

Calculation of Nonradiative Electron Transition Rates in a Lattice-Localized-Electron System

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We outline a method for the calculation of (nonradiative) electron transition rates between pure electronic states (for an impurity or defect electron trapped in a crystalline lattice) which employs functions that may be directly correlated with the radiative spectral functions obtained from the interaction of the electron with an externally applied electromagnetic field. In order to handle a possibly strong electron-lattice distortion V_d , we have introduced a canonical transformation $[\exp i\mathcal{R}](H_0+V_d)[\exp(-i\mathcal{R})]$ to H_0+V_d , our unperturbed Hamiltonian, to insure the use of pure electronic states with our transition-inducing perturbation V_u . We have chosen Cr^{3+} and V^{3+} in corundum as a physical example for the theory, since their d electrons appear experimentally to exhibit a strong V_d type of coupling to the $194\text{-cm}^{-1} E_u$ mode of the Al_2O_3 lattice. Particular emphasis has been given to the temperature dependence of the ${}^4T_2 \rightarrow {}^2E$ and ${}^4T_2 \rightarrow {}^4A_2$ transition rates for Cr^{3+} .

I. INTRODUCTION

WE should like to calculate the (nonradiative) electron transition probability per unit time between pure electronic states for an impurity or defect electron trapped in a crystalline lattice. As a simple model we choose a two-component electron-phonon system consisting of a single trapped electron interacting with the surrounding lattice. The Hamiltonian operator H for such a system in quantized form may be expressed as

$$H=H'+V_u, \quad H'=H_0+V_d, \quad H_0=H_A+H_B, \quad (1a)$$

$$H_A=\sum_i \epsilon_i a_i^\dagger a_i, \quad H_B=\sum_n \omega_n (b_n^\dagger b_n + \frac{1}{2}), \quad (1b)$$

$$V_d=\sum_{i,n} v_{i,n} a_i^\dagger a_i (b_n + b_n^\dagger), \quad v_{i,n} \text{ real} \quad (1c)$$

$$V_u=\sum_{\substack{i,j,n \\ i \neq j}} v_{ij,n} a_i^\dagger a_j (b_n + b_n^\dagger), \quad v_{ij,n}=v_{ji,n} \text{ real} \quad (1d)$$

where b_n^\dagger and b_n are the standard raising and lowering operators for the emission or absorption of a phonon in mode n and a_i^\dagger and a_i are the creation and annihilation operators for electrons in the state i —the quantities ω_n and ϵ_i being the respective phonon and electron energies. The interaction V_d , linear in its phonon coordinates, whose matrix elements $v_{i,n}$ connect like electronic states is the electron-phonon interaction operator responsible for the displacement of the centers of oscillation of the phonons by the electron—considered for the case of the F center by Huang and Rhys,¹ by Lax,² by O'Rourke,³ and by Markham,⁴ among others. The interaction V_u , also linear in its phonon coordinates, whose matrix elements $v_{ij,n}$ connect unlike electronic states, is the electron-phonon interaction operator responsible for nonradiative decay whose transition probability per unit time we wish to calculate using perturbation theory

¹ K. Huang and A. Rhys, Proc. Roy. Soc. (London) **A204**, 406 (1950).

² M. Lax, J. Chem. Phys. **20**, 1752 (1952).

³ R. C. O'Rourke, Phys. Rev. **91**, 265 (1953).

⁴ J. J. Markham, Rev. Mod. Phys. **31**, 956 (1959).

(as done for the case of shallow impurity levels in Ge and Si by Kane⁵). Although V_d and V_u may be identified separately with two physical extremes (e.g., F centers and shallow impurities in Ge and Si), they combine to form the total electron-phonon interaction which is linear in the phonon coordinate, and should both be considered in the majority of calculations.

In calculating a transition probability per unit time by means of perturbation theory we are given a perturbation, in our case V_u , and a pair of Schrödinger equations

$$i(\partial/\partial t)|\Psi(t)\rangle = H|\Psi(t)\rangle, \quad i(\partial/\partial t)|\Phi(t)\rangle = H'|\Phi(t)\rangle, \quad (2)$$

$$H=H'+V_u, \quad \hbar=1,$$

and are expected to derive a solution incorporating the matrix elements

$$\langle \Phi_i(t) | V_u | \Phi_f(t) \rangle, \quad |\Phi(t)\rangle = e^{-iH't} |\Phi\rangle \quad (3)$$

between two states of the Hamiltonian H' . As long as we are interested in calculating a transition probability between two states of H' the procedure can be relatively simple. In our case, however, we are dealing with a two-component system A, B and are interested in a transition probability involving only one component A , the electron. Since H' contains a potentially strong interaction V_d between A and B so that $|\Phi\rangle$ is not directly factorable into $|A\rangle|B\rangle$, we must first introduce a canonical transformation

$$|\Phi\rangle = e^{-i\mathcal{R}} |A\rangle |B\rangle \quad (4)$$

subject to the requirement

$$\bar{H}_0 \equiv e^{i\mathcal{R}} H' e^{-i\mathcal{R}} = \bar{H}_A + \bar{H}_B, \quad (5)$$

in order to insure the use of pure electronic states with V_u . If it is possible to satisfy (5) we can express our matrix elements (3) using (4) and (5) as

$$\langle A_i | \langle B_i | \bar{V}(t) | B_f \rangle | A_f \rangle, \quad (6a)$$

⁵ E. O. Kane, Phys. Rev. **119**, 40 (1960).

where

$$\bar{V}(t) = [\exp i\bar{H}_0 t] \bar{V} [e^{-i\bar{H}_0 t}], \quad \bar{V} = e^{i\mathcal{R}} V_u e^{-i\mathcal{R}}. \quad (6b)$$

The advantages of the canonical transformation are clearly demonstrated upon considering

$$\sum_{if} p_0(\Phi_i) w_0(\Phi_i, \Phi_f) = \sum_{if} p_0(A_i) w_0(A_i, A_f), \quad (7)$$

an expression connecting the thermally weighted densities of states p_0 and transition elements⁶ w_0 of Φ with those of A . Using an equilibrium weighting factor and employing standard methods⁷ for calculating a transition probability per unit time, we set

$$p_0(\Phi_i) = \langle \Phi_i | e^{-\beta H'} | \Phi_i \rangle / \sum_j \langle \Phi_j | e^{-\beta H'} | \Phi_j \rangle, \quad \beta = 1/k_B T, \quad (8a)$$

$$w_0(\Phi_i, \Phi_f) = \lim_{\tau \rightarrow \infty} (1/\tau) \int_0^\tau dt \int_0^\tau dt'$$

$$\times \langle \Phi_i | e^{iH't'} V_u e^{-iH't'} | \Phi_f \rangle \langle \Phi_f | e^{iH't'} V_u e^{-iH't'} | \Phi_i \rangle. \quad (8b)$$

It is now necessary that we make explicit use of (4) in (8a), (8b), and (7) in order to establish that

$$p_0(A_i) = \langle A_i | \exp(-\beta \bar{H}_A) | A_i \rangle / \sum_j \langle A_j | \exp(-\beta \bar{H}_A) | A_j \rangle, \quad (9a)$$

$$w_0(A_i, A_f) = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau dt \int_0^\tau dt' \times \langle \langle A_i | \bar{V}(t) | A_f \rangle \langle A_f | \bar{V}(t') | A_i \rangle \rangle, \quad (9b)$$

where

$$\langle \dots \rangle = \sum_i \langle B_i | \exp(-\beta \bar{H}_B) \dots | B_i \rangle / \sum_i \langle B_i | \exp(-\beta \bar{H}_B) | B_i \rangle, \quad (9c)$$

$|B_f\rangle$ has been removed by summing over final states, and $e^{-\beta \bar{H}_B}$ has been absorbed by $w_0(A_i, A_f)$. A brief sketch of the canonical transformation as applied to our electron-phonon system is presented in Appendix A and will be referred to occasionally in Secs. II and III of this paper. It states briefly that given the transformation

$$\mathcal{R} = \sum_i g_i a_i^\dagger a_i = \sum_n C_n (b_n - b_n^\dagger), \quad (10a)$$

$$g_i = i \sum_n v_{i,n} (b_n - b_n^\dagger) / \omega_n, \quad C_n = i \sum_i v_{i,n} a_i^\dagger a_i / \omega_n, \quad (10b)$$

we obtain the set of transformed operators

$$\bar{a}_i \equiv e^{i\mathcal{R}} a_i e^{-i\mathcal{R}} = e^{-i\sigma_i} a_i, \quad \bar{a}_i^\dagger = e^{i\sigma_i} a_i^\dagger, \quad (11a)$$

$$\bar{b}_n \equiv e^{i\mathcal{R}} b_n e^{-i\mathcal{R}} = b_n + iC_n, \quad \bar{b}_n^\dagger = b_n^\dagger + iC_n, \quad (11b)$$

⁶ All transition elements w_0 appearing in a given representation of (7) are of the same order in the perturbation strength.

⁷ See, e.g., L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Co., New York, 1949), Chap. 8.

and the Hamiltonian

$$\bar{H}_0 \equiv e^{i\mathcal{R}} (H_0 + V_a) e^{-i\mathcal{R}} = H_0 - \sum_{n,i} v_{i,n}^2 a_i^\dagger a_i / \omega_n \quad (12a)$$

satisfying requirement (5), such that

$$\bar{H}_A = H_A - \sum_{n,i} v_{i,n}^2 a_i^\dagger a_i / \omega_n, \quad \bar{H}_B = H_B. \quad (12b)$$

Note that the subscript i (as used in this paper) indicates the initial state of the system only when it is used in conjunction with the subscript f which indicates the final state of the system; otherwise it is a general index equivalent to j or k .

