

## Numerical investigation of the $(s + p) \otimes T_{1u}$ system: II. Reduction factors and emission spectra

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**Abstract.** The eigenvalue problem of the ideal  $(s + p) \otimes T_{1u}$  pseudo-Jahn–Teller system is solved numerically. Reduction factors and emission spectra at finite temperatures are computed for representative values of the electronic 2s–2p spacing in all coupling regimes. In addition, zero- and one-phonon lines of emission and of absorption are calculated in the strong-coupling limit.

### 1. Introduction

In the preceding paper (Grevsmühl 1981, to be referred to as I) the eigenvalue problem of the ideal  $(s + p) \otimes T_{1u}$  pseudo-Jahn–Teller system was investigated numerically and the vibronic eigenstates and absorption spectra were calculated. Here we continue this investigation and present the results for the reduction factors and the emission spectra at finite temperatures for representative values of the vibronic coupling strength and of the electronic 2s–2p spacing.

In order to compare the properties with the results in the strong coupling region, the orthogonal transformation of Ham (1973) is used to obtain explicit expressions for the eigenfunctions and to calculate the zero- and one-phonon lines of emission and of absorption.

### 2. Reduction factors

As the threefold degeneracy of the electronic 2p states can only be lifted by a perturbation of symmetry  $E_g$ ,  $T_{2g}$  or  $T_{1g}$  of  $O_h$ , it is of considerable interest to investigate numerically how the properties of these states compare with those of the lowest type-I vibronic states with  $J = 1$ , which also transform in cubic symmetry  $O_h$  as  $T_{1u}$ .

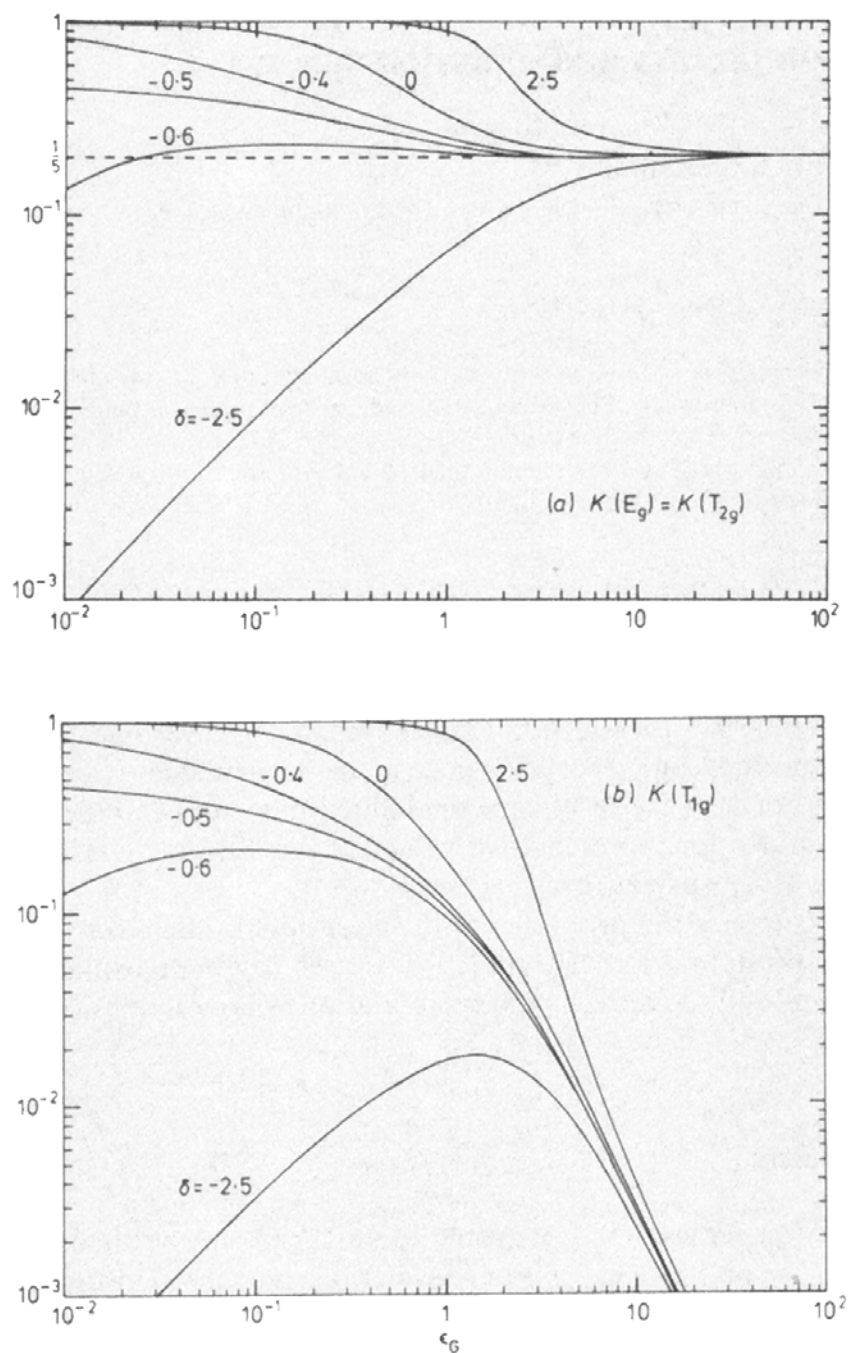
Following Ham (1965, 1973) we may define reduction factors  $K$  for the  $(s + p) \otimes T_{1u}$  system as the ratio of the response of the lowest triplet vibronic state to that of the electronic 2p state for an external field of  $E_g$ ,  $T_{2g}$  or  $T_{1g}$  symmetry.

