

Theory of Optical Band Shape for $A_{1g} - T_{1u}$ Transition. II

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A theory of the optical band shape for $A_{1g} - T_{1u}$ transitions is developed based on the method of the characteristic function. It covers the region of weak coupling between the electrons and the phonon modes of a_{1g} , e_g and t_{2g} symmetries, and takes account of the phonon dispersion. It is found that the cumulant function of the characteristic function can be described by a two-time phonon correlation function which includes the multi-phonon correlation due to the Jahn-Teller effect. A Dyson equation of the phonon correlation function is solved under specific conditions where the contribution from the e_g modes is neglected and the phonons have a Lorentzian dispersion. Analytical expressions are given for intensity, peak shift and broadening of a few lower phonon side bands, and it is found that the one phonon side band of the t_{2g} mode shifts to higher frequencies than that of the a_{1g} mode.

1. Introduction

Several approaches have been proposed for the formulation of the optical band shape of Jahn-Teller systems¹. Among others, a formulation which was derived by Wagner² and by Vekhter et al.³ for the $E \times e$ Jahn-Teller system is quite interesting, since it has an analytical character. In its derivation, these authors use an approximation called the Independent Ordering Approximation (IOA). As shown by Wagner², this approximation gives correct results in two extreme cases, the weak coupling limit and the strong coupling limit, where the character of the spectral shape is well-known from other approximations. In the case of intermediate coupling, however, the character of the spectral shape given by the IOA has not yet been investigated in detail.

For this reason, in part I⁴ we applied the IOA to the $A_{1g} - T_{1u}$ transition and calculated spectral shapes mainly in the case of intermediate coupling. The result could explain at least qualitatively the peculiar feature of the spectral shape of an Ag^- center in alkali halides⁵ that a three-headed curve appears at high temperatures, and one of its peaks disappears at low temperatures. Thus the theory turned out to have a wider applicability than the semiclassical theory of Toyozawa and Inoue⁶.

In the case of weak coupling and low temperature, however, one often observes sharp phonon structures in the spectral function. By analysing such structures together with the global profile of

the spectrum, we can expect to get better insight into the nature of the electron-phonon interaction associated with the absorption center. After the previous paper was published, however, it became apparent that the IOA gives unreasonably broad phonon structures in the weak coupling case, even though we took account of the phonon dispersion rigorously. This broadening arises from the fact that the spectral shape of the IOA is given as a superposition of nondegenerate shape functions with different Huang-Rhys factors [cf. Eqs. (38) and (39) in Part I], and that sharp phonon structures associated with each nondegenerate shape function are broadened to a width of about $S_2^3 \omega/2$, namely the Huang-Rhys factor of the t_{2g} mode times the phonon frequency ω . In the weak coupling limit, where this broadening is much smaller than the broadening due to the phonon dispersion, the IOA gives reasonable results, but in other cases it is not appropriate to treat the phonon structure within the framework of the IOA*. Therefore, it is desirable to improve the foregoing treatment if we want to consider phonon structures in detail in the case of weak coupling and low temperature.

In Part II, we will extend the characteristic function method, which was first derived by Lax⁸ and was applied only to the singlet-singlet transition, so as to be applicable to the $A_{1g} - T_{1u}$ transition. Although such an attempt was undertaken by McCumber⁹ on the $E \times e$ problem, the cumulant ex-

* The statement in part I that the IOA covers all regions of the temperature and of the linear electron phonon coupling strength is misleading. Muramatsu and Nasu⁷ discussed the magnitude of the error of the spectral shape brought about by using the IOA for the intermediate coupling case.

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pansion was terminated with only the two-phonon correlation function in his formulation. In the present work it will be shown that the cumulant function can be expressed by a two-time phonon correlation function which includes multi-phonon correlations due to the Jahn-Teller effect. The effect of multi-phonon correlations (higher than the two-

phonon) cannot be neglected even in the case of weak coupling such that the zero, one and two phonon side bands dominate in the spectral function. To take account of the phonon dispersion, a Dyson equation of the phonon correlation function will be solved under specific conditions.

2. General Formulation of Optical Band Shape

Throughout this paper, we will follow the notation used in Part I. As a starting point, we will expand straightly the characteristic function $W_{23}(t)$ due to e_g and t_{2g} modes, define by Eq. (25) in Part I, with respect to the Huang-Rhys factors **,

$$W_{23}(t) = \sum_{n=0}^{\infty} \sum_{\Gamma_1}^{2,3} \dots \sum_{\Gamma_n}^{2,3} \sum_{\kappa_1 i_1} \dots \sum_{\kappa_n i_n} [(-1)^n / 2^n] S_{\Gamma_1 \kappa_1}^2 \dots S_{\Gamma_n \kappa_n}^2 \omega_{\Gamma_1 \kappa_1}^2 \dots \omega_{\Gamma_n \kappa_n}^2 \\ \times \int_0^t dt_1 \dots \int_0^{t_{2n-1}} dt_{2n} \sum_d T_c [\tau_{\Gamma_1 i_1}(t_{m_1}) \tau_{\Gamma_1 i_1}(t_{m_2}) \dots \tau_{\Gamma_n i_n}(t_{m_{2n-1}}) \tau_{\Gamma_n i_n}(t_{m_{2n}})] \\ \times \varphi(\omega_{\Gamma_1 \kappa_1}, t_{m_1} - t_{m_2}) \dots \varphi(\omega_{\Gamma_n \kappa_n}, t_{m_{2n-1}} - t_{m_{2n}}). \quad (1)$$