II. TRANSITION PROBABILITY

The emphasis in this paper is on simplicity. Thus we shall accept a loss in generality and introduce the simplifying assumption that

$$v_{ij,n} \simeq \lambda_{ij}^0 (v_{i,n} - v_{j,n}), \quad \lambda_{ij}^0 = -\lambda_{ji}^0 \text{ are real} \quad (13)$$

into our calculation. Requirement (13) is a form of electron-phonon decoupling approximation frequently encountered in electron-lattice theory⁸ under various guises and becomes meaningful when n is restricted to a specified set of allowable phonon modes. We shall assume in using (13) that our interaction ($V_a + V_u$) can be restricted to a set of phonon modes capable of satisfying this approximation.

Returning to (1d) we write, using (13),

$$V_u = \sum_{\substack{i,j \\ i \neq j}} \lambda_{ij}^0 [V_a a_i^\dagger a_j];$$

and upon replacing V_a by $(H' - H_0)$ we obtain, with the aid of (6b), (1b), and (11a),

$$\bar{V}(t) = - \sum_{\substack{i,j \\ i \neq j}} \lambda_{ij}^0 \left(i \frac{d}{dt} + \omega_{ij} \right) (\bar{a}_i^\dagger(t) \bar{a}_j(t)), \quad \omega_{ji} = \epsilon_i - \epsilon_j. \quad (14)$$

Putting (14) into (9b) and using (11a), (12a), and (12b), we can express $w_0(A_i, A_f)$ as

$$w_0(A_i, A_f) = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau dt \int_0^\tau dt' dt'' \lambda_{if}^0 \lambda_{fi}^0 \times \left(i \frac{d}{dt} + \omega_{fi} \right) \left(i \frac{d}{dt'} + \omega_{fi} \right) \times e^{i\bar{a}_{fi}(t-t')} \langle e^{i[\sigma_i(t) - \sigma_f(t)]} e^{i[\sigma_f(t') - \sigma_i(t')] } \rangle, \quad (15a)$$

where

$$\bar{\omega}_{fi} = \omega_{fi} - \sum_n (v_{i,n}^2 - v_{f,n}^2) / \omega_n. \quad (15b)$$

⁸ Approximation (13) is based on the more rigid assumption that the contribution $V_n(q_n, \mathbf{r})$ of the n th lattice mode to the electron-lattice perturbation potential can be approximated as $V(\mathbf{r}) \lambda_n q_n$, where q_n is the lattice normal coordinate and λ_n is a parameter independent of \mathbf{r} .

The integrand of (15a) is an oscillating function of $(t-t')$, as the time and thermal development operators within the trace commute. Since we will have no contribution to $w_0(A_i, A_f)$ from terms involving d/dt , d/dt' or $d^2/dt dt'$, expression (15a) may be rewritten as simply

$$w_0(A_i, A_f) = 2\pi(\lambda_{if}^0)^2 \omega_f^2 K_{ij}^0(\bar{\omega}_{fi}) \quad (16)$$

in terms of the spectral function

$$K_{ij}^0(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} ds e^{i\omega s} K_{ij}^0(s), \quad (17a)$$

$$K_{ij}^0(s) = \langle e^{i[a_i(s)-a_j(s)]} e^{i(a_j-a_i)} \rangle$$

after transforming to the coordinates t and $s=t-t'$. It is sometimes convenient to express $K_{ij}^0(s)$ as

$$K_{ij}^0(s) = N_{ij}^2 [1 + L_{ij}(s)], \quad (17b)$$

where N_{ij} is the normalizing factor

$$\langle e^{i(a_i-a_j)} \rangle \quad (17c)$$

and $L_{ij}(s)$ is a correlation function. In this case

$$w_0(A_i, A_f) = 2\pi(\lambda_{if}^0)^2 \omega_f^2 N_{ij}^2 L_{ij}(\bar{\omega}_{fi}), \quad \bar{\omega}_{fi} \neq 0 \quad (18)$$

where $L_{ij}(\omega)$ is the transform of $L_{ij}(s)$. The function $w_0(A_i, A_f)$ is the zeroth-order approximation to the electron transition probability per unit time.

By substituting (8a) and (8b) into expression (7), we see that

$$\sum_{ij} p_0(A_i) w_0(A_i, A_f) = \int_{-\infty}^{\infty} ds \text{Tr} e^{-\beta H'} e^{iH's} V_u e^{-iH's} V_u / \text{Tr} e^{-\beta H'} \quad (19)$$

(after changing coordinates and commuting the time and thermal exponentials). The trace here can designate the sum over any complete set of states for our system. As H' does not alter the electronic state of the system, we can write

$$p_0(A_i) w_0(A_i, A_f) = \int_{-\infty}^{\infty} ds \text{Tr} e^{-\beta H'} e^{iH's} Q_{ij} e^{-iH's} Q_{ji} / \text{Tr} e^{-\beta H'}, \quad (20a)$$

where we have used (1d) and (19), and where

$$Q_{ij} = \sum_n v_{ij,n} a_i^\dagger a_j (b_n + b_n^\dagger). \quad (20b)$$

Expression (20a) represents a special case of the function

$$R_{ij}^\omega(X, Y) = \frac{1}{2\pi} \int_{-\infty}^{\infty} ds e^{i\omega s} R_{ij}^s(X, Y), \quad (21)$$

$$R_{ij}^s(X, Y) = \text{Tr} e^{-\beta Y} e^{iYs} X_{ij} e^{-iYs} X_{ji} / \text{Tr} e^{-\beta Y},$$

where X and Y are time-independent operators. Com-

muting β past X in $R_{ij}^s(X, Y)$ with the aid of the operator $\exp[-i\beta(d/ds)]$, we obtain⁹

$$\exp[-i\beta(d/ds)] R_{ij}^s(X, Y) = R_{ji}^{-s}(X, Y). \quad (22)$$

Upon taking the inverse transform using (22), we can equate integrands and write¹⁰

$$R_{ji}^{-\omega}(X, Y) = e^{-\beta\omega} R_{ij}^\omega(X, Y), \quad (23)$$

so that [inserting (20a) into (23)]

$$p_0(A_i) w_0(A_i, A_j) = p_0(A_j) w_0(A_j, A_i),$$

showing that $w_0(A_i, A_j)$ satisfies the conditions for thermal equilibrium. But suppose that instead of letting Y equal H' , we let it equal H and express

$$R_{ij}^0(Q, H) \cong p_1(A_i) w_1(A_i, A_j). \quad (24)$$

If we can satisfy (24), relation (23) guarantees that

$$p_1(A_i) w_1(A_i, A_j) = p_1(A_j) w_1(A_j, A_i).$$

Following Van Hove,¹¹ we take the diagonal part of $\exp(\beta\bar{H}_0) \exp(-\beta\bar{H})$ and $\exp(i\bar{H}_0 s) \exp(-i\bar{H} s)$ in (24). As an approximation this is equivalent to letting

$$\pm i\hat{\epsilon}_i s \rightarrow \pm i\hat{\epsilon}_i s - \Gamma_i |s|, \quad \beta\hat{\epsilon} \rightarrow \beta\hat{\epsilon} \quad (25a)$$

in the time and thermal exponentials of $p_0(A_i) w_0(A_i, A_j)$, where $\hat{\epsilon}_i$ is the energy of the i th electronic state after it has been shifted by both V_u and V_d , and¹²

$$2\Gamma_i = \sum_{k \neq i} w_1(A_i, A_k) + \text{additional terms}. \quad (25b)$$

If we are to satisfy (14) with H' replaced by H , we must also replace λ_{ij}^0 , as defined in (13), by λ_{ij}^1 such that

$$v_{ij,n} \simeq \lambda_{ij}^1 (v_{i,n} - v_{j,n}) + \sum_{k \neq i,j} (\lambda_{kj}^1 v_{ik,n} - \lambda_{ik}^1 v_{kj,n}). \quad (26)$$

Substituting (25a) into expression (16), we now obtain

$$w_1(A_i, A_f) = 2\pi(\lambda_{if}^1)^2 \omega_f^2 K_{ij}^1(\hat{\omega}_{fi}), \quad \hat{\omega}_{fi} = \hat{\epsilon}_i - \hat{\epsilon}_f, \quad (27a)$$

$$K_{ij}^1(s) = e^{-(\Gamma_i + \Gamma_f)|s|} K_{ij}^0(s), \quad (27b)$$

as a higher-order approximation to $w(A_i, A_f)$. Expression (27a), along with (16) and (18), provides the basis for our consideration of the nonradiative electron transition probability in solids. Since both $K_{ij}^0(\omega)$ and $K_{ij}^1(\omega)$ can be interpreted as radiative spectral functions—with the argument ω taken relative to the zero-phonon

⁹ If O is a linear operator and A and B are analytic functions it is trivial to show that $(\exp O)AB = [(\exp O)A] \times [(\exp O)B]$. To arrive at (22) we set $O = -i\beta d/ds$, $A = \exp(-\beta Y + isY)$, $B = X_{ij} \times \exp(-isY)$.

¹⁰ Expression (23) can also be proved from methods developed by D. N. Zubarev, Usp. Fiz. Nauk. **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 328 (1960)].

¹¹ L. Van Hove, Lecture Notes, University of Washington, 1958 (unpublished); Physica **21**, 901 (1955); **22**, 343 (1956); **23**, 441 (1957).

¹² In expression (25b) we lump into the category of (additional terms) broadening due to the existence of additional interactions, strain, etc. In so doing we assume that these mechanisms can be approximated by a Lorentzian profile.

position—we observe that our expressions for the non-radiative transition probability closely parallel expressions for the radiative absorption and emission properties of the system. In order to demonstrate this, we shall briefly discuss the radiative spectral functions as they apply to our electron-phonon model. In particular, we shall construct spectral functions based on the radiative absorption coefficient, contrast their description of emission and absorption, and demonstrate their equivalence to $K_{ij}^0(\omega)$ and $K_{ij}^1(\omega)$.

