

Energy gap law for vibrational relaxation of a molecule in a dense medium

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In this paper we advance a model Hamiltonian for direct vibrational relaxation of a guest molecule in a host lattice. General expressions for the vibrational relaxation rate constant are derived utilizing the generating function method, elucidating the gross features of this class of multiphonon relaxation phenomena. Explicit theoretical results were obtained for the vibrational relaxation rate in two temperature regions: for moderately low temperatures below the characteristic Debye temperature and in the high temperature limit. In the low temperature range the vibrational relaxation rate exhibits a nearly exponential variation with the order of the multiphonon processes, revealing the energy gap law, an appreciable isotope effect, and a strong temperature dependence. The predicted energy gap law is compatible with the available experimental data.

I. INTRODUCTION

Recent experimental observations¹⁻¹⁰ of medium induced vibrational relaxation (VR) of a guest molecule in a solid or liquid¹¹⁻¹⁶ fall into two general categories:

A. Sequential dissipation of vibrational energy into the medium, which proceeds in two steps. First, a high frequency intramolecular vibration is converted via intramolecular and medium induced coupling into lower frequency intramolecular vibrational modes. Second, medium-molecule coupling induces VR of the latter modes resulting in the excitation of the medium phonons. Such processes were recently studied in the ground and electronically excited states of large molecules in solution at room temperature, utilizing the techniques of picosecond spectroscopy,¹⁻⁵ which result in VR decay times τ_{VR} in the range of $\tau_{VR} = 5-20$ psec.

B. Direct vibrational energy dissipation into the medium. The molecule-medium coupling results in a direct VR process, without the participation of other intramolecular modes. Such a physical situation prevails for the VR of a diatomic molecule and for the relaxation of the lowest frequency vibrational excitation of a polyatomic molecules. Such VR processes were observed in the electronically excited $A^3\Sigma_u$ state of N_2 in solid rare gases⁷ ($\tau_{VR} = 10^3 - 10$ msec at low temperatures), in high vibrational levels of the ground $X^1\Sigma_g$ state of N_2 ($\tau_{VR} \sim 1$ sec at 4°K), for VR in the ground electronic state of CO in solid Ar ($\tau_{VR} > 10$ msec at 8°K),^{7,9} and for the

970 cm^{-1} vibration of NH_3 in solid N_2 ($\tau_{VR} = 2 \mu$ sec at 8°K).⁸

Medium induced VR phenomena can be handled in terms of a multiphonon process of a high order, occurring within a single electronic configuration. Such a theory, which rests on a quantum mechanical treatment of a harmonic oscillator subjected to a linear coupling with a phonon bath, was recently developed.^{12,14,17} Equivalent results can be obtained utilizing the first order solution of the Pauli master equation,^{13,18,19} which results in conventional kinetic equations for the diagonal matrix elements of the density matrix. Consider the VR of a single "harmonic" guest molecule embedded in a phonon bath, assuming that the molecule-medium coupling is linear in each of the intramolecular normal modes and disregarding the rare possibility of interference effects, so that the molecular vibrations are not coupled via their interaction with the medium. We can thus consider independently the decay of each harmonic molecular oscillator, characterized by the coordinate Q and by the frequency ω . Specifying the medium modes in terms of the phonon frequencies $\{\omega_\nu\}$, the occupation numbers $\{v_\nu\}$, and the coordinates $\{q_\nu\}$, the molecule-medium coupling is taken in the form

$$H_{mL} = QF(\{q_\nu\}), \quad (I. 1)$$

where $F(q_1, q_2 \dots)$ is a general function of the medium phonon coordinates. The VR rate for the transition between the initial state $|I\rangle = |1, \Pi_\nu v_\nu\rangle$ to the final state $|0, \Pi_\nu v'_\nu\rangle$ is given by^{15,13b,17}

$$\gamma = \frac{\pi}{\hbar B^2} [1 - \exp(-\beta \hbar \omega)] \sum_{\{v_\nu\}} \sum_{\{v'_\nu\}} \prod_\nu \frac{\exp(-\beta v_\nu \hbar \omega_\nu)}{Z_\nu} \left| \left\langle \prod_\nu v_\nu \left| F(\{q_\nu\}) \right| \prod_\nu v'_\nu \right\rangle \right|^2 \delta \left[\sum_\nu (v'_\nu - v_\nu) \hbar \omega_\nu - \hbar \omega \right], \quad (I. 2)$$

where $B^2 = \mu\omega/\hbar$ (with μ the effective mass of the molecular oscillator), $\beta = (k_B T)^{-1}$ and $Z_\nu = [1 - \exp(-\beta\hbar\omega_\nu)]^{-1}$ is the partition function for the ν th mode. The experimentally relevant observable for monitoring the VR involves the time evolution $n(t)$ of the population of the molecular oscillator^{12,20}

$$n(t) = n(0) \exp(-\gamma t) + [1 - \exp(-\gamma t)] \langle n \rangle_T, \quad (\text{I. 3})$$

where $\langle \rangle_T$ denotes thermal averaging.

