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Pressure-dependent properties of absorption- and emission-band shapes of impurities in solids

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Pressure dependences are determined for a number of properties of absorption- and emission-band shapes of vibrationally assisted electronic transitions within impurities in solids. The vibrational coupling of the impurity to the lattice includes both linear and quadratic interaction terms, as well as different pressure couplings in the ground and excited electronic states. The pressure-dependent properties that are examined include the zero-phonon-line energy, the first three moments, the centroid shift from the zero-phonon line, and the Stokes shift. In general, all these properties have pressure dependences that involve the quadratic interaction parameter and the difference in the pressure coupling to the ground and excited electronic states. These pressure-dependent effects are shown to arise through a pressure-dependent Huang-Rhys factor and a pressure-dependent energy separation between the minima of the electronic ground and excited states.

I. INTRODUCTION

There have been numerous studies reporting the effects of pressure on absorption- and emission-band shapes of solutes, gases, and impurities in solids. These have included both experimental and theoretical work, and have dealt with electronic effects *per se*, and also effects introduced through vibrational interactions with the electronic states. The experimental studies have primarily dealt with the readily measurable pressure-induced frequency shifts of the peaks of the band shapes. These shifts have been related to the pressure dependence of the crystal-field parameters for ion complexes and also for extrinsic impurities in solids.[1-3] The main concern of this paper is with the effects of hydrostatic pressure on those absorption- and emission-band shapes that are caused by vibrationally assisted electronic transitions within a single impurity ion (either intrinsic or extrinsic) in a solid.

Pressure-induced frequency shifts of band shapes have been extensively reported for impurities in alkali halides,[4-6] in II-VI compounds,[3,7,8] and in other host lattices.[2,9] There have been considerably fewer experimental studies of the pressure dependence of the half-width, peak intensity, and oscillator strength of such bands.[6,7,10-12] There is some indication that with increasing pressure the near-infrared band of Cr^{2+} in ZnS shifts to higher frequency, narrows, increases in peak intensity, and decreases in overall strength.[7] Surprisingly, there does not appear to be any reported experimental work concerning the pressure dependence of the moments of these band shapes. A good review of the experimental studies through 1965 is provided by Drickamer.[13]

As with the experimental work, most theoretical work has centered on the pressure-induced frequency shifts of the peaks of these bands,[4,6-8,10,14,15] although there has been some work reported concerning the pressure dependence of the half-width and peak intensity.[10-12,16] The early configuration-coordinate study by Johnson and Williams[4] likened the effects of pressure to those induced by a piston performing the work necessary to transfer the impurity and its surrounding from one configuration equilibrium position to another. With this interpretation, they were able to successfully fit the pressure-induced frequency shift of the absorption band in KCl:Tl. Henry, Schnatterly, and Slichter[14] investigated the effects on similar band shapes of both uniaxial stress and hydrostatic pressure. For an impurity ion whose electronic ground- and excited-state vibrational frequencies are equal, they find that the first three moments of an absorption-band shape are altered under the effect of hydrostatic pressure in such a way that the band is displaced in frequency. The over-all band shape, however, is unchanged. Koda *et al.*[8] constructed configuration-coordinate diagrams for a variety of impurities in ZnS from observed pressure-induced frequency shifts of the band maxima. Jacobs[6] concluded that for the *F* center in several alkali halides, the main pressure-induced frequency shift in the peak position is due to variation of the interatomic distances with pressure, while only a small fraction is due to optical lattice vibrations. He also predicted that unequal vibrational frequencies in the ground and excited electronic states could result in pressure-dependent half-widths, as well as frequency shifts of peak positions. This has been reiterated by others.[10-12]

The theoretical work of Drickamer, Frank, and Slichter[10] deals with a configuration-coordinate approach to understanding the effects of pressure on impurity band shapes. For equal pressure coupling in the ground and excited electronic states, they show that the peak position is pressure dependent, while the half-width is pressure dependent only if the ground and excited electronic states have different vibrational frequencies. Their approach was extended by others,[11,12] and served as a basis for a more complete study by Lin,[15] who generalized the approaches of both Johnson and Williams,[4] and Drickamer, Frank, and Slichter[10] in an attempt to obtain a theoretical foundation of their models. In his approach, Lin considers situations where the ground and excited electronic states have different vibrational frequencies and, simultaneously, where the pressure coupling to the ground and excited electronic states can be different. The theoretical model he develops is applicable to frequency shifts of electronic spectra, electronic relaxation, and transformation of electronic structures.