III. RADIATIVE SPECTRAL FUNCTIONS

The dominant contribution to the absorption coefficient α between the electronic states $\epsilon_2 > \epsilon_1$ may be expressed in the Kubo formalism¹³ as

$$\alpha_{12}(\omega) \sim -2 \lim_{\epsilon \rightarrow 0} \text{Im} G_{12}^{21}(\omega + i\epsilon, H), \quad (28a)$$

where

$$G_{ji}^{ij}(E, H) = -\frac{i}{2\pi} \int_0^\infty ds e^{iEs} [K_{ji}(s, H) - K_{ij}(-s, H)], \quad \text{Im} E > 0, \quad (28b)$$

$$K_{ji}(s, H) = \text{Tr} e^{-\beta H} e^{iHs} a_j^\dagger a_i e^{-iHs} a_i^\dagger a_j / \text{Tr} e^{-\beta H}, \quad \hbar = 1, \quad (28c)$$

$$K_{ji}(s - i\beta, H) = K_{ij}(-s, H), \quad (28d)$$

$$K_{ji}(s, H) = K_{ji}^*(-s, H),$$

express the difference between the radiative absorption and emission characteristics of the system in terms of temperature-dependent double-time Green's functions of the variety introduced by Bogoliubov *et al.*¹⁴ Defining a spectral-absorption function¹⁵

$$K_{12}(\omega, H) = \frac{1}{2\pi\rho_1} \int_{-\infty}^\infty ds e^{i\omega s} K_{12}(s, H), \quad (29)$$

$$\int_{-\infty}^\infty d\omega K_{12}(\omega, H) = 1,$$

such that for a one-electron system [using (9a) and (25a)]

$$\rho_i = p_1(A_i) = [\exp(-\beta\epsilon_i)] / \sum_j \exp(-\beta\epsilon_j), \quad (30)$$

we see from a comparison of (28c), (29), and (21) that

$$\rho_1 K_{12}(\omega, H) = R_{12}^\omega(a^\dagger a, H). \quad (31)$$

¹³ R. Kubo, J. Phys. Soc. (Japan) **12**, 570 (1957).

¹⁴ N. N. Bogoliubov and S. V. Tyablikov, Dokl. Akad. Nauk. SSSR **126**, 53 (1959) [English transl.: Soviet Phys.—Doklady **4**, 589 (1959)].

¹⁵ Expressions relating Green's functions to spectral functions are presented in Ref. 10.

Substituting (31) into (23) we obtain

$$K_{21}(-\omega, H) = \exp[-\beta(\omega - \bar{\omega}_{12})] K_{12}(\omega, H), \quad (32)$$

a relation contrasting the emission and absorption properties of the system. Had we used the spectral function $K_{12}(\omega, H')$ —with $\bar{\epsilon}_1$ replacing ϵ_1 in ρ_1 —we would have arrived at

$$K_{21}(-\omega, H') = \exp[-\beta(\omega - \bar{\omega}_{12})] K_{12}(\omega, H') \quad (33)$$

instead of (32). Assuming $\epsilon_2 \gg \epsilon_1$ and confining ourselves to temperatures below 300°K so that we may set $\rho_2 \sim 0$, $\rho_1 \sim 1$, we need only to calculate the absorption part of $G(E, H)$ in order to obtain α . In this case we find, after inserting (29) into (28b),

$$\alpha_{12}(\omega) \sim K_{12}(\omega, H).$$

In place of $K_{12}(\omega, H')$ and $K_{12}(\omega, H)$ we prefer for the purposes of this paper to use $K_{12}^0(\omega - \bar{\omega}_{12})$ and $K_{12}^1(\omega - \bar{\omega}_{12})$ as defined in Sec. II. To demonstrate their equivalence, we observe from (14) and (16) that the effective part of Q_{ij} in (20b) as far as the transition probability per unit time is concerned may be expressed as

$$(Q_{ij})_{\text{eff}} = -\lambda_{ij}^0 \omega_{ij} a_i^\dagger a_j. \quad (34)$$

Substituting first (34) and then (28c) into (20a) and dividing by $p_0(A_i)$, we see that

$$p_0(A_i) e^{i\bar{\omega}_{12} t} K_{ij}^0(s) = K_{ij}(s, H') \quad (35)$$

by comparing integrands with (16). Similarly for the case of H we would obtain

$$p_1(A_i) \exp[i\bar{\omega}_{12} s] K_{ij}^1(s) = K_{ij}(s, H). \quad (36)$$

Applying (29) and the analogous expression for $K_{12}(\omega, H')$ to (35) and (36), we thus arrive at

$$K_{12}^1(\omega - \bar{\omega}_{12}) = K_{12}(\omega, H), \quad (37)$$

$$K_{12}^0(\omega - \bar{\omega}_{12}) = K_{12}(\omega, H').$$

If we are to work with $K_{ij}^0(\omega)$ and $K_{ij}^1(\omega)$ we must first construct expressions for N_{ij} and $L_{ij}(s)$ as defined by (17a), (17b), and (17c). Derivations of $K_{ij}^0(s)$ are to be found in the literature.¹⁻⁴ We illustrate in Appendix B an example from which we obtain

$$N_{ij} = \langle e^{i[\sigma_i(s) - \sigma_j(s)]} \rangle$$

$$= \exp \left\{ -\frac{1}{2} \sum_n \frac{(v_{i,n} - v_{j,n})^2}{\omega_n^2} (2N_n + 1) \right\}, \quad (38a)$$

$$L_{ij}(s) = \exp \left\{ \sum_n \frac{(v_{i,n} - v_{j,n})^2}{\omega_n^2} \right. \\ \left. \times [N_n e^{i\omega_n s} + (N_n + 1) e^{-i\omega_n s}] \right\} - 1, \quad (38b)$$

where

$$N_n = (e^{\beta\omega_n} - 1)^{-1},$$

in agreement with standard theory. It is obvious from (38a) and (38b), and (17a) and (17b) that

$$K_{ij}^0(\omega) = K_{ji}^0(\omega); \quad (39)$$

and by substituting, in order, the second part of (37) and then (39) into (33), we obtain

$$K_{12}^0(-\Delta_{12}) = e^{-\beta\Delta_{12}} K_{12}^0(\Delta_{12}), \quad \Delta_{12} = \omega - \bar{\omega}_{12}, \quad (40)$$

a relation predicting the symmetry of the absorption spectrum relative to the zero-phonon energy $\bar{\omega}_{12}$. We are now in a position to consider an application to the theory.

IV. AN APPLICATION: Cr^{3+} AND V^{3+} IN CORUNDUM

Associated with the transitions ${}^4A_2 \rightarrow {}^4T_2$ (Cr^{3+} in Al_2O_3) and ${}^3T_1 \rightarrow {}^3T_2$ (V^{3+} in Al_2O_3) McClure¹⁶ has experimentally observed at 5°K well-defined spectra containing regularly spaced vibrational structure indicative of coupling to the 194-cm^{-1} E_u mode of the corundum lattice. In applying our one-electron $\epsilon_1 \rightarrow \epsilon_2$ model to Cr^{3+} and V^{3+} (which have 3 and 2 electrons, respectively, in the d state) we are confining ourselves to the calculation of spectral functions and transition probabilities arising from one-electron $d-d$ transitions and neglecting electron-electron coupling. To eliminate additional complications we shall also ignore splitting by the trigonal field of the corundum lattice¹⁷ and spin-orbit effects.

A. Corundum Lattice (Al_2O_3)

We limit our consideration of the corundum lattice to a band centered at 194 cm^{-1} satisfying requirements (13) and (26). From Eqs. (38a) and (38b), we conclude that our interest in the matrix elements $v_{i,n}$ and the phonon distribution function (implicit in the summation over phonon modes) is through the expressions

$$S_{ij}(\beta) = \sum_n (v_{i,n} - v_{j,n})^2 (2N_n + 1) / \omega_n^2, \quad (41a)$$

$$I_{ij}^{\pm}(\beta, s) = \sum_n (v_{i,n} - v_{j,n})^2 (N_n + \frac{1}{2} \mp \frac{1}{2}) e^{\pm i\omega_n s} / \omega_n^2, \quad (41b)$$

where

$$I_{ij}^{\pm}(\beta, s - i\beta) = I_{ij}^{\mp}(\beta, -s), \quad (41c)$$

$$I_{ij}^{+}(\beta, 0) + I_{ij}^{-}(\beta, 0) = S_{ij}(\beta).$$

We shall therefore [1] assume a continuous set of phonon modes exerting a maximum influence at 194 cm^{-1} , [2] require that $I_{ij}^{\pm}(\beta, s)$ provide adequate convergence of $L_{ij}(s)$ to zero for large $|s|$, and [3] demand that $I_{ij}^{\pm}(\beta, s)$

¹⁶ D. S. McClure, J. Chem. Phys. **36**, 2757 (1962); see also R. M. MacFarlane, J. Chem. Phys. **39**, 3118 (1963).