For any electronic operator  $O^{\Gamma\gamma}$  transforming as the  $\gamma$ -component of the irreducible representation  $\Gamma$  we define

$$\langle \Psi_{1,0}^{1M} | O^{\Gamma\gamma} | \Psi_{1,0}^{1M'} \rangle = K_{j=0}^{J=1}(\Gamma) \langle 21M | O^{\Gamma\gamma} | 21M' \rangle \quad (1)$$

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provided the last factor is non-zero. The size of the matrix elements and thus the magnitude of the initial linear splitting of the level are proportional to the appropriate reduction factor, which itself depends only on the coupling strength of the electron-phonon interaction.



**Figure 1.** Reduction factors  $K_0^1(E_g) \equiv K_0^1(T_{2g})$  (a) and  $K_0^1(T_{1g})$  (b) versus stabilisation energy  $\epsilon_G = \kappa^2$  for various values of  $\delta$ .  $\delta$  and  $\epsilon_G$  are defined in 1, §2. Note the double logarithmic scale.

Representative electronic operators of symmetry  $E_g$ ,  $T_{2g}$  and  $T_{1g}$  may be defined in terms of the electronic orbital angular momentum, as done by Ham (1973). Non-zero matrix elements of these operators within the lowest type-I vibronic level (18) with  $J = 1$  may then be calculated and the reduction factors be expressed in terms of the

coefficients  $b$  and  $c$ :

$$\begin{aligned}
 K_0^1(T_{1g}) &= \sum_{N=0}^{\infty} \{ |c(1, 0, 2N)|^2 - \frac{1}{2} |b(1, 0, 2N + 2)|^2 \} \\
 K_0^1(E_g) \equiv K_0^1(T_{2g}) &= \sum_{N=0}^{\infty} \{ |c(1, 0, 2N)|^2 + \frac{1}{10} |b(1, 0, 2N + 2)|^2 \}. \quad (2)
 \end{aligned}$$

The electronic operators transform in the full rotational symmetry of this vibronic model as a set of functions belonging to  $J = 2$  with parity  $\Lambda' = +1$ . The reduction factors for operators of  $E_g$  and  $T_{2g}$  symmetry are therefore the same as long as we limit ourselves to linear coupling.

The expressions (2) correspond to the ones given by Ham (1973) in terms of the  $f_2$  and  $f_3$  coefficients of the coupled differential equations. For the strong-coupling limit he was able to predict the values  $K_0^1(T_{1g}) = 0$  and  $K_0^1(E_g) = \frac{1}{5}$ . This means that in this limit the magnetic splitting of the lowest type-I vibronic state with  $J = 1$  is completely quenched, whereas the effect of applied strain is not. The strain splitting of this level is reduced by 80% compared with the splitting of the electronic  $2p$  states.

The overall variation of the reduction factors with  $\varepsilon_G$  (see figure 1) depends crucially on the value of the electronic  $2s-2p$  separation parameter  $\delta$ , i.e. on the type of state at zero coupling strength. In the weak-coupling region we find through a simple perturbation approach the following expressions:

for  $\delta < -\frac{1}{2}$

$$\begin{aligned}
 K_0^1(E_g) &= \left( |\delta| + \frac{1}{4|\delta|} \right) K_0^1(T_{1g}) \\
 K_0^1(T_{1g}) &= \frac{|\delta|\varepsilon_G}{2(\delta^2 - \frac{1}{4})^2}
 \end{aligned}$$

for  $\delta = -\frac{1}{2}$

$$K_0^1(E_g) = K_0^1(T_{1g}) = \frac{1}{2}(1 - \varepsilon_G^{1/2})$$

and for  $\delta > -\frac{1}{2}$

$$K_0^1(E_g) = K_0^1(T_{1g}) = 1 - \frac{\varepsilon_G}{4(\delta + \frac{1}{2})^2}.$$

Figure 1 shows that the weak- and strong-coupling expressions hold reasonably well. For  $\delta \ll -\frac{1}{2}$ ,  $K_0^1(T_{1g})$  becomes very small also in the intermediate-coupling region and decreases as  $|\delta|$  increases. Note for  $\delta < 0$ ,  $K_0^1(E_g)$  is less than  $\frac{1}{5}$  as this asymptotic value is approached. In the interval  $-1 \lesssim \delta < 0$ ,  $K_0^1(E_g)$  exhibits a slight 'dip' at intermediate and strong coupling strengths which is reflected in a reduction of the total  $p-(J-1)$  admixture of the state.

### 3. Emission spectra

#### 3.1. Spontaneous emission at zero temperature

The investigation of the vibronic eigenstates in the preceding paper revealed that at all coupling strengths the lowest energy level is of type-I with  $j = 0$  and either  $J = 0$  or  $J = 1$ . Spontaneous emission for 0 K can therefore occur only from one of these states.

