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The Jahn–Teller band shape for an $^nS \rightarrow ^nP$ transition: a 'universal' band shape for magnetic circular and linear dichroism

M C M O'Brien

Department of Theoretical Physics, University of Oxford, 1 Keble Road, Oxford OX1 3NP, UK

Abstract. This paper extends the calculations for the $^2S \rightarrow ^2P$ band shape with degenerate and equally coupled τ_2 and ε vibrations to be usable for any spin as long as the spin–orbit coupling is sufficiently small compared with the Jahn–Teller coupling. It turns out that the similarity between the calculations for states of different spins is such that the only numerical calculations that need to be made are those for the doublet states, for which the matrices are already set up and the techniques established.

1. Introduction

Measurements of absorption and magnetic circular dichroism (MCD) spectra of the $^2S \rightarrow ^2P$ transitions for a variety of impurity atoms in noble-gas matrices over the years have provided a rich source of Jahn–Teller-dominated profiles (Zeringue *et al* 1983, Lund *et al* 1984, Vala *et al* 1984, Rose *et al* 1986, Samet *et al* 1989). These have been very well matched by theoretical profiles based on a model that assumes equal coupling to a set of five vibrational modes of τ_{2g} and ε_g symmetry, with these modes having the same frequency (O'Brien 1985, Rose *et al* 1986, Samet *et al* 1989). The fit is best when the vibrational frequency is taken to be as small as possible relative to the Jahn–Teller energy, and this condition together with the equal coupling can be taken to mean that the surroundings of the ion are behaving like a soft elastic continuum. The broadening resulting from coupling to symmetric modes of vibration is usually small compared with the Jahn–Teller band width, enabling the Jahn–Teller profile to be particularly well resolved. In this strong-coupling regime the cluster (single-frequency) approximation is particularly good, but the method of calculation by numerical diagonalisation of large matrices gets much more difficult as the coupling strength increases.

All the calculations done so far are for singlet and doublet spin states and, if states of higher spin were to be tackled in the same way, the matrices to be diagonalised would be very much larger. For this reason a method of calculating band shapes is proposed here that can predict those of higher spin on the basis of calculations for $S = \frac{1}{2}$ only. This works if the spin–orbit coupling is weak compared with the Jahn–Teller coupling and results in 'universal' band shapes that are independent of spin. These calculations were prompted by work by Rivoal and his collaborators (Rivoal and Vala 1987, Vala *et al* 1987, Rivoal 1988) on systems that satisfy these criteria, and for which the band shapes

can be very nicely fitted. For these higher spins it is also possible to get another band shape by measuring the magnetic linear dichroism (MLD), and that band shape is also calculated in what follows.

2. Moments analysis of MCD and MLD

The method of moments has been very widely used for 20 years or so for extracting information from band shapes, and the theory has been discussed elsewhere, but that is not what we need it for here. We shall use it only to show the equivalence of band shapes for different spins by showing that all the moments can be related by a constant factor and shall derive only as much of the theory as is needed for that purpose.

The method uses the fact that, if a transition is allowed into an uncoupled state, $|0\rangle$, which is coupled to a set of states by a Hamiltonian $\mathcal{H}$, then the nth moment of the band about the uncoupled energy of $|0\rangle$ is given by

$$\mu_n = \langle 0 | \mathcal{H}^n | 0 \rangle. \tag{1}$$

For an $^nS \rightarrow {}^nP$ transition the state $|0\rangle$ is whichever component of the P state is produced from the S state by the particular polarisation of light being used. An average has to be taken over the spin multiplicity of the ground state; so

$$\mu_n = \text{Av}(S_z) \langle 0, S_z | (\mathcal{H}_{\text{ph}} + \mathcal{H}_{\text{JT}} + \zeta l \cdot S)^n | 0, S_z \rangle. \tag{2}$$

Now the MCD is zero if $\zeta = 0$; so, for the MCD band shape for small ζ, we must pick terms with a single power of $l \cdot S$ and, as this is the only part of the Hamiltonian that operates on the spin variable, we can replace $l \cdot S$ by $l_z S_z$ and get

$$\mu_n = \langle S_z \rangle_{\text{Av}} \zeta \langle 0 | \mathcal{P} [l_z (\mathcal{H}_{\text{ph}} + \mathcal{H}_{\text{JT}})^{n-1}] | 0 \rangle \tag{3}$$

where the operator $\mathcal{P}$ permutes the factors. The importance of this result is not in a direct calculation of the moments, which is an intractable problem, but in showing that all these MCD moments are related to each other by the factor $\zeta \langle S_z \rangle_{\text{Av}}$, and so, to first order in ζ, the shape of all the MCD bands can be derived from the one most easily calculated, that for $S = \frac{1}{2}$.

