Theory of nonradiative quenching of hot luminescence in F centers

Masami Kusunoki
Physics Laboratory, The Faculty of Engineering,
Meiji University, Kawasaki, Kanagawa, 214 Japan
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A quantitative theory of nonradiative quenching of hot luminescence in F centers excited by an extremely short laser pulse is given on the basis of the Franck-Condon principle in optical excitation and the momentariness of nonradiative transitions (NRT) in the cases of strong electron–(accepting mode) phonon coupling. The treatment given differs from the qualitative considerations by Dexter, Klick, and Russell and Bartram and Stoneham in two important aspects, namely, the strength of the coupling between the $1s$-like ground state and the $2p$-like excited state as well as the damping constant of the lattice vibration are taken into account. It will be shown that the coupling strength via a promoting-mode phonon is just intermediate so that its nonperturbative treatment in the region of crossing of the two potential surfaces is essentially required. For strong electron-phonon coupling, the interferences between different passages through the crossing point X are found to cancel out mainly due to the initial wide distribution of the excitation spectrum. This fact is taken into account by applying the Landau-Zener formula of NRT's for mutually independent passages through X. Accordingly, a systematic method to determine the classical motions of the lattice is presented. It will be shown that the system may have many more chances to pass over X for damping oscillation on the $2p$ potential surface than on the $1s$ potential surface as long as the damping is slow. In this way, the probability for an excited F center to return to its ground state will be numerically calculated for $\frac{1}{4} < \Lambda < \frac{1}{2}$ where Λ is the excited-state lattice relaxation energy divided by the optical-absorption energy. The result shows that the Dexter, Klick, and Russell postulate that $\Lambda < \frac{1}{4}$ might be a sufficient and necessary condition for luminescence is inadequate.

I. INTRODUCTION

The problem of nonradiative transitions (abbreviated as NRT) by multiphonon emission has been of considerable experimental and theoretical interest for a long time since the pioneering works of Huang and Rhys[1] and Kubo.[2] One purpose of the theory has been how more generally[3–7] and/or how with better approximations (non-Condon schemes[4,8–11]) to calculate the first-order transition rates between nonsteady electronic states prepared by some experiment. Under the condition that the transition probability is much smaller than unity (in either limit of weak or strong coupling), the formalism for instance given by Kubo and Toyozawa[4] has sometimes successfully been applied to studies[12,13] of energy transfer between localized electronic states in crystals[12,14,15] and in photosynthetic systems,[16–18] electron-hole recombination in semiconductors,[5,13,19] relaxation of vibrationally excited molecules,[12,20] NRT in small molecules,[21] and in large molecules,[22] and so on.

Nevertheless, the problem of the nonradiative quenching of F-center luminescence has long been unsatisfactorily understood with recourse to only a qualitative mechanism[13,23,24] originally suggested by Dexter, Klick, and Russell (DKR)[23] on the basis of a schematic application of a two-state configuration coordinate diagram as shown in Fig. 1. They[23] proposed that if point B lies above intersection point X (i.e., $E_X < \langle V \rangle$), then after one period or a few periods of the vibration following the light absorption process, the system will cross over X with so high probability that the complete quenching of luminescence may occur. Bartram and Stoneham (BS)[24] demonstrated that it is impossible to prove that there is no luminescence when $E_X < \langle V \rangle$, but then in most ionic crystals luminescence has been sought in vain. Mott[13] has recently discussed this problem in connection with the potential curve crossing problem in molecular collisions, which has long been tackled by many researchers in that field[25–28] to surpass or generalize the pioneering works of Landau[29] and Zener[30] (LZ). At present no superior theory to LZ's has appeared except for two limits of weak or strong coupling between terms.[26] The so-called LZ formula[29,30] which can be used for the arbitrary coupling strength is known to be valid more generally than its derivation would indicate.[29] However, we still have no quantitative theory of NRT in solids which is applicable to the case of intermediate coupling between the $1s$-like ground state $|g\rangle$ and the $2p$-like excited state $|e\rangle$ in F centers.

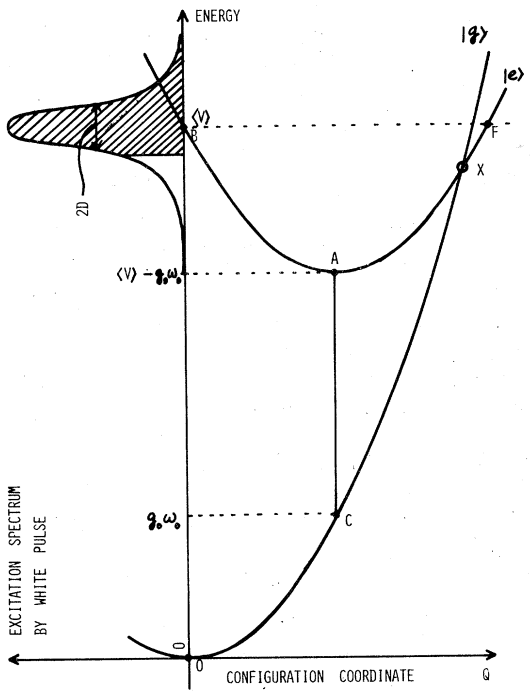

FIG. 1. Two-state configuration coordinate diagram. The excitation spectrum by a very short laser pulse is also depicted. Only the vibration quanta in its shaded part can pass over X during at least one vibration period and therefore contribute to NRT through X.

The purpose of this paper is to develop such theory in the case where the electron-phonon coupling is so strong that a classical approximation may be used to describe the lattice relaxation. We suppose that the electron initially being in the $1s$ state with the lattice in thermal equilibrium is excited into the $2p$ state at $t=0$ by a very short laser pulse, conforming to the Franck-Condon principle. It should be noted that due to the Heisenberg uncertainty principle the excitation spectrum is half-infinitely distributed[31] as shown in Fig. 1 even at low temperatures. Only the vibration quanta with high initial energies lying in the shaded part of the excitation spectrum can pass over X during at least one vibration period and therefore contribute to NRT through X. Among these vibrations, one with comparatively low initial energy will make a double passage through X with low velocities for which the LZ formula breaks down. However, we can estimate that such vibrations can occupy only a small portion in the shaded part of excitation spectrum in the case of strong electron-phonon coupling. But, even for the other vibration quanta which can make double passages through X with high velocities, the transition probability for such a double passage does not simply conform to the LZ formula[29] but, in addition to it, contains an interference term coming from the successive passages through X.[19] The problem of NRT in solids is very simplified by the strong cancellation of the interference terms coming from the sum over all the possible double passages.[6,19] In this way, we find that the LZ formula can be used as a reasonable basis of the intermediate-coupling theory of NRT in solids.

To develop such a theory, the accurate description of the classical lattice vibration in the region of crossing must be determined. Then, it is essentially important to take into account the irreducible energy flow from the configuration coordinate system to the other modes. In Sec. III, limiting ourselves to the linear electron-phonon coupling situation, we present a general formalism of such "classical" approximation. The term classical is used to distinguish it from the conventional semiclassical approximation, although both give the exact equal transition probability in the weak-coupling limit at high temperatures as shown in Sec. IV. The system of F center in ionic crystals, described in Sec. II, will be shown in Secs. II, IV, and V to be just in the case of intermediate coupling. Then, we must solve a series of differential equations because, after a "real" NRT occurs near X, the potential surface on which the lattice moves classically jumps from $|g\rangle$ to $|e\rangle$ or from $|e\rangle$ to $|g\rangle$. Section VI will be devoted to solving them by use of the LZ approximation. The results will be discussed and summarized in Sec. VII.

II. DESCRIPTION OF THE SYSTEM

A. Model Hamiltonian

Let us consider an interaction of an electron trapped at some crystal imperfection with the surrounding lattice. We denote the jth normal coordinate of the lattice vibration in the absence of the electron by Q_j. When the electron is added at the trapped center, its interaction with the imperfect lattice can be expanded up to the first power of Q_j. If we further take a quadratic approximation for the potential energy, we can write the Hamiltonian of this system[1,4] as

$$\begin{aligned}\mathcal{H}(r,Q) &= H_E + H_{EL} + H_L \\ &= \left(\frac{p^2}{2m} + V(r)\right) - \sum_j u_j(r) Q_j \\ &\quad + \tfrac{1}{2}\sum_j (P_j^2 + \omega_j^2 Q_j^2) \ , \end{aligned} \tag{2.1}$$

where H_E is the electronic Hamiltonian with $Q_j=0$ for all j, H_{EL} describes the fluctuating potential due to the electric field of the vibrational modes at the defect, and H_L is the lattice energy when there is no electron.

As is well known, the electron in F center is in a

discrete bound state such as a $1s$-like ground state, or $2p$-like excited states and so on. Throughout this paper, the Jahn-Teller effect of threefold degeneracy of $2p$-state will be completely neglected because our concern is not in the polarization characteristics[32] but in the sum over all polarizations. Thus, we can adopt a simple two-state model used by many authors. Now, let

$$|g\rangle = \psi_g(\vec{r}, \vec{Q}_0) \quad \text{and} \quad |e\rangle = \psi_e(\vec{r}, \vec{Q}_0) \tag{2.2}$$

be the eigenfunctions of $H_E + H_{EL}$ with $Q_j = Q_{j0}$ for the $1s$-like ground state and the $2p$-like excited state, respectively, where $\vec{Q}_0 = \{Q_{j0}\}$ is conveniently chosen as the lattice equilibrium position of the $|g\rangle$ state defined above, i.e., $Q_{j0} = \langle g|u_j|g\rangle/\omega_j^2$.[9] Then, the Hamiltonian (2.1) can be represented as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{T} = (|g\rangle H_g \langle g| + |e\rangle H_e \langle e|) + (|g\rangle T_{ge} \langle e| + |e\rangle T_{eg} \langle g|) \ , \tag{2.3}$$

with the definitions

$$H_g \equiv \sum_j \omega_j (b_j^\dagger b_j + \tfrac{1}{2}) \ , \tag{2.4}$$

$$V \equiv H_e - H_g = \langle V\rangle + \delta V = \langle V\rangle - \sum_j (g_j)^{1/2} \omega_j (b_j + b_j^\dagger)$$

$$= \langle e|H_E|e\rangle - \langle g|H_E|g\rangle - \sum_j \left[\frac{(\langle e|u_j|e\rangle - \langle g|u_j|g\rangle)}{(2\omega_j)^{1/2}}\right](b_j + b_j^\dagger) \ , \tag{2.5}$$

$$T_{eg} = T_{ge}^\dagger = -\sum_j \left[\frac{\langle e|u_j|g\rangle}{(2\omega_j)^{1/2}}\right](b_j + b_j^\dagger) \ , \tag{2.6}$$

where b_j ($b_j^\dagger$) is an annihilation (creation) operator of the jth phonon. After Sharf and Silvey,[9] we shall call this the "crude adiabatic representation (CAR)" in order to distinguish it from the conventional adiabatic representation (AR). The Hamiltonian in the latter representation was first obtained by Kubo and Toyozawa[4] using the unitary transformation

$$\begin{aligned} |1\rangle &= \cos\chi|g\rangle - \sin\chi|e\rangle \ , \\ |2\rangle &= \sin\chi|g\rangle + \cos\chi|e\rangle \ , \end{aligned} \tag{2.7}$$

with

$$\chi = \tfrac{1}{2}\tan^{-1}(2T_{eg}/V) \ . \tag{2.8}$$

The result is given by

$$\mathcal{H} = |1\rangle\{H_g + \tfrac{1}{2}[V - (V^2 + 4T_{eg}^2)^{1/2}]\}\langle 1| - |1\rangle i\dot{\chi}\langle 2| + |2\rangle i\dot{\chi}\langle 1| + |2\rangle\{H_g + \tfrac{1}{2}[V + (V^2 + 4T_{eg}^2)^{1/2}]\}\langle 2| \ . \tag{2.9}$$

In the CAR, the nonradiative transition is caused by the bare transfer matrix T_{eg}, while in the AR it is caused by the off-diagonal matrix element of the lattice kinetic energy K [$i\dot{\chi} = \langle 2|K|1\rangle = (K\chi)$] which exhibits a resonance type of strong dependence on the lattice coordinate. The problem is which representation can be a better starting point of perturbation theory.