The rate of spontaneous emission of light of energy  $\varepsilon$  and polarisation  $\eta$  resulting from a transition from a  $(2J + 1)$ -fold degenerate state  $\Psi_{l,j}^{JM}$  with energy  $\varepsilon(l, jJ)$  to the

vibronic states  $\Psi_{N'J'M'}$  (1s) with energies  $\varepsilon(N'J', 1s) = -\varepsilon_0 + 2N' + J' + \frac{3}{2}$  is then given by (Dexter 1958, Fowler 1968, p 61)

$$i_{\eta}(IjJ, \varepsilon) = \frac{C'}{2J+1} \sum_{M=J, J-1, \dots, -J} \sum_{N'J'M'} |\langle \Psi_{1,j}^{JM} | D_{\eta} | \Psi_{N'J'M'}(1s) \rangle|^2 \\ \times \delta(\varepsilon(I, jJ) - \varepsilon(N'J', 1s) - \varepsilon)$$

where  $C' = (F_{\text{eff}}/F_0)^2 4ne^3/3\hbar^4 c^3$ , and  $n$  is the refractive index of the medium,  $c$  the speed of light in vacuum and  $(F_{\text{eff}}/F_0)^2$  the local field correction. Furthermore, we ignore the variation of  $C'$  over the energy range of the states  $\Psi_{N'J'M'}(1s)$  to which the transitions occur, on the assumption that the width of the emission band is small compared with its mean energy.

The electric dipole moment operator  $D$  for linearly polarised light takes the form  $D_{\eta} = e\eta$  with  $\eta = x, y, \text{ or } z$ . Substituting its matrix elements (I16) into the expression above leaves us with a sum over  $M (= J, J-1, \dots, -J)$  which can easily be carried out since the energies in the delta functions do not depend on  $M$ . With the sums

$$\sum_M \frac{(J+M)(J-M)}{J(2J-1)} = \sum_M \frac{(J+M+1)(J+1-M)}{(J+1)(2J+3)} = \frac{1}{3}(2J+1)$$

the emission spectrum from a general state  $\Psi_{1,j}^{JM}$  is then given by

$$I_{\eta}^e(IjJ, \varepsilon) = |c(J, j, J-1)|^2 \delta(\varepsilon(I, jJ) - \varepsilon(0(J-1), 1s) - \varepsilon) \\ + \sum_{N=0}^{\infty} [ |b(J, j, J+2N+1)|^2 + |c(J, j, J+2N+1)|^2 ] \\ \times \delta(\varepsilon(I, j, J) - \varepsilon(N(J+1), 1s) - \varepsilon) \quad (3)$$

where we put  $I_{\eta}^e = 3i_{\eta}/C'D^2$ , for convenience. Note that  $c \equiv 0$  for  $J = 0$  (see equation (I8)).

The total probability per unit time of the emission of a photon of polarisation  $\eta$  is found by integrating the spectrum (3) over the energy. Summing the result over all polarisations yields

$$N(jJ) = \frac{\tau_r(p)}{\tau_r(jJ)} = 1 - \sum_{N=0}^{\infty} |a(J, j, J+2N)|^2 \quad (4)$$

where  $\tau_r(jJ)$  and  $\tau_r(p) = (C'D^2)^{-1}$  are the radiative lifetimes of the state  $\Psi_{1,j}^{JM}$  and a 2p electronic state, respectively.  $(1/N)$  can be regarded as the normalisation constant of the spectrum (3) (see Ham 1973, equation (5.8b)). As the admixture of the s- $J$  states is given by  $\sum_N |a|^2$ ,  $N$  represents the total p-admixture of the p- $(J+1)$  and p- $(J-1)$  states (see equation (I8)). In the case of zero coupling strength  $N$  will either be equal to 1 for a pure p state or equal to zero for an s state. In the strong-coupling limit the energetically low-lying type-I vibronic states have equal admixtures of 2s and 2p electronic states, and in this case we find  $N = \frac{1}{2}$ , independent of the electronic 2s-2p spacing and independent of  $j$  and  $J$ .

When we calculate the spontaneous emission spectrum at absolute zero from equation (3), there are three possibilities. Either a type-I state with  $j = J = 0$  is lowest, or a type-I state with  $j = 0, J = 1$ , or both. The first possibility occurs for  $\delta \leq 0$  for all coupling strengths, but for  $\delta > 0$  only in the intermediate or strong coupling region.

The  $(2N + 1)$ -phonon emission lines ( $N = 0, 1, 2, \dots$ ) are then given by

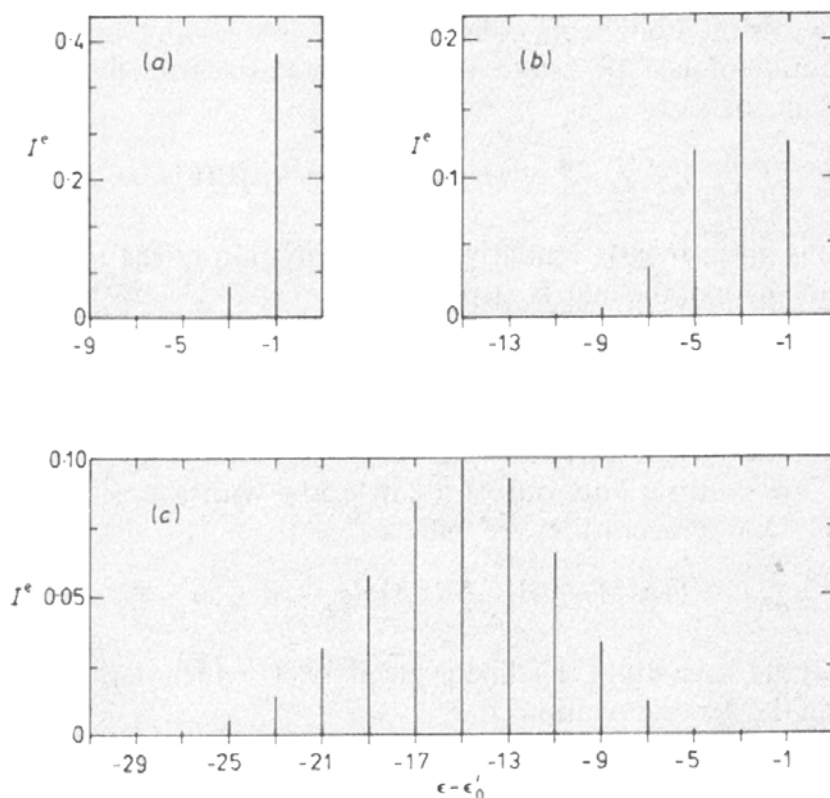
$$M^e(2N + 1) = |b(0, 0, 2N + 1)|^2. \quad (5)$$