The intent of the present work is to build on the theoretical framework developed by Lin, and to investigate specifically how hydrostatic pressure affects various properties of vibrationally assisted electronic absorption- and emission-band shapes of impurities in solids. Prime concern here is with zero-phonon energies, peak positions, half-widths, the first three moments of the bands (indeed, all higher-order moments also), and the Stokes shift between absorption and emission. Since a band shape is completely specified once all its moments are determined, it is of importance to determine the dependence of these moments on pressure. The pressure dependences of these moments are, in turn, sufficient to describe completely the pressure dependence of the band shape.

II. THEORETICAL DEVELOPMENT

Consider an impurity ion located within a solid that is subjected to an external hydrostatic pressure P. The total ground-state Hamiltonian H_a, including the electronic, vibrational, and pressure contributions is written as the sum of the Hamiltonian $H_a(0)$ in the absence of pressure and the perturbation $H_a(P) - H_a(0)$ that is induced by the pressure. The pressure produces a change in the nuclear displacements s_j, which in turn perturb $H_a(0)$. Accordingly, we expand $H_a(P)$ in a Taylor expansion in the s_j about $H_a(0)$,

$$H_a(P) = H_a(0) + \sum_{j=1}^{N}\left[\left(\frac{\partial H_a}{\partial s_j}\right)_{s_{j0}}(s_j) + \sum_{n=2}^{\infty}\left(\frac{\partial^n H_a}{n!\,\partial s_j^n}\right)_{s_{j0}}(s_j)^n\right], \quad (1)$$

plus higher-order terms having factors like $\partial^n H_a/\partial s_j^k \partial s_k^{n-k}$. The occurrence of such terms is not essential to the present development, but they do contribute to higher-order effects. The $P=0$ nuclear displacements are s_{j0}, and j designates the jth of the N possible nuclear displacements. The nuclear displacements are linearly related to the pressure and also to the nuclear coordinates $R_{0j} + \Delta R_j$ and, thereby, to the normal coordinates q_j through β_j, the modulus of compressibility when the pressure is nonzero

$$s_j = P\beta_j(R_{0j} + \Delta R_j) = P\beta_j\left(R_{0j} + \sum_k a_{jk} q_k\right). \quad (2)$$

The ΔR_j are displacements that are caused by nuclear vibration. Here, β_j is taken as pressure independent; in some instances, however, it is pressure dependent. This is considered further in Sec. III. The expressions $\partial^n H_a/\partial s_j^n$ for all n, including $n=0$, in Eq. (1) are evaluated at $P=0$, and are therefore pressure independent. They are, accordingly, not evaluated at the equilibrium positions that occur for nonzero pressure, so we perform a Taylor expansion of the $(\partial^n H_a/\partial s_j^n)_{s_{j0}}$ in the ΔR_l about the pressure-induced equilibrium. Since the Taylor expansion is performed on a quantity that is evaluated at $P=0$, the change ∂s_l in the nuclear displacement is equal to the change $\partial \Delta R_l$ in the nuclear coordinate. Then

$$\left(\frac{\partial^n H_a}{\partial s_j^n}\right)_{s_{j0}} = \left(\frac{\partial^n H_a}{\partial s_j^n}\right)_{R_{0j}} + \sum_{l=1}^{N}\left(\frac{\partial^{n+1} H_a}{\partial s_j^n \partial s_l}\right)_{R_{0l}} \times \sum_k a_{lk} q_k + \sum_{l=1}^{N}\sum_{m=2}^{\infty}\left(\frac{\partial^{n+m} H_a}{m!\,\partial s_j^n \partial s_l^m}\right)_{R_{0l}} \times \left(\sum_k a_{lk} q_k\right)^m, \quad (3)$$