¹⁷ Since we choose to ignore the trigonal field splitting our transition ${}^4A_2 \rightarrow {}^4T_2$ in Cr^{3+} will correspond physically to the spin-allowed perpendicularly polarized component ${}^4A_2 \rightarrow {}^4T_2({}^4E)$. In the case of V^{3+} our transition ${}^3T_1 \rightarrow {}^3T_2$ will encompass both polarizations.

satisfy requirement (41c). Writing¹⁸

$$\mu_{12}^n = \int_{-\infty}^{\infty} d\omega (\omega - \bar{\omega}_{12})^n K_{12}^0(\omega - \bar{\omega}_{12})$$

$$= i^n \left[(d^n/dt^n) \int_{-\infty}^{\infty} d\omega e^{-i(\omega - \bar{\omega}_{12})t} K_{12}^0(\omega - \bar{\omega}_{12}) \right]_{t=0}$$

for the n th moment of the absorption band associated with an electronic transition $\epsilon_1 \rightarrow \epsilon_2$ ($\epsilon_2 > \epsilon_1$) in the impurity, we see (using (17a), (17b), and (17c), and (38a) and (38b) along with assumption [1] and (41a)) that the first moment μ_{12}^1 is

$$\mu_{12}^1 = \sum_n (v_{1,n} - v_{2,n})^2 / \omega_n \simeq \bar{\omega} S, \quad (42a)$$

$$S = S_{12}(\infty), \quad \bar{\omega} = 194\text{ cm}^{-1}.$$

Also using assumption [1] and (41a) one finds

$$S_{12}(\beta) \simeq S[2N(\bar{\omega}) + 1], \quad N(\bar{\omega}) = (e^{\beta\bar{\omega}} - 1)^{-1}. \quad (42b)$$

Since we have not assumed an exact knowledge of either the electron-phonon coupling or the phonon distribution function, it is useless to attempt an exact solution of $I_{12}^{\pm}(\beta, s)$. For low temperatures we shall modify $I_{12}^{\pm}(\beta, s)$ by writing

$$I_{12}^{\pm}(\beta, s) \simeq SN(\bar{\omega}) e^{\beta\bar{\omega}/2} \sum_n e^{\pm i\omega_n(s + i\beta/2)} / \sum_n 1, \quad (43a)$$

using assumption [1] and (41b). Letting

$$\sum_n e^{\pm i\omega_n z} / \sum_n 1 = \exp[\pm i\bar{\omega}z - \bar{\Gamma}(|z| - |\text{Im}z|)] \quad (43b)$$

and substituting (43b) into (43a) we obtain

$$I_{12}^{\pm}(\beta, s) = S(N(\bar{\omega}) + \frac{1}{2} \mp \frac{1}{2}) e^{\pm i\bar{\omega}s - \bar{\Gamma}(1 + \frac{1}{2}i\beta|s| - |\frac{1}{2}\beta|)}, \quad (44)$$

a simple expression satisfying requirements [2] and [3]¹⁹ for some temperature range

$$T_{\min} < T = 1/k_B\beta < T_{\max}.$$

This compact formulation introduces an additional parameter $\bar{\Gamma}$ from which we can establish an effective width of $2\bar{\Gamma}$ for our phonon band. It provides a reasonable approximation to use with (38a) and (38b) as long as T is not allowed to become too large²⁰ or too small.²¹

¹⁸ When constructing moments we shall consider $K_{ij}^0(\omega - \bar{\omega}_{ij})$ as providing an adequate description of our line shape.

¹⁹ The necessary condition that (44) satisfy the first part of (41c) and thus [3] is that the ratio $K_{12}^0(-\Delta_{12})/K_{12}^0(\Delta_{12})$ calculated using (44) provide adequate agreement with relation (40). The ability of (44) to meet this condition is discussed in Sec. IV C.

²⁰ Although μ_{12}^1 when computed using approximation (44) is identical to (42a), higher moments of the line tend to become distorted in this approximation with increase in temperature (see Appendix C). Since the cutoff T_{\max} is a function of $\bar{\Gamma}$, it will be determined in Sec. IV B.

²¹ In the limit of infinite β expression (44) becomes purely oscillatory over time, and its substitution into (38b) would yield a series of δ -type functions rather than a continuous spectrum for $K_{12}^0(\omega - \bar{\omega}_{12})$.

We shall arbitrarily assign $T_{\min} = 50^\circ\text{K}$ [since an exact expression for $I_{12}^\pm(\beta, s)$, dependent as it is upon N_n , should show little variation between 0 and 50°K] and insert it into our calculation in place of the true temperature when $T < 50^\circ\text{K}$. We shall consider T_{\max} in Sec. IVB. For $T \gg 300^\circ\text{K}$ we can come close to satisfying [2] and [3] by invoking the "slow-modulation approximation",²² in which case inserting (42b) into (41b) we approximate

$$I_{12}^+(\beta, s) + I_{12}^-(\beta, s) \simeq \{ [2N(\bar{\omega}) + 1] \times [1 - \frac{1}{2}\bar{\omega}^2 s^2] - is\bar{\omega} \} S. \quad (45)$$

When using expression (45) it is preferable to work directly with $K_{ij}^0(s)$ [through (17b)] as (45) prevents the possible formation of δ character in $K_{ij}^0(\omega)$ and eliminates the need for $L_{ij}(s)$. Writing

$$\Gamma = \Gamma_1 + \Gamma_2 \quad (46)$$

we see upon combining (27b), (17b), (38a) and (38b), (41a) and (41b), (42b), and (44) that $K_{12}^0(\omega - \bar{\omega}_{12})$ and $K_{12}^1(\omega - \bar{\omega}_{12})$ are completely defined in terms of their arguments and the parameters $\bar{\omega}$, S , $\bar{\Gamma}$, and Γ . However, at very high temperatures—inserting (45) in place of (44)—they are defined in terms of their arguments and the parameters $\bar{\omega}$, S , and Γ .

B. Determination of Parameters

In order to determine S , $\bar{\Gamma}$, and Γ we return to the experimental observations of McClure.^{16,17} Using (42a) we estimate from the band structure of his experimental curves for Cr^{3+} and V^{3+} at 5°K that upon setting $\epsilon_1 \rightarrow \epsilon_2$, respectively, equal to ${}^4A_2 \rightarrow {}^4T_2$ and ${}^3T_1 \rightarrow {}^3T_2$,

$$S(\text{Cr}^{3+}) \simeq S(\text{V}^{3+}) \simeq 6. \quad (47)$$

Assuming $\bar{\Gamma} > \Gamma$ we conclude that the half-width of the first vibrational component for Cr^{3+} and V^{3+} is characteristic of $\bar{\Gamma}$ and estimate, using these same curves, that

$$\bar{\Gamma}(\text{Cr}^{3+}) \simeq \bar{\Gamma}(\text{V}^{3+}) \simeq 0.15\bar{\omega}. \quad (48)$$

The half-width Γ at 5°K we approximate directly from the zero-phonon component and write

$$\Gamma(\text{Cr}^{3+}) \simeq 0.075\bar{\omega}, \quad \Gamma(\text{V}^{3+}) \simeq 0.037\bar{\omega}. \quad (49)$$

Although S and $\bar{\Gamma}$ (like $\bar{\omega}$) may be taken as independent of temperature, Γ as defined by (46) and (25b) merits further discussion.

For the sake of argument let us assume that $\Gamma(\text{Cr}^{3+})$ is determined primarily from the transition elements $w_1(A_i, A_k)$, which, though temperature-dependent, should increase $\Gamma(\text{Cr}^{3+})$ only by a factor of 2.5 between absolute zero and room temperature.²³ Since there are

²² The "slow-modulation approximation" expands $\exp(\pm i\omega_n s)$ in (41b) to second order in s . It provides a more accurate description of μ_{12}^* at moderate to high temperatures than (44) and is preferable for use at all temperatures in calculations far out on the high-energy wing. (See Appendix C.)

²³ It is shown in Fig. 3 that $w_1({}^4T_2, {}^2E)$, the prime contributor to 4T_2 relaxation, increases by a factor of 2.5 between 50 and 300°K .

no important contributions from the ground state, (49) would indicate a zero-temperature lifetime $(2c\Gamma_2)^{-1}$ for 4T_2 of 1.2×10^{-12} sec. However, experimental measurements by Pollack^{24,25} at room temperature appear to indicate a much greater lifetime of the order of 2×10^{-9} sec. We shall assume that this large discrepancy arises primarily from the necessary inclusion of strain broadening in any realistic estimate of $\Gamma(\text{Cr}^{3+})$. In fact, we shall further assume that strain broadening is the dominant contributing factor to both $\Gamma(\text{Cr}^{3+})$ and $\Gamma(\text{V}^{3+})$, in which case (assuming no structural change in the material), we can estimate that Γ is essentially temperature-independent.

Having established S , $\bar{\Gamma}$, and Γ we shall now determine T_{\max} . Proceeding as in the derivation of μ_{12}^1 in (42a) (see also Appendix C) we find that the dominant contribution to μ_{12}^2 at high temperatures comes from

$$i^2 \left[\frac{d^2}{dt^2} (I_{12}^+(\beta, t) + I_{12}^-(\beta, t)) \right]_{t=0}.$$

At $T = 400^\circ\text{K}$ and $\Gamma = 0.15\bar{\omega}$ we find a positive distortion of 14% in μ_{12}^2 by using approximation (44) instead of the exact expression (41a) in conjunction with assumption [1]. Since this distortion due to $\bar{\Gamma}$ becomes even more pronounced for higher even moments we shall assign $T_{\max} = 400^\circ\text{K}$ for $\bar{\Gamma} = 0.15\bar{\omega}$. In fact, this tendency of (44) to overestimate higher moments of the line-shape limits its use to very low temperatures when $K^0(\omega)$ or $K^1(\omega)$ must be evaluated far out on the high-energy wing ($\omega > 20\bar{\omega}$). In this region approximation (45) with a 5% negative distortion of μ_{12}^4 at 0°K (Appendix C) is preferable at all temperatures.