Complementary to this, a type-I state with  $j = 0, J = 1$  is lowest only for  $\delta > 0$  and for weaker coupling. The emission spectrum consists now of zero-phonon and  $(2N + 2)$ -phonon lines ( $N = 0, 1, 2, \dots$ ) which are given by

$$\begin{aligned} M^e(0) &= |c(1, 0, 0)|^2 \\ M^e(2N + 2) &= |b(1, 0, 2N + 2)|^2 + |c(1, 0, 2N + 2)|^2. \end{aligned} \quad (6)$$

The third possibility occurs when the two lowest energy levels are accidentally degenerate which can be the case only for  $\delta > 0$ .

The emission spectra from the lowest type-I state with  $J = 0$  have been drawn in the case of electronic  $2s-2p$  degeneracy ( $\delta = 0$ ) for various values of  $\varepsilon_G$  (figure 2). The positions of the delta functions are given by  $\varepsilon'_0 - (2N + 1)$  with  $\varepsilon'_0 = \varepsilon(I, 00) + \varepsilon_0 - \frac{3}{2}$ , where  $N = 0, 1, 2, \dots$ ,  $\varepsilon_0$  is taken as a given constant and  $\varepsilon(I, 00)$  is obtained from the computations of I. The spectra have uniform spacings which are independent of  $\varepsilon_G$  (and  $\delta$ ). The total  $2p$  admixtures  $N(00)$  have also been included and are given by the sums of the strengths of all the delta functions of the spectra.



**Figure 2.** Emission spectra at  $T = 0$  K for  $\delta = 0$  versus  $\varepsilon - \varepsilon'_0$  where  $\varepsilon'_0 = \varepsilon(I, 00) + \varepsilon_0 - \frac{3}{2}$ . The  $n$ -phonon line has the position  $(-n) \cdot \varepsilon(I, 00)$  and  $N(00)$  denote the energy and the total  $2p$  admixtures respectively of the lowest type-I state with  $J = 0$ . (a)  $\varepsilon_G = 1$ ,  $\varepsilon(I, 00) = -0.16$ ,  $N(00) = 0.43$ ; (b)  $\varepsilon_G = 4$ ,  $\varepsilon(I, 00) = -3.42$ ,  $N(00) = 0.49$ ; (c)  $\varepsilon_G = 16$ ,  $\varepsilon(I, 00) = -15.48$ ,  $N(00) = 0.50$ .

For weak coupling the overlap integrals between the type-I vibronic states with  $j = J = 0$  and the states  $\Psi_{N'J'M'}(1s)$  with small  $N'$  are largest and the few-phonon lines dominate. The emission spectra are then strongly affected by the kind of state which is lowest at  $\varepsilon_G = 0$ . As the coupling strength increases, the influence of the many-phonon lines becomes appreciably prominent, as expected from the semiclassical theory of Toyozawa and Inoue (1966), and the spectra resemble Poisson distributions.

### 3.2. Emission at finite temperature

For temperatures greater than zero the thermal average over the initial states from which spontaneous emission occurs and which are each weighted with the customary Boltzmann factor has to be taken into account. There are now two contributions to the spectrum, one of them comes from the type-I vibronic states with energies  $\varepsilon(I, jJ)$  the other from the type-II states with energies  $\varepsilon(\text{II}, NJ)$  (see paper I, § 2.3). In analogy to (3) the total emission spectrum is then given by

$$I_{\eta, T}^c = (1/A)[A_I I_{\eta, T}^c(\text{I}) + A_{\text{II}} I_{\eta, T}^c(\text{II})] \quad (7)$$

where  $A = A_I + A_{\text{II}}$  with

$$A_I = \sum_{jJ} (2J + 1) \exp[-\varepsilon(\text{I}, jJ)/\beta]$$

$$A_{\text{II}} = \sum_{NJ} (2J + 1) \exp[-\varepsilon(\text{II}, NJ)/\beta]$$

and  $\beta = kT/\hbar\omega$ .  $k$  is the Boltzmann constant and  $T$  the absolute temperature.