B. Estimation of transfer matrix element in F centers

As is well known, the fluctuation part of the electron-lattice interaction in the case of ionic crystals can be written[1,4]

$$H_{EL} = \frac{\omega_0}{N^{1/2}}\left[\frac{8\pi}{v_a}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\right]^{1/2} \times \sum_j [-Q_j(e\vec{r}\cdot\hat{\vec{k}})\cos\vec{k}\cdot\vec{r} + Q_j(e\vec{r}\cdot\hat{\vec{k}})\sin\vec{k}\cdot\vec{r}] \ , \tag{2.10}$$

where the jth mode of the optical longitudinal vibration is specified by the wave vector $\vec{k}$ ($\hat{\vec{k}} \equiv \vec{k}/|k|$) and the angular frequency ω_0 (which is assumed to be constant), ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants, respectively, v_a the volume of the unit cell, N the total number of unit cells, and e the electronic charge. It is further well known[33] that as regards a hydrogenic defect the promoting mode (for which $\langle e|u_{jp}|g\rangle \neq 0$) and the accepting mode (for which $\langle e|u_{ja}|e\rangle \neq \langle g|u_{ja}|g\rangle$) must have odd and even parities, respectively. Thus, in our system, these two roles of the lattice vibration are respectively played by the first and second terms of Eq. (2.10) which are distinct by symmetry.[13,33] Therefore, the replacement of T_{eg}^2 by its thermal average $\langle T_{eg}^2\rangle$ may be considered to be a good approximation. As a suitable starting point of the estimation of $\langle e|u_{jp}|g\rangle$, we can assume that the electric field of promoting modes is roughly uniform over the F center.[1] These considerations lead to

$$\langle T_{eg}^2\rangle \equiv \frac{\mathrm{Tr}(e^{-H_g/kT}T_{eg}^2)}{\mathrm{Tr}(e^{-H_g/kT})} = \frac{4\pi\omega_0}{3v_a}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)(2n_0 + 1)|\langle e|e\vec{r}|g\rangle|^2 \ , \tag{2.11}$$

where

$$n_0 \equiv n(\omega_0) = [\exp(\omega_0/kT) - 1]^{-1}$$

is the Bose-Einstein distribution function, T being the temperature.

The rate of radiative transition from the relaxed excited state to the ground state was first calculated by Huang and Rhys,[1] which is given by

$$\gamma \simeq (4/3c^3)|\langle e|e\vec{r}|g\rangle|^2(\langle V\rangle - g_0\omega_0)^3 \ , \tag{2.12}$$

where c is the light velocity and

$$g_0=(\langle e|u_{ja}|e\rangle-\langle g|u_{ja}|g\rangle)^2/2\omega_0^3$$

is called as Huang-Rhys factor.

From Eqs. (2.11) and (2.12), we get the formula to estimate T_{eg} from the optical data

$$T_{eg}\sim(\langle T_{eg}^2\rangle)^{1/2}=\left[\frac{\pi c^3(2n_0+1)\omega_0\gamma}{v_a(\langle V\rangle-g_0\omega_0)^3}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\right]^{1/2} . \quad (2.13)$$

By use of the well-known data on KBr in which $g_0\omega_0/\langle V\rangle=0.223$,[24] $g_0\simeq 22$, $\omega_0\simeq 3.0\times 10^{13}$/sec, $\epsilon_0=4.78$, $\epsilon_\infty=2.33$, $v_a=2.86\times 10^{-22}$ cm^3, and $\gamma\simeq 10^7$/sec for a dipole allowed transition, we can obtain a typical numerical estimate as

$$\tilde{T}_{eg}\equiv T_{eg}/\omega_0\sim 1.34(2n_0+1)^{1/2} . \quad (2.14)$$

As will be shown in Secs. IV and V, the above intensity corresponds to the intermediate-coupling situation when the system passes through X. Physically speaking, the system after the passage will be evenly distributed among two electronic states.

III. GENERAL FORMULATION

A. Transient polarization after optical excitation

By reference to Fig. 1, let us suppose that the F center is excited from the $|g\rangle$ state into the $|e\rangle$ state by an extremely short laser pulse at $t=0$. After that, the phonon wave packet will pass back and forth over X with or without nonradiative change of its electronic state. Since $\gamma\simeq 10^{-6}\omega_0$ in alkali halides, we can neglect radiative damping almost completely during 10^5 times period of vibration. Therefore, our problem is simply to solve the time-dependent Schrödinger equation

$$i\dot{\psi}(t)=\mathcal{H}\psi(t)=(\mathcal{H}_0+\mathcal{T})\psi(t) , \quad (3.1)$$

for $t\ll\gamma^{-1}$ under the initial condition

$$\psi(0)=|e\rangle|\{n_j\}\rangle\equiv|e\rangle\prod_j\left(\frac{(b_j^\dagger)^{n_j}}{(n_j!)^{1/2}}\right)|0) , \quad (3.2)$$

where $|0)$ is the vacuum state of phonon field.

Exactly speaking, T_{eg} must have an upper limit in order that a mixing of the $|e\rangle$ and $|g\rangle$ states can be neglected around point 0 in Fig. 1. From Eqs. (2.7) and (2.8), this condition is found to be

$$T_{eg}<<\langle V\rangle . \quad (3.3)$$

Then, the wave function can be written

$$\psi(t)=\exp(-i\mathcal{H}t)\psi(0)=[e^{-iH_gt}a_g(t)|g\rangle+e^{-iH_et}a_e(t)|e\rangle]|\{n_j\}) , \quad (3.4)$$

with the probability amplitude operators

$$a_\lambda(t)=\langle\lambda|e^{i\mathcal{H}_0t}e^{-i\mathcal{H}t}|e\rangle=\langle\lambda|\exp_+\left[-i\int_0^t d\tau\,\mathcal{T}(\tau)\right]|e\rangle;\quad \lambda=e \text{ or } g , \quad (3.5)$$

where $\exp_{+(-)}$ denotes the time-ordered exponential with increasing (decreasing) time towards the left and from Eq. (2.3)

$$\mathcal{T}(\tau)\equiv e^{i\mathcal{H}_0\tau}\mathcal{T}e^{-i\mathcal{H}_0\tau}=|g\rangle T_{ge}(\tau)\langle e|+|e\rangle T_{eg}(\tau)\langle g| , \quad (3.6)$$

with

$$T_{\lambda\lambda'}(\tau)\equiv e^{iH_\lambda\tau}T_{\lambda\lambda'}e^{-iH_{\lambda'}\tau};\quad \lambda\lambda'=eg \text{ or } ge . \quad (3.7)$$

The physical quantity to be calculated is the transient probability for the system to be found in the $|e\rangle$ or $|g\rangle$ state. From Eq. (3.4), this is given by

$$P_\lambda(t)\equiv\langle\psi(t)|\lambda\rangle\langle\lambda|\psi(t)\rangle=\mathrm{Tr}[a_\lambda(t)\rho_g a_\lambda^\dagger(t)] , \quad (3.8)$$

with the canonical density matrix

$$\rho_g=|\{n_j\}\rangle\langle\{n_j\}|=e^{-H_g/kT}/\mathrm{Tr}(e^{-H_g/kT}) . \quad (3.9)$$

$P_e(t)$ and $P_g(t)$ are related by the conservation of the probability

$$P_e(t)+P_g(t)=1 . \quad (3.10)$$

B. Perturbational expansion method

The only nonvanishing matrix elements of the time-ordered expansion[34] of $a_e(t)$ in Eq. (3.5) with Eq. (3.6) are the even terms. This is given by

$$a_e(t)=\sum_{n=0}^{\infty}(-1)^n\int_0^t d\tau_1\int_0^{\tau_1}d\tau_2\cdots\int_0^{\tau_{2n-2}}d\tau_{2n-1}\int_0^{\tau_{2n-1}}d\tau_{2n}\,(\Lambda(\tau_1,\tau_2)\cdots\Lambda(\tau_{2n-1},\tau_{2n}) , \quad (3.11)$$

where

$$\Lambda(\tau,\tau') \equiv T_{eg}(\tau)\,T_{ge}(\tau') \quad . \tag{3.12}$$

By use of Eq. (3.11) and its Hermite conjugate, $P_e(t)$ given by Eq. (3.8) can be written[34]

$$P_e(t) = \sum_{n=0}^{\infty} (-1)^n C_n(t) \quad , \tag{3.13}$$

with $C_0(t) = 1$ and

$$C_n(t) \equiv \hat{I}_n(t|\tau_1,\tau_2;\cdots;\tau_{2n-1},\tau_{2n}) \times \langle \Lambda(\tau_1,\tau_2)\cdots\Lambda(\tau_{2n-1},\tau_{2n})\rangle \quad , \tag{3.14}$$

for $n \geq 1$, where the integral operators $\{\hat{I}_n\}$ are found to be given by

$$\hat{I}_1(t|\tau_1,\tau_2) = \int_0^t d\tau_1 \int_0^t d\tau_2 \quad , \tag{3.15}$$

$$\hat{I}_2(t|\tau_1,\tau_2;\tau_3,\tau_4) = \int_0^t d\tau_4 \int_0^{\tau_4} d\tau_3 \int_0^{\tau_3} d\tau_2 \int_0^{\tau_2} d\tau_1 + \int_0^t d\tau_1 \int_0^{\tau_1} \tau_2 \int_0^{\tau_2} d\tau_3 \int_0^{\tau_3} d\tau_4 + \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \int_0^t d\tau_3 \int_0^{\tau_3} d\tau_4 \cdots \tag{3.16}$$

In general, $\hat{I}_n$ is diagrammatically shown in Fig. 2(a) where the upper (lower) time branch corresponds to the increasing (decreasing) time sequence in $a_e(t)$ $[a_e^\dagger(t)]$ towards the left and the solid and dotted lines indicate the propagations of the system in $|e\rangle$ and $|g\rangle$ states, respectively. Indeed, it is important to note that the sum of Fig. 2(a) can be reclassified into the sum of 2^{n-1}-type diagrams as shown in Fig. 2(b) for $n=1$ and $n=2$, where a pair of parallel solid (or dotted) lines both starting from τ_i and ending in τ_j $(\tau_i < \tau_j)$ expresses a propagator of the system in $|e\rangle$ (or $|g\rangle$) state. Further, NRT occurs during every time region strung by a circular arc which stands for a pair of solid and dotted lines both starting from τ_i and ending in τ_j $(\tau_i < \tau_j)$. We can say that the NRT is "real" or "virtual" according to whether the electronic state changes or not in that transition.