Here $\varphi(\omega, t)$ is the unperturbed phonon correlation function,

$$\varphi(\omega, t) = \langle n(\omega) \rangle e^{-i\omega t} + \{ \langle n(\omega) \rangle + 1 \} e^{i\omega t},$$

$\langle n(\omega) \rangle$ is the thermal average of the phonon number,

$$\langle n(\omega) \rangle = (e^{\hbar\omega/kT} - 1)^{-1},$$

and \sum_d means the summation over all possible combinations, in which integers from 1 to $2n$ are grouped into n pairs. We denote a combination d by a set of n pairs (m_{2j-1}, m_{2j}) ($j=1, \dots, n$), where $m_{2j-1} < m_{2j}$,

$$d = (m_1, m_2) \dots (m_{2n-1}, m_{2n}). \quad (2)$$

The total number of these combinations is $(2n-1)!!$. From Eq. (1), it follows that

$$J_{23}(t) \equiv \text{Tr}[W_{23}(t)]/3 = \sum_{n=0}^{\infty} (S_3^2/2)^n \sum_d f_{nd}(b) U_{nd}(t), \quad (3)$$

where $f_{nd}(b)$ is the trace of the time ordered product of matrices in Eq. (1),

$$f_{nd}(b) = \frac{1}{3} \text{Tr} \left\{ \sum_{\substack{i_1, \dots, i_n \\ \Gamma_1, \dots, \Gamma_n = 2, 3}} T_c [\tau_{\Gamma_1 i_1}(t_{m_1}) \tau_{\Gamma_1 i_1}(t_{m_2}) \dots \tau_{\Gamma_n i_n}(t_{m_{2n-1}}) \tau_{\Gamma_n i_n}(t_{m_{2n}})] b^{2(3n - \Gamma_1 - \dots - \Gamma_n)} \right\}, \quad (4)$$

and

$$U_{nd}(t) = (-1)^n \int d\omega_1 \dots \int d\omega_n \sigma_3(\omega_1) \dots \sigma_3(\omega_n) \omega_1^2 \dots \omega_n^2 \\ \times \int_0^t dt_1 \dots \int_0^{t_{2n-1}} dt_{2n} \varphi(\omega_1, t_{m_1} - t_{m_2}) \dots \varphi(\omega_n, t_{m_{2n-1}} - t_{m_{2n}}). \quad (5)$$

Here, we have confined ourselves as in Part I, to the specific case that the projected densities of e_g and t_{2g} modes are equal,

$$\sigma_2(\omega) = \sigma_3(\omega), \quad \text{and put } S_2^2/S_3^2 = b^2.$$

** τ_{3i} ($i=1, 2, 3$) used here is normalized in the following manner,

$$\text{Tr} \left(\sum_{i=1}^3 \tau_{3i}^2 \right) / 3 = 1,$$

and is different from Eq. (9) in part I only by a normalization factor $2^{-\frac{1}{2}}$.

It is convenient to represent $U_{nd}(t)$ by a simple diagram. For example, in the case where $n=2$ and $d=(1,3)(2,4)$, $U_{nd}(t)$ is represented by the diagram shown below,

$$U_{2d}(t) = \int d\omega_1 \int d\omega_2 \sigma_3(\omega_1) \sigma_3(\omega_2) \omega_1^2 \omega_2^2 \int_0^t dt_1 \dots \int_0^{t_3} dt_4 \varphi(\omega_1, t_1 - t_3) \varphi(\omega_2, t_2 - t_4)$$

$$= \begin{array}{c} \text{---} \text{---} \text{---} \text{---} \\ \times \quad \times \quad \times \quad \times \\ t_1 \quad t_2 \quad t_3 \quad t_4 \end{array}, \quad (6)$$

where ---- means the phonon line and the vertices \times correspond to the t_1, \dots, t_{2n} in the order of left to right. Then we have

$$J_{23}(t) = 1 + (S_3^2/2) (1 + b^2) (\times \times) + (S_3^2/2)^2 \{ (1 + b^2)^2 (\times \times \times \times + \times \times \times \times) + (\frac{1}{2} - b^2 + b^4) (\times \times \times \times) \} + \dots \quad (7)$$

Numerical values of $f_{nd}(b)$ of higher order diagrams cannot be known without numerical computations, but a diagram:

$$\begin{array}{ccccccc} 1 & 2 & & n-1 & n \\ \times & \times & \times & \times & \times & \dots & \times & \times & \times \end{array} \quad (8)$$

is readily seen to have the value

$$f_{nd}(0) = 2^{-(n-1)}, \quad (9)$$

because

$$\tau_{3i} \tau_{3j} \tau_{3i} = 0 \quad (i \neq j).$$

The products of $U_{n_i d_i}(t)$ ($i=1, \dots, k$) can be expanded as a linear combination of $U_{nd}(t)$ of order n ,

$$\prod_{i=1}^k (U_{n_i d_i})^{m_i} = \sum_d M(d_1^{m_1}, \dots, d_k^{m_k}; d) U_{nd}, \quad (10)$$

where n is given by

$$n = \sum_{i=1}^k m_i n_i.$$

The coefficient $M(d_1^{m_1}, \dots, d_k^{m_k}; d)$ is determined by dividing each time integral of $U_{n_i d_i}$ ($i=1, \dots, k$) into integrals of order $2n$. For example,

$$\begin{aligned} (\times \times) (\times \times \times \times) &= 3 (\times \times \times \times \times \times) \\ &+ 2 (\times \times \times \times \times \times + \times \times \times \times \times \times + \times \times \times \times \times \times) \\ &+ (\times \times \times \times \times \times + \times \times \times \times \times \times + \times \times \times \times \times \times) \\ &+ (\times \times \times \times \times \times + \times \times \times \times \times \times + \times \times \times \times \times \times). \end{aligned} \quad (11)$$