The contribution of the type-I states to the emission spectrum can then be calculated by using the results of § 3.1

$$I_{\eta, T}^c(\text{I}) = A_I^{-1} \sum_{jJ} (2J + 1) \exp[-\varepsilon(\text{I}, jJ)/\beta] I_{\eta}^c(\text{I } jJ, \varepsilon) \quad (8)$$

where  $I_{\eta}^c(\text{I } jJ, \varepsilon)$  is given by (3). Similarly, the contribution of the type-II states can be obtained with the help of the matrix elements

$$\langle \Psi_{\text{II}, N}^{JM} | D_z | \Psi_{N'J'M'}(1s) \rangle = DM [J(J + 1)]^{-1/2} \delta_{N', N} \delta_{J', J} \delta_{M', M} \quad \text{for } J \geq 1. \quad (9)$$

The energy difference between all the states involved in the contribution  $I_{\eta, T}^c(\text{II})$  is thus independent of  $N$  and  $J$  and given by  $\varepsilon(\text{II}, NJ) - \varepsilon(NJ, 1s) = \varepsilon_0 - \delta$ . This part of the spectrum therefore consists only out of a single line with a position independent of coupling strength and temperature. We find

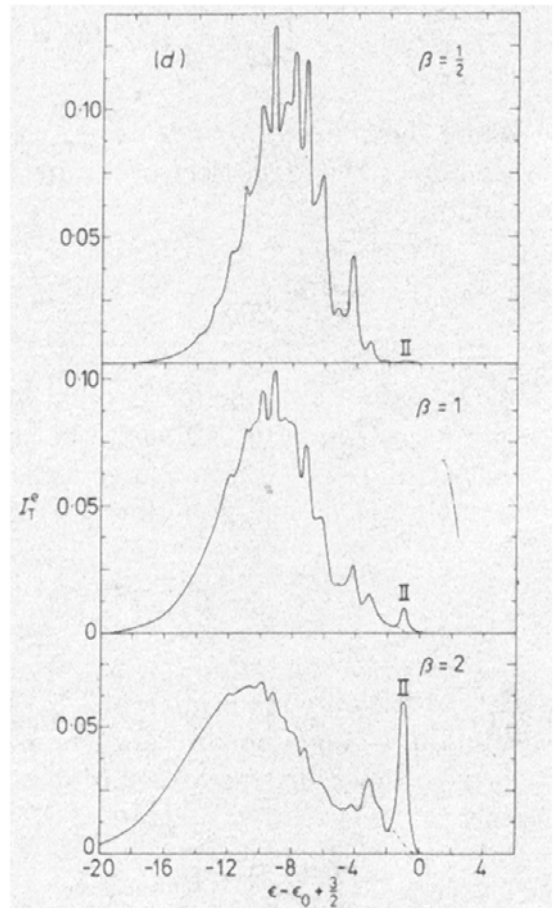
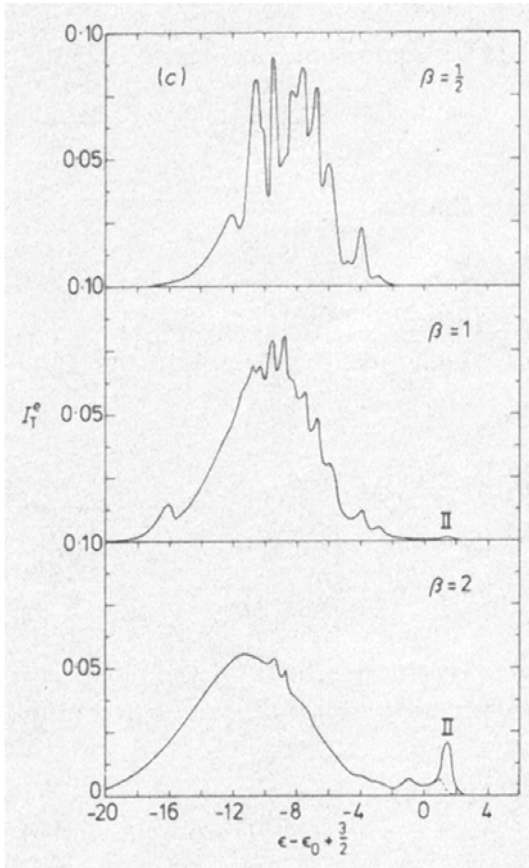
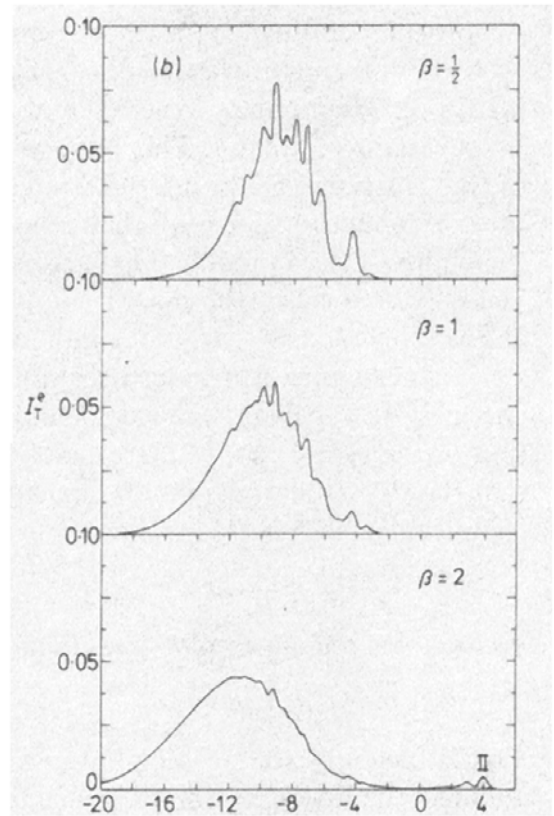
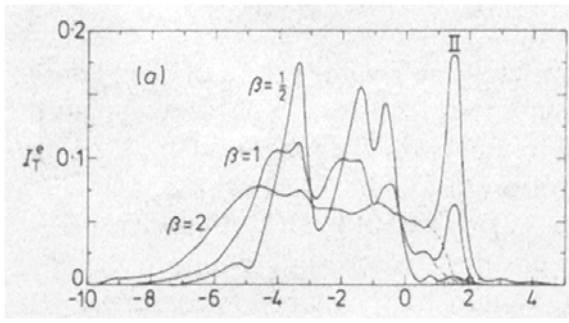
$$I_{\eta, T}^c(\text{II}) = A_{\text{II}}^{-1} \sum_{NJ} (2J + 1) \exp[-\varepsilon(\text{II}, NJ)/\beta] \delta(\varepsilon_0 - \delta - \varepsilon) = \delta(\varepsilon_0 - \delta - \varepsilon). \quad (10)$$