where use has been made of the second half of Eq. (2). For $n=1$, the first term on the right-hand side of Eq. (3) vanishes because $\partial H_a/\partial s_j$ is now evaluated at equilibrium. Equations (2) and (3) are now substituted into Eq. (1) and it is noted that $\sum_k a_{jk} q_k$ is negligible in comparison with the larger term R_{0j}. The leading terms of the resulting expression are

$$H_a(P) = H_a(0) + P\sum_{j=1}^{N}\beta_j R_{0j} \times \sum_{l=1}^{N}\left(\frac{\partial^2 H_a}{\partial s_j \partial s_l}\right)_{R_{0l}} \sum_k a_{lk} q_k. \quad (4)$$

The electronic potential of the ground state is then given by $E_a(P) = \langle\phi_a|H_a(P)|\phi_a\rangle$, where the ϕ_a

are the purely electronic wave functions; we define $E_a(0)$ similarly. The pressure-independent coefficient C_{ak} is introduced

$$C_{ak}=\sum_{j=1}^{N}\beta_j R_{0j}\sum_{l=1}^{N}\langle\phi_a|\left(\frac{\partial^2 H_a}{\partial s_j \partial s_l}\right)_{R_{0l}}|\phi_a\rangle a_{lk} . \tag{5}$$

Then the expression for the electronic ground-state potential becomes

$$E_a(P)=E_a(0)+P\sum_k C_{ak}q_k . \tag{6}$$

It has been shown elsewhere[17,18] that

$$E_a(0)=\sum_k E_{0ak}+\tfrac{1}{2}\omega_k^2 q_k^2 , \tag{7}$$

where E_{0ak} represents the equilibrium energy of the kth vibrational mode of the electronic ground state and ω_k is the vibrational frequency of the kth vibrational mode. Combining Eqs. (6) and (7) and rearranging, we get

$$E_a(P)=\sum_k\left[E_{0ak}-\frac{1}{2}\left(\frac{PC_{ak}}{\omega_k}\right)^2 + \tfrac{1}{2}\omega_k^2(q_k+PC_{ak}\omega_k^{-2})^2\right] . \tag{8}$$

The derivation of the vibrational potential for the electronic excited state proceeds analogously to that of the electronic ground state (see Ref. 18 for the derivation for $P=0$). In the derivation we introduce the ratio R_k of the electronic excited-state vibrational frequency of the kth vibrational mode to that of the electronic ground state of the same vibrational mode. We shall consider the general case where $R_k \neq 1$. R_k is usually not significantly different from unity, although it can vary for impurities in alkali halides.[11] All the results simplify to those of the linear interaction by merely setting R_k equal to unity. The quadratic interaction parameter R_k is so named because it is a measure of the degree to which E_b-E_a is quadratic in q_k. R_k is taken as pressure independent, in accordance with available data.[11] The Huang-Rhys factor, $S_k=R_k\omega_k q_{ek}^2/2\hbar$, on the other hand (see below) is a measure of the degree to which E_b-E_a is linear in q_k (at $P=0$). Here, q_{ek} is the equilibrium normal coordinate of the kth vibrational mode of the electronic excited state. Because the pressure coupling to the electronic excited state could be different from that of the electronic ground state—due to the atomic orbitals being rearranged with respect to one another—the coefficient $V_k=C_{bk}/C_{ak}$ is introduced to allow for asymmetry in the electronic ground-state and electronic excited-state pressure couplings

$$E_b(P)=\sum_k E_{0bk}-[(S_k R_k\hbar\omega_k)^{1/2} + PV_kC_{ak}[(2)^{1/2}R_k\omega_k]^{-1}]^2 + \tfrac{1}{2}R_k^2\omega_k^2\left[q_k+\left(\frac{2S_k\hbar}{R_k\omega_k}\right)^{1/2} + \left(\frac{PV_kC_{ak}}{R_k^2\omega_k^2}\right)\right]^2 . \tag{9}$$