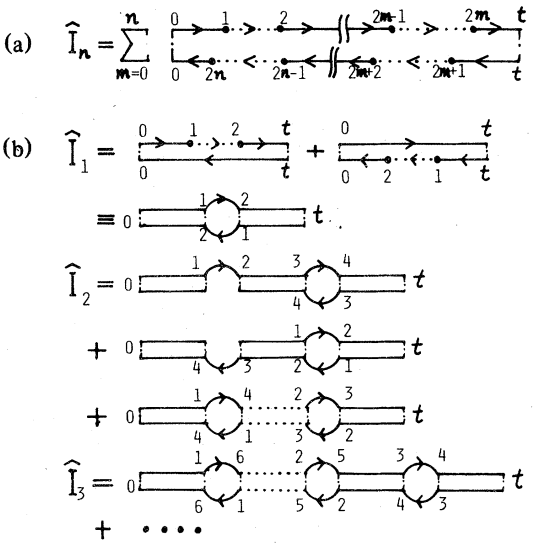

FIG. 2. (a) Diagrammatic representation of the integral operators $\hat{I}_n(t|\tau_1,\tau_2;\ldots;\tau_{2n-1},\tau_{2n})$ operating to the correlator $\langle\Lambda(\tau_1,\tau_2)\cdots\Lambda(\tau_{2n-1},\tau_{2n})\rangle$; a solid (dotted) line in the upper or lower time branch indicates the forward or backward propagation of the system in the $|e\rangle$ $(|g\rangle)$ state. (b) Reclassification of $\hat{I}_n$; A NRT occurs during every time region strung by a circular arc which stands for a pair of solid and dotted lines.

The calculations of the correlation functions $\langle\Lambda(\tau_1,\tau_2)\cdots\Lambda(\tau_{2n-1},\tau_{2n})\rangle$ can be easily performed for Eqs. (2.4) and (2.5) when T_{eg} is constant. Especially for $n=1$, the result is well known[4] that

$$\langle\Lambda(\tau_1,\tau_2)\rangle = T_{eg}^2\langle e^{iH_e\tau_1}e^{iH_g(\tau_2-\tau_1)}e^{-iH_e\tau_2}\rangle = T_{eg}^2\exp\left[-G+G(\tau_2-\tau_1)-i(\tau_2-\tau_1)\left(\langle V\rangle-\int_0^\infty d\omega\,\omega g(\omega)\right)-2i\int_0^\infty d\omega\, g(\omega)(\sin\omega\tau_2-\sin\omega\tau_1)\right] , \tag{3.17}$$

where the interaction spectrum $g(\omega)$, $G(\tau)$, and the interaction strength G are defined by

$$g(\omega) \equiv \sum_j g_j[\delta(\omega-\omega_j)-\delta(\omega+\omega_j)] = -g(-\omega) \quad , \tag{3.18}$$

$$G(\tau) \equiv \int_{-\infty}^{\infty} d\omega\,[n(\omega)+1]e^{i\omega\tau}g(\omega) \quad , \tag{3.19}$$

$$G \equiv G(0) = \int_0^\infty d\omega\,[2n(\omega)+1]g(\omega) \quad . \tag{3.20}$$

Higher-order correlation functions can similarly be evaluated as[34]

$$\langle\Lambda(\tau_1,\tau_2)\cdots\Lambda(\tau_{2n-1},\tau_{2n})\rangle = T_{eg}^2\exp\left[-nG+\sum_{h=1}^{2n}\sum_{m=h+1}^{2n}(-1)^{m-h+1}G(\tau_m-\tau_h) - i\left(\langle V\rangle-\int_0^\infty d\omega\,\omega g(\omega)\right)\sum_{h=1}^{2n}(-1)^h\tau_h - 2i\int_0^\infty d\omega\, g(\omega)\sum_{h=1}^{2n}(-1)^h\sin\omega\tau_h\right] . \tag{3.21}$$

C. Semiclassical approximation

We further restrict ourselves to systems with strong electron-phonon coupling as is the case in many ionic crystals and semiconductors. This condition is specified by the nearly zero Debye-Waller factor ($e^{-G} \simeq 0$) or by the large second moment of the correlator (3.17), i.e.,

$$D^2 = \int_0^\infty d\omega\, \omega^2 g(\omega)[2n(\omega)+1] \equiv \bar{\omega}^2 G >> \bar{\omega}^2 \ , \tag{3.22}$$

where $\bar{\omega}$ is a mean frequency of vibration. Then, a NRT event occurring during every time region strung by a pair of circular arcs in Fig. 2(b) would end within a much shorter time of order D^{-1} than a mean period of vibration $2\pi/\bar{\omega}$, so that the motion of the system may be described classically. In this approximation, the system has no time to stay in two electronic states at the same time in agreement with the classical picture.

D. Determination of classical motions

We present a systematic way to determine such classical motions. First, the integral operator $\hat{I}_n$ classified as Fig. 2(b) must be known. Second, the changes of time variables must be made in a way that the ith transition ($i=1,2,\ldots$, in the order of increasing times) occurs during the times

$$\tau_{2h} = \eta_i + \tfrac{1}{2}\xi_i \quad \text{and} \quad \tau_{2m-1} = \eta_i - \tfrac{1}{2}\xi_i \ , \tag{3.23}$$

with h, $m = 1,2,\ldots,n$. Third, the logarithm of the correlator should be expanded in a series of powers of ξ_1, the duration time of the ith NRT, for $i=1,2,\ldots,n$. Then, n first moments describe the corresponding classical motion: (i) Case of $n=1$; Eq. (3.17) with Eqs. (3.19) and (3.20) can be expanded as

$$\langle \Lambda(\eta_1 - \tfrac{1}{2}\xi_1, \eta_2 + \tfrac{1}{2}\xi_2)\rangle \simeq T_{eg}^2 \exp[-i\,\Omega(\eta_1)\xi_1 - \tfrac{1}{2}D^2\xi^2 + O(\xi^3)] \ . \tag{3.24}$$

In the above, as is well known,

$$\Omega(\eta) = \langle V\rangle - 2\int_0^\infty d\omega\, \omega g(\omega)(1-\cos\omega\eta) \tag{3.25}$$

is the Franck-Condon energy of the virtual NRT which starts from $\langle V\rangle$ at $\eta=0$ and thereafter displays a damping oscillation on the $|e\rangle$ potential surface around the relaxed energy given by

$$\Omega(\infty) = \langle V\rangle_e \equiv \langle V\rangle - 2\int_0^\infty d\omega\, \omega g(\omega) \ . \tag{3.26}$$

(ii) Case of $n=2$; Then, as seen from Fig. 2(b), we have a virtual and a real double transition. The corresponding correlators (3.21) are respectively expanded as

$$\langle \Lambda(\eta_1 - \tfrac{1}{2}\xi_1, \eta_1 + \tfrac{1}{2}\xi_1)\Lambda(\eta_2 - \tfrac{1}{2}\xi_2, \eta_2 + \tfrac{1}{2}\xi_2)\rangle \simeq T_{eg}^4 \exp[-i\,\Omega(\eta_1)\xi_1 - i\,\Omega(\eta_2)\xi_2 + O(\xi^2)] \tag{3.27}$$

and

$$\langle \Lambda(\eta_1 - \tfrac{1}{2}\xi_1, \eta_2 + \tfrac{1}{2}\xi_2)\Lambda(\eta_2 - \tfrac{1}{2}\xi_2, \eta_1 + \tfrac{1}{2}\xi_1)\rangle \simeq T_{eg}^4 \exp\{-i\,\Omega(\eta_1)\xi_1 - i[\Omega(\eta_2) + \langle V\rangle - \Omega(\eta_2 - \eta_1)]\xi_2 + O(\xi^2)\} \ . \tag{3.28}$$

(iii) Case of $n=3$; Then, we have four kinds of classical paths. Only a diagram expressing a new kind of classical motion is depicted in Fig. 2(b), in which the first, second, and third NRT's are real, real, and virtual, respectively. The corresponding correlator of Eq. (3.21) is given by

$$\langle \Lambda(\eta_1 - \tfrac{1}{2}\xi_1, \eta_2 + \tfrac{1}{2}\xi_2)\Lambda(\eta_3 - \tfrac{1}{2}\xi_3, \eta_3 + \tfrac{1}{2}\xi_3)\Lambda(\eta_2 - \tfrac{1}{2}\xi_2, \eta_1 + \tfrac{1}{2}\xi_1)\rangle$$
$$\simeq T_{eg}^6 \exp\{-i\,\Omega(\eta_1)\xi_1 - i[\Omega(\eta_2) + \langle V\rangle - \Omega(\eta_2 - \eta_1)]\xi_2 - i[\Omega(\eta_3) + \Omega(\eta_3 - \eta_2) - \Omega(\eta_3 - \eta_1)]\xi_3 + O(\xi^2)\} \ . \tag{3.29}$$

From these expressions, we find that so long as any real NRT does not occur, the classical motion of the lattice is unchanged and can be described by $\Omega(\eta)$. When the first and last real NRT has occurred at η_1, the system thereafter continues to display a damping oscillation around point 0 on the $|g\rangle$ potential surface and can be specified by the Franck-Condon energy $\Omega(\eta_2) + \langle V\rangle - \Omega(\eta_2 - \eta_1)$ at η_2. Furthermore, when two real NRT's have occurred at η_1 and η_2 ($\eta_1 < \eta_2$), the lattice vibrates again on the $|e\rangle$ potential surface with a slightly different Franck-Condon energy $\Omega(\eta_3) + \Omega(\eta_3 - \eta_2) - \Omega(\eta_3 - \eta_2)$ at η_3.

In the semiclassical approximation, the logarithm of the correlators (3.21) are expanded up to the second moments which the temperature dependence of $P_e(t)$ is described. Unfortunately, however, the integrations of the higher-order terms than the first are practically impossible to perform for the sinusoidal classical motions mentioned above.

E. Definition of a kind of "classical" approximation

Instead of it, limiting us to high temperatures, we propose a kind of classical approximation in which the temperature dependence is introduced into the calculation only as the initial boundary condition of subsequent classical motion. This is based on the Franck-Condon principle in optical excitation and the momentariness of NRT's in the case of strong electron-phonon coupling.

To formulate this approximation, let us derive single equations of $a_e(t)$ and $a_g(t)$. Substituting Eq. (3.4) into Eq. (3.1), we have two equations for the probability-amplitude operators

$$i\dot{a}_g(t) = T_{ge}(t)a_e(t) = T_{ge}\exp_-\left[-i\int_0^t d\tau\, V^{(e)}(\tau)\right]a_e(t) \quad (3.30)$$

and

$$i\dot{a}_e(t) = T_{eg}(t)a_g(t) = T_{eg}\exp_-\left[i\int_0^t d\tau\, V^{(g)}(\tau)\right]a_g(t) \ , \quad (3.31)$$

where $V^{(\lambda)}(t)$ is the Heisenberg representation of V in the $|\lambda\rangle$ state and takes the form

$$V^{(e)}(t) \equiv e^{iH_e t}Ve^{-iH_e t} = \Omega(t) + \delta V^{(g)}(t) \quad (3.32)$$

or

$$V^{(g)}(t) \equiv e^{iH_g t}Ve^{-iH_g t} = \langle V\rangle + \delta V^{(g)}(t) \ . \quad (3.33)$$

Elimination of a_g or a_e from Eqs. (3.30) and (3.31) leads to the single equation

$$\ddot{a}_e(t) - iV^{(e)}(t)\,\dot{a}_e(t) + T_{eg}^2 a_e(t) = 0 \quad (3.34)$$

or

$$\ddot{a}_g(t) + iV^{(g)}(t)\,\dot{a}_g(t) + T_{eg}^2 a_g(t) = 0 \ . \quad (3.35)$$

From Eqs. (3.32) and (3.33), we find that the classical motions of $V^{(e)}(t)$ in Eq. (3.34) and $V^{(g)}(t)$ in Eq. (3.35) display damping oscillations around the respective equilibrium points, $\langle V\rangle_e$ and $\langle V\rangle$. Especially when the system remains in the $|e\rangle$ state from the start, the mean classical motion of $V^{(e)}(t)$ is given by $\Omega(t)$ as was shown in Sec. III D. Therefore, it is reasonable to assume that a projection of the remaining term $\delta V^{(g)}(t)$ in Eq. (3.32) onto the configuration coordinate space gives the thermal fluctuation of the Franck-Condon energy at the absorption process, δV_Q. Let the coordinate and the momentum of the lattice thermal vibration in the configuration coordinate space be $Q(t) = Q\sin\omega_0 t$ and $P(t) = Q\omega_0\cos\omega_0 t$, respectively. Then, from Eqs. (2.4) and (2.5), the lattice energy and the Franck-Condon energy have the forms

$$E_Q = \tfrac{1}{2}[P(t)^2 + \omega_0^2 Q(t)^2] = \tfrac{1}{2}\omega_0^2 Q^2 \quad (3.36)$$

and

$$V_Q = \langle V\rangle + \delta V_Q = \langle V\rangle - (2g_0\omega_0)^{1/2}Q\sin\theta \ , \quad (3.37)$$

respectively, where $\theta = \omega_0 t$. Thus, the initial boundary condition can be imposed by replacing the mean Franck-Condon energy $\langle V\rangle$ in the classical motions of $V^{(e)}(t)$ and $V^{(g)}(t)$ by V_Q given by Eq. (3.37).