As shown in Fig. 1, the time integrals of the two diagrams appearing on the left-hand side of Eq. (11) can be divided into 15 areas to give time integrals of order 6,

$$\int_0^t dt_1 \int_0^{t_1} dt_2 \times \int_0^t dt_3 \dots \int_0^{t_5} dt_6 \rightarrow \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \dots \int_0^{t_5} dt_6$$

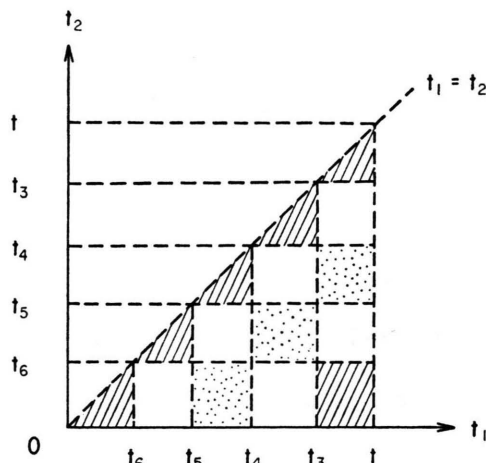


Fig. 1. Dividing the time integral into 15 areas.

each of which corresponding to a diagram of order $n=3$. The dotted areas correspond to the first term of the right-hand side of Eq. (11) and $M=3$, the white areas correspond to the second term and $M=2$, and the shaded areas correspond to the remaining terms and $M=1$. M can also be easily determined by considering the topological structure of the diagrams. By a similar method we get the following relation:

$$(\times \text{---} \times)^2 = 2 (\times \text{---} \times \times \text{---} \times + \times \text{---} \times \times \text{---} \times + \times \text{---} \times \times \text{---} \times), \quad (12)$$

and a more general theorem:

$$(\times \text{---} \times)^n = n! \quad (\text{sum of all the diagrams of order } n). \quad (13)$$

Equation (31) in Part I can be derived using this theorem, if we approximate $f_{nd}(b)$ by its averaged value in Eq. (3), assuming that it is independent of the phonon correlation, $U_{nd}(t)$;

$$f_{nd}(b) \rightarrow \left\{ \sum_d f_{nd}(b) \right\} / (2n-1)!!.$$

Hereafter we call $M(d_1^{m_1}, \dots, d_k^{m_k}; d)$ the coefficient of the diagram d when it is factorized into m_i diagrams of the type d_i ($i=1, \dots, k$). If d is a reducible diagram in which not all the phonon lines are connected and is composed of m_i irreducible diagrams of a type d_i ($i=1, \dots, k$) with all phonon line connected, $M(d_1^{m_1}, \dots, d_k^{m_k}; d)$ depends only on its components,

$$M(d_1^{m_1}, \dots, d_k^{m_k}; d) = \prod_{i=1}^k (m_i!), \quad (14)$$

and is independent of the arrangement of the constituent diagrams. An example of this theorem is seen in the last term of Equation (11).

Writing the cumulant expansion of $J_{23}(t)$ in the form,

$$J_{23}(t) = \exp \left[\sum_{n=0}^{\infty} (S_3^2/2)^n \sum_d f'_{nd}(b) U_{nd}(t) \right], \quad (15)$$

we get the relation,

$$f'_{nd}(b) = f_{nd}(b) - \sum' \left[\prod_{i=1}^k \frac{\{f'_{n_i d_i}(b)\}^{m_i}}{m_i!} \right] M(d_1^{m_1}, \dots, d_k^{m_k}; d), \quad (16)$$

by comparing Eq. (3) with Equation (15). Here \sum' means the summation over all possible ways of factorization of the diagram d into m_i lower order diagrams of type d_i and of order n_i ($i=1, \dots, k$) under the condition,

$$n = \sum_{i=1}^k n_i m_i.$$

A great advantage of the cumulant expansion in Eq. (15) is the cancellation of $f'_{nd}(b)$ for reducible diagram; the cancellation is expected from the general property of the cumulant expansion as was shown by Kubo¹⁰, but in our specific case it can be proved by using Eqs. (14) and (16) if necessary. Then the cumulant function $U(t)$ is

$$U(t) \equiv \ln[J_{23}(t)] = \sum_{n=1}^{\infty} (S_3^2/2)^n \sum_d^{\text{ir}} f'_{nd}(b) U_{nd}(t), \quad (17)$$

where \sum_d^{ir} means the summation over all the irreducible diagrams. A computer calculation of $f'_{nd}(b)$ yields,

$$\begin{aligned} U(t) = & (S_3^2/2) (1+b^2) (\text{diagram with 2 crosses and 1 arc}) - \frac{1}{2} (S_3^2/2)^2 (1+6b^2) (\text{diagram with 3 crosses and 2 arcs}) \\ & + (S_3^2/2)^3 [(1+9b^2 + 27b^4/4) (\text{diagram with 4 crosses and 3 arcs}) \\ & + \frac{1}{4} (1+15b^2 + 9b^4) (\text{diagram with 5 crosses and 4 arcs}) + \dots] \end{aligned} \quad (18)$$