According to (7) the strength of this line is given by  $A_{\text{II}}$  which depends on  $\delta$  and  $\beta$  but not on  $\varepsilon_G$ . Using the general relation

$$\sum_{k=0}^{\infty} a^{kx} = \frac{1}{1 - a^x} \quad (a > 1, x < 0)$$

we find from (7)

$$A_{\text{II}} = \frac{\exp[(\delta - \frac{\varepsilon}{2})/\beta] [3 - \exp(-1/\beta)]}{[1 - \exp(-2/\beta)][1 - \exp(-1/\beta)]^2}. \quad (11)$$



**Figure 3.** Emission spectra at finite temperatures for  $\beta = kT/\hbar\omega = \frac{1}{2}, 1, 2$ . (a)  $\delta = 0$ ,  $\epsilon_G = 1$ ; (b)  $\delta = -\frac{5}{2}$ ,  $\epsilon_G = 4$ ; (c)  $\delta = 0$ ,  $\epsilon_G = 4$ ; (d)  $\delta = \frac{5}{2}$ ,  $\epsilon_G = 4$ . The broadening parameter is given by  $H = 0.5$ . The contributions from the type-II states are indicated; the broken lines indicate spectra without these contributions.

At low temperatures  $A_{II}$  is approximately given by  $3 \exp[(\delta - \frac{5}{2})/\beta]$ .

The total emission spectrum (7) has been computed for several values of  $\delta$ ,  $\varepsilon_G$  and  $\beta$  (figure 3). To simulate experimental measurements the delta functions were replaced by gaussians of areas 1. This imposes some requirements on the magnitude and width of the gaussians. Denoting the strength and position of a delta function by  $M$  and  $L$ , the corresponding gaussian then reads  $2M \exp\{-2[(\varepsilon - L)/H]^2/H(2\pi)^{1/2}\}$  where  $H$  is the width of the function. The factor  $2/H(2\pi)^{1/2}$  ensures that the integration over all  $\varepsilon$  yields  $M$ . However, the magnitude is in general altered by the same factor, unless we choose  $H = 2/(2\pi)^{1/2}$ . In the computation we put  $H = 0.5$ .

As the temperature increases, the spectra are smoothed and shift towards lower energies. As  $\delta$  increases, the areas under the bands become larger as well. The contribution of the type-II states increases with  $\beta$  and  $\delta$  but decreases for increasing  $\varepsilon_G$ . Note that the structure of the bands (apart from the type-II peak) does not appear to depend significantly on  $\delta$ .

#### 4. Emission and absorption lines in the strong-coupling limit

##### 4.1. Vibronic eigenstates

For sufficiently strong coupling, i.e. when the conditions  $2\varepsilon_G \gg |\delta|$  and  $\varepsilon_G \gg 1$  are fulfilled, the lowest vibronic eigenstates are of type-I which have the general form (Ham 1973)

$$\Psi_1(JM) = (2)^{-1/2} F_1(q) \left[ |JM, J, s\rangle - \left(\frac{J}{2J+1}\right)^{1/2} |JM, J-1, p\rangle + \left(\frac{J+1}{2J+1}\right)^{1/2} |JM, J+1, p\rangle \right] \quad (12)$$

where the states  $|JM, L, l\rangle$  are linear combinations of the products of the spherical harmonics  $y_L^m$  and the electronic states  $|ll_z\rangle$ . The radial function  $F_1(q)$  fulfils the differential equation

$$\left( -\frac{\partial^2}{2\partial q^2} - \frac{\partial}{q\partial q} + \frac{1}{2}(q - q_0)^2 - \varepsilon_G + \frac{J^2 + J + 1}{4\varepsilon_G} - \varepsilon \right) F_1(q) = 0. \quad (13)$$

We introduce the function  $G_1(q) = qF_1(q)$ . In order for the solutions to be regular, the condition  $G_1(q=0) = 0$  has to be satisfied. If we limit ourselves to values of  $q$  in the vicinity of  $q_0 \gg 1$ , i.e. to energetically low-lying eigensolutions, and introduce the new variable  $x = q - q_0$ , equation (13) takes the form

$$\left( \frac{d^2}{dx^2} + 2\varepsilon - x^2 + 2\varepsilon_G - \frac{J^2 + J + 1}{2\varepsilon_G} \right) G_1(x) = 0. \quad (14)$$

$G_1(x)$  exists only in the interval  $-q_0 \leq x < \infty$ . For  $q_0 \gg 1$  it is at least for the low-lying solutions a good approximation to extend this interval to  $-\infty < x < \infty$ . Equation (14) then becomes the radial equation of the linear harmonic oscillator with the energy eigenvalues

$$\varepsilon(I, jJ) = j + \frac{1}{2} - \varepsilon_G + (J^2 + J + 1)/4\varepsilon_G \quad (15)$$



and the normalised eigenfunctions

$$G_1^j(x) = (\pi^{1/2} 2^j j!)^{-1/2} \exp(-x^2/2) H_j(x) \quad (16)$$

with  $j, J = 0, 1, 2, \dots$ .  $H_j(x)$  are the Hermite polynomials defined by Messiah (1969, p 491). In particular, the ground state  $j = 0$  reads

$$G_1^0(q - q_0) = \pi^{-1/4} \exp[-(q - q_0)^2/2]. \quad (17)$$

In equation (14) the term in  $J$  is a constant, and the functions  $G_1^j$  are therefore independent of  $J$ .