In Sec. III D, it was shown that only real transitions can change the classical motion of the lattice. Corresponding to it, the classical approximations of Eqs. (3.34) and (3.35) are composed of a series of equations:

(i) When no real NRT occurred in the past, Eq. (3.34) is approximated by

$$\ddot{a}_{e0}^c(t) - i\,\Omega_0(t)\dot{a}_{e0}^c(t) + T_{eg}^2 a_{e0}^c(t) = 0 \ , \quad (3.38)$$

with the initial condition $a_{e0}^c(t) = 1$ where

$$\Omega_0(t) \equiv \Omega(t) + \delta V_Q = \Omega(t) - 2(g_0\omega_0 E_Q)^{1/2}\sin\theta \ . \quad (3.39)$$

(ii) When a real NRT occurred at $\eta_1 (< t)$ where $\Omega_0(\eta_1) \simeq 0$, Eq. (3.35) is approximated by

$$\ddot{a}_{g1}^c(t) + i\,\Omega_1(t)\dot{a}_{g1}^c(t) + T_{eg}^2 a_{g1}^c(t) = 0 \ , \quad (3.40)$$

where

$$\Omega_1(t) \equiv \Omega(t) + \langle V\rangle - \Omega(t-\eta_1) + \delta V_Q \ . \quad (3.41)$$

(iii) When two real NRT's occurred at η_1 and η_2 $(\eta_1 < \eta_2 < t)$ where $\Omega_0(\eta_1) \simeq 0$ and $\Omega_1(\eta_2) \simeq 0$, Eq. (3.34) is approximated by

$$\ddot{a}_{e2}^c(t) - i\,\Omega_2(t)\dot{a}_{e2}^c(t) + T_{eg}^2 a_{e2}^c(t) = 0 \ , \quad (3.42)$$

where

$$\Omega_2(t) \equiv \Omega(t) + \Omega(t-\eta_2) - \Omega(t-\eta_1) + \delta V_Q \quad (3.43)$$

and so on. The approximate numerical solution of these equations will be given in Sec. VI. As a final step, we must take its thermal average defined by

$$\langle P_{gQ}^c(\infty)\rangle \equiv \frac{\frac{1}{2\pi}\int_0^{2\pi} d\theta \int_0^\infty dE_Q\, e^{-E_Q/kT}P_{gQ}^c(\infty)}{\int_0^\infty dE_Q\, e^{-E_Q/kT}} \ . \quad (3.44)$$

In the weak-coupling limit and in the absence of nonthermal classical motion, the similar approach was used first by Soules and Duke[14] in the problem of the resonant energy transfer and recently by Henry and Lang[19] in the problem of the nonradiative capture by multiphonon emission in semiconductors.

IV. WEAK-COUPLING LIMIT

In this section, we calculate the lowest-order transition probability in a double passage through X in the two approximations; semiclassical and "classical". We prove that their results exactly agree with the thermal average of the LZ formula since the interference effect coming from the double crossing becomes negligible as a consequence of the lattice thermal average.

A. Semiclassical calculation of $C_1(2\pi/\omega_0)$

From Eqs. (3.14), (3.15), and (3.24), $C_1(t)$ becomes

$$C_1(t) \simeq T_{eg}^2 \int_{-t}^{t} d\xi_1 \int_{|\xi_1|/2}^{t-|\xi_1|/2} d\eta_1 \exp[-i\,\Omega(\eta_1)\xi_1 - \tfrac{1}{2}D^2\xi_1^2] \quad . \tag{4.1}$$

At the time t satisfying the unequality

$$t >> \sqrt{2}/D \quad , \tag{4.2}$$

Eq. (4.1) can be approximated as

$$C_1(t) \simeq T_{eg}^2 \int_{-\infty}^{\infty} d\xi_1 \int_0^t d\eta_1 \exp[-i\,\Omega(\eta_1)\xi_1 - \tfrac{1}{2}D^2\xi_1^2] = \frac{2\pi T_{eg}^2}{D} \int_0^t d\eta_1 \exp\left[-\frac{\Omega(\eta_1)^2}{2D^2}\right] \quad . \tag{4.3}$$

It is found that the integral (4.3) rapidly converges as the system moves away from X where $\Omega(\eta_1)=0$. To carry out the integral at $t=2\pi/\bar{\omega}$, we adopt a single frequency model specified by

$$g(\omega) = g_0[\delta(\omega-\omega_0) - \delta(\omega+\omega_0)] \tag{4.4}$$

only in Secs. IV and V and assume that X is not so far apart from the turning point that $\Omega(\eta)$ may be expanded around it like

$$\Omega(\eta) = \langle V\rangle - 2g_0\omega_0(1-\cos\omega_0\eta) \simeq \langle V\rangle - 4g_0\omega_0 + g_0\omega_0^3(\eta-\pi/\omega_0)^2 \quad . \tag{4.5}$$

This approximation would hold fairly well when X lies on the right-hand side of A, i.e.,

$$\langle V\rangle > 2g_0\omega_0 >> \omega_0 \quad . \tag{4.6}$$

Since then from Eq. (3.22)

$$D = D_0 \equiv \omega_0[g_0(2n_0+1)]^{1/2} << \sqrt{2}\omega_0 g_0 < \langle V\rangle/\sqrt{2} \quad , \tag{4.7}$$

where $n_0 = n(\omega_0)$, the upper and lower boundaries of the integral (4.3) can be replaced by ∞ and $-\infty$, respectively. As a result, we obtain

$$C_1\left(\frac{2\pi}{\omega_0}\right) \simeq \frac{(2\pi)^{1/2}T_{eg}^2}{D_0} \times \int_{-\infty}^{\infty} dx \exp\left[-\frac{(\langle V\rangle - 4g_0\omega_0 + g_0\omega_0^3x^2)^2}{2D_0^2}\right] = \frac{\sqrt{\pi}\,\Gamma(\frac{1}{4})\,\tilde{T}_{eg}{}^2}{2^{1/4}g_0^{3/4}(2n_0+1)^{1/4}}\,\mathfrak{F}(z) \quad , \tag{4.8}$$

with

$$\mathfrak{F}(z) = \exp(-z^2)\left[F(\tfrac{1}{4},\tfrac{1}{2};z^2) + \frac{2\sqrt{2}\pi z}{\Gamma(\frac{1}{4})^2}F(\tfrac{3}{4},\tfrac{3}{2};z^2)\right] \quad , \tag{4.9}$$

$$z \equiv (4g_0\omega_0 - \langle V\rangle)/\sqrt{2}D_0 < [2g_0/(2n_0+1)]^{1/2} \quad , \tag{4.10}$$

in which $F(\alpha,\beta;z)$ is a confluent hypergeometric function which has an asymptotic expansion for large $|z|$ as given by

$$F(\alpha,\beta;z) = \sum_{m=0}^{\infty}\frac{z^m}{m!}\frac{(\alpha)_m}{(\beta)_m} = \frac{\Gamma(\beta)}{\Gamma(\beta-\alpha)}(-z)^{-\alpha}\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\frac{(\alpha)_n(\alpha-\beta+1)_n}{z^n} + \frac{\Gamma(\beta)}{\Gamma(\alpha)}e^{z}z^{\alpha-\beta}\sum_{n=0}^{\infty}\frac{(1-\alpha)_n(\beta-\alpha)_n}{n!z^n} \quad , \tag{4.11}$$

where $(\zeta)_n \equiv \Gamma(n+\zeta)/\Gamma(\zeta)$. For $z>0$, the mean classical motion of the system experiences a double passage at the times

$$t_{1\mp} = \pi/\omega_0 \mp [(4g_0\omega_0 - \langle V\rangle)/g_0\omega_0^3]^{1/2} \quad , \tag{4.12}$$

with the velocities

$$\mp v_1 \equiv \left(\frac{d\Omega(\eta)}{d\eta}\right)_{\eta=t_{1\mp}} = \mp 2[g_0\omega_0^3(4g_0\omega_0 - \langle V\rangle)]^{1/2} = \mp 2^{5/4}(g_0\omega_0^3 D_0 z)^{1/2} \tag{4.13}$$

and then only the second term of Eq. (4.11) contributes to Eq. (4.8); that is

$$C_1\left(\frac{2\pi}{\omega_0}\right) = 2C_1^{LZ}\sum_{n=0}^{\infty}\frac{1}{n!z^{2n}}(\tfrac{1}{4})_n(\tfrac{3}{4})_n \quad , \tag{4.14}$$

$$\simeq 2C_1^{LZ} \tag{4.15}$$

especially for $z>>1$, where

$$C_1^{LZ} \equiv 2\pi T_{eg}^2/v_1 \tag{4.16}$$

is the first-order single-pass transition probability for

the mean classical motion of the system, predicted by the LZ theory.[29,30] Here, it should be remarked that the factor other than $2C_1^{LZ}$ in Eq. (4.14) does not mean the breakdown of the LZ formula as was recently concluded by Nasu and Kayanuma[35] (although they have not derived its explicit form) but describes the effect of an ensemble average of the LZ formula over the initial excited state, as will be shown later. On the other side of $z<0$, only the first term of Eq. (4.11) contributes to Eq. (4.8) to give

$$C_1\left(\frac{2\pi}{\omega_0}\right)=\frac{2^{1/4}\pi T_{eg}^2}{\omega_0(g_0\omega_0 D_0)^{1/2}}\frac{e^{-z^2}}{(|z|)^{1/2}} \times\sum_{n=0}^{\infty}\frac{(-1)^n}{n!z^{2n}}\left(\frac{1}{4}\right)_n\left(\frac{3}{4}\right)_n \tag{4.17}$$

$$\simeq[2^{1/4}\pi T_{eg}^2/\omega_0(g_0\omega_0 D_0|z|)^{1/2}]e^{-z^2} \tag{4.18}$$

especially for $z\lesssim -1$. It is found that at high temperatures the NRT for $z\lesssim -1$ occurs with the effective activation energy given by, from Eqs. (4.7) and (4.9),

$$E^*=(4g_0\omega_0-\langle V\rangle)^2/4g_0\omega_0 =\Delta E_{XF}+4g_0\omega_0-\langle V\rangle\ , \tag{4.19}$$

which is smaller than the energy difference between X and F ($\equiv\Delta E_{XF}=E_X-\langle V\rangle$). Even at $T=0$, the excitation spectrum depicted in Fig. 1 can be approximated by a Gaussian when $g_0>>1$ although it vanishes for $E<\langle V\rangle-g_0\omega_0$, because only the vibration quanta with energies larger than E_X ($>\langle V\rangle-g_0\omega_0$) can make NRT's as was explained in Sec. I. Therefore, our formula is applicable to all temperatures. Especially for

$$z=(4g_0\omega_0-\langle V\rangle)/\omega_0(2g_0)^{1/2}\lesssim -1$$

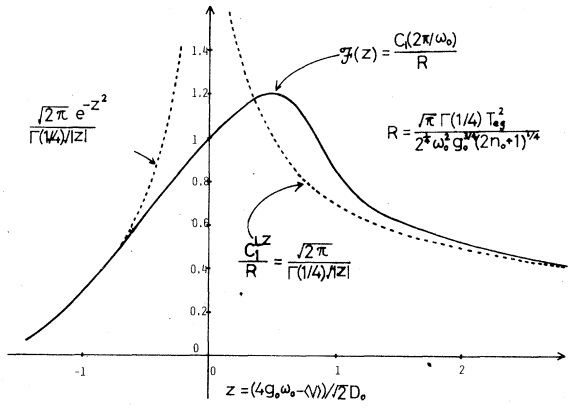

FIG. 3. Double-pass transition probability $C_1(2\pi/\omega_0)$ in the weak-coupling limit as a function of $4g_0\omega_0-\langle V\rangle$. C_1^{LZ} is that predicted by the Landau and Zener theory.