The $f'_{nd}(0)$ for the diagram (8) is,

$$f'_{nd}(0) = (-2)^{-(n-1)}, \quad (19)$$

which may be confirmed from Eqs. (9) and (16). The first term in Eq. (18) denotes the one phonon correlation and the rest comes from multi-phonon correlation due to a Jahn-Teller effect. How to manage the higher order terms is an essential problem in the theory of the phonon side bands of the Jahn-Teller system. In the case of the phonon of total symmetry, such as the a_{1g} modes in O_h , the expansion in Eq. (18) terminates with only the first term as shown in Eq. (24) in Part I. The matrix character of the Jahn-Teller interaction in Eq. (8) in Part I precludes the cancellation which is necessary for the expansion to terminate.

Here we define a perturbed phonon correlation function $\varphi'(\omega, t_1, t_2)$ which includes the multi-phonon correlation due to the Jahn-Teller effect:

$$\begin{aligned} \varphi'(\omega, t_1, t_2) = & \varphi(\omega, t_1 - t_2) \\ & + (S_3^2/2) \frac{(1+6b^2)}{2(1+b^2)} \int d\omega_1 \sigma_3(\omega_1) \omega_1^2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \varphi(\omega, t_1 - t_3) \varphi(\omega_1, t_2 - t_4) + \dots, \end{aligned} \quad (20)$$

and the cumulant function is written,

$$U(t) = - (S_3^2/2) (1+b^2) \int d\omega \sigma_3(\omega) \omega^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \varphi'(\omega, t_1, t_2). \quad (21)$$

Equation (20) can be rewritten in the form of a Dyson equation,

$$\begin{aligned} \varphi'(\omega, t_1, t_2) = & \varphi(\omega, t_1 - t_2) + (S_3^2/2) \frac{(1+6b^2)}{2(1+b^2)} \int d\omega_1 \sigma_3(\omega_1) \omega_1^2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \varphi(\omega, t_1 - t_3) \varphi'(\omega_1, t_2, t_4) \\ & + (S_3^2/2)^2 \int d\omega_1 \int d\omega_2 \sigma_3(\omega_1) \sigma_3(\omega_2) \omega_1^2 \omega_2^2 \int_0^{t_2} dt_3 \dots \int_0^{t_5} dt_6 \\ & \times \left\{ \frac{(1+9b^2+27b^4/4)}{(1+b^2)} \varphi(\omega, t_1 - t_4) \varphi(\omega_1, t_2 - t_5) \varphi'(\omega_2, t_3, t_6) \right. \\ & + \frac{(1+15b^2+9b^4)}{4(1+b^2)} [\varphi(\omega, t_1 - t_5) \varphi(\omega_1, t_2 - t_4) \varphi'(\omega_2, t_3, t_6) \\ & \quad \left. + \varphi(\omega, t_1 - t_4) \varphi(\omega_1, t_3 - t_5) \varphi'(\omega_2, t_2, t_6)] \right. \\ & \left. + \frac{b^2(1-3b^2+9b^4/4)}{(1+b^2)^2} \varphi(\omega, t_1 - t_3) \varphi(\omega_1, t_2 - t_5) \varphi(\omega_2, t_4, t_6) \right\} + \dots \end{aligned}$$

Hereafter we will confine ourselves to absolute zero temperature, then $\varphi'(\omega, t_1, t_2)$ simply becomes,

$$\varphi'(\omega, t_1, t_2) = \exp(i\omega t_1) g(\omega, t_2), \quad (22)$$

where $g(\omega, t_2)$ is the solution of the following equation,

$$\begin{aligned} g(\omega, t_2) = & e^{-i\omega t_2} + \frac{S_3^2}{2} \frac{(1+6b^2)}{2(1+b^2)} \int d\omega_1 \sigma_3(\omega_1) \omega_1^2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 e^{i(\omega_1 t_3 - \omega t_2)} g(\omega_1, t_4) \\ & + (S_3^2/2)^2 \int d\omega_1 \int d\omega_2 \sigma_3(\omega_1) \sigma_3(\omega_2) \omega_1^2 \omega_2^2 \int_0^{t_2} dt_3 \dots \int_0^{t_5} dt_6 \\ & \times \left\{ \frac{(1+9b^2+27b^4/4)}{(1+b^2)} \exp[-i\omega t_4 + i\omega_1(t_2 - t_5) + i\omega_2 t_3] g(\omega_2, t_6) \right. \\ & + \frac{(1+15b^2+9b^4)}{4(1+b^2)} \{ \exp[-i\omega t_5 + i\omega_1(t_2 - t_4) + i\omega_2 t_3] \\ & \quad \left. + \exp[-i\omega t_4 + i\omega_1(t_3 - t_5) + i\omega_2 t_2] \} g(\omega_2, t_6) \right. \\ & \left. + \frac{b^2(1-3b^2+9b^4/4)}{(1+b^2)^2} \exp[-i\omega t_3 + i\omega_1(t_2 - t_5) + i\omega_2 t_4] g(\omega_2, t_6) \right\} + \dots \end{aligned} \quad (23)$$