For the MLD we have to carry this process to second order in ζ, because the contribution to first order in ζ is zero. To work this out we must be more specific about the state labelled $|0, S_z\rangle$ in equation (2). For the MLD, two measurements are taken: one with polarisation such that the electric vector is along the magnetic field which provides the quantisation for S_z, and the other with it perpendicular. Consequently we can write

$$\mu_n = \text{Av}(S_z) [\langle z, S_z | (\mathcal{H}_{\text{ph}} + \mathcal{H}_{\text{JT}} + \zeta l \cdot S)^n | z, S_z \rangle - \langle x, S_z | (\mathcal{H}_{\text{ph}} + \mathcal{H}_{\text{JT}} + \zeta l \cdot S)^n | x, S_z \rangle] \tag{4}$$

where $|x\rangle$ and $|z\rangle$ are real P states. The terms linear in ζ can be seen to be zero because the P states are real and l is a purely imaginary operator. The non-zero ζ^2 terms must come from operator products such as $l_x l_x$ that are diagonal in the real P states, and not from products such as $l_x l_y$ that are not. This determines which parts of the $(l \cdot S)^2$ operator must be used and means effectively that the average over spins must be a linear combination of $\langle S_x^2 \rangle_{\text{Av}}$, $\langle S_y^2 \rangle_{\text{Av}}$ and $\langle S_z^2 \rangle_{\text{Av}}$. These averages are related to each other, and the linear combination that goes to zero in zero applied field is $\langle S(S + 1) - 3S_z^2 \rangle_{\text{Av}}$. Once this part of μ_n has been extracted, what remains of the ζ^2 part is independent of S; so there is a universal band shape for the MLD just as there is for the MCD. This band has

no zeroth or first moment. We cannot find it as directly as we can the MCD because $\langle S(S + 1) - S_z^2 \rangle_{Av}$ goes to zero in the $S = \frac{1}{2}$ states.

3. Band shapes for small ζ

Because the spin–orbit coupling is small, the appropriate coupling scheme to use is one in which the orbital P states are first coupled to the phonon states and suitably symmetrised to produce states which are classified by an angular momentum quantum number. These vibronic states are labelled D_n in what follows, where n is the aforesaid angular momentum quantum number. This scheme was used by O'Brien (1976, hereafter referred to as I) and it was shown there that all integral angular momentum quantum numbers appear except zero. It is the states with $L = 1$ that contain the uncoupled P state, and consequently contribute to the allowed S $\to$ P transition. We next couple in the spin to get states of total angular momentum J, and find these occur as follows:

$$S \otimes D_1 : J = S + 1 \qquad S \qquad S - 1$$

$$S \otimes D_2 : J = S + 2 \qquad S + 1 \qquad S$$

$$S \otimes D_3 : J = S + 3 \qquad S + 2 \qquad S + 1$$

$$\cdots\cdots$$

(For the special case $S = \frac{1}{2}$ the last column is missing.) The simplest set of states will be for $J = S - 1$, which contains only D_1 vibronic states in its basis. Reference to I shows that these derive from vibrational states of two different angular momenta, 0 and 2. The matrix elements of $\zeta \mathbf{l} \cdot \mathbf{S}$ occur only on the diagonal of the standard matrix in the basis of the uncoupled states, and the matrix elements are of the form

$$\zeta \langle 1, L; 1\|l\|1, L; 1\rangle\langle 1, S; J\|l \cdot S\|1, S; J\rangle \tag{5}$$

where

$$\langle 1, S; J\|l \cdot S\|1, S; J\rangle = \tfrac{1}{2}[J(J + 1) - 2 - S(S + 1)]. \tag{6}$$

Here $L = 0$ or 2, the first reduced matrix element in (5) allows for the coupling of the electronic angular momentum with the vibrational states, and the second reduced matrix element allows for variations in the choice of J and S. Thus we see that the matrix is independent of the choice of S except for a scaling of ζ by the factor (6).

