being too large, asymptotically. O'Brien (1989) suggests a

$$\Delta \propto k_\tau \exp(-ck_\tau^2) \tag{18}$$

law, without predicting a value of c. More recently Polinger (1990) has recalculated the splitting, using numerical integration of the WKB theory, and produced the result shown in figure 3. The points between $k = 2$ and $k = 8$ fit well to $a = 0.578$, $b = 1.070$ and $c = -0.732$, or

$$\Delta = 1.78k_\tau^{1.07} \exp(-0.732k_\tau^2) \tag{19}$$

and figure 3 shows this result as remarkably similar to the numerical ones.

7. The zero-phonon line in $T \otimes \tau$

The intensity of the zero-phonon line in $T \otimes \tau$ can be found immediately from our matrix calculations, and is shown in table 5 for a variety of values of k_τ. In vibronic bands without Jahn–Teller coupling this intensity is well known to be $\exp(-S)$ where S, the Huang–Rees factor, is the energy of the zero-phonon level below the uncoupled state. The analogue in the case of a Jahn–Teller system would be to have an intensity of $\exp(-E_{JT})$, but in these systems there are usually geometric effects which alter this simple rule. As can be seen from the table our numerical results suggest that at strong coupling the intensity is tending to something like $1.76\exp(-E_{JT})$, where the numerical coefficient is changing rather little. Since, to the author's knowledge, this intensity has not been calculated before, we present the calculation that follows.

We start by remarking that at strong coupling the vibronic wave function for $T \otimes \tau$ is isolated in a set of wells that are localised in the vibrational phase space by the formation of minima in the lowest adiabatic potential energy surface. As all these wells are related by symmetry we can start by concentrating on the overlap of the uncoupled ground state with one of them. We accordingly consider the well in the

(1, 1, 1) direction in the space of the three vibrational coordinates, and make a suitable choice of basis and simultaneously rotate and displace the axes so that the Jahn–Teller interaction matrix and potential energy that started by looking like

$$\tfrac{1}{2}(X^2+Y^2+Z^2)+k_\tau\begin{pmatrix}0 & Z & Y\\ Z & 0 & X\\ Y & X & 0\end{pmatrix} \tag{20}$$

ends up looking like

$$\tfrac{1}{2}(X^2+Y^2+Z^2)+k_\tau\begin{pmatrix}Z\sqrt{3}-Y\sqrt{\frac{2}{3}} & X\sqrt{\frac{2}{3}} & Y/\sqrt{3}\\ X\sqrt{\frac{2}{3}} & Z\sqrt{3}+Y\sqrt{\frac{2}{3}} & X/\sqrt{3}\\ Y/\sqrt{3} & X/\sqrt{3} & 0\end{pmatrix}$$
$$+\begin{pmatrix}\frac{4}{3}k_\tau^2 & 0 & 0\\ 0 & \frac{4}{3}k_\tau^2 & 0\\ 0 & 0 & -\frac{2}{3}k_\tau^2\end{pmatrix} \tag{21}$$

where X, Y, Z are measured from the position of the $1, 1, 1$ minimum, which is at a distance $(2/\sqrt{3})k_\tau$ from the origin along the new Z direction.

We now need the effective potential energy in the neighbourhood of this minimum, and to get it we use perturbation theory as far as the third order on the Jahn–Teller matrix, noticing that the energy to go in the denominators is $2k_\tau^2$. The result is a potential energy

$$V=\tfrac{1}{2}(X^2+Y^2+Z^2)-\frac{1}{6}(X^2+Y^2)+\frac{1}{4k_\tau\sqrt{3}}(X^2+Y^2)Z+\frac{1}{24k_\tau\sqrt{6}}(3X^2Y-Y^3). \tag{22}$$

The first two terms together give a harmonic potential of the form $\frac{1}{2}Z^2+\frac{1}{3}(X^2+Y^2)$, so to this approximation the states are harmonic oscillator states with a frequency 1 in the Z direction and a frequency $\alpha=\sqrt{(2/3)}$ in the X and Y directions. The uncoupled state is just a three-dimensional harmonic oscillator of frequency 1 at the origin of coordinates, and the overlap with the distorted oscillator states centred at $Z=(2/\sqrt{3})k_\tau$ is obtained straightforwardly as

$$\frac{2\sqrt{\alpha}}{1+\alpha}\exp(-\tfrac{1}{3}k_\tau^2) \tag{23}$$

where the exponential is the usual term coming from the overlap of oscillators with centres displaced by $(2/\sqrt{3})k_\tau$.