Further developments require the numerical solution of Eq. (23), but from Eqs. (21) and (22) we can clarify the physical meaning of the cumulant function; $U(t)$. Without loss of generality $g(\omega, t)$ can be casted into a Fourier transform,

$$g(\omega, t) = c(\omega) e^{-i\omega t} + \int d\omega' \varrho(\omega, \omega') e^{i\omega' t}, \quad (24)$$

where $\varrho(\omega, -\omega) = 0$. The functions $c(\omega)$ and $\varrho(\omega, \omega')$ must satisfy the initial conditions of Eq. (23): $g(\omega, 0) = 1$ and $(\partial/\partial t)g(\omega, t)|_{t=0} = -i\omega$, then we obtain

$$c(\omega) + \int d\omega' \varrho(\omega, \omega') = 1, \quad c(\omega) - \int d\omega' \frac{\omega'}{\omega} \varrho(\omega, \omega') = 1. \quad (25, 26)$$

From Eq. (24) the characteristic function turns out to have the following simple t dependence,

$$J(t) = \exp[-I - it\Delta\Omega + \int d\omega \sigma_T(\omega) e^{i\omega t}] \quad (27)$$

where $I, \Delta\Omega$ and $\sigma_T(\omega)$ are given by

$$I = (S_1^2/2) + (S_3^2/2) (1+b^2) \left\{ \int d\omega \sigma_3(\omega) \left[c(\omega) - \int d\omega' \varrho(\omega, \omega') \frac{\omega}{\omega' + \omega} \right] \right\}, \quad (28)$$

$$\Delta\Omega = (S_1^2/2) \langle \langle \omega \rangle \rangle_1 + (S_3^2/2) (1+b^2) \int d\omega \sigma_3(\omega) c(\omega) \omega, \quad (29)$$

$$\begin{aligned} \sigma_T(\omega) = & (S_1^2/2) \sigma_1(\omega) + (S_3^2/2) \left\{ \sigma_3(\omega) \left[c(\omega) - \int d\omega' \varrho(\omega, \omega') \frac{\omega}{\omega'} \right] \right. \\ & \left. + \int d\omega' \sigma_3(\omega') \int d\omega'' \varrho(\omega', \omega'') \frac{\omega'^2}{\omega''(\omega' + \omega'')} \delta(\omega - \omega'' - \omega') \right\}. \end{aligned} \quad (30)$$

The physical meaning of $I, \Delta\Omega$ and $\sigma_T(\omega)$ can easily be recognized by comparing them with the characteristic function of the a_{1g} mode alone:

$$W_1(t) = \exp \left[- (S_1^2/2) \{ i t \langle \langle \omega \rangle \rangle_1 + 1 - \int d\omega \sigma_1(\omega) e^{i\omega t} \} \right]. \quad (31)$$

That is, I is the Debye Waller factor; $\exp(-I)$ determines the relative intensity of the zero phonon line to the sum of phonon side bands. $\Delta\Omega$ is the self-energy which gives the frequency shift of the zero phonon line. $\sigma_T(\omega)$ is the reduced multi-phonon density; a superposition of the multi-fold convolutions gives the multi-phonon side bands. It contains most of the informations concerning the structure peculiar to the band shape for A_{1g} — T_{1u} transition. Contrary to $\sigma_1(\omega)$ of the a_{1g} mode alone, $\sigma_T(\omega)$ may be negative for certain frequencies and will be finite for larger frequencies than the maximum frequency of the phonons associated with the ground state of the impurity, as an effect of the multi-phonon correlation. According to the above discussion on $\sigma_T(\omega)$, $\varrho(\omega, \omega')$ in Eq. (24) must satisfy the condition,

$$\varrho(\omega, \omega') = 0 \quad (\omega' \leq -\omega). \quad (32)$$

Otherwise, phonon side bands would appear in the lower frequency side of the zero phonon line as can be seen from the second line of Eq. (30), but this is unreasonable, for there can be no phonon absorption process at absolute zero temperature.

Eventually, the Fourier transform of Eq. (27) gives the shape function $K(\Omega)$,

$$K(\Omega) = e^{-I} \sum_{n=0}^{\infty} \frac{1}{n!} \sigma_T^n(\Omega - \Omega_0 + \Delta\Omega), \quad (33)$$

which is a generalization of the expression of a_{1g} mode alone:

$$K(\Omega) = \exp \left[-S_1^2/2 \right] \sum_{n=0}^{\infty} \frac{1}{n!} (S_1^2/2)^n \sigma_1^n \left(\Omega - \Omega_0 + \frac{S_1^2}{2} \langle \langle \omega \rangle \rangle_1 \right), \quad (34)$$

where σ_T^n and σ_1^n are the n -fold convolution functions of σ_T and σ_1 respectively,

$$\sigma_T^n(\omega) = \int d\omega_1 \dots \int d\omega_n \left[\prod_{n'=1}^n \sigma_T(\omega_{n'}) \right] \delta(\omega_1 + \dots + \omega_n - \omega), \quad (35)$$

$$\sigma_1^n(\omega) = \int d\omega_1 \dots \int d\omega_n \left[\prod_{n'=1}^n \sigma_1(\omega_{n'}) \right] \delta(\omega_1 + \dots + \omega_n - \omega). \quad (36)$$