If the absorption band shape for this particular J-value of $S - 1$ were worked out and expanded in powers of ζ, then we should find that the absorption intensity as a function of energy x could be written

$$I^{(S-1)}(x) = I_0(x) + \zeta' I_1(x) + \zeta'^2 I_2(x) + \ldots \tag{7}$$

for $S > \frac{1}{2}$ where

$$\zeta' = \tfrac{1}{2}\zeta[J(J + 1) - 2 - S(S + 1)] = -\zeta(S + 1) \tag{8}$$

and the functions $I_0, I_1, I_2, \ldots$ are independent of S. These functions will depend on the Jahn–Teller coupling strength, and they are defined by the above two equations. We omit a degeneracy factor, $(2J + 1)$, from the transition probability as well as the numerical value of any transition matrix elements. In the special case $S = \frac{1}{2}$ the lowest value of

J is $\frac{1}{2}$, so for $I^{(1/2)}(x)$ we must take

$$\zeta' = \frac{1}{2}\zeta[\frac{1}{2}(\frac{1}{2} + 1) - 2 - \frac{1}{2}(\frac{1}{2} + 1)] = -\zeta \tag{9}$$

giving

$$I^{(1/2)}(x) = I_0(x) - \zeta I_1(x) + \zeta^2 I_2(x) + \dots. \tag{10}$$

The next set of states to consider is those with $J = S$. The matrix for these states falls into two blocks; one deriving from $S \otimes D_1$, to which transitions are allowed, and one from $S \otimes D_2$ to which transitions are forbidden if $\zeta = 0$. A consideration of the moments of the band derived from such a matrix shows that to order ζ^2 there are two contributions: one in which both the ζ-factors are within the $S \otimes D_1$ block, and one in which both the ζ-factors connect $S \otimes D_1$ to $S \otimes D_2$, and this second contribution only comes in to order ζ^2. Consequently we can now write the absorption intensity as

$$I^{(S)}(x) = I_0(x) + \zeta' I_1(x) + \zeta'^2 I_2(x) + \zeta''^2 I_{12}(x) + \dots \tag{11}$$

for $S > \frac{1}{2}$, where I_0, I_1 and I_2 are the same as before, and

$$\zeta' = \frac{1}{2}\zeta[J(J + 1) - 2 - S(S + 1)] = -\zeta \quad \text{for} \quad J = S. \tag{12}$$

To get the correct reduced matrix element for $\zeta \mathbf{l} \cdot \mathbf{S}$ between the blocks, we have to use the equation (Judd 1963, equation (3.36))

$$\langle l, S; J \| \mathbf{l} \cdot \mathbf{s} \| l', S; J \rangle = (-1)^{S+J+l} \begin{Bmatrix} l' & S & J \\ S & l & 1 \end{Bmatrix} \langle l' \| l \| l \rangle \langle S \| S \| S \rangle \tag{13}$$

and, to avoid extra work, use the formula twice to give

$$\zeta''/\zeta' = \begin{Bmatrix} 2 & S & J \\ S & 1 & 1 \end{Bmatrix} \Big/ \begin{Bmatrix} 1 & S & J \\ S & 1 & 1 \end{Bmatrix}. \tag{14}$$