We next look at the third-order term proportional to $(X^2+Y^2)Z$, and notice that it has the effect of shifting the distorted well nearer to the origin on average. Although this term only enters to order $1/k_\tau$, it will alter the overlap by a factor of order one because of the exponential variation of the overlap with distance. To calculate this extra overlap we need a solution of the Schrödinger equation that is valid to order $1/k_\tau$, and must avoid the lack of convergence resulting from the fact that the potential becomes negative when $Z(X^2+Y^2)$ or $(3X^2Y-Y^3)$ becomes large and negative. We do this by putting in a trial solution, and forcing the constants in it so that it becomes a solution to the required order. The trial solution is

$$\psi=\frac{\alpha^{1/2}}{\pi^{3/4}}\{\exp[-\tfrac{1}{2}(Z+\beta(X^2+Y^2)+\gamma)^2-\tfrac{1}{2}\alpha(X^2+Y^2)]\}[1-\mu(3X^2Y-Y^3)] \tag{24}$$

which is to be a solution to first order in β, γ and μ, and is normalised to the same order. The partial differentials of this are

$$\partial\psi/\partial Z = [-Z + \beta(X^2 + Y^2) + \gamma]\psi \tag{25}$$

$$\partial^2\psi/\partial Z^2 = -\psi + [Z + \beta(X^2 + Y^2) + \gamma]^2\psi \tag{26}$$

that is

$$\partial^2\psi/\partial Z^2 \approx [-1 + Z^2 + 2Z\beta(X^2 + Y^2) + 2Z\gamma]\psi \tag{27}$$

$$\partial\psi/\partial X = \{-\alpha X - 2\beta X[Z + \beta(X^2 + Y^2) + \gamma]\}\psi - 6\mu XY\psi \tag{28}$$

that is

$$\partial\psi/\partial X \approx (-\alpha X - 2\beta XZ - 6\mu XY)\psi \tag{29}$$

and

$$\partial^2\psi/\partial X^2 \approx (-\alpha - 2\beta Z - 6\mu Y)\psi + (-\alpha X - 2\beta XZ - 6\mu XY)^2\psi \tag{30}$$

that is

$$\partial^2\psi/\partial X^2 \approx (-\alpha + \alpha^2X^2 - 2\beta Z + 4\alpha\beta X^2Z - 6\mu Y + 12\alpha\mu X^2Y)\psi \tag{31}$$

which, with a similar result for the Y derivatives, gives

$$\nabla^2\psi \approx (-1 - 2\alpha + Z^2 + \alpha^2(X^2 + Y^2) + (2 + 4\alpha)\beta Z(X^2 + Y^2) + (2\gamma - 4\beta)Z + 6\mu(3X^2Y - Y^3))\psi \tag{32}$$

Substituting this into the Schrödinger equation shows that this trial wave function is a solution of energy $\frac{1}{2}(1 + 2\alpha)$ in a potential

$$V = \tfrac{1}{2}(Z^2 + \alpha^2(X^2 + Y^2)) + (1 + 2\alpha)\beta(X^2 + Y^2)Z + 6\alpha\mu(3X^2Y - Y^3) + (\gamma - 2\beta)Z \tag{33}$$

which can be made the same as the potential (3) by putting

$$\gamma = 2\beta \tag{34}$$

$$\beta = \frac{1}{(1 + 2\alpha)4k_\tau\sqrt{3}} \tag{35}$$

$$\mu = \frac{1}{144\alpha k_\tau\sqrt{6}} \tag{36}$$

and this result is correct to order $1/k_\tau$.

We must now calculate the overlap of this wave function with the uncoupled harmonic oscillator wave function centred at the origin, which is, in these coordinates

$$\psi_0 = \frac{1}{\pi^{3/4}}\exp\left[-\frac{1}{2}\left(Z + \frac{2}{\sqrt{3}}k_\tau\right)^2 - \frac{1}{2}(X^2 + Y^2)\right] \tag{37}$$

To work out the overlap integral we rearrange the terms in the exponent to the form, correct to order $1/k_\tau$, as follows

$$\psi\psi_0 = \frac{\alpha^{1/2}}{\pi^{3/2}}\left\{\exp\left[-\frac{1}{3}k_\tau^2 + \frac{2}{\sqrt{3}}k_\tau\beta - \left(Z + \frac{1}{2}\beta(X^2 + Y^2 + 2) + \frac{1}{\sqrt{3}}k_\tau\right)^2 - \frac{1}{2}\left(1 + \alpha - \frac{2}{\sqrt{3}}k_\tau\beta\right)(X^2 + Y^2)\right][1 - \mu(3X^2Y - Y^3)]\right\}. \tag{38}$$