We now consider just the kth vibrational mode, and drop the k subscript. Additionally, we shift both the ground-state and excited-state potential energies by the same amount, $P^2C_a^2/2\omega^2-E_{0a}$. This shift produces no effect in either the optical absorption spectra or the optical emission spectra that result from these potentials because these spectra depend on the difference in the ground-state and excited-state potentials. We also drop the a and b subscripts, and denote these pressure-shifted potentials as $U_a(P)$ and $U_b(P)$. For many impurity centers, a single configuration coordinate does not provide an accurate description of the system, and any realistic model should include a variety of interacting modes.[19] Keil[17b] finds that the presence of terms in $q_i q_j$ can be essentially deleted by appropriate choice of configuration coordinates. The potentials then become

$$U_a(P)=\tfrac{1}{2}\omega^2(q+PC\omega^{-2})^2 , \tag{10a}$$

$$U_b(P)=E_0-SR\hbar\omega-PVC\left(\frac{2S\hbar}{R\omega}\right)^{1/2}-\frac{P^2C^2(V^2-R^2)}{2R^2\omega^2} + \tfrac{1}{2}R^2\omega^2\left[q+\left(\frac{2S\hbar}{R\omega}\right)^{1/2}+\frac{PVC}{R^2\omega^2}\right]^2 . \tag{10b}$$

We introduce the pressure-shifted coordinate Q and the pressure-shifted Huang-Rhys factor S',

$$Q\equiv q+PC\omega^{-2}, \tag{11a}$$

$$S'\equiv[S^{1/2}+PC(V-R^2)(2R^3\hbar\omega^3)^{-1/2}]^2 ; \tag{11b}$$

the value of S' is pressure independent if $V=R^2$. Using Eqs. (11) and the definition

$$U_0\equiv E_0-PCR^2\left(\frac{2S'\hbar}{R\omega}\right)^{1/2}-\frac{P^2C^2(R^2-1)}{2\omega^2} , \tag{12}$$

Eqs. (10) become

$$U_a(P)=\tfrac{1}{2}\omega^2Q^2 , \tag{13a}$$

$$U_b(P)=U_0-S'R\hbar\omega+\tfrac{1}{2}R^2\omega^2\left[Q+\left(\frac{2S'\hbar}{R\omega}\right)^{1/2}\right]^2 . \tag{13b}$$

The ground-state equilibrium is located at $q_e=-PC\omega^{-2}$, and the ground-state vibrational motion is simple harmonic motion about the equilibrium. The excited-state vibrational motion is likewise simple harmonic, but with a different frequency $(R\omega)$ than that (ω) of the ground state, and possesses an equilibrium position that is shifted in both energy and normal coordinate from that of the ground state.

Note that for $P=0$, S' reduces to S, U_0 reduces to E_0, and Q reduces to q. In fact, Eqs. (13) are identical to the $P=0$ results with two exceptions: (i) the Huang-Rhys factor S is appropriate when $P=0$ is replaced by S' [Eq. (11b)] when $P\neq 0$; (ii) the energy E_0, appropriate when $P=0$, is replaced by U_0 [Eq. (12)] when $P\neq 0$. That these two replacements are all that is required to transform E_a and E_b to $U_a(P)$ and $U_b(P)$ means that any property of the band shape depending solely on these quantities can be readily transformed to its pressure-dependent form. We now consider a few examples of such pressure-shifted properties of the band shapes.

The eigenvalues of Eqs. (13) are

$$\epsilon_a=(i+\tfrac{1}{2})\hbar\omega\ , \tag{14a}$$

$$\epsilon_b=U_0-S'R\hbar\omega+(f+\tfrac{1}{2})R\hbar\omega\ , \tag{14b}$$

where i is the vibrational quantum number of the electronic ground state a, and f is the vibrational quantum number of the electronic excited state b.