The formulae for these two $6j$ symbols are (Rotenberg *et al* 1959)

$$\begin{Bmatrix} 1 & S & J \\ S & 1 & 1 \end{Bmatrix} = (-1)^{1+S+J} \frac{2[S(S + 1) + 2 - J(J + 1)]}{[2S(2S + 1)(2S + 2) \times 4 \times 5 \times 6]^{1/2}} \tag{15}$$

$$\begin{Bmatrix} 2 & S & J \\ S & 1 & 1 \end{Bmatrix} = (-1)^{2+S+J} \left[\frac{2(J + S + 3)(2 + S - J)(2 + J - S)(J + S - 1)}{2S(2S + 1)(2S + 2) \times 3 \times 4 \times 5} \right]^{1/2} \tag{16}$$

so that

$$\zeta''/\zeta' = -[6(J + S + 3)(2 + S - J)(2 + J - S)(J + S - 1)]^{1/2}$$
$$\times [S(S + 1) + 2 - J(J + 1)] \tag{17}$$

and if $J = S$ this gives

$$\zeta'' = -[6(2S - 1)(2S + 3)]^{1/2} \zeta. \tag{18}$$

when $S = \frac{1}{2}$ the matrix with the double-block structure is that for $J = \frac{3}{2}$; so we use the above equations with $J = S + 1$ to get

$$I^{(3/2)}(x) = I_0(x) + \zeta' I_1(x) + \zeta'^2 I_2(x) + \zeta''^2 I_{12}(x) + \dots \tag{19}$$

with

$$\zeta' = \frac{1}{2}\zeta[\frac{3}{2}\frac{5}{2} - 2 - \frac{1}{2}\frac{3}{2}] = \frac{1}{2}\zeta \tag{20}$$

and

$$\zeta'' = -3[2S(S + 2)]^{1/2}\zeta = -[\tfrac{45}{2}]^{1/2}\zeta \tag{21}$$

which is obtained by putting $J = S + 1$ in equation (17). Finally we can look at the $J = S + 1$ states. The matrix here has a three-block structure, but the $S \otimes D_3$ block connects only to the $S \otimes D_2$ block, and not directly to the $S \otimes D_1$ block. Consequently this third block can be ignored to second order in ζ, and the absorption intensity can be written immediately as

$$I^{(S+1)}(x) = I_0(x) + \zeta'I_1(x) + \zeta'^2I_2(x) + \zeta''^2I_{12}(x) + \ldots \tag{22}$$

with

$$\zeta' = \tfrac{1}{2}\zeta[(S + 1)(S + 2) - 2 - S(S + 1)] = \zeta S \tag{23}$$

and

$$\zeta'' = -3[2S(S + 2)]^{1/2}\zeta \tag{24}$$

as above.

What this analysis shows is that we can find the band shapes up to second order in ζ just by using the method already set up to find the $S = \tfrac{1}{2}$ band shapes for various small values of ζ.

4. The MCD band shape

To find the MCD band shape we can work with the states for $S = \tfrac{1}{2}$. When a spin of $\tfrac{1}{2}$ is coupled to a P state the states formed are $J = \tfrac{1}{2}$ and $J = \tfrac{3}{2}$, and the MCD band is made up of an appropriate linear combination of $I^{(1/2)}(x)$ and $I^{(3/2)}(x)$. The dipole transition operators from the ground ^2S state produce the components of P without altering the spin components, and the probability of each operator producing each state can be calculated with the following results:

spin component			$J = \tfrac{3}{2}$	$J = \tfrac{1}{2}$
σ_+	on	$|+\rangle$	1	0
σ_+	on	$|-\rangle$	$\tfrac{1}{3}$	$\tfrac{2}{3}$
σ_-	on	$|+\rangle$	$\tfrac{1}{3}$	$\tfrac{2}{3}$
σ_-	on	$|-\rangle$	1	0

For MCD the dipole operator is $\sigma_+ - \sigma_-$; so the MCD band shape should be

$$I^{(MCD)}(x) = [p(+) - p(-)][\tfrac{2}{3}I^{(3/2)}(x) - \tfrac{2}{3}I^{(1/2)}(x)] \tag{25}$$

where $p(+)$ and $p(-)$ are the probabilities of the spin components in the initial states. These probabilities can be written as a thermal average over spin states to give

$$I^{(MCD)}(x) = 2\langle S_z\rangle_{Av}[\tfrac{2}{3}I^{(3/2)}(x) - \tfrac{2}{3}I^{(1/2)}(x)]. \tag{26}$$

taken to first order in ζ this gives, for the $S = \frac{1}{2}$ states,

$$I^{(MCD)}(x) = 2\langle S_z\rangle_{Av}\zeta I_1(x) \tag{27}$$

and this is now a general expression for small ζ and any spin.