at $T=0$, it approaches a constant,

$$C_1\left(\frac{2\pi}{\omega_0}\right)_{T=0}=\frac{\sqrt{2}\pi t_{eg}^2}{\omega_0[g_0\omega_0(\langle V\rangle-4g_0\omega_0)]^{1/2}} \times\exp\left[-\frac{(\langle V\rangle-4g_0\omega_0)^2}{2g_0\omega_0^2}\right]\ . \tag{4.20}$$

$F(z)$ as a function of z is plotted in Fig. 3. Since it has a maximum 1.2 at $z\simeq 0.52$, the weak-coupling condition can be estimated as

$$\tilde{T}_{eg}<<\left[\frac{2^{1/4}g_0^{3/4}(2n_0+1)^{1/4}}{1.2\sqrt{\pi}\,\Gamma(\frac{1}{4})}\right]^{1/2}\sim 1.3(2n_0+1)^{1/8} \tag{4.21}$$

for the typical value of $g_0=25$.

B. Classical calculation of $C_1(2\pi/\omega_0)$

In the classical approximation defined in Sec. III E, $C_1(2\pi/\omega_0)$ can be easily evaluated by the formula

$$C_1\left(\frac{2\pi}{\omega_0}\right)=\frac{1}{2\pi}\int_0^{2\pi}d\theta \times\int_0^{\infty}d\left(\frac{E_Q}{kT}\right)e^{-E_Q/kT}\left|a_g^{cl}\left(\frac{2\pi}{\omega_0}\right)\right|^2\ , \tag{4.22}$$

where $a_g^{cl}(t)$ is the first-order classical probability amplitude of NRT given by [from Eq. (3.31) with $a_e(t)=1$ and the replacement of $V^{(e)}(t)$ by $\Omega_0(t)$]

$$a_g^{cl}\left(\frac{2\pi}{\omega_0}\right)=-iT_{eg}\int_0^{2\pi/\omega_0}dt\exp[-i\int_0^t dt'\,\Omega_0(t')]\ . \tag{4.23}$$

The problem takes essentially the same path as that of Henry and Lang,[19] although their case does not include nonthermal motions. Substituting Eq. (3.39) with Eq. (4.5) into Eq. (4.23) and putting

$$\nu=[\langle V\rangle-2g_0\omega_0-2(g_0\omega_0E_Q)^{1/2}\sin\theta]/\omega_0\ , \tag{4.24}$$

we obtain

$$a_g^{cl}\left(\frac{2\pi}{\omega_0}\right)=\left(\frac{2\pi T_{eg}}{i\omega_0}\right)e^{-i\pi\nu}J_\nu(2g_0)\ , \tag{4.25}$$

where the Bessel function of order ν defined by

$$J_\nu(2g_0)=\frac{1}{\pi}\int_0^{\pi}dx\cos(2g_0\sin x-\nu x) \tag{4.26}$$

can be approximated by the Airy function as

$$J_\nu(2g_0)\simeq\frac{1}{\pi}\int_0^{\infty}dx\cos[(2g_0-\nu)x-g_0x^3] =\frac{1}{g_0^{1/3}}\mathrm{Ai}\left(\frac{\nu-2g_0}{g_0^{1/3}}\right)\ , \tag{4.27}$$

when $2g_0 >> 1$ and under the condition (4.6).

In this model, the lattice vibration with the initial condition specified by E_Q and θ experiences a double passage at the times

$$t_{1Q\mp} = \{\pi \mp [(2g_0 - \nu)/g_0]^{1/2}\}/\omega_0 \ , \tag{4.28}$$

with the velocities

$$\mp v_{1Q} = \left[\frac{d\Omega_0(t)}{dt}\right]_{t=t_{1Q\mp}}$$

$$= \mp 2(g_0\omega_0^3)^{1/2}(4g_0\omega_0 kT)^{1/4}(z+\sqrt{\epsilon}\sin\theta)^{1/2} \ , \tag{4.29}$$

where we introduced two dimensionless variables

$$z \equiv (4g_0\omega_0 - \langle V\rangle)/(4g_0\omega_0 kT)^{1/2} \tag{4.30}$$

and

$$\epsilon \equiv E_Q/kT \ . \tag{4.31}$$

The problem is much simplified by noting that the argument of the Airy function in Eq. (4.27), given by

$$-y \equiv \frac{\nu - 2g_0}{g_0^{1/3}} = -\frac{v_{1Q}^2}{4\omega_0^4 g_0^{4/3}}$$

$$= -2g_0^{1/6}\left(\frac{kT}{\omega_0}\right)^{1/2}(z+\sqrt{\epsilon}\sin\theta) \ , \tag{4.32}$$

involves a thermal fluctuation of the magnitude $\delta y \sim 4g_0^{1/6}(kT/\omega_0)^{1/2}$ sufficiently larger than 1 for $g_0 >> 1$ and $kT \gtrsim \omega_0$. This means that, when taking the thermal average of $\mathrm{Ai}(-y)^2$, one can use the approximate expression accurate only for $|y| \gtrsim 1$,

$$\langle \mathrm{Ai}(-y)^2\rangle \simeq \langle \Theta(y)[1+\sin(\tfrac{1}{3}y^{3/2})]/2\pi\sqrt{y}\,\rangle$$

$$\sim \langle \Theta(y)/2\pi\sqrt{y}\,\rangle \tag{4.33}$$

for all y. In the above, the thermal average of the sinusoidal behavior of $\mathrm{Ai}(-y)^2$ for $y \gtrsim 1$, which expresses the interference between the double passages, practically vanishes because the thermal fluctuation of the phase $\frac{1}{3}y^{3/2}$ in Eq. (4.33) largely exceeds 2π. Therefore, from Eqs. (4.22), (4.25), and (4.33) with Eq. (4.32), we obtain

$$C_1\left(\frac{2\pi}{\omega_0}\right) \simeq \frac{1}{2\pi}\int_0^2 d\theta \int_0^\infty d\epsilon\, e^{-\epsilon}\frac{4\pi T_{eg}^2}{v_{1Q}} \times \Theta(z+\sqrt{\epsilon}\sin\theta) \ , \tag{4.34}$$

which is nothing but the thermal average of the LZ formula

$$C_{1Q}^{LZ} \equiv (4\pi T_{eg}^2/v_{1Q})\Theta(z+\sqrt{\epsilon}\sin\theta) \ .$$

Finally, let us prove that Eq. (4.34) exactly agrees with the semiclassical result (4.8) at high temperatures. Substituting Eq. (4.29) into Eq. (4.34) and using the expansion formula

$$\frac{\theta(z+\sqrt{\epsilon}\sin\theta)}{(z+\sqrt{\epsilon}\sin\theta)^{1/2}} = \mathrm{Re}\sum_{n=0}^{\infty}(-1)^n\frac{(2n-1)!!}{(2n)!!}\frac{(\sqrt{\epsilon}\sin\theta)^n}{z^{n+1/2}} \tag{4.35}$$

to perform the integrals over ϵ and θ, we easily obtain

$$C_1\left(\frac{2\pi}{\omega_0}\right) = 2\,\mathrm{Re}\left[C_1^{LZ}\sum_{n=0}^{\infty}\frac{1}{n!z^{2n}}(\tfrac{1}{4})_n(\tfrac{3}{4})_n\right] \ , \tag{4.36}$$

where $\mathrm{Re}Z$ means the real part of Z. It is convenient to define Eq. (4.36) in terms of Mellin-Barness–type integral,[36]

$$C_1\left(\frac{2\pi}{\omega_0}\right) = 2\,\mathrm{Re}\left[C_1^{LZ}\frac{1}{2\pi i}\int_{0^+-i\infty}^{0^++i\infty} ds\,(-1)^s z^{-2s}\Gamma(s)\Gamma(-s+\tfrac{1}{4})\Gamma(-s+\tfrac{3}{4})\right] \ . \tag{4.}$$

Carrying out the contour integral inside the $\mathrm{Re}z > 0$ plane and using the Kummer's transformation formula: $F(\alpha,\gamma;x) = e^x F(\gamma-\alpha,\gamma;-x)$, we finally arrive at the semiclassical result (4.8).

This exact agreement of the semiclassical and classical results at high temperatures strongly suggests that our classical approximation to be applied to high temperatures could be generalized to all temperatures simply by replacing $2kT/\omega_0$ in the final result by $2n(\omega_0)+1$. By doing so, the term of "thermal average" can be sublated into ensemble average over the initial state excited by a very short laser pulse.

V. STRONG-COUPLING LIMIT

In this section, we shall examine the condition for strong-coupling limit. Then, it is necessary in the zeroth approximation to start with the adiabatic wave functions, $|1\rangle$ and $|2\rangle$ given by Eq. (2.7) with Eq. (2.8). The initial wave function $\psi(0)$ given by Eq. (3.2) is assumed to be transformed into the more realistic form

$$\psi(0) \simeq |2\rangle|\{n_j\}\rangle \tag{5.1}$$

under the supposed condition (3.3). Then, in the

system with the Hamiltonian (2.9), the probability amplitude $a_1(t)$ for the first-order NRT from $|2\rangle$ to $|1\rangle$ is easily obtained in an operator form,

$$a_1(t) = \langle 1|\psi(t)\rangle \simeq -\int_0^t d\tau \exp(i\tau\{H_g + [V - \tfrac{1}{2}(V^2+4T_{eg}^2)^{1/2}]\})\,\dot{\chi}(\tau)\exp(-i\tau\{H_g + [V + \tfrac{1}{2}(V^2+4T_{eg}^2)^{1/2}]\}) \quad . \tag{5.2}$$

The existing quantum-mechanical calculations of NAT (nonadiabatic transition) probability are all based on the substitutions of H_g and H_e for $H_g + [V - \frac{1}{2}(V^2+4T_{eg}^2)^{1/2}]$ and $H_g + [V + \frac{1}{2}(V^2+4T_{eg}^2)^{1/2}]$, respectively.[10,11] But, such an approximation would apparently lead to its overestimation. We believe that a more reliable estimate can be obtained in the classical approximation without substitutions, which is defined by

$$a_1(t) \simeq a_1^c(t) \equiv -\int_0^t d\tau\,\dot{\chi}^c(\tau) \times \exp\left[-i\int_0^\tau d\tau' [\Omega_0(\tau')^2 + 4T_{eg}^2]^{1/2}\right], \tag{5.3}$$

with

$$\chi^c(\tau) \equiv \frac{d}{d\tau}\left[\frac{1}{2}\tan^{-1}\left(\frac{2T_{eg}}{\Omega_0(\tau)}\right)\right] = -\frac{T_{eg}\,\dot{\Omega}_0(\tau)}{\Omega_0(\tau)^2 + 4T_{eg}^2} \quad . \tag{5.4}$$