The three lowest moments (and only these three[20]) of the band shapes are given by

$$M_n=f_{ab}A_i\langle\chi_i|(E_b-E_a)^n|\chi_i\rangle \tag{15}$$

for absorption, and similarly for emission except for replacing i by f and f_{ab} by f_{ba}. The χ_i are the electronic ground-state vibrational wave functions and f_{ab} is a coefficient that is not important for the present discussion [see Lax[20] for a derivation of Eq. (15) and a discussion of its limitations]. The notation A_i means a thermal average over all i, and when performed, involves $\theta=\hbar\omega/k$, and, of course, the temperature T. The wave functions and the potentials are all of the same form for Q at $P\neq 0$ as they are for q at $P=0$. Accordingly, to transform the moments for $P=0$ to those for $P\neq 0$, one simply replaces S by S' and E_0 by U_0. For convenience we use the notation $m_n=M_n/M_0$, and we present the second central moment m_{c2} (the second moment taken about the band centroid, m_1) instead of the second moment m_2, because m_{c2} can often be related to the half-width of the band. The emission moments are denoted by the subscript ϵ, and are obtained analogously to those for absorption. Table I lists the pressure dependences of the zero-phonon transition energy (for a transition between $i=0$ and $f=0$), the first moment (centroid) and second central moment of the band shape, the energy separation of the band centroid and the zero-phonon line, and the Stokes shift $\Delta(P)$ representing the energy separation of the absorption and emission centroids. These pressure dependences were obtained by making the substitutions S' for S, and U_0 and E_0 in the quantities in the second column from the left that give the well-known $P=0$ results. There are no terms proportional to P^3, so that the sum of the three right-hand-most columns gives the quantity in the left-hand column.

III. DISCUSSION

The zero-phonon line has a pressure-dependent position E_{zp} regardless of the value of S, R, or V (except in the trivial case where $R=1$, $V=1$, and $S=0$). Since R is usually on the order of unity (0.9 to 1.1), the zero-phonon line energy linearly decreases with P for low pressure; but it can be quadratically increasing or decreasing at high pressure, depending on the sign of R^2-V^2.

The zeroth moment is pressure independent. This is not surprising because here, where electronic effects are not considered, the zeroth moment is related to the number of absorbing centers. The centroid always has a pressure dependence regardless of whether $R=1$, $V=1$, or $S=0$, as long as all three do not occur simultaneously. Note that the pressure dependence of m_1 is different from that of E_{zp}, so that one is always shifted with respect to the other. This shift, $m_1(P)-E_{zp}(P)$, is given in Table I. It is pressure independent only when there is a strictly linear interaction $(R=V=1)$. Note that, depending on the values of R and V, this shift can display a minimum, a maximum or be a monotonically increasing or decreasing function of P. For bands that are near-Gaussian in shape (usually the case for $S\gtrsim 3$), the centroid closely approximates the peak position, and the above statements concerning the pressure dependence of the centroid can be taken to apply (with the near-Gaussian caveat) to the peak position as well. For such near-Gaussian bands, m_{c2} is related to the full width γ at half-maximum (half-width) by $\gamma=(8\ln 2)^{1/2}(m_{c2})^{1/2}$. For $V=R^2$ there is no pressure dependence of m_{c2} (and thereby the half-width). This appears to be the usual case experimentally. Typically, $R\simeq 1$ (although there can be exceptions), and since reported pressure dependences of many experimentally measured half-widths are either small or not detected,[8] this implies that V also is very close to unity. There are, however, instances[10,11] where the band does display a pressure dependent half-width that can be a linear or quadratic function of pressure. For low pressure and $R>|V^{1/2}|$, the half-width can even decrease with increasing pressure. For near-Gaussian-shaped bands, the

TABLE I. Pressure dependences of properties relevant to absorption- and emission-band shapes. The expression for any quantity in the left-hand column is given by the sum of the expressions in the three other columns.