5. The MLD band shape

The smallest spin to give a non-zero MLD in an $^nS \to ^nP$ transition is $S = 1$; so we start there. We couple the P states to a spin, $S = 1$, and get the explicit forms for the three different J-states. The possible values of J are 0, 1, 2; so the MLD band shape will be made up of a linear combination of $I^{(S-1)}(x)$, $I^{(S)}(x)$ and $I^{(S+1)}(x)$ with $S = 1$. The dipole transition operators from the ground ^3S state produce the three components of the P state without altering the spin components; so the probability that each operator produces each J-state can be calculated from the explicit forms of the coupled states, with the following results:

spin component			$J = 2$	$J = 1$	$J = 0$
σ_+	on	$|+1\rangle$	1	0	0
σ_+	on	$|0\rangle$	$\frac{1}{2}$	$\frac{1}{2}$	0
σ_+	on	$|-1\rangle$	$\frac{1}{6}$	$\frac{1}{2}$	$\frac{1}{3}$
σ_-	on	$|+1\rangle$	$\frac{1}{6}$	$\frac{1}{2}$	$\frac{1}{3}$
σ_-	on	$|0\rangle$	$\frac{1}{2}$	$\frac{1}{2}$	0
σ_-	on	$|-1\rangle$	1	0	0
σ_z	on	$|+1\rangle$	$\frac{1}{2}$	$\frac{1}{2}$	0
σ_z	on	$|0\rangle$	$\frac{2}{3}$	0	$\frac{1}{3}$
σ_z	on	$|-1\rangle$	$\frac{1}{2}$	$\frac{1}{2}$	0

For MLD the operator is $\sigma_z - \frac{1}{2}(\sigma_+ + \sigma_-)$; so the probabilities are

		$J = 2$	$J = 1$	$J = 0$
from	$|+1\rangle$	$-\frac{1}{12}$	$\frac{1}{4}$	$-\frac{1}{6}$
from	$|0\rangle$	$\frac{1}{6}$	$-\frac{1}{2}$	$\frac{1}{3}$
from	$|-1\rangle$	$-\frac{1}{12}$	$\frac{1}{4}$	$-\frac{1}{6}$.

the MLD band shape should thus be

$$I^{(MLD)}(x) = [(p(0) - \tfrac{1}{2}p(+1) - \tfrac{1}{2}p(-1)][\tfrac{1}{3}I^{(S-1)}(x) - \tfrac{1}{2}I^{(S)}(x) + \tfrac{1}{6}I^{(S+1)}(x)] \tag{28}$$

where $p(0)$, $p(+1)$ and $p(-1)$ are the probabilities of the spin components in the initial states. These probabilities can be written as a thermal average over spin states, so that

$$I^{(MLD)}(x) = \tfrac{1}{12}\langle S(S + 1) - 3S_z^2\rangle_{Av}[2I^{(S-1)}(x) - 3I^{(S)}(x) + I^{(S+1)}(x)]. \tag{29}$$

Substituting $S = 1$ in the equations (7), (11) and (22) and putting them in equation (29) gives

$$I^{(MLD)}(x) = \tfrac{1}{2}\langle S(S+1) - 3S_z^2\rangle_{Av}[\zeta^2 I_2(x) - 6\zeta^2 I_{12}(x)] \tag{30}$$