To proceed further, we adopt the same model for the system discussed in Sec. IV. Substituting Eq. (3.39) with Eq. (4.5) into Eq. (5.3) with Eq. (5.4) and introducing the dimensionless variables

$$b \equiv (2T_{eg})^{3/2}/\sqrt{g_0} \quad , \tag{5.5}$$

$$\xi(\tau) \equiv (g_0/2T_{eg})^{1/2}(\omega_0\tau - \pi) \quad , \tag{5.6}$$

and with use of Eq. (4.31)

$$\zeta \equiv [4g_0\omega_0 - \langle V\rangle + 2(g_0\omega_0 E_Q)^{1/2}\sin\theta]/2T_{eg} = \langle\zeta\rangle + (g_0\omega_0 kT\epsilon)^{1/2}\sin\theta/T_{eg} \quad , \tag{5.7}$$

we obtain at $t = 2\pi/\omega_0$

$$a_1^c\left(\frac{2\pi}{\omega_0}\right) \simeq \int_{-\infty}^{\infty} d\xi\,\frac{\xi}{(\xi^2-\zeta)^2+1} \times \exp\left[ib\int_{\xi(0)}^{\xi} d\xi\,[(\xi^2-\zeta)^2+1]^{1/2}\right] \quad , \tag{5.8}$$

where we have replaced the integral region of $-|\xi(0)| < \xi < |\xi(0)|$ by $-\infty < \xi < \infty$ by taking account of the conditions (3.3) and (4.6), i.e.,

$$\tilde{T}_{eg} << 2g_0 < \langle\tilde{V}\rangle \equiv \langle V\rangle/\omega_0 \quad . \tag{5.9}$$

The integral (5.8) was approximately performed by Nikitin[26] in the problem of NRT near the turning point in atomic collisions. But in our case the thermal average of $|a_1^c(2\pi/\omega_0)|^2$ must be taken to obtain the NAT probability

$$P_{21}\left(\frac{2\pi}{\omega_0}\right) = \frac{1}{2\pi}\int_0^{2\pi} d\theta \int_0^{\infty} d\epsilon\, e^{-\epsilon}\left|a_1^c\left(\frac{2\pi}{\omega_0}\right)\right|^2 \quad . \tag{5.10}$$

Nikitin's result[26] is given by

$$|a_1^c(2\pi/\omega_0)|^2 = \begin{cases} 2\exp(-\pi b/4\sqrt{\zeta}) \ , & \text{for } \zeta >> 1 \ , \\ \sim \exp[-\frac{1}{4}\pi b(1.57 - 1.11\zeta)] \ , & \text{for } |\zeta| << 1 \ , \\ \sim \exp(-\frac{1}{4}\pi b|\zeta|^{3/2}) \ , & \text{for } -\zeta >> 1 \ , \end{cases} \tag{5.11}$$

which is a monotonically increasing function of ζ in the region where the above first-order perturbation theory is applicable, i.e.,

$$2\exp[-\pi b/4(\langle\zeta\rangle)^{1/2}] << 1 \quad \text{or} \quad \langle\zeta\rangle < (\tfrac{1}{4}\pi b)^2 \quad . \tag{5.12}$$

Thus, the strong-coupling condition is found to be

$$b >> 1 \quad \text{or} \quad T_{eg} >> \tfrac{1}{2}g_0^{1/3} \simeq 1.4, \quad \text{for } g_0 = 22 \ . \tag{5.13}$$

The above conditions (5.9), (5.12), and (5.13) stand together as far as $g_0 >> 1$.

Finally, let us consider the effect of thermal average. Since the thermal fluctuation of ζ is small ($\Delta\zeta \equiv \zeta - \langle\zeta\rangle \simeq \sqrt{g_0}/T_{eg} << 2g_0^{1/6} \simeq 3.3$ for $g_0 = 22$), the solution (5.11) in the first approximation takes the form

$$|a_1^c(2\pi/\omega_0)|^2 \simeq \exp[2(\beta\epsilon T_{eg}kT/\omega_0)^{1/2}\sin\theta] \times |a_1^c(2\pi/\omega_0)|^2_{\zeta\to\langle\zeta\rangle} \quad , \tag{5.14}$$

with

$$\beta = \begin{cases} \pi^2/32\langle\zeta\rangle^3 \ , & \text{for } \langle\zeta\rangle >> 1 \ , \\ 1.52 \ , & \text{for } |\langle\zeta\rangle| << 1 \ , \\ 9\pi^2|\langle\zeta\rangle|/32 \ , & \text{for } -\langle\zeta\rangle >> 1 \ . \end{cases} \tag{5.15}$$

Substituting Eq. (5.14) into Eq. (5.10) and performing the integral, we obtain

$$P_{21}(2\pi/\omega_0) \simeq \exp(\beta T_{eg} kT/\omega_0)\,|a_1^c(2\pi/\omega_0)|^2_{\zeta\to\langle\zeta\rangle} \ . \tag{5.16}$$

Thus, we found that NRT is enhanced in the region of $\langle\zeta\rangle$ given by Eq. (5.12). At the largest value of $\langle\zeta\rangle = (\frac{1}{4}\pi b)^2 >> 1$, the enhancement factor takes its minimum,

$$\exp(\beta T_{eg} kT/\omega_0) = \exp[2^6 g_0^3/\pi^4 (2T_{eg})^8] << \exp(2^6 g_0^{1/3}/\pi^4) \simeq 6.3 \ ,$$

for $g_0 = 22$. As $\langle\zeta\rangle$ decreases, the enhancement factor increases remarkably although $P_{21}(2\pi/\omega_0)$ decreases. Therefore, we find that the strong-coupling condition (5.13) is revised due to the thermal average.

VI. NONRADIATIVE QUENCHING OF HOT LUMINESCENCE IN *F* CENTERS

In this section, we present a modified theoretical justification of the quenching mechanism of luminescence originally proposed by DKR[23] and later used to predict the occurrence of luminescence from available optical-absorption data by BS.[24] The sufficient (not necessary) condition for luminescence to be observed at low temperatures, used by BS, is composed only of

$$\Lambda^{-1} \equiv \langle V\rangle/g_0\omega_0 > 4 \ . \tag{6.1}$$

In addition to g_0, Λ, and T, we take into account two other important parameters; i.e., the damping constant of lattice vibration Γ_0 and the strength of coupling between terms A. With use of them, the intensity of F-center luminescence itself will be calculated.

A. Model for dissipative system

The damping constant Γ_0, which expresses the irreducible energy flow from the configuration coordinate system to the other modes, is introduced by a model of interaction spectrum given by

$$g(\omega) = \frac{g_0}{\pi}\left[\frac{\Gamma_0}{(\omega-\omega_0)^2+\Gamma_0^2} - \frac{\Gamma_0}{(\omega+\omega_0)^2+\Gamma_0^2}\right] . \tag{6.2}$$

Γ_0 may have two different origins; the nonmonochromaticy of normal mode frequencies and the anharmonic interactions between normal modes.

Substituting Eq. (6.2) into Eq. (3.25) and performing the integral, we obtain

$$\Omega(t) = \langle V\rangle_e + 2g_0(\omega_0^2+\Gamma_0^2)^{1/2} e^{-\Gamma_0 t}\cos(\omega_0 t+\phi_0) \ , \tag{6.3}$$

with

$$\tan\phi_0 = \Gamma_0/\omega_0 \equiv \tilde{\Gamma}_0 \ . \tag{6.4}$$

In the existence of the damping of lattice vibration, the condition (6.1) that X is not accessible by the mean classical motion must be corrected,

$$\min\Omega(t) = \Omega\left(\frac{\pi-2\phi_0}{\omega_0}\right) = g_0\omega_0(\Lambda^{-1} - 2 - 2e^{-\Gamma_0(\pi-2\phi_0)/\omega_0}) > 0 \ . \tag{6.5}$$

Then, the transition probability $P_{gQ}^c(\infty)$ with $\delta V_Q = 0$ vanishes. Meanwhile, the purpose of this paper is to evaluate $P_{gQ}^c(\infty)$ when the first turning point of the mean classical vibration occurs in the region above X but not so far apart from it, i.e.,

$$2 < \Lambda^{-1} < 2(1+e^{-\Gamma_0(\pi-2\phi_0)/\omega_0}) \equiv \Lambda_c^{-1} \ . \tag{6.6}$$

This is a necessary condition for the luminescence to be quenched. By use of this condition and Table I of BS,[24] we can obtain a rough estimation of Γ_0: Since the F-center luminescence in host LiF is substantially quenched with $\Lambda = 0.323$, $\pi\tilde{\Gamma}_0 << 0.6$ must be satisfied. Therefore, we assume that

$$\pi\tilde{\Gamma}_0 << 1 \ . \tag{6.7}$$

B. Calculation of mean classical motions

The mean Franck-Condon energies of virtual or real NRT's, given by Eqs. (3.39), (3.41), and (3.43) with $\delta V_Q = 0$, are evaluated as follows: (i) When any real NRT did not occur in the past,

$$\Omega_0(t) = \Omega(t) = \text{Eq. (6.3)} \ . \tag{6.8}$$

(ii) When only a real NRT occurred at $\eta_1 (< t)$ in the past,

$$\Omega_1(t) = \langle V\rangle + 4g_0(\omega_0^2+\Gamma_0^2)^{1/2} S_1 e^{-\Gamma_0(t-\phi_1/\omega_0)} \times\cos(\omega_0 t+\phi_0+\phi_1) \ , \tag{6.9}$$

with

$$\tan\phi_1 \equiv \sin\omega_0\eta_1/(e^{-\Gamma_0\eta_1} - \cos\omega_0\eta_1) \ , \tag{6.10}$$

$$S_1 \equiv 2^{-1} e^{\Gamma_0\phi_1/\omega_0}(1 - 2\cos\omega_0\eta_1 e^{\Gamma_0\eta_1} + e^{2\Gamma_0\eta_1})^{1/2} \ . \tag{6.11}$$

(iii) When only two real NRT's occurred at η_1 and η_2 $(\eta_1 < \eta_2 < t)$ in the past,

$$\Omega_2(t) = \langle V\rangle - 2g_0\omega_0 + 2g_0(\omega_0^2+\Gamma_0^2)^{1/2} S_2 e^{-\Gamma_0 t} \times\cos(\omega_0 t+\phi_0+\phi_2) \ , \tag{6.12}$$

with

$$\tan\phi_2 = \frac{e^{\Gamma_0\eta_1}\sin\omega_0\eta_1 - e^{\Gamma_0\eta_2}\sin\omega_0\eta_2}{1+e^{\Gamma_0\eta_2}\cos\omega_0\eta_2 - e^{\Gamma_0\eta_1}\cos\omega_0\eta_1} \quad , \tag{6.13}$$

$$\begin{aligned} S_2 = [&1+e^{2\Gamma_0\eta_1}(1-2\cos\omega_0\eta_1) \\ &+e^{2\Gamma_0\eta_2}(1+2\cos\omega_0\eta_2) \\ &-2e^{\Gamma_0(\eta_1+\eta_2)}\cos\omega_0(\eta_2-\eta_1)]^{1/2}e^{\Gamma_0\phi_2/\omega_0} \quad , \end{aligned} \tag{6.14}$$

and so on. Since NRT occurs principally near X where the above Franck-Condon energy vanishes, we can approximate $\Omega_i(t)$ $(i=0,1,2,\ldots)$ by a parabola around the lth turning point giving the local minimum under the conditions (6.6) and (6.7),

$$\text{(i)}\quad \Omega_0(t) \simeq \langle V\rangle_e + 2g_0\omega_0 e^{-\Gamma_0 t_0^{(l)}} \times[-1+\tfrac{1}{2}(\omega_0^2+\Gamma_0^2)(t-t_0^{(l)})^2] \quad , \tag{6.15}$$