#### 4.2. Zero- and one-phonon lines of emission and absorption

With the explicit expressions for the vibronic type-I states given above we are now able to calculate the zero- and one-phonon lines of emission and of absorption in the strong-coupling limit. Emission and absorption involve again the vibronic states  $\Psi_{N'J'M'}$  (1s) of (I14) which are now required as explicit functions of the polar coordinates  $(q, \theta, \varphi)$ . Following Flügge (1965) we find the wavefunctions of the 3D harmonic oscillator with energies  $\varepsilon = 2n + l + \frac{3}{2}$  to

$$\Psi_{nlm}(q, \theta, \varphi) = C_{nl} q^l \exp(-q^2/2) F(-n, l + \frac{3}{2}; q^2) y_l^m(\theta, \varphi) \quad (18)$$

where  $C_{nl}$  denotes the normalisation constant and  $y_l^m$  the spherical harmonics defined by Messiah (1969, p 494). The confluent hypergeometric series  $F(\alpha, \beta; z)$  is for  $\alpha = -n$  given by a polynomial of  $n$ th power

$$F(-n, \beta; z) = \sum_{s=0}^n (-1)^s \frac{\Gamma(n+1)\Gamma(\beta)}{\Gamma(n-s+1)\Gamma(\beta+s)} \frac{z^s}{s!} \quad (19)$$

where the gamma function is defined by  $\Gamma(x+1) = x!$ ,  $x \in \mathbf{R}$ . For  $n = 0$ :  $F(0, \beta; z) = 1$ .

The transition matrix elements may be calculated in analogy to (I16). The emission spectrum at zero temperature occurs from a type-I state with  $j = J = M = 0$  and is found from (3):

$$I^e(\text{I00}, \varepsilon) = \frac{1}{2} \sum_{N'=0}^{\infty} |x_{N', J'=1}^{j=0}|^2 \delta(\varepsilon(\text{I}, 00) - \varepsilon(N'1, 1s) - \varepsilon) \quad (20)$$

where

$$x_{N', J'=1}^0 = \int_0^{\infty} q^2 f_{N', J'=1}(q) F_1^0(q) dq$$

and

$$f_{N', J'=1}(q) = C_{N', J'=1} q \exp(-q^2/2) F(-N', \frac{5}{2}; q^2).$$

Transitions occur only to the states (I14) with  $J' = 1$ , and the spectrum consists purely of odd-phonon lines.

For  $N' = 0$  the strength of the one-phonon line in the strong-coupling limit is then given by

$$M_{\text{SCL}}^e(1) = \frac{1}{2} |x_{01}^0|^2 = (4/3\pi) \exp(-2\varepsilon_G) |Z_1| \quad (21)$$

where we used  $q_0^2 = 2\varepsilon_G$  (see Ham 1973).  $Z_1$  denotes the definite integral

$$Z_1 = \int_0^{\infty} q^2 \exp[-q^2 + (2\varepsilon_G)^{1/2} q] dq. \quad (22)$$

Introducing  $\exp[(2\varepsilon_G)^{-1/2}q] = \sum_{t=0}^{\infty} [(2\varepsilon_G)^{1/2}q]^t/t!$  the integration over  $q$  can be carried out (Bronstein and Semendjajew 1967, p 350):

$$Z_1 = \sum_{t=0}^{\infty} \frac{(2\varepsilon_G)^{t/2}}{2t!} \Gamma\left(\frac{t+3}{2}\right).$$

It is now convenient to introduce the error function defined by Gradshteyn and Ryzhik (1965) as

$$\operatorname{erf}(x) = \frac{2}{\pi^{1/2}} \int_0^x \exp(-t^2) dt = \frac{2}{(2\pi)^{1/2}} \exp(-x^2) \sum_{k=0}^{\infty} \frac{(2^{1/2}x)^{2k+1}}{(2k+1)!!}$$

where  $(2k+1)!! = 1 \times 3 \times 5 \times \dots \times (2k+1)$ . Making use of the properties of the gamma function, we arrive at

$$M_{\text{SCL}}^e(1) = (1/6\pi) \exp(-2\varepsilon_G) \left| \frac{1}{2}(2\pi)^{1/2}(\varepsilon_G + 1) \exp(\varepsilon_G/2) \{1 + \operatorname{erf}[(\varepsilon_G/2)^{1/2}]\} + \varepsilon_G^{1/2} \right|^2 \quad (23)$$

since  $\varepsilon_G \gg 1$  we may write in very good approximation  $\operatorname{erf}[(\varepsilon_G/2)^{1/2}] \approx 1$  and find

$$M_{\text{SCL}}^e(1) = \frac{1}{3}(\varepsilon_G + 1)^2 \exp(-\varepsilon_G). \quad (24)$$