In this form the integral over Z is of standard Gaussian type, and can be done immediately. In integrating over X and Y we notice that the term in μ integrates out to zero. The final result of these manoeuvres is to get the overlap in the form

$$S_{\text{vib}} =< \psi\psi_0 >= \frac{2\alpha^{1/2}}{1+\alpha-2/\sqrt{3}k_\tau\beta} \exp\left(-\tfrac{1}{3}k_\tau^2 + \frac{2}{\sqrt{3}}k_\tau\beta\right) \tag{39}$$

which is somewhat larger than the overlap in (4).

We must next allow for the overlap of the *electronic* wave functions. Suppose the electronic wave function in the uncoupled state is $(1,0,0)$ in the original basis. After the change of basis and rotation used to produce equation (2), the basis for the lowest state at the bottom of the well is $(1/\sqrt{3})(1,1,1)$ so the overlap of the electronic states contributes a factor $1/\sqrt{3}$. In principle we should also allow for the change in the electronic basis over the well, but it can be seen that the admixtures to order $1/k_\tau$ integrate out, so this only comes into the overlap to order $1/k_\tau^2$.

Table 5. Zero-phonon line intensities.

k_τ	Intensity	$\exp(-\frac{2}{3}k_\tau^2)$	Intensity/$\exp(-\frac{2}{3}k_\tau^2)$
3	4.5636×10^{-3}	2.4787×10^{-3}	1.8411
4	4.1771×10^{-5}	2.3309×10^{-5}	1.7921
5	1.0232×10^{-7}	5.7777×10^{-8}	1.7709
6	6.6494×10^{-11}	3.7709×10^{-11}	1.7614

So far we have got the overlap of the uncoupled state with a ground state in one of the wells that appear in the lowest APES of the strongly coupled $\mathrm{T}\otimes\tau$ system. At this point it is necessary to allow for the variation of the phase over this lowest APES, and we do it following O'Brien (1989) by a mapping that doubles the space. Using that mapping we have eight wells at the vertices of a cube, and the lowest states are linear combinations of the lowest state in each well that have $\mathrm{T}_{1\mathrm{u}}$ and $\mathrm{A}_{2\mathrm{u}}$ symmetry. After the signs of the electronic overlaps have been allowed for, the only state with a non-zero overlap to the $(1,0,0)$ uncoupled state is the T_{1ux} state, as might be expected from the symmetry. For all other states the overlaps to the eight wells cancel, but for this state they all have the same sign and add up to give an overlap

$$\frac{1}{\sqrt{3}}\frac{8}{\sqrt{8}}S_{\text{vib}} \tag{40}$$

where the factor $1/\sqrt{8}$ allows for the normalisation of the T_{1ux} linear combination in the approximation we are working in. A final numerical factor must be included to adjust the normalisation of the uncoupled state. It must now be normalised over the doubled space, which introduces a further factor $1/\sqrt{2}$ into the overlap.

It only remains to put in the values already obtained for α and β and square the overlap to get the zero-phonon line intensity as

$$\tfrac{4}{3}S_{\text{vib}}^2 = 1.607\,95\exp(-\tfrac{2}{3}k_\tau^2)\,. \tag{41}$$

Comparison with table 5 shows a small but significant discrepancy between this result and the result of the numerical calculations.

8. Conclusion

The mixture of numerical and analytical methods described in this paper suffice to show how the various reduction factors change with relative and absolute coupling strengths, and the variation of these parameters between the different styles of Jahn–Teller coupling should produce recognisably different patterns, from which something about the coupling could be deduced. Apart from the differences between B_{E} and B_{T}, it is worth noticing the difference too between the rates at which $K(\mathrm{T}_1)$ is approaching zero in the different coupling regimes. In particular for $\mathrm{T} \otimes \epsilon$ there is a substantially larger range of coupling strengths for which the second-order term dominates the first-order one.

The result on the tunnelling splitting underlines the difficulty of getting the asymptotic form for it numerically, but the agreement with the WKB calculation is encouraging. The remaining small difference may be related to the proximity of other potential energy surfaces (Polinger 1990).

The small difference between the numerical and analytic forms for the zero-phonon line intensity may be due to the use of perturbation theory in an inappropriate region.

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