C. Low-Temperature Investigations: Approximation (44)

We shall designate any temperature for which $T < 300^\circ\text{K}$ as a low temperature and shall use approximation (44) in all calculations applied to this range where the argument of $K^0(\omega)$ or $K^1(\omega)$ is less than $20\bar{\omega}$. We found it desirable to first check the ratio $K_{12}^0(-\Delta_{12})/K_{12}^0(\Delta_{12})$ in this range in order to demonstrate that this approximation is really consistent with the symmetry requirement of [3]¹⁹ and is thus justified. Using (17a) and (17b), (38a) and (38b), (41a) and (41b), (42b), and (44) in conjunction with (47) and (48), the computation of $K_{12}^0(\Delta_{12})$ as a function of Δ_{12} was performed numerically on an IBM 7094 (Mark I) computer. We compared tabulated values of $K_{12}^0(-\Delta_{12})/K_{12}^0(\Delta_{12})$ up through $\Delta_{12} = 2\bar{\omega}$ obtained by this procedure with values derived from relation (40). Over the range considered a suitable agreement to within a factor of 3 was found to exist between tabulated and derived values even at temperatures as low as 50°K —substan-

²⁴ P. Kisliuk and C. A. Moore, Phys. Rev. **160**, 307 (1967).

²⁵ S. A. Pollack, J. Appl. Phys. **38**, 5083 (1967).

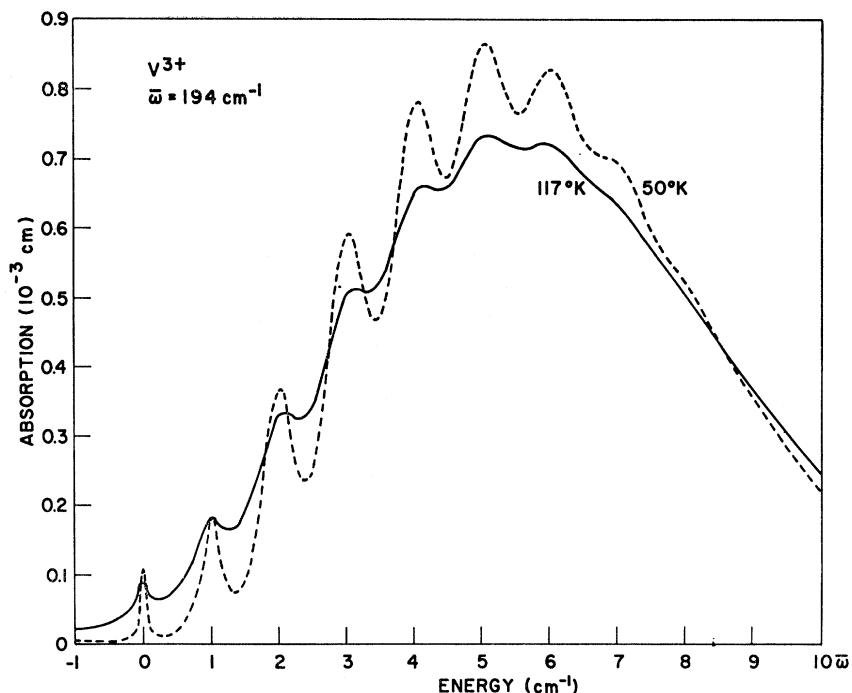


FIG. 1. Plots of the spectral absorption function $K_{12}^1(\Delta_{12})$ versus Δ_{12} for V^{3+} over the region $-\bar{\omega} \rightarrow 10\bar{\omega}$ at 50 and 117°K using approximation (45). The spectral function may be expressed in seconds by dividing its value in centimeters by the velocity of light.

tiating our argument. The spectrum of $K_{12}^0(\Delta_{12})$ has not been plotted since it differs only slightly from $K_{12}^1(\Delta_{12})$.

In order to illustrate the functional form of $K_{12}^1(\Delta_{12})$ prescribed by (44) we plot, in Fig. 1, $K_{12}^1(\Delta_{12})$ versus Δ_{12} for V^{3+} at 50 and 117°K. Using (27b) and (49)—in addition to those relations used in the computation of $K_{12}^0(\Delta_{12})$ —the computation of $K_{12}^1(\Delta_{12})$ was performed numerically at a rate corresponding to approximately 23 input values of the argument per minute. An increment of $0.1\bar{\omega}$ was used over the range $-2.5\bar{\omega} \leq \Delta_{12} \leq 10\bar{\omega}$. We notice in Fig. 1 a slight deviation of the energy $(\Delta_{12})_n$ at the n th vibrational peak from $n\bar{\omega}$. This deviation is due principally to Γ and becomes more pronounced for the case of Cr^{3+} ($\Gamma=0.15\bar{\omega}$). We define this deviation as Δ_n where

$$(\Delta_{12})_n = n\bar{\omega} + \Delta_n, \quad n > 0;$$

values of $\Delta_n/\bar{\omega}$ for Cr^{3+} at 50°K are given in Table I.

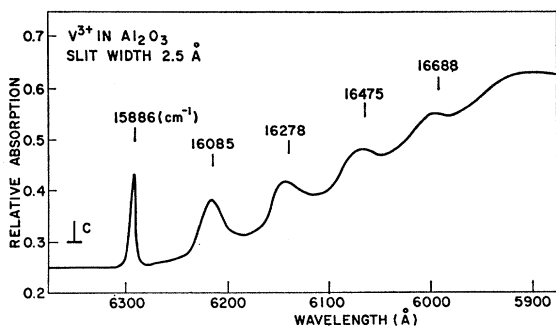


FIG. 2. Vibrational structure of the perpendicularly polarized component of the first strong absorption band of V^{3+} at about 5°K as obtained experimentally by McClure (Ref. 16).

These values were obtained from a numerical computation of $K_{12}^1(\Delta_{12})$ for Cr^{3+} using an increment of $0.01\bar{\omega}$, in order to more accurately establish the peaks. The deviation Δ_n is seen to first rise positively and then return to zero at Δ_6 in qualitative agreement with the experimental 5°K spectrum for Cr^{3+} presented by McClure. The line profile for V^{3+} at 50°K presented in Fig. 1 agrees quite well with McClure's experimental data (Fig. 2) although the vibrational satellites do not damp out as rapidly with increasing phonon number as in the experimental case. No experimental comparison is available at 117°K. The one-phonon annihilation peak observable numerically at 50 and 80°K for $K_{12}^0(\Delta_{12})$ appears abnormally suppressed for $K_{12}^1(\Delta_{12})$ due to the insufficient attenuation of phonon-creation elements by the Lorentzian broadening factor used in the calculation of $K_{12}^1(\Delta_{12})$. For this reason we have not indicated the presence of an annihilation peak in Fig. 1.

Before considering the question of transition probabilities, we must first determine λ_{ij}^1 and $\bar{\omega}_{ij}$. Ignoring coupling to states $k \neq i, j$ and energy shifts due to V_u ,

TABLE I. Values for the ratio of Δ_n (the deviation of the position of the n -phonon peak from $n\bar{\omega}$ obtained from a numerical computation of the spectral function) to $\bar{\omega}$ for V^{3+} indicating the extent of error in the calculation of the peak position.

| n | $\Delta_n/\bar{\omega}$ |
|-----|-------------------------|
| 1 | 0.01 ± 0.003 |
| 2 | 0.02 ± 0.003 |
| 3 | 0.04 ± 0.003 |
| 4 | 0.06 ± 0.003 |
| 5 | 0.05 ± 0.003 |
| 6 | 0.00 ± 0.003 |

we see from (26) and (25a) that we can set

$$\lambda_{ij}^1 = \lambda_{ij}^0, \quad \bar{\omega}_{ij} = \bar{\omega}_{ij}. \quad (50)$$

Let us confine our discussion of transition probabilities to Cr^{3+} and define an ϵ_l such that

$$\epsilon_l < \epsilon_2 = \epsilon(4T_2) \quad (51)$$

will include all states with energy less than ϵ_2 . We observe from the combined experimental spectrum¹⁶ of Cr^{3+} that transitions involving only ϵ_l are sharp lines. Thus it is reasonable to conclude that the coupling

$$v_{l,n} = 0. \quad (52)$$

Using (52) we now write

$$\bar{\omega}_{l2} = \omega_{l2} - \bar{\omega}S \quad (53)$$

by comparing (15b) with (42a). Also using (52), (38a) and (38b), (17a) and (17b), (39), (27b), and assuming Γ to be independent of l , we see that

$$K_{2l}^0(\omega) = K_{21}^0(\omega) = K_{12}^0(\omega), \quad (54)$$

$$K_{2l}^1(\omega) = K_{21}^1(\omega) = K_{12}^1(\omega),$$

and inserting expressions (50) and (53) into (27a) we obtain

$$w_1(A_2, A_l) = 2\pi(\lambda_{2l}^0)^2(\bar{\omega}_{l2} + \bar{\omega}S)^2 K_{2l}^1(\bar{\omega}_{l2}). \quad (55)$$

Expressions (54) act as a bridge between the radiative spectral functions previously determined for ${}^4A_2 \rightarrow {}^4T_2$ and the transition probability per unit time (55). In Fig. 3 we have plotted $w_1(A_2, A_l)/2(\lambda_{2l}^0)^2$ as a function of $\bar{\omega}_{l2}$ for Cr^{3+} at 50, 117, and 300°K. At $\bar{\omega}_{l2} \simeq 2300 \text{ cm}^{-1}$ ($11.9\bar{\omega}$), which is the ${}^4T_2 \rightarrow {}^2E$ energy difference, we have drawn a vertical line whose intercepts indicate the temperature dependence of the ${}^4T_2 \rightarrow {}^2E$ transition rate. The transition rate ${}^4T_2 \rightarrow {}^4A_2$ is not indicated, as it occurs far out in the wings at $\bar{\omega}_{l2} \simeq 86\bar{\omega}$. It will be considered, using approximation (45), in Sec. IV D. Figure 3 is illuminating in that it exhibits not only the temperature dependence for the rate of a nonradiative