3. Calculation under Specific Conditions

In the case of very weak coupling $S_3^2/2 \ll 1$ and $b^2 < 1$, the cumulant expansion developed in Eq. (18) provides useful results. We terminate the cumulant expansion in Eq. (18) with two terms:

$$I = S_1^2/2 + S_3^2(1+b^2)/2 - (S_3^2/2)^2 \frac{(1+6b^2)}{2} \int d\omega_1 \int d\omega_2 \sigma_3(\omega_1) \sigma_3(\omega_2) \left\{ 1 + \frac{\omega_1 \omega_2}{(\omega_1 + \omega_2)^2} \right\}, \quad (37)$$

$$\Delta\Omega = (S_1^2/2) \langle \langle \omega \rangle \rangle_1 + (S_3^2/2) (1+b^2) \langle \langle \omega \rangle \rangle_3 - (S_3^2/2)^2 \frac{(1+6b^2)}{2} \int d\omega_1 \int d\omega_2 \sigma_3(\omega_1) \sigma_3(\omega_2) \frac{\omega_1 \omega_2}{\omega_1 + \omega_2}, \quad (38)$$

$$\begin{aligned} \sigma_T(\omega) = & (S_1^2/2) \sigma_1(\omega) + (S_3^2/2) (1+b^2) \sigma_3(\omega) \\ & - (S_3^2/2)^2 (1+b^2) \sigma_3(\omega) \int d\omega_1 \frac{\omega_1}{\omega_1 - \omega} \sigma_3(\omega_1) \\ & - (S_3^2/2)^2 \frac{(1+6b^2)}{2} \int d\omega_1 \int d\omega_2 \frac{\omega_1 \omega_2}{(\omega_1 + \omega_2)^2} \sigma_3(\omega_1) \sigma_3(\omega_2) \delta(\omega_1 + \omega_2 - \omega). \end{aligned} \quad (39)$$

The first and second terms of Eq. (39) are the reduced one phonon densities coming from the one phonon correlation, which also reflects on the zero phonon line as shown in the first and second terms of Eqs. (37)

and (38). The last term of Eq. (39) is the reduced two phonon density due to the two phonon correlation, which corrects the zero phonon line and the reduced one phonon density as shown in the third terms of Eqs. (37), (38) and (39).

Let us consider the one and two phonon side bands. Using the Green's function method, Boese and Wagner¹¹ had shown that the peak of the corrected one phonon side band shifts to higher frequencies than that of the original by the effect of the denominator $(\omega_1 - \omega)$ in the first term of Eq. (39), but even in the case of weak coupling $S_3^2/2 \sim 0.2$ ($b^2 = 0$), the correction term will exceed the original when ω is near the peak of $\sigma_3(\omega)$ by the effect of the denominator. For the same reason higher order corrections arising from the diagram (8) exceed the original, whereas corrections from other types of diagrams may all be small in this coupling region. It is understood from the topological structure of the diagrams that the former type gives the reduced two phonon density correcting the zero phonon line and the reduced one phonon density. The latter types such as the third, fifth and sixth diagrams in Eq. (18) give the reduced three phonon density correcting the zero phonon line and the reduced one and two phonon densities. Consequently, the latter corrections will be much smaller than that of the former in the weak coupling region where zero, one and two phonon side bands dominate in the spectral function. Then we solve the integral Eq. (23) neglecting terms higher than the second and the effect of the e_g mode. To avoid useless mathematical complexities, we consider the specific case where the phonons have a Lorentzian dispersion centered at ω_0 with the width $\gamma \omega_0$,

$$\sigma_1(\omega) \omega^2 = \sigma_3(\omega) \omega^2 = \omega_0 \frac{\gamma}{\pi \{ (\omega/\omega_0 - 1)^2 + \gamma^2 \}}, \quad (40)$$

where γ is much smaller than unity, $\gamma \ll 1$. The phonon correlation functions φ, φ' integrated over frequencies take very simple forms,

$$\int d\omega \sigma_3(\omega) \omega^2 \varphi(\omega, t) = \omega_0^2 \exp[i\omega_0'(t)], \quad (41)$$

$$\text{and} \quad \int d\omega \sigma_3(\omega) \omega^2 \varphi'(\omega, t_1, t_2) = \omega_0^2 \exp[i\omega_0'(t_1)] g(t_2), \quad (42)$$

$$\text{where} \quad \omega_0'(t) = \omega_0 t(1 + i\gamma t/|t|). \quad (43)$$

The integral equation for $g(t_2)$ is then

$$g(t_2) = e^{-i\omega_0'(t_2)} + \left(\frac{S_3^2}{2}\right) \frac{\omega_0^2}{2} e^{i\omega_0'(t_2)} \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 e^{-i\omega_0'(t_4)} g(t_4). \quad (44)$$

Equation (44) can be transformed into a second order linear differential equation, which is easily solved, and we get,

$$g(t) = \{e^{-i\omega_0'(t)} + c_1 \exp[i\omega_0'(t)(\lambda_1 - 1)] + c_2 \exp[i\omega_0'(t)(\lambda_2 - 1)]\} \left\{1 + \frac{S_3^2 \omega_0^2 t^2}{8[\omega_0'(t)]^2}\right\}^{-1}, \quad (45)$$