Quantity	Pressure-independent term	Linear-pressure term	Quadratic-pressure term
Absorption			
$m_0(P)$	f_{ab}		
$m_1(P)$	$E_0+\frac{1}{4}(R^2-1)\hbar\omega\coth(\theta/2T)$	$-PCR^2(2S\hbar/R\omega)^{1/2}$	$+P^2C^2(1+R^2-2V)/2\omega^2$
$m_{c2}(P)$	$(\hbar\omega)^2SR^3\coth(\theta/2T)$	$+2PC\sqrt{S}R^3(\hbar\omega)^2(V-R^2)$	$+P^2C^2(V-R^2)^2R^3(\hbar\omega)^2$
	$+\frac{1}{8}(R^2-1)^2(\hbar\omega)^2\coth^2(\theta/2T)$	$\times(2R^2\hbar\omega^3)^{-1/2}\coth(\theta/2T)$	$\times(2R^3\hbar\omega^3)^{-1}\coth(\theta/2T)$
$m_1(P)-E_{zp}(P)$	$\frac{1}{2}(2SR+1-R)\hbar\omega$	$+PC(V-R^2)(2S\hbar/R\omega)^{1/2}$	$+P^2C^2(1-V^2)/2\omega^2$
	$+\frac{1}{4}(R^2-1)\hbar\omega\coth(\theta/2T)$		
Emission			
$m_{\epsilon 0}(P)$	f_{ba}		
$m_{\epsilon 1}(P)$	$E_0-(1+R^2)S\hbar\omega R^{-1}$	$+PCR^{-2}(2S\hbar/R\omega)^{1/2}$	$+P^2C^2V(2\omega^2R^4)^{-1}$
	$+\frac{1}{4}(R^2-1)\hbar\omega R^{-1}\coth(R\theta/2T)$	$\times(R^2-V-R^2V)$	$\times(2R^2-V-R^2V)$
$m_{c\epsilon 2}(P)$	$(\hbar\omega R^{-1})^2S\coth(R\theta/2T)$	$+2PC\sqrt{S}(V-R^2)(\hbar\omega R^{-1})^2$	$+P^2C^2(V-R^2)^2(\hbar\omega R^{-1})^2$
	$+\frac{1}{8}(R^2-1)^2(\hbar\omega R^{-1})^2\coth^2(R\theta/2T)$	$\times(2R^3\hbar\omega^3)^{-1/2}\coth(R\theta/2T)$	$\times(2R^3\hbar\omega^3)^{-1}\coth(R\theta/2T)$
$E_{zp}(P)-m_{\epsilon 1}(P)$	$\frac{1}{2}(R-1-2SR)\hbar\omega+(1+R^2)S\hbar\omega R^{-1}$	$-PCR^{-2}(R^2-V)(2S\hbar/R\omega)^{1/2}$	$+P^2C^2(V-R^2)^2/2\omega^2R^4$
	$+\frac{1}{4}(R^2-1)\hbar\omega R^{-1}\coth(R\theta/2T)$		
$E_{zp}(P)$	$E_0+\frac{1}{2}[R(1-2S)-1]\hbar\omega$	$-PVC(2S\hbar/R\omega)^{1/2}$	$+P^2C^2(R^2-V^2)/2R^2\omega^2$
$\Delta(P)$	$(1+R^2)S\hbar\omega R^{-1}+(1/4R)(R^2-1)\hbar\omega$	$+PCR^{-2}(V-R^2)(1+R^2)$	$+P^2C^2(V-R^2)^2(1+R^2)$
	$\times[R\coth(\theta/2T)-\coth(R\theta/2T)]$	$\times(2S\hbar/R\omega)^{1/2}$	$\times(2\omega^2R^4)^{-1}$

product of γ and the peak intensity is proportional to M_0, which is constant. Hence the peak intensity is a function of P, and varies approximately inversely as $\gamma(P)$.