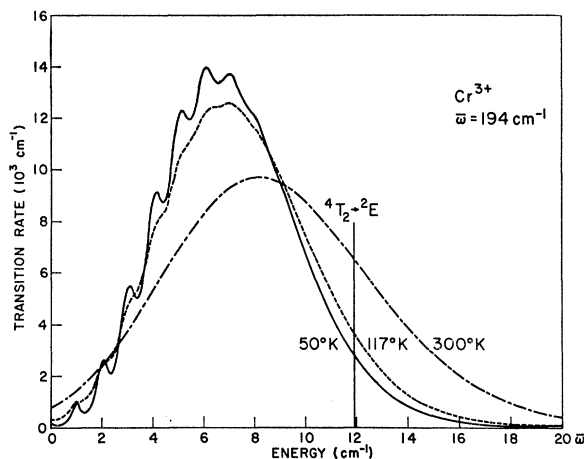


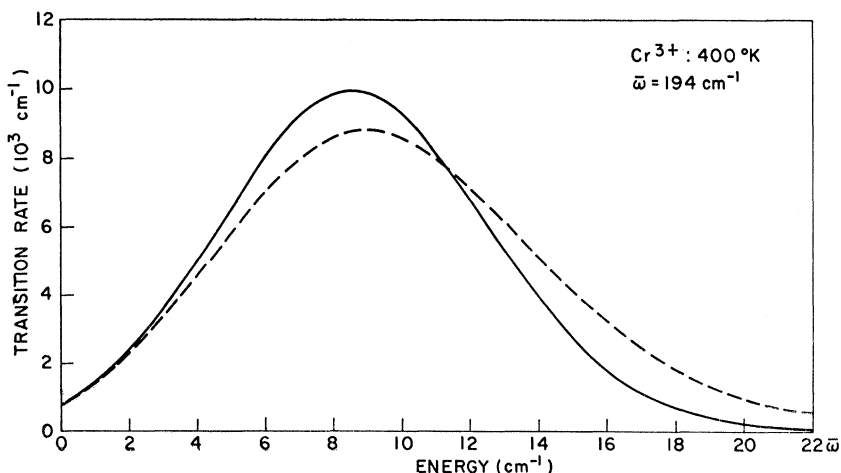
FIG. 3. Plots of the transition rate $w_1(A_2, A_l)/2(\lambda_{2l}^0)^2$ versus $\bar{\omega}_{l2}$ for Cr^{3+} over the region $0 \rightarrow 20\bar{\omega}$ at 50, 117, and 300°K with a vertical line at $11.9\bar{\omega}$ to indicate the transition ${}^4T_2 \rightarrow {}^2E$. The transition rate may be expressed in inverse seconds by multiplying its value in inverse centimeters by the velocity of light.

transition occurring in Cr^{3+} but also the dependence of the transition amplitude on electronic energy-level separation. Although the theory predicts transitions to higher energy states, these have amplitudes derivable from negative values of the argument $\bar{\omega}_{l2}$ in (55) and as a result are suppressed. We have made no attempt to consider them in this paper.

D. High-Temperature Investigations

Thus far in calculating $w_1(A_2, A_l)$ we have used approximation (44) at low temperatures in the region $\bar{\omega}_{l2} < 20\bar{\omega}$. The question arises as to whether we can use (44) in this region at temperatures $T > 300^\circ\text{K}$. In Fig. 4 we have plotted $w_1(A_2, A_l)/2(\lambda_{2l}^0)^2$ as a function of $\bar{\omega}_{l2}$ at 400°K using both approximation (44) and approximation (45). Since (44) comes much closer to satisfying (41c) than (45) at 400°K it more accurately reflects the shape of the envelope in the region of small $\bar{\omega}_{l2}$

FIG. 4. Plots of the transition rate $w_1(A_2, A_l)/2(\lambda_{2l}^0)^2$ versus $\bar{\omega}_{l2}$ for Cr^{3+} over the region $0 \rightarrow 22\bar{\omega}$ at 400°K obtained by using approximation (44) (dotted line) and approximation (45) (solid line).



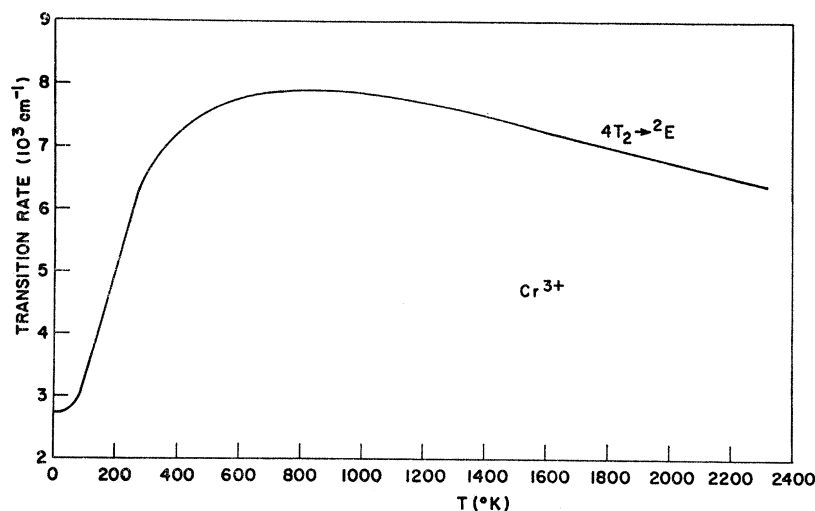


FIG. 5. Plot of the transition rate $w_1(A_2, A_1)/2(\lambda_2^0)^2$ for ${}^4T_2 \rightarrow {}^2E$ of Cr^{3+} as a function of temperature up to the melting point of Al_2O_3 .

values ($\bar{\omega}_{12} < 12\bar{\omega}$). Above 800°K our calculations indicate that approximation (44) appears to have no advantage over approximation (45) in any region of the spectrum. In Fig. 5 we have plotted $w_1({}^4T_2, {}^2E)/2[\lambda^0({}^4T_2, {}^2E)]^2$ (${}^4T_2 \rightarrow {}^2E$ occurring at $\bar{\omega}_{12} \sim 12\bar{\omega}$) as a function of temperature using (44) at temperatures up through 400°K , and using (45) at temperatures above 400°K up to 2300°K (the melting point of Al_2O_3). We observe a peak for $w_1({}^4T_2, {}^2E)$, occurring at around 800°K , which appears to be rather flat. This peak lies in that region where we have shifted from approximation (44) over to approximation (45). The rise observed for $w_1({}^4T_2, {}^2E)$ with increase in temperature between 50 and 800°K is gradual.

In the case of $w_1({}^4T_2, {}^4A_2)$ (${}^4T_2 \rightarrow {}^4A_2$ occurring at $\bar{\omega}_{12} \sim 86\bar{\omega}$), the rise in amplitude with increase in temperature is quite abrupt. For this reason in Fig. 6 we have plotted $w_1({}^4T_2, {}^4A_2)/2[\lambda^0({}^4T_2, {}^4A_2)]^2$ versus temperature (solid line) on a logarithmic scale so that we might compare this rapid increase with the more stand-

ard temperature variation given by²⁴

$$[N(\bar{\omega}) + 1]^{(\bar{\omega}_{12} + \bar{\omega}S)/\bar{\omega}}, \quad (56)$$

the transition rate for the decay of an excited electron of energy²⁶ $\bar{\omega}_{12} + \bar{\omega}S$ by the excitation of $(\bar{\omega}_{12} + \bar{\omega}S)/\bar{\omega}$ quanta of energy $\bar{\omega}$ (dotted line). Although we feel that the perturbation methods leading to (56) are not directly applicable to our case ($S=6$), Fig. 6 illustrates the fact that our results predict even a greater change of $w_1({}^4T_2, {}^4A_2)$ with temperature than is normally considered. We have therefore normalized the dotted curve to agree with our solid curve at 0°K .

One aspect of our calculation of $w_1({}^4T_2, {}^4A_2)$ requires further explanation. The Lorentzian broadening factor $e^{-\Gamma|s|}$ appearing in (27b) is physically unacceptable to use in calculating $K^1(\omega)$ in the far wings, as it falls off too slowly to use with approximation (45), which describes $K^0(\omega)$ as a Gaussian. We therefore replace $e^{-\Gamma|s|}$ in (27b) by $e^{-0.3607\Gamma^2s^2}$, its Gaussian half-height

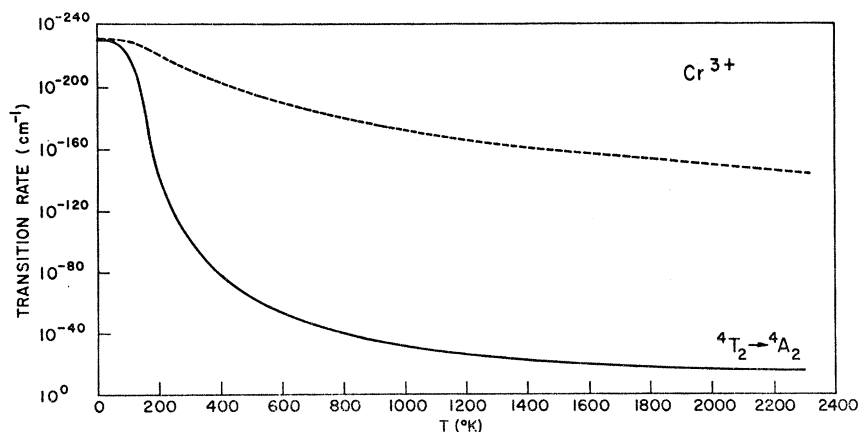


FIG. 6. Logarithmic plot of the transition rate $w_1(A_2, A_1)/2(\lambda_2^0)^2$ for ${}^4T_2 \rightarrow {}^4A_2$ of Cr^{3+} as a function of temperature (solid line) as compared with similar plot using the more standard but not applicable perturbation approach given by (56) (dotted line).