where $I_2(x)$ and $I_{12}(x)$ are also defined in section 3. This calculation verifies that the MLD only appears to second order in ζ, and is a general form for small ζ and any spin.
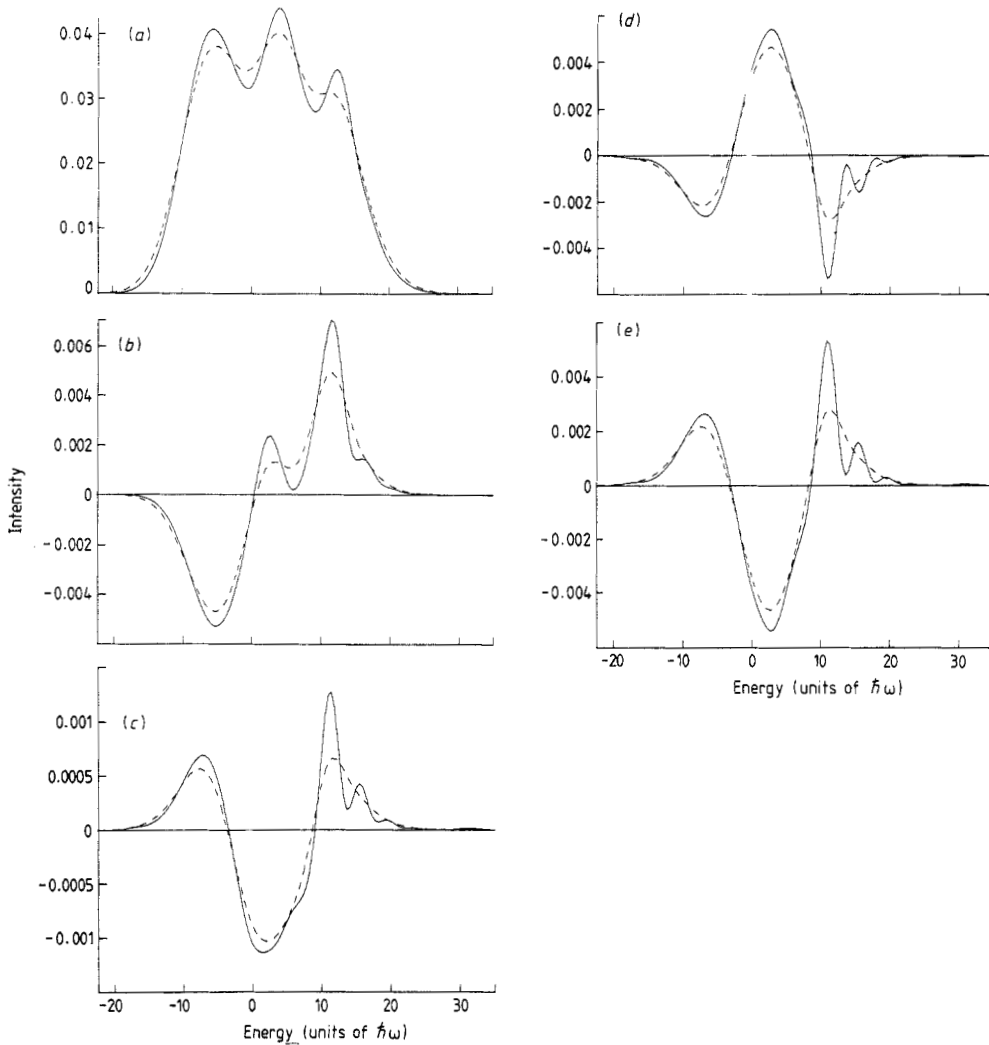
Figure 1. Band profiles calculated as described in the text. The same coupling strength, $k = 14.49\hbar\omega$, is used throughout, and $\zeta = 0.05k\hbar\omega$: (a) absorption profiles $I_0(x)$; (b) MCD profiles $-\zeta I_1(x)$; (c) $2\zeta^2 I_2(x)$; (d) $45\zeta^2 I_{12}(x)$; (e) MLD profiles $\tfrac{15}{2}$, $[\zeta^2 I_2(x) - 6\zeta^2 I_{12}(x)]$. The absorption profiles are normalised to unity, and the intensities of the other profiles are related to the absorption intensities as described in the text. Two different widths of Gaussian smoothing are used and the convoluted function is $(\sigma/\pi)^{1/2}\exp(-\sigma x^2)$: ——, $\sigma = 0.3$; –––, $\sigma = 0.1$.