The emission results are closely analogous to those of absorption. The location of the zero-phonon line for emission is coincident with that of absorption [see Eq. (14)]. As for the absorption band shapes, the zeroth emission moment is pressure independent, the emission centroid is always pressure dependent, and the second central moment for emission is quite similar in form to that of absorption. Also, as for absorption, the pressure dependence of the second central moment (hence the half-width) for emission vanishes if $V=R^2$. The separation of the emission centroid and the zero-phonon line is pressure independent if $V=R^2$, whereas for this to occur for absorption it is required that $V=R^2=1$.

The Stokes shift $\Delta(P)$ is the separation of the absorption and emission centroids. It is pressure independent only if $V=R^2$, but otherwise always has a pressure dependence.

The compressibility in the vicinity of an impurity has been found to be essentially the same as that for the host lattice for many impurity-host systems.[8] But for impurity ions whose radii are significantly different from those of the ions they replace, the local compressibility may differ from that of the host lattice. Additionally, experimentally measured compressibilities have been found to be pressure dependent.[21] The compressibility of the volume V at constant temperature T is

$$\beta=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T . \tag{16}$$

Lazarus,[22] Lawson,[23] and Slater[24] give an expression for $V(P)$, based on work by Bridgman[21] and Slater,[21] from which

$$\beta=(A-2BP)/(1-AP+BP^2) . \tag{17}$$

For KCl, $A=5.68\times10^{-6}$ bar^{-1}, $B=-7.24\times10^{-11}$ bar^{-2}, and, both here and typically, $B/A\simeq-10^{-5}$ bar^{-1}.[22] Thus, for pressures less than about 0.5 kbar, β is constant and equal to A, whereas for pressures between about 0.5 and 2 kbar, $\beta\simeq A-2BP$ and linearly increases with increasing pressure. For higher pressures β is a more complex function of P.

This variation of β with P introduces a second-order effect in those expressions in Table I that involve C. This can be corrected to a first approximation by giving β, and thereby C, the pressure dependence of Eq. (17).

IV. CONCLUDING REMARKS

The aim of this paper has been to obtain expressions for the pressure dependences of the main properties of absorption and emission band shapes within impurities in solids. These are tabulated in Table I. These pressure dependences are shown to be describable through a definition of a pressure-dependent Huang-Rhys factor and a pressure-dependent energy separation between the minima of the electronic ground and excited states. The figures of merit for these optical transitions are f_{ab} (also, f_{ba}), E_0, R, θ, S, V, and C. All but the last two can be determined, at least, in principle, from measurements made at atmospheric pressure. A determination of the five remaining unknown parameters from an atmospheric-pressure absorption or emission measurement requires highly accurate data—especially if a moments technique is employed. Nevertheless, such a determination is possible if unwanted effects are not present or are carefully removed. In addition, several of these five parameters can be pressure dependent. For example, the pressure dependence of the compressibility introduces additional constants to be specified. To determine V and C, pressure-dependent studies are required. V and C can be obtained from such nonatmospheric pressure measurements using the expressions listed in Table I. In fact, it would be informative to analyze the pressure-dependent moments of band shapes to obtain values of C and V.

For the linear interaction ($R=1$), the convolution approach of Ritter[25] has been found[26] to accurately portray the exact quantum-mechanical band shape. The technique applies to cases of reasonably large S ($\gtrsim 3$) and gives a continuous line shape rather than the δ-function spectrum of the exact quantum-mechanical treatment, and is accordingly easier to compare to experimental spectra. The convolution approach is relevant also to pressure studies. As mentioned in the previous sections, all that is required is the definition of S' and U_0.

For high pressures, the pressure dependences of Table I may not be followed because of departures from the approximations made in the derivation of the relations in Table I. These include the possible continuous dependence of the vibrational frequencies on pressure, the mixing of vibrational modes, the requirement of several normal coordinates for adequate discriptions of the band shapes, and the pressure dependence of the compressibility.

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