Similarly, we can calculate the emission spectrum from the type-I state with  $j = 0$ ,  $J = 1$ , only. The transitions to the ground state (I14) with  $N' = J' = 0$  then define a zero-phonon line, the strength of which is in the strong-coupling limit given by

$$M_{\text{SCL}}^e(0) = \frac{1}{6} |x_{00}^0|^2 = (2/3\pi) \exp(-2\varepsilon_G) |Z_2|^2 \quad (25)$$

where

$$Z_2 = \int_0^{\infty} q \exp[-q^2 + (2\varepsilon_G)^{1/2}q] dq \quad (26)$$

can be calculated in the same way as above. We find

$$M_{\text{SCL}}^e(0) = (1/6\pi) \exp(-2\varepsilon_G) \left| 1 + \frac{1}{2}(2\pi\varepsilon_G)^{1/2} \exp(\varepsilon_G/2) \{1 + \operatorname{erf}[(\varepsilon_G/2)^{1/2}]\} \right|^2. \quad (27)$$

Again we put  $\operatorname{erf}[(\varepsilon_G/2)^{1/2}] \approx 1$  for  $\varepsilon_G \gg 1$  and obtain

$$M_{\text{SCL}}^e(0) = \frac{1}{3} \varepsilon_G \exp(-\varepsilon_G). \quad (28)$$

The absorption lines from the ground state (I14) with  $N' = J' = 0$  to the lowest-lying type-I states of strong coupling can be calculated in a similar manner. Of course, the ( $j = 0$ ) absorption line is identical to the zero-phonon emission line. The strength of the ( $j = 1$ ) absorption line is defined by the transition probability to the type-I state with  $j = J = 1$  and found to be

$$M_{\text{SCL}}^a(1) = \frac{1}{6} |x_{00}^1|^2 = (4/3\pi) \exp(-2\varepsilon_G) |Z_1 - (2\varepsilon_G)^{1/2} Z_2|^2 \quad (29)$$

where  $Z_1, Z_2$  are given by (22) and (26), respectively. We obtain

$$M_{\text{SCL}}^a(1) = (1/6\pi) \exp(-2\varepsilon_G) \left| \frac{1}{2}(2\pi)^{1/2}(\varepsilon_G - 1) \exp(\varepsilon_G/2) \{1 + \operatorname{erf}[(\varepsilon_G/2)^{1/2}]\} + \varepsilon_G^{1/2} \right|^2. \quad (30)$$

With the strong-coupling condition  $\varepsilon_G \gg 1$  this expression reduces to

$$M_{\text{SCL}}^a(1) = \frac{1}{3}(\varepsilon_G - 1)^2 \exp(-\varepsilon_G). \quad (31)$$

In figure 4 the expressions (23), (27), and (30) have been plotted against  $\varepsilon_G^{1/2}$  together with the computed values for  $\delta = 0$  of §§3 and I4. Good agreement between the lines is found for intermediate and strong coupling.

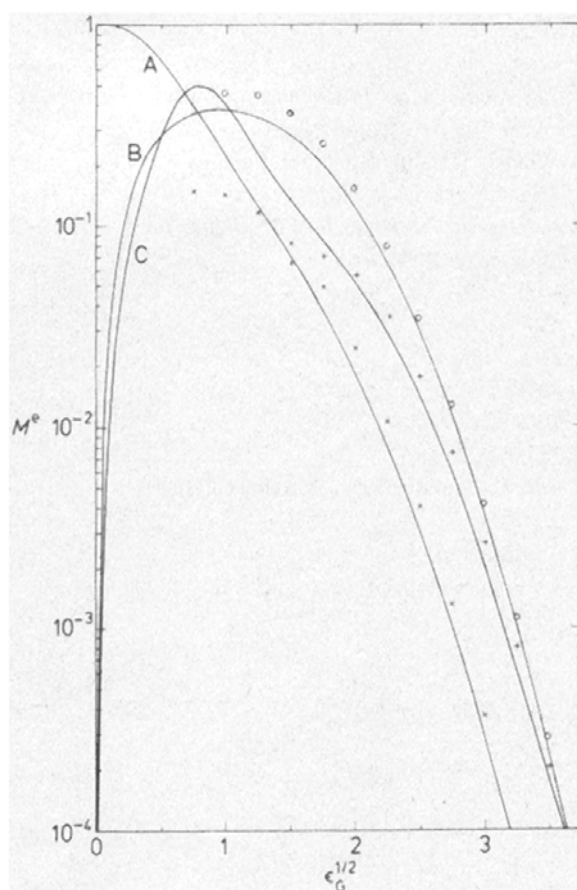


Figure 4. A, strength of zero-phonon line; B, one-phonon emission line; and C ( $j = 1$ ) absorption line for  $\delta = 0$  versus coupling strength  $\epsilon_G^{1/2}$ . The exact lines have been plotted together with the strong-coupling expressions (27)  $\times$ , (23)  $\circ$ , and (30)  $+$ .

## 5. Conclusion

The numerical results presented in this and the preceding paper should prove useful in the analysis of systems where  $2s$  and  $2p$  electronic states interact in cubic symmetry via a triply degenerate odd-parity vibrational mode. As has been demonstrated for the relaxed excited state of the F centre in alkali halides (Ham and Grevsmühl 1973, Kayanuma 1976, Grevsmühl 1976, Imanaka *et al* 1977, Thomchick and Ham 1980), the coupling of such systems may be found in the weak or intermediate region. Recently, Pooler (1980) has calculated by means of an analytical method some of the properties of the vibronic eigenstates in strong coupling such as reduction factors and radiative lifetimes of the low-lying states. Our numerical studies are in excellent agreement with his results and provide the link to both weak and strong coupling expressions.

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