λ_1, λ_2 are roots of the following quadratic equation,

$$\lambda^2 - 3\lambda + 2 \left\{1 + \frac{S_3^2 \omega_0^2 t^2}{8[\omega_0'(t)]^2}\right\} = 0, \quad (46)$$

and c_1 and c_2 are constants to be determined from the initial conditions, Eqs. (25) and (26). Neglecting the dispersion except the effect of broadening of the phonon lines, we get

$$I = (S_1^2/2) + (S_3^2/2) (1 - S_3^2/16)/(1 + S_3^2/8)^2, \quad (47)$$

$$\Delta\Omega = \left(\frac{S_1^2}{2} + \frac{S_3^2}{2} \frac{1}{(1 + S_3^2/8)}\right) \omega_0, \quad (48)$$

$$\begin{aligned} \sigma_T(\omega) = & (S_1^2/2) \frac{\gamma}{\pi \omega_0 \{ (\omega/\omega_0 - 1)^2 + \gamma^2 \}} \\ & + (S_3^2/2)^2 \frac{1}{4(1 + S_3^2/8)} \left\{ \frac{\text{Re}(\lambda_2)}{\text{Re}(\lambda_2 - \lambda_1) \text{Re}(\lambda_1 - 1) \text{Re}(\lambda_1)} \right. \\ & \times \frac{\gamma \text{Re}(\lambda_1) + \text{Im}(\lambda_1)}{\pi \omega_0 \{ [\omega/\omega_0 - \text{Re}(\lambda_1)]^2 + [\gamma \text{Re}(\lambda_1) + \text{Im}(\lambda_1)]^2 \}} \\ & \left. + \frac{\text{Re}(\lambda_1)}{\text{Re}(\lambda_1 - \lambda_2) \text{Re}(\lambda_2 - 1) \text{Re}(\lambda_2)} \frac{\gamma \text{Re}(\lambda_2) + \text{Im}(\lambda_2)}{\pi \omega_0 \{ [\omega/\omega_0 - \text{Re}(\lambda_2)]^2 + [\gamma \text{Re}(\lambda_2) + \text{Im}(\lambda_2)]^2 \}} \right\}. \quad (49) \end{aligned}$$

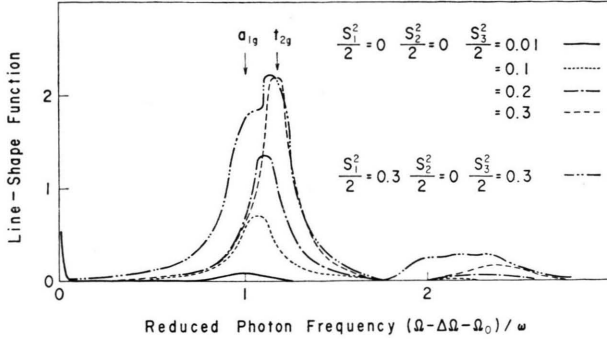


Fig. 2. The shape functions as a function of $S_1^2/2$ and $S_3^2/2$ at absolute zero temperature according to Eqs. (33), (47), (48) and (49). The phonons are assumed to have a Lorentzian dispersion ($\gamma=0.1333$) denified in Equation (40).

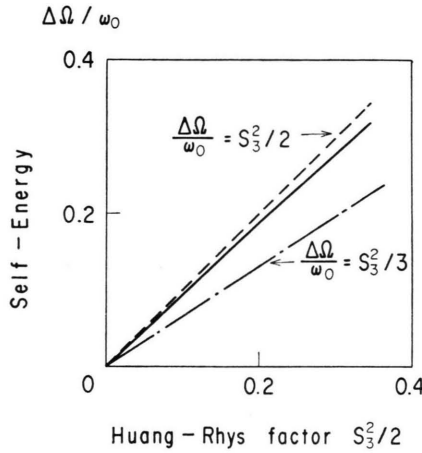


Fig. 3. The self-energy $\Delta\Omega/\omega_0$ as a function of $S_3^2/2$ according to Equation (48).

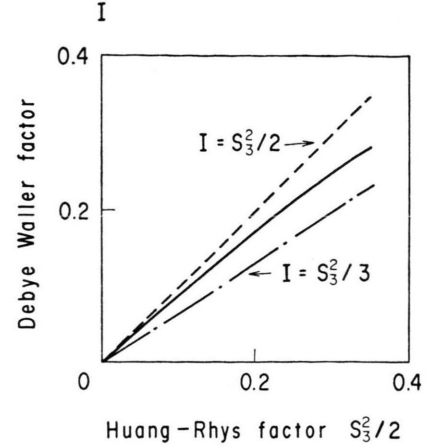


Fig. 4. The Debye Waller factor I as a function of $S_3^2/2$ according to Equation (47).

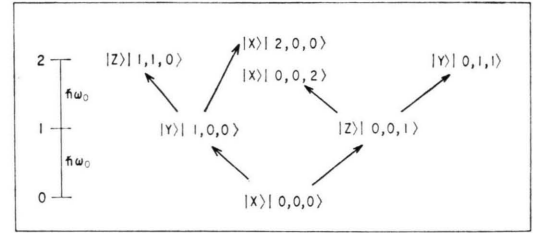


Fig. 5. The lower three levels excited by x polarized light. $|X\rangle$, $|Y\rangle$ and $|Z\rangle$ denote the wave functions of the electron of T_{1u} symmetry, and $|n_1, n_2, n_3\rangle$ denotes the wave function of the phonon of t_{2g} symmetry in which the phonon numbers of the xy , yz and zx modes are n_1 , n_2 and n_3 .