for $|t-t_0^{(l)}| < \frac{1}{2}\pi$ $(l=1,2,\ldots)$, with

$$t_0^{(l)} = (2l-1)\pi/\omega_0 - 2\phi_0/\omega_0 \quad . \tag{6.16}$$

$$\text{(ii)}\quad \Omega_1(t) \simeq \langle V\rangle + 4g_0\omega_0 S_1 e^{-\Gamma_0 t_0^{(l)}} \times[-1+\tfrac{1}{2}(\omega_0^2+\Gamma_0^2)(t-t_1^{(l)})^2] \quad , \tag{6.17}$$

for $|t-t_1^{(l)}| < \frac{1}{2}\pi$, with

$$t_1^{(l)} = t_0^{(l)} - \phi_1/\omega_0 > \eta_1 \quad . \tag{6.18}$$

$$\text{(iii)}\quad \Omega_2(t) \simeq \langle V\rangle_e + 2g_0\omega_0 S_2 e^{-\Gamma_0 t_0^{(l)}} \times[-1+\tfrac{1}{2}(\omega_0^2+\Gamma_0^2)(t-t_2^{(l)})^2] \quad , \tag{6.19}$$

for $|t-t_2^{(l)}| < \frac{1}{2}\pi$, with

$$t_2^{(l)} = t_0^{(l)} - \phi_2/\omega_0 > \eta_2 > \eta_1 \quad , \tag{6.20}$$

and so on. Especially, in this approximation, respective classical motions of the lattice experience the nth double passage through X at the times

$$\text{(i)}\quad t_{0\mp}^{(n)} = t_0^{(n)} \mp \left[\frac{2\Lambda-(1-2\Lambda)\exp(\Gamma_0 t_0^{(n)})}{\Lambda(\omega_0^2+\Gamma_0^2)}\right]^{1/2} , \tag{6.21}$$

$$\text{(ii)}\quad t_{1\mp}^{(n)} = t_0^{(n)} \mp \left[\frac{4\Lambda S_1-\exp(\Gamma_0 t_0^{(n)})}{2\Lambda S_1(\omega_0^2+\Gamma_0^2)}\right]^{1/2} , \tag{6.22}$$

$$\text{(iii)}\quad t_{2\mp}^{(n)} = t_2^{(n)} \mp \left[\frac{2\Lambda S_2-(1-2\Lambda)\exp(\Gamma_0 t_0^{(n)})}{\Lambda S_2(\omega_0^2+\Gamma_0^2)}\right]^{1/2} , \tag{6.23}$$

around the nth turning point with the velocities

$$\begin{aligned} \text{(i)}\quad \mp v_0^{(n)} &= \left(\frac{d\Omega_0(t)}{dt}\right)_{t=t_{0\mp}^{(n)}} \\ &= \mp 2\omega_0(\omega_0^2+\Gamma_0^2)^{1/2}g_0^{3/4}[Z_0(\Gamma_0 t_0^{(n)})]^{1/2} \quad , \end{aligned} \tag{6.24}$$

where

$$Z_0(x) \equiv \sqrt{g_0}[2e^{-2x} - (\Lambda^{-1}-2)e^{-x}] \quad . \tag{6.25}$$

$$\begin{aligned} \text{(ii)}\quad \mp v_1^{(ln)} &= \left(\frac{d\Omega_1(t)}{dt}\right)_{t=t_{1\mp}^{(n)}} \\ &= \mp 2\omega_0(\omega_0^2+\Gamma_0^2)^{1/2}g_0^{3/4}[Z_1^{(l)}(\Gamma_0 t_0^{(n)})]^{1/2} \quad , \end{aligned} \tag{6.26}$$

where

$$Z_1^{(l)}(x) = 2\sqrt{g_0}S_1(4S_1e^{-2x} - \Lambda^{-1}e^{-x}) \quad . \tag{6.27}$$

$$\begin{aligned} \text{(iii)}\quad \mp v_2^{(lmn)} &= \left(\frac{d\Omega_2(t)}{dt}\right)_{t=t_{2\mp}^{(n)}} \\ &= \mp 2\omega_0(\omega_0^2+\Gamma_0^2)^{1/2}g_0^{3/4} \\ &\quad \times[Z_2^{(lm)}(\Gamma_0 t_0^{(n)})]^{1/2} \quad , \end{aligned} \tag{6.28}$$

where

$$Z_2^{(lm)}(x) = \sqrt{g_0}S_2[2S_2e^{-2x} - (\Lambda^{-1}-2)e^{-x}] \quad , \tag{6.29}$$

and so on. Here, we have supposed that the first and the second real NRT's have occurred in the regions of $\eta_1 \simeq t_0^{(l)}$ and $\eta_2 \simeq t_0^{(m)}$, respectively $(l \geqslant m)$. Since the mean velocity of the lattice must vary continuously at any real NRT event, S_1 and S_2 in Eqs. (6.27) and (6.29) should be determined by the relations;

$$v_0^{(l)} = v_1^{(ll)}$$

or

$$Z_0(\Gamma_0 t_0^{(l)}) = Z_1^{(l)}(\Gamma_0 t_0^{(l)}) \quad , \tag{6.30a}$$

and

$$v_1^{(lm)} = v_2^{(lmm)}$$

or

$$Z_1^{(l)}(\Gamma_0 t_0^{(m)}) = Z_2^{(lm)}(\Gamma_0 t_0^{(m)}) \quad . \tag{6.30b}$$

Substituting Eqs. (6.25), (6.27), and (6.29) into Eqs. (6.30a) and (6.30b), we get

$$S_1 \to S_1^{(l)} = \{e^{\Gamma_0 t_0^{(l)}} + [(4\Lambda)^2 - 8\Lambda(1-2\Lambda)e^{\Gamma_0 t_0^{(l)}} + e^{2\Gamma_0 t_0^{(l)}}]^{1/2}\}/8\Lambda \tag{6.31}$$

and

$$S_2 \to S_2^{(lm)} = \frac{1}{2}\left(\frac{1}{2\Lambda}-1\right)e^{\Gamma_0 t_0^{(m)}} + \left[\frac{1}{4}\left(\frac{1}{2\Lambda}-1\right)^2 e^{2\Gamma_0 t_0^{(m)}} + S_1^{(l)}\left(4S_1^{(l)} - \Lambda^{-1}e^{\Gamma_0 t_0^{(m)}}\right)\right]^{1/2} . \tag{6.32}$$

We plot in Fig. 4 the relations of $Z_0(x)$ vs x (solid lines), $Z_1^{(l)}(x)$ vs x (broken lines which stem from solid lines), and $Z_2^{(lm)}(x)$ vs x (dotted lines which stem from broken lines) for various values of Λ in the typical case of $g_0=25$ and $\pi\tilde{\Gamma}_0=0.1$. Discrete allowed points are indicated by open circles, which are located at

$$x=\Gamma_0 t_0^{(n)} \simeq (2n-1)\pi\tilde{\Gamma}_0$$
$$=0.1(2n-1), \quad n=1,2,...$$

and must lie on the upper half plane because only positive $Z_0(x)$, $Z_1^{(l)}(x)$ and $Z_2^{(lm)}(x)$ can give real velocities at X. To avoid complexity, many lines were omitted.

From this calculation, we find a very important fact that the chances for the system to make real NRT's from $|e\rangle$ to $|g\rangle$ principally through X are exceedingly higher than those to return back into $|e\rangle$ again through X. For instance, in the case of $\Lambda=0.35$, $g_0=25$, and $\pi\tilde{\Gamma}_0=0.1$, there are four chances of the former but no chance of the latter. The physical reason is simple: As seen from Eqs. (6.15), (6.17), and (6.19) ($S_1\simeq S_2\simeq 1$), it comes from the special situation that the amplitude of damping oscillation on the $|g\rangle$ potential surface is about twice larger than that on the $|e\rangle$ potential surface. As $\tilde{\Gamma}_0$ increases (decreases), the chances mentioned above decrease (increase) rapidly.

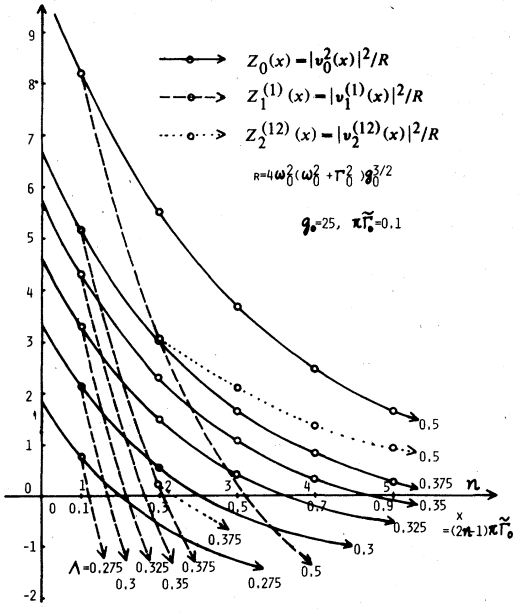

FIG. 4. Square velocities at X as functions of time, for various values of Λ in the typical case of $g_0=25$ and $\pi\tilde{\Gamma}_0=0.1$. Real allowed points are indicated by open circles.

C. Calculation of NRT probability

To solve Eqs. (3.38), (3.40), and (3.42) with the characteristic frequencies given by Eqs. (6.15), (6.17), and (6.19), after Landau,[29] we also assume that the interference between the double passages near each turning point of lattice vibration may be neglected although in our system this assumption can be justified only after taking the thermal average of classical transition probability in the same way as in Sec. IV B. Then, the probability for a transition from $|e\rangle$ (or $|g\rangle$) to $|g\rangle$ (or $|e\rangle$) in a double passage through X may be estimated from the LZ formula.[29,30] If the four kinds of velocities on X are all equally given by the expression

$$v(Z)=2\omega_0(\omega_0^2+\Gamma_0^2)^{1/2}g_0^{3/4}\sqrt{Z} \tag{6.33}$$

apart from their signs as is the case in the present approximation, this formula takes the form

$$P(Z)=\begin{cases} 2\exp\left(-\dfrac{A}{\sqrt{Z}}\right)\left[1-\exp\left(-\dfrac{A}{\sqrt{Z}}\right)\right], & \text{for } Z>0, \\ 0, & \text{for } Z<0, \end{cases} \tag{6.34}$$

with the strength of coupling between terms defined by

$$A \equiv \pi\tilde{T}_{eg}^2/g_0^{3/4}[1+(\Gamma_0/\omega_0)^2]^{1/2}$$
$$\sim \pi\tilde{T}_{eg}{}^2/g_0^{3/4} . \tag{6.35}$$

We depict in Fig. 5 the graphs of $P(Z)$ vs Z for vari-

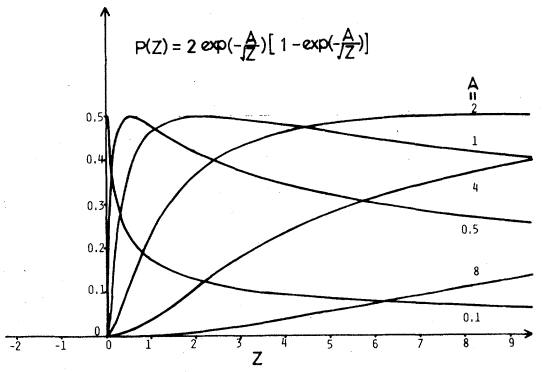

FIG. 5. Landau-Zener formula $P(Z)$ for the double-pass transition probability as a function of Z defined by Eq. (6.33): the velocity on X. A is the coupling strength defined by Eq. (6.35). Note that $P(Z)$ is nearly constant $\lesssim 0.5$ for $0<Z<8$ in the cases of intermediate coupling ($A=0.5$ and $A=1$).

ous values of A: $A=0.1$ (weak-coupling case), $A=0.5\sim1$ (intermediate-coupling case) and $A=8$ (strong-coupling case). When $\tilde{T}_{eg}$ is given by Eq. (2.14) and $g_0=22$, A takes the values $\simeq0.5$ at $T=0$, $\simeq1$ at $T=\omega_0$, and $\simeq2$ at $T=2\omega_0$. It is important to note that $P(Z)$ as a function of Z behaves like a step function $\sim\frac{1}{2}\Theta(Z)$ for $Z<Z_0(0)\simeq8$, only in these intermediate-coupling cases where we are concerned with. This property brings about an important conclusion that the final transition probability $P_g^c(\infty)$ is maximized in such cases of intermediate coupling.