6. Numerical methods, results and comparison with experiment

In a previous paper (O'Brien 1985) we have used the method of diagonalising large matrices in the basis of the uncoupled states to calculate the quantities now called $I^{(3/2)}(x)$ and $I^{(1/2)}(x)$ for various values of the coupling strength and ζ. Now we want to use the same routines to find the various profiles $I_1(x)$, $I_2(x)$, etc, which means running them for small values of ζ and taking linear combinations. For instance

$$[I^{(1/2)}(x)]_\zeta + [I^{(1/2)}(x)]_{-\zeta} - 2[I^{(1/2)}(x)]_0 \simeq 2\zeta^2 I_2(x) \tag{31}$$

and

$$[I^{(3/2)}(x)]_\zeta + [I^{(3/2)}(x)]_{-\zeta} - 2[I^{(3/2)}(x)]_0 \simeq \zeta^2[\tfrac{1}{2}I_2(x) + 45I_{12}(x)]. \tag{32}$$

It was necessary to check the convergence of the ζ-expansion by trying a range of small values of ζ, and the checking was done by generating profiles and comparing them visually. It turned out that taking a very small but non-zero value of ζ introduced extra inaccuracies in the numerical process, and care had to be taken to allow for this.

An assortment of band profiles are shown in figure 1. The coupling strength chosen
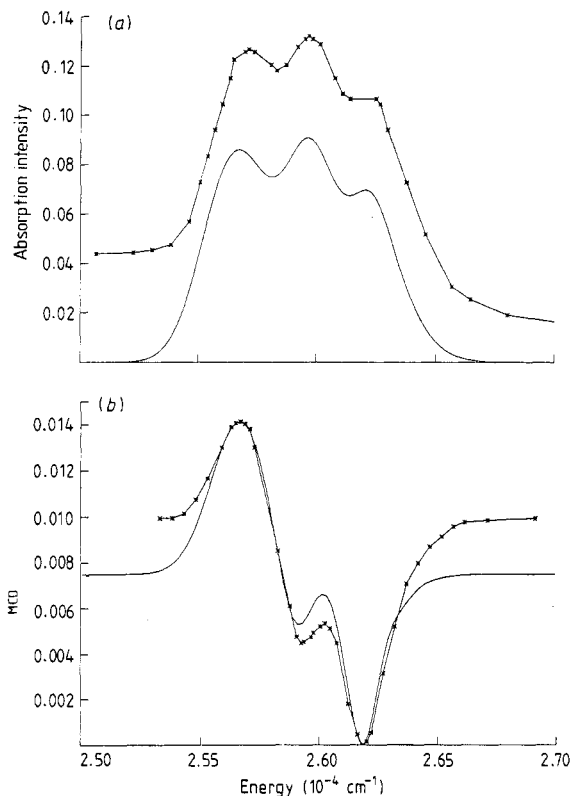
Figure 2. Fit to data on Mn in Kr (from Rivoal (1988)) for (a) absorption and (b) MCD (the shift of zero on the MCD band is ignored as coming from coupling to a neighbouring level): ——, theoretical data; *——*, experimental data at (a) $T = 5.84$ K and (b) $T = 5.96$ K, $B = 1.5$ T. The experimental plots are on the same scale. The theoretical absorption is scaled from the MCD assuming $\zeta = 7$ cm^{-1}.

was as large as could conveniently be handled. As usual the band shapes were produced by smoothing a set of lines, using a Gaussian convolution, and the effect of using two different widths is shown. In an actual measured band this smoothing would correspond to coupling to the totally symmetric mode of vibration, and a variety of different amounts of smoothing are found experimentally.

In figure 2 is shown the fit to the absorption and MCD measurements on Mn in Kr made by Rivoal (1988). The transition here is $^6S \rightarrow {}^6P$ and ζ is very small; so the theoretical fit should be good. The fitting parameters were chosen to fit the two main peaks of the MCD band, and the vertical scale for the absorption was calculated using the measured ζ of 7 cm^{-1}. Apart from baseline problems the agreement looks good. The MLD was looked for but did not appear above noise; this theory predicts a peak MLD smaller than the peak MCD by a factor of 0.16 at the temperature used.

Other examples of these band shapes can be seen in the $^7S \rightarrow z^7P$ transition for Cr in Kr and Xe (Vala *et al* 1987) and in the 'blue triplet' for K in Kr (Samet *et al* 1989). It is to be hoped that the success of these fits might lead to more examples being found.

Acknowledgments

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