The peak of the one phonon side band of the t_{2g} mode shifts to higher frequencies than that of the a_{1g} mode as shown in Figure 2. $\Delta\Omega/\omega_0$ and I fall into the region between $S_3^2/2$ and $S_3^2/3$ as shown in Figs. 3 and 4. The lower bound corresponds to the classical treatment of the $T \times t$ problem, and the upper bound corresponds to the case of nondegeneracy or the a_{1g} mode. Let us consider the case of very weak coupling, $S_3^2 \ll 1$ in the $T \times t$ problem, neglecting the phonon dispersion. Figure 5 shows zero, one and two phonon states which are relevant to the absorption of light polarized in the x direction. The two fold degeneracy of the one phonon state is removed by the second order perturbation as shown by Moffitt and Thorson¹². One of them has T_{2u} symmetry with the wave function

$$(|Y\rangle|1,0,0\rangle - |Z\rangle|0,0,1\rangle)/2^{1/2}$$

according to Fig. 5, and shifts to the lower frequency side of the original one phonon state, for it does not couple to the zero phonon state. The other state of T_{1u} symmetry with the wave function

$$(|Y\rangle|1,0,0\rangle + |Z\rangle|0,0,1\rangle)/2^{1/2}$$

shifts to higher frequencies, and the separation from the zero phonon state is $\hbar\omega_0(1 + S_3^2/4)$, and in this case $\Delta\Omega/\omega_0$ and I become $S_3^2/2$. They are equal to the results of Eqs. (47), (48) and (49) when $S_3^2/2 \ll 1$. In the case of the strong coupling limit $S_3^2/2 \gg 1$, the three-fold degeneracy of the T_{1u} electronic state is completely removed by the static Jahn-Teller effect, and the adiabatic potential energy sur-

face (APES) has a minimum point at the trigonally-distorted configuration as shown by Öpik and Pryce¹³. In the vicinity of this point APES has the following form¹⁴:

$$\text{APES} = E^p + (2/3)^{1/2} S_3 q_z \hbar \omega_0 + \hbar \omega_0 (q_z^2 + q_x^2 + q_y^2)/2,$$

where q_z is the coordinate of the phonon which induces the trigonal distortion, and q_x and q_y are phonon coordinates orthogonal to q_z . In this case

$$I = \Delta\Omega/\omega_0 = S_3^2/3.$$

Our results shown in Fig. 3 become close to the above results as the coupling increases.

Incidentally, we will consider the broadening of the zero phonon line at very low temperatures in the case of weak coupling $S_3^2/2 \ll 1$ and $b^2 < 1$. In the case of the singlet-singlet transition, the linear interaction with phonons does not lead to any broadening of the zero phonon line at finite temperatures, but the matrix character of the Jahn-Teller interaction causes a broadening of the zero phonon line. The second diagram in Eq. (18) includes the Raman term

$$\frac{1}{2} (S_3^2/2)^2 (1 + 6b^2) \int d\omega_1 \int d\omega_2 \sigma_3(\omega_1) \sigma_3(\omega_2) \left[\frac{2\omega_1\omega_2}{(\omega_1 - \omega_2)^2} \langle n(\omega_1) \rangle \{ \langle n(\omega_2) \rangle + 1 \} \{ e^{-i(\omega_1 - \omega_2)t} - 1 \} \right], \quad (50)$$

which gives a broadening when the two frequencies nearly coincide. The asymptotic form of $J(t)$ for larger t , $|t| \gg 2\pi/\langle \omega \rangle_3$ is

$$J(t) = \exp[-it\Delta\Omega - \Gamma|t| + O(t^0)]. \quad (51)$$

The damping term in Eq. (51) comes from Eq. (50) making use of the property that

$$(1 - e^{-ixt})/x^2 \rightarrow \pi t \delta(x) + i\pi \delta'(x)t/|t|,$$

for $|t| \rightarrow +\infty$, and

$$\Gamma = \pi(1 + 6b^2) (S_3^2/2)^2 \int d\omega_1 \{ \sigma_3(\omega_1) \}^2 \langle n(\omega_1) \rangle \{ \langle n(\omega_1) \rangle + 1 \}. \quad (52)$$

Then the spectral shape of the zero phonon line $K_0(\Omega)$ becomes Lorentzian,

$$K_0(\Omega) \propto \frac{\Gamma}{\pi \{ (\Omega - \Omega_0 + \Delta\Omega)^2 + \Gamma^2 \}}. \quad (53)$$

4. Discussion and Conclusion

We have developed the theory of the optical band shape for the $A_{1g}-T_{1u}$ transition based on the method of the characteristic function. The physical meaning of the cumulant function of the characteristic function is clarified by introducing the perturbed phonon correlation function. The Dyson equation of the phonon correlation function was solved under specific conditions and analytical expressions are derived for intensity, peak-shift, broadening and splitting of a few lower phonon side bands. It is found that the one phonon side band of the t_{2g} mode shifts to higher frequencies than that of the a_{1g} mode as an effect of the multi-phonon correlation. It should be mentioned that the straightforward expansion of the phonon correlation function converges very slowly as shown in Section 3. If we want to go up to the two phonon

side band, at least all the higher order diagrams that contribute to the reduced two phonon density must be taken into account together with the corrections to the lower phonon side bands.

Although practical calculations may be somewhat complicated, there will be no further difficulty in extending the theory to higher phonon side bands or other singlet-multiplet transitions in the case of weak coupling.

In Sect. 3, we have treated the specific case where the coupling is predominantly in a narrow range of the phonon frequencies as represented by Eq. (40), but Eq. (23) has a more general character and can be solved numerically for arbitrary $\sigma_3(\omega)$ if necessary.

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