By use of the numerical results as shown in Figs. 4 and 5, we can numerically calculate $P_g^c(\infty)$ given by the LZ formula

$$\begin{aligned}P_g^c(\infty)\simeq{}&P(Z_0(\Gamma_0t_0^{(1)}))\{[1-P(Z_1^{(1)}(\Gamma_0t_0^{(2)}))][1-P(Z_1^{(1)}(\Gamma_0t_0^{(3)}))+\cdots]\\&+P(Z_1^{(1)}(\Gamma_0t_0^{(2)}))[P(Z_2^{(12)}(\Gamma_0t_0^{(3)}))+\cdots]\cdots\}\\&+[1-P(Z_0(\Gamma_0t_0^{(1)}))]\{P(Z_0(\Gamma_0t_0^{(2)}))[1-P(Z_1^{(2)}(\Gamma_0t_0^{(3)}))+\cdots]\\&+[1-P(Z_0(\Gamma_0t_0^{(2)}))][P(Z_0(\Gamma_0t_0^{(3)}))+\cdots]\cdots\}\ .\end{aligned}\tag{6.36}$$

The results are drawn in Fig. 6 in the cases of $A=0.5$, 1, and 2 with $\pi\tilde{\Gamma}_0=0.1$ and $g_0=25$. For example, for $A=1$ and $\Lambda=0.3$, we have only $Z_0(\Gamma_0t_0^{(1)})=2.155$ and $Z_0(\Gamma_0t_0^{(2)})=0.549$ from Fig. 4 and then we can read from Fig. 5 $P(2.155)=0.500$ and $P(0.549)=0.385$ to get the final result: $P_g^c(\infty)=0.500+(1-0.500)0.385=0.693$. Then, we say that the quantum yield is 30.7%. Small dips of $P_g^c(\infty)$ around $\Lambda\gtrsim0.37$ in the cases of $A=0.5$ and 1 indicate the appearance of back transfer into the $|e\rangle$ state for larger values of Λ. In general, $P_g^c(\infty)=1$ at $\Lambda=0.5$ independent of $\pi\tilde{\Gamma}_0$ and A and $P_g^c(\infty)=0$ for $\Lambda<\Lambda_c$.

D. Ensemble average of $P_{gQ}^c(\infty)$ in the initial state

The ensemble average of $P_{gQ}^c(\infty)$ over the initial state excited by a very short laser pulse plays two important roles: (a) the interference between different passes through X coming from different boundary conditions strongly cancels out; (b) the NRT through X becomes possible even for $\Lambda\leqq\Lambda_c$ and at $T=0$. The first point is already taken into account by applying the LZ formula. Next, we demonstrate the second point at high temperatures by choosing an approximate form of $P_{gQ}^c(\infty)$ near $\Lambda\sim\Lambda_c$ for $A=0.5$ and 1,

$$\begin{aligned}P_{gQ}^c(\infty)&=\alpha[1-\Lambda_c(\Lambda^{-1}+\delta V_Q/g_0\omega_0)]^{1/2}\\&\quad\times\Theta(\Lambda_c^{-1}-\Lambda^{-1}-\delta V_Q/g_0\omega_0)\\&=\alpha(4\Lambda_c^2kT/g_0\omega_0)^{1/4}(z+\sqrt{\epsilon}\sin\theta)^{1/2}\\&\quad\times\Theta(z+\sqrt{\epsilon}\sin\theta)\ ,\end{aligned}\tag{6.37}$$

where

$$z\equiv(2g_0\omega_0\Lambda_c^{-1}-\langle V\rangle)/4(g_0\omega_0kT)^{1/2}\ .\tag{6.38}$$

The integrals over ϵ and θ in Eq. (3.44) with Eq. (6.37) can be performed in the same manner as in Sec. IV B. The result is given by

$$P_{gQ}^c(\infty)=\alpha(4\Lambda_c^2kT/g_0\omega_0)^{1/4}G(z)\ ,\tag{6.39}$$

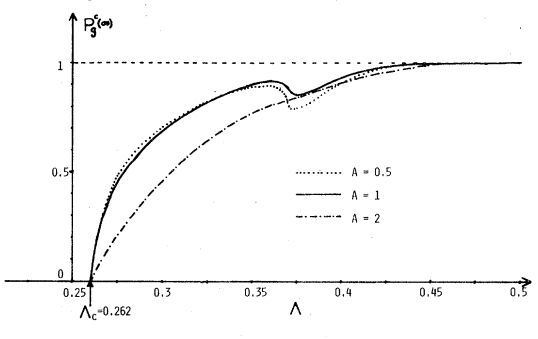

FIG. 6. Landau-Zener formula for the total transition probabilities at ∞, as functions of Λ, in the cases of intermediate coupling. Its thermal average as shown in Fig. 7 gives the quenching rate of luminescence.

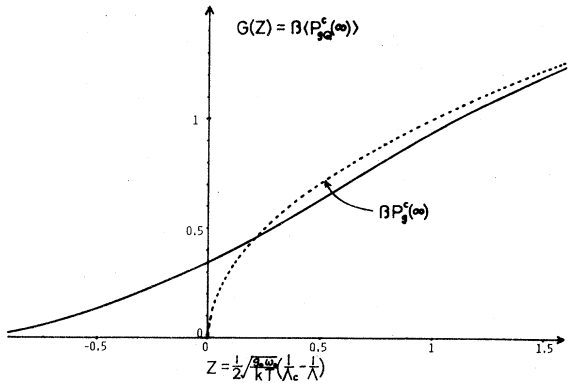

FIG. 7. Effect of thermal fluctuation of initial boundary condition around a marginal point of the Landau-Zener formula $P_g^c(\infty)$ indicated by a dotted line.

with

$$G(z)=\frac{(2\pi)^{1/2}}{8\Gamma(\frac{5}{4})}\mathrm{Re}\left[(1+i)F(-\tfrac{1}{4},\tfrac{1}{2};-z^2)+\frac{2^{5/2}}{\pi}\Gamma(\tfrac{5}{4})^2 z(1-\bar{z})F(\tfrac{1}{4},\tfrac{3}{2};-z^2)\right], \tag{6.40}$$

which has asymptotic forms

$$G(z)=\begin{cases}\sqrt{z}\,(1-1/16z^2+\cdots), & \text{for } z>>1,\\ 0.346+0.511z, & \text{for } |z|<<1,\\ \sqrt{2}|z|^{-3/2}e^{-z^2}, & \text{for } -z>>1.\end{cases} \tag{6.41}$$

The numerical calculation of $G(z)$ for $-1<z<1.5$ is depicted in Fig. 7. It is found that for $z>1$ the effect of thermal average can be neglected within an error of 5%.

VII. DISCUSSION AND SUMMARY

DKR[23] proposed in their original paper that the crossover at X sometimes occurs with high probability ($\lesssim 1$) so that the condition (6.1) may be necessary and sufficient. This postulate seems to have been ascertained for luminescences for F centers in alkali halides, alkaline-earth oxides, and MgF_2 by BS.[24] Accordingly, Mott[13] has conjectured that since the LZ formula for a double passage through X, $P(Z)$, is in no case greater than 0.5 and will normally be much less, the crossover with high probability would occur when the turning point of lattice vibration coincides with X where the LZ formula breaks down.

In Sec. IV, however, we have shown that the transition probability for a double passage through X, C_1, obtained in the semiclassical approximation, is nothing except for the thermal average of the LZ formula C_{1Q}^{LZ}. This proof strongly suggests that DKR's postulate and Mott's conjecture can never be the case since the thermal average of the LZ formula $P(Z)$ is also in no case greater than 0.5. Thus, the appreciable quenching of F-center luminescence naturally requires that there must occur many chances to pass through X with nearly maximum probability ($\lesssim 0.5$) for each transfer in the course of lattice relaxation in such a way that the probability of back transfers from $|g\rangle$ to $|e\rangle$ is strongly suppressed in virtue of some special situation. Indeed, we have shown that this is just the case in Sec. VI.

The essential features of our theory are summarized as follows: (a) The NRT occurs almost instantaneously according to the Franck-Condon principle with strong electron-phonon coupling. This justifies the classical approximation used in this paper. In this approximation, the temperature dependence is introduced into the calculation only as the initial boundary condition of subsequent classical motions. In Sec. III D, a systematic way to determine such classical motions has been presented. It should be noted that only "real" NRT can change the classical motion of the lattice: As after a real NRT occurs, the center of vibration jumps from A to 0 or from 0 to A. (b) The NRT occurs principally when the system passes through X in the configuration coordinate space where the Franck-Condon energy of NRT vanishes. It should be noted that when the system is excited by a white pulse, the shaded part of the excitation spectrum depicted in Fig. 1 may be approximated by a part of Gaussian even at low temperatures. Here, only the lattice vibration in the shaded part can pass over X and contribute to NRT. Therefore, the wider the area of such shaded part is, the more the probability of NRT increases. As $\tilde{\Gamma}_0$ increases, that area decreases. (c) The damping of lattice vibration in the configuration coordinate space is essentially important for the system to end in the lower state, as was indicated by Stoneham.[13] As shown in Fig. 4, we have found that the system may have many more chances to pass over X for the damping oscillation on the $|e\rangle$ potential surface than on the $|g\rangle$ potential surface so long as $\pi\tilde{\Gamma}_0 << 1$. This means that the total probability of forward transfers ($|e\rangle \rightarrow |g\rangle$) is much larger than that of back transfers ($|g\rangle \rightarrow |e\rangle$). But it does not mean immediately that the luminescence is strongly quenched, because it is required that the transition probabilities for these double passages take about the nearly maximum values ($\gtrsim 0.5$). (d) The strength of coupling between terms can be specified by A defined by Eq. (6.35). The cases of $A<<1$, $A\sim 1$, and $A>>1$ correspond to weak, intermediate, and strong couplings, respectively. We have shown that F centers in ionic crystals are in the cases of intermediate coupling. This fact brings about the property of $P(Z)$ mentioned above and so is essentially important for the understanding of the strong quenching of F-center luminescence. It should be remarked, however, that the quenching is not complete in our theory contrary to DKR's postulate and perhaps some data for $0.25<\Lambda<0.4$ in Table I of BS[24] although the accuracies of experiments are unknown. (e) Applicability of the LZ formula is based on the existence of any mechanism of phase randomization, such as an energetic spread of the initial boundary condition due to nonmonochromaticy of incident light and/or thermal fluctuation in addition to the damping of localized vibration. Recent numerical analysis of transient NRT in a single mode model ($\Gamma_0=0$)[37] is consistent with this statement.

Even for a monochromatic excitation, if temperature is sufficiently high, the LZ formula would be applicable as its effects in optical spectra of molecules were recently investigated by Averbukh *et al.*[38] Therefore, the excitation spectrum of luminescence at high temperatures can be a direct experimental

evidence of the relation of $1-\langle P^c_{gQ}(\infty)\rangle$ vs Λ (Figs. 6 and 7) with the replacement of Λ^{-1} defined in Eq. (6.1) by $\Lambda^{-1}\equiv\Omega_0/g_0\omega_0$ where Ω_0 is the frequency of incident light. We believe that such evidence has already been found by Street *et al.*[39,40] on the problem of nonradiative recombination in amorphous semiconductors.[41,42]

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