²⁶ In this case V_d becomes part of the perturbation and the unperturbed energy ω_{12} is given by (53).

equivalent, so that, by use of (45), $w_1(A_2, A_i)$ becomes

$$w_1(A_2, A_i) = 2\pi^{1/2}\Omega^{-1}(\lambda_{2i}^0)^2(\bar{\omega}_{12} + \bar{\omega}S)^2 \times \exp[-(\bar{\omega}_{12} - \bar{\omega}S)^2/\Omega^2], \quad (57a)$$

with

$$\Omega = [2S(2N(\bar{\omega}) + 1)\bar{\omega}^2 + 1.443\Gamma^2]^{1/2}. \quad (57b)$$

For $S=6$, $\Gamma=0.15\bar{\omega}$ it was possible to obtain three-figure accuracy in Ω at all temperatures by neglecting the second term within the square root in (57b).

V. SUMMARY AND CONCLUSIONS

We have attempted in this paper to outline a method for the calculation of the (nonradiative) electron-transition probability per unit time between pure electronic states for an impurity or defect electron trapped in a crystalline lattice. In order to handle a possibly strong electron-lattice distortion V_d we have introduced a canonical transformation

$$e^{i\mathcal{R}}(H_0 + V_d)e^{-i\mathcal{R}}$$

of $H_0 + V_d$, our unperturbed Hamiltonian, to insure the use of pure electronic states with our perturbation V_u . To simplify our formalism and computation we have permitted some loss in generality by introducing the assumption that the matrix elements $v_{ij,n}$ and $v_{i,n}$ of V_u and V_d are related by the expression

$$v_{ij,n} \simeq \lambda_{ij}^0(v_{i,n} - v_{j,n}), \quad \lambda_{ij}^0 = -\lambda_{ji}^0 \text{ are real.} \quad (58)$$

In so doing we have restricted our consideration of the lattice to a set of phonon modes satisfying this condition. As a result we obtain a simple expression for our (nonradiative) transition probability per unit time, which can be correlated to the radiative spectral function $K_{ij}(\omega)$ between the electronic states i and j with argument ω taken relative to the zero-phonon energy position. Because of this fact we have discussed in general the radiative spectral functions and developed their properties. Of particular importance is the relation

$$K_{12}^0(-\Delta_{12}) = e^{-\beta\Delta_{12}}K_{12}^0(\Delta_{12}), \quad \Delta_{12} = \omega - \bar{\omega}_{12},$$

predicting the symmetry of the absorption spectrum (for the Hamiltonian $H_0 + V_d$) relative to the zero-phonon energy $\bar{\omega}_{12}$.

We have chosen Cr^{3+} and V^{3+} in corundum as a physical example for the theory since their d electrons appear experimentally to exhibit a strong V_d -type coupling to the 194-cm^{-1} E_u mode of the Al_2O_3 lattice. As we have not assumed an exact knowledge of the form of either the electron-phonon coupling or the phonon distribution for this example, we have used two approximations in order to develop the theory. In the first approximation we look for a simple algebraic form for the expressions $I_{12}^{\pm}(\beta, s)$, defined in (41b), which will insure that they provide adequate convergence of $L_{12}(s)$ (our correlation function) to zero for large $|s|$ and satisfy as far as possible the symmetry requirement

(41c). This procedure provides for the proper symmetry of the spectral function in the neighborhood of the zero-phonon line, in addition to permitting its numerical calculation. The approximation is limited at very low temperatures by the fact that one obtains a set of δ -type functions for the function $K_{12}^0(\omega)$ at absolute zero. Although this limitation does not alter the spectral contour, it distorts the degree of resolution of the satellite vibrational peaks at very low temperatures. In order to compensate for this peculiarity we have established a low-temperature cutoff of 50°K . It is to be expected that the exact expressions for $I_{12}^{\pm}(\beta, s)$, as given by (41b), should exhibit little change between 0 and 50°K . At high temperatures the approximation is limited by its overestimation of the moments of the spectrum. The problem here is more serious, with the result that the approximation is not acceptable for use with the chosen example at temperatures $T > 400^\circ\text{K}$. It is also not acceptable for use in calculating spectral amplitudes far out on the high-energy wing (as required in calculating the ${}^4T_2 \rightarrow {}^4A_2$ transition rate in Cr^{3+}) at any temperature. On the positive side (see Fig. 1), the spectral function $K_{12}^1(\omega)$ at 50°K for $\omega < 20\bar{\omega}$ compares favorably with McClure's experimental data, although the vibrational satellites do not damp off as fast with increasing phonon number as might be expected. As a result we have used this approximation to compute $w_1({}^4T_2 \rightarrow {}^2E)$ occurring at an electron difference of $12\bar{\omega}$ at temperatures up through 400°K .

As a second approximation for $I_{12}^{\pm}(\beta, s)$ we have introduced the "slow modulation" formulation by expanding $\exp(\pm i\omega_n s)$ in (41b) to second order in s . Although the line shape in the neighborhood of the zero-phonon position is acceptable only at very high temperatures in this approximation, its estimation for the moments of the line at $S=6$ is quite-good; and we have used it at all temperatures where amplitudes far out on the high-energy wing are desired.²⁷ From this approximation we obtain a Gaussian form for both $K_{12}^0(\omega)$ and $K_{12}^1(\omega)$ (upon requiring that strain and other related broadening mechanisms become Gaussian) and in this manner we obtain a very simple and compact expression for $w_1(A_2, A_i)$, given by (57a) and (57b). The temperature dependence of the transition rates for ${}^4T_2 \rightarrow {}^2E$ and ${}^4T_2 \rightarrow {}^4A_2$ in Cr^{3+} plotted in Figs. 5 and 6 shows a flat peak for ${}^4T_2 \rightarrow {}^2E$ at about 800°K and a rapid increase for ${}^4T_2 \rightarrow {}^4A_2$ above 50°K . The rate for ${}^4T_2 \rightarrow {}^4A_2$ peaks only at physically unrealizable temperatures above $100\,000^\circ\text{K}$. It is to be emphasized that nowhere in our treatment of the electron-phonon interaction do we require that the distortion V_d be a perturbation.

We plan in a later paper to eliminate assumption (58) and consider the more general case where more than

²⁷ At $S=6$ the spectrum peaks far enough to the high-energy side of the zero-phonon position that a good approximation to the higher-order moments should predict reasonable amplitudes far out on the high-energy wing.

one region in the phonon spectrum may be involved in the calculation of transition rates. For example, $v_{i,n}$ may show strong coupling at acoustic phonon frequencies while $v_{ij,n}$ exhibits a maximum coupling at optical phonon modes. Also, we shall consider a more exact method for handling $I_{12}^{\pm}(\beta,s)$ involving some estimation of the nature of the electron-phonon coupling coefficients and phonon distribution function, along with a numerical calculation of the summation over phonon modes contained in $I_{12}^{\pm}(\beta,s)$ —missing in approximations (44) and (45) of this paper.

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APPENDIX A: CANONICAL TRANSFORMATION

Following a suggestion of Kane⁵ we introduce a canonical transformation

$$\bar{a}_i = e^{i\mathcal{R}} a_i e^{-i\mathcal{R}}, \tag{A1a}$$

$$\bar{b}_n = e^{i\mathcal{R}} b_n e^{-i\mathcal{R}}, \tag{A1b}$$

$$\mathcal{R} = \sum_i g_i a_i^\dagger a_i, \quad g_i = i \sum_n v_{i,n} (b_n - b_n^\dagger) / \omega_n, \tag{A1c}$$

$$[g_i, g_j] = 0,$$

of the operators a^\dagger, a and b^\dagger, b of our system, such that

$$\bar{H}_0 \equiv e^{i\mathcal{R}} (H_0 + V_d) e^{-i\mathcal{R}} = H_0 - \sum_{n,i} v_{i,n}^2 a_i^\dagger a_i / \omega_n. \tag{A2}$$

Writing

$$\mathcal{R} = \sum_n C_n (b_n - b_n^\dagger), \quad C_n = i \sum_i v_{i,n} a_i^\dagger a_i / \omega_n, \tag{A3}$$

it is a trivial matter to show, from the definition of \mathcal{R} in (A1a), (A1b), and (A1c), that

$$\bar{a}_i = e^{-i\theta_i} a_i, \quad \bar{a}_i^\dagger = e^{i\theta_i} a_i^\dagger, \tag{A4a}$$

$$\bar{b}_n = b_n + iC_n, \quad \bar{b}_n^\dagger = b_n^\dagger + iC_n. \tag{A4b}$$

If we picture \bar{b} as an operator of the distorted lattice and express our lattice momentum and position operators p, q in accordance with (1c) and (1d) as

$$p \sim b - b^\dagger, \quad q \sim b + b^\dagger,$$

we can establish from (A3) and (A4b) that

$$\bar{p}_n = p_n, \quad \bar{q}_n = q_n - 2 \sum_i v_{i,n} a_i^\dagger a_i / \omega_n. \tag{A5}$$

Expressions (A5) illustrate the fact that the distortion arising due to V_d is that of position, not momentum, and in terms of q has a value of $2iC$. The exponential

phonon operator $\exp(-ig_i)$ may be designated as the creation operator for the “phonon cloud” that surrounds the electron in the i th state as a result of this distortion. Comparing (A1c) with (A3), we see that a replacement of C_n by $iv_{i,n}/\omega_n$ implies a replacement of \mathcal{R} by g_i . Thus, using (A1b), we may replace (A4b) by

$$e^{i\theta_i} b_n e^{-i\theta_i} = b_n - v_{i,n} / \omega_n, \quad e^{i\theta_i} b_n^\dagger e^{-i\theta_i} = b_n^\dagger - v_{i,n} / \omega_n, \tag{A6}$$

and write the commutator expressions

$$[b_n(t), e^{\pm i\theta_i(t')}] = \pm (v_{i,n} / \omega_n) e^{-i\omega_n(t-t')} e^{\pm i\theta_i(t')}, \tag{A7a}$$

$$[b_n^\dagger(t), e^{\pm i\theta_i(t')}] = \pm (v_{i,n} / \omega_n) e^{i\omega_n(t-t')} e^{\pm i\theta_i(t')}, \tag{A7b}$$

where

$$g_i(t) = e^{iH_B t} g_i e^{-iH_B t}, \quad b_n(t) = e^{iH_B t} b_n e^{-iH_B t} = e^{-i\omega_n t} b_n, \text{ etc.}$$

Letting (A7a) operate on $|0\rangle$ —the vacuum state of our system—we see that for an electron in the i th state,

$$b_n |c\rangle_i = (-v_{i,n} / \omega_n) |c\rangle_i, \quad |c\rangle_i = e^{-i\theta_i} |0\rangle, \tag{A8}$$

and $|c\rangle_i$ is an eigenstate of b_n with eigenvalue $(-v_{i,n} / \omega_n)$. Thus, a state of the “phonon cloud” is likewise an eigenstate of the lowering operator b . If a simplified form for $|c\rangle_i$ is desired we can write

$$|c\rangle_i = \exp(-\frac{1}{2} \sum_n v_{i,n}^2 / \omega_n^2) \exp(-\sum_n v_{i,n} b_n^\dagger / \omega_n) |0\rangle$$

using (A1c) and a well-known identity,²⁸ where we have now eliminated the “annihilation” portion of g_i from $|c\rangle_i$. Finally, within the framework of our one-electron system²⁹ we see from (1d), (A3), and (A4b) that we can express

$$\bar{V} = \sum_{\substack{i,j,n \\ i \neq j}} v_{ij,n} q_{i,n} e^{i(\theta_i - \theta_j)} a_i^\dagger a_j, \tag{A9a}$$

$$= \sum_{\substack{i,j,n \\ i \neq j}} v_{ij,n} e^{i(\theta_i - \theta_j)} q_{j,n} a_i^\dagger a_j, \tag{A9b}$$

in terms of a position coordinate operator

$$q_{i,n} = b_n + b_n^\dagger - 2v_{i,n} / \omega_n.$$

Expressions (A9a) and (A9b) illustrate the fact that it is the relative distortion characterized by $\exp i(\theta_i - \theta_j)$ that is physically important.

APPENDIX B: PROOF OF RELATIONS (38a) AND (38b)

Lax² has demonstrated that the spectral function $K_{ij}(\omega, H')$ —which we have defined in expression (29)—can be written (we use our notation) as

$$K_{ij}(\omega, H') = \frac{1}{2\pi} \int_{-\infty}^{\infty} ds e^{i(\bar{a}_{ij} - \omega)s + f_{ij}(s)},$$

²⁸ We employ the identity $e^{x+y} = e^{-\frac{1}{2}[x,y]} e^x e^y$, where the commutator $[x,y]$ is a c number. See, e.g., H. F. Baker, Proc. Math. Soc. (London) 3, 24 (1905).

²⁹ The operator $a_i^\dagger a_j^\dagger a_k a_l$ acting upon one-electron states is zero.

where

$$f_{ij}(s) = \sum_n \frac{(v_{i,n} - v_{j,n})^2}{\omega_n^2} \times [i \sin \omega_n s - (2N_n + 1)(1 - \cos \omega_n s)]. \quad (\text{B1})$$

Replacing s by $-s$ in (B1) and applying (37) we obtain

$$K_{ij}^0(\omega - \bar{\omega}_{ij}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} ds e^{i(\omega - \bar{\omega}_{ij})s + f_{ij}(-s)}. \quad (\text{B2})$$

It is now a simple matter to introduce (17a) and (17b) into (B2) and prove (38a) and (38b).

APPENDIX C: MOMENTS OF $K_{12}^0(\omega - \bar{\omega}_{12})$

Expressing the n th moment of $K_{ij}^0(\omega - \bar{\omega}_{ij})$ as

$$\mu_{ij}^n = i^n \left[\left(\frac{d^n}{dt^n} \int_{-\infty}^{\infty} d\omega e^{-i(\omega - \bar{\omega}_{ij})t} K_{ij}^0(\omega - \bar{\omega}_{ij}) \right) \right]_{t=0},$$

we obtain upon inserting (17a) and (17b)

$$\mu_{ij}^n = i^n \left[\left(\frac{d^n}{dt^n} e^{-S_{ij}(\beta)} e^{I_{ij}(\beta, t)} \right) \right]_{t=0},$$

$$I_{ij}(\beta, t) = I_{ij}^+(\beta, t) + I_{ij}^-(\beta, t),$$

where use has been made of (38a) and (38b) and the definitions (41a) and (41b). The first four moments are

$$\mu_{ij}^0 = 1,$$

$$\mu_{ij}^1 = i \left[\frac{d}{dt} I_{ij}(\beta, t) \right]_{t=0},$$

$$\mu_{ij}^2 = i^2 \left[\frac{d^2}{dt^2} I_{ij}(\beta, t) + \left(\frac{d}{dt} I_{ij}(\beta, t) \right)^2 \right]_{t=0},$$

$$\mu_{ij}^3 = i^3 \left[\frac{d^3}{dt^3} I_{ij}(\beta, t) + 3 \left(\frac{d}{dt} I_{ij}(\beta, t) \right) \left(\frac{d^2}{dt^2} I_{ij}(\beta, t) \right) + \left(\frac{d}{dt} I_{ij}(\beta, t) \right)^3 \right]_{t=0},$$

$$\mu_{ij}^4 = i^4 \left[\frac{d^4}{dt^4} I_{ij}(\beta, t) + 3 \left(\frac{d^2}{dt^2} I_{ij}(\beta, t) \right)^2 + 4 \left(\frac{d}{dt} I_{ij}(\beta, t) \right) \left(\frac{d^3}{dt^3} I_{ij}(\beta, t) \right) + 6 \left(\frac{d}{dt} I_{ij}(\beta, t) \right)^2 \times \left(\frac{d^2}{dt^2} I_{ij}(\beta, t) \right) + \left(\frac{d}{dt} I_{ij}(\beta, t) \right)^4 \right]_{t=0}.$$

We shall now compute these moments for $K_{12}^0(\omega - \bar{\omega}_{12})$ using first the exact expression for $I_{ij}(\beta, t)$ given by (41b) (used in conjunction with assumption [1]), using second approximation (44), and using finally the "slow modulation" approximation (45). From the exact expression [computing $\mu_{12}(e)$] we obtain

$$\begin{aligned} \mu_{12}^0(e) &= 1, \\ \mu_{12}^1(e) &= \bar{\omega} S, \\ \mu_{12}^2(e) &= \bar{\omega}^2 [2N(\bar{\omega}) + 1] S + \bar{\omega}^2 S^2, \\ \mu_{12}^3(e) &= \bar{\omega}^3 S + 3\bar{\omega}^3 [2N(\bar{\omega}) + 1] S^2 + \bar{\omega}^3 S^3, \\ \mu_{12}^4(e) &= \bar{\omega}^4 [2N(\bar{\omega}) + 1] S + 3\bar{\omega}^4 [2N(\bar{\omega}) + 1]^2 S^2 \\ &\quad + 4\bar{\omega}^4 S^2 + 6\bar{\omega}^4 [2N(\bar{\omega}) + 1] S^3 + \bar{\omega}^4 S^4. \end{aligned}$$

Using (44) [computing $\mu_{12}(1)$] we obtain

$$\begin{aligned} \mu_{12}^0(1) &= \mu_{12}^0(e), \\ \mu_{12}^1(1) &= \mu_{12}^1(e), \\ \mu_{12}^2(1) &= \mu_{12}^2(e) + (2\bar{\Gamma}/\beta) [2N(\bar{\omega}) + 1] S, \\ \mu_{12}^3(1) &= \mu_{12}^3(e) + (6\bar{\Gamma}/\beta) \bar{\omega} S + (6\bar{\Gamma}/\beta) \bar{\omega} [2N(\bar{\omega}) + 1] S^2, \\ \mu_{12}^4(1) &= \mu_{12}^4(e) + (6\bar{\Gamma}/\beta) \bar{\omega}^3 [2N(\bar{\omega}) + 1]^2 S^2 \\ &\quad + (12\bar{\Gamma}^2/\beta^2) [2N(\bar{\omega}) + 1]^2 S^2 + (24\bar{\Gamma}/\beta) \bar{\omega}^2 S^2 \\ &\quad + (12\bar{\Gamma}/\beta) \bar{\omega}^2 [2N(\bar{\omega}) + 1] S^3 \\ &\quad + [(12\bar{\Gamma}/\beta) \bar{\omega}^2 + (12\bar{\Gamma}^2/\beta^2) + (24\bar{\Gamma}/\beta^3)] \\ &\quad \times [2N(\bar{\omega}) + 1] S, \end{aligned}$$

and using (45) [computing $\mu_{12}(2)$] we obtain

$$\begin{aligned} \mu_{12}^0(2) &= \mu_{12}^0(e), \\ \mu_{12}^1(2) &= \mu_{12}^1(e), \\ \mu_{12}^2(2) &= \mu_{12}^2(e), \\ \mu_{12}^3(2) &= \mu_{12}^3(e) - \bar{\omega}^3 S, \\ \mu_{12}^4(2) &= \mu_{12}^4(e) - \bar{\omega}^4 [2N(\bar{\omega}) + 1] S - 4\bar{\omega}^4 S^2. \end{aligned}$$

One sees immediately from these expressions that (44) tends to overestimate and (45) tends to underestimate the moments. Only at very low temperatures is (44) preferred, (45) being superior at most temperatures especially when used with large values of S .