Equations (I. 1)–(I. 3) constitute a useful theoretical framework for the study of VR processes of class B and for the first step in type A processes. Utilizing a special form for the molecule–medium coupling,^{12,14}

$$H_{mL} = \sum_{\{\nu\}} G_{\{\nu\}} \left(\prod_{\nu} q_{\nu} \right) Q, \quad (\text{I. 4})$$

and adopting the rotating wave and the random phase approximations, we were able¹⁴ to provide explicit expressions for the temperature dependence of γ , without specifying the exact form of the multiphonon coupling term $G_{\{\nu\}}$. In retrospect, our temperature effect for the physically relevant temperature range ($\beta\hbar\omega \ll 1$) just correspond to a multiphonon emission process of the order

$$N = \omega / \langle \omega_{\nu} \rangle, \quad (\text{I. 5})$$

where $\langle \omega_{\nu} \rangle$ is a mean lattice frequency, of the order of the Debye frequency. We have also conjectured¹⁴ that for a multiphonon process of a high order, the major contribution of the coupling Hamiltonian (I. 4) to γ originates from a term of the form $G_{\{\nu\}} = \bar{A} \delta^N$, where \bar{A} and δ are constants for a given guest–host system and $\delta \ll 1$. Such a relation amounts to an energy gap law (EGL) for VR, as it implies that

$$\ln \gamma \propto -\omega / \langle \omega_{\nu} \rangle. \quad (\text{I. 6})$$

It will be useful and important to derive some algorithms for the characterization of VR processes, specifying the general dependence of γ on the molecular frequency, i. e., the EGL, on the phonon spectrum of the bath, and also on the temperature. Such a program requires the specification of the molecule–medium coupling in greater detail than that given by Eq. (I. 4). In this context, Sun and Rice¹¹ have applied the Jackson–Mott²¹ model for vibrational relaxation for VR in solids. This approach rests on a binary collision approximation which is not directly applicable for a dense medium. Recently, Diestler¹⁶ has attempted to handle the VR problem of diatomic molecules in solid rare gases assuming that the origins of the lattice normal modes are displaced between different vibrational states of the host molecule. He then phenomenologically obtains a rate expression for two level VR relaxation which is identical with the well-known result for multiphonon electronic relaxation.^{22–27} The weakness of this approach lies in the initial assumption concerning the parallel displacement of the lattice modes, which cannot be rigorously justified. The temperature dependence obtained by Diestler is of the form $\gamma \propto [\langle n_{\nu} \rangle_T + 1]^N$, which is characteristic of any multiphonon emission process and which does not reflect on the validity of his model.

We would like to advance a new model Hamiltonian for

medium induced VR processes, which will enable us to elucidate the gross features of such processes. The present approach may be also useful for the study of intramolecular energy redistribution^{13,28a,b} and of coupled electronic–vibrational relaxation processes in large molecules. A similar model has recently been invoked by Lin,^{13b} who, however, obtained useful results only for the strong coupling limit.

II. A MODEL HAMILTONIAN FOR VIBRATIONAL RELAXATION

Let us invoke the customary approach for the molecular VR, assuming that the dominating impurity–medium intermolecular interactions which contribute to Eq. (I. 1) involves short range repulsive terms.²¹ We must thus adopt for a moment a molecular physics type of approach, focusing attention on the repulsive interaction between the impurity molecule and its $j = 1, 2, \dots, J$ nearest neighbors. We adopt a grossly simplified picture for the coupling between a diatomic molecule and its nearest neighbor medium atoms. First, we consider a collinear configuration of the molecule and the perturbing atom. This picture was common in model calculations of “linear” collision processes²⁹ and is strictly applicable only for a linear chain. Second, we assume that in the collinear configuration the interaction potential depends on the separation between the perturbing atom and the closer atom in the diatomic.²⁹ Third, we assert that the intramolecular frequency is sufficiently high and that the intramolecular displacement Q are small (relative to the reciprocal characteristic repulsive length), whereupon the coupling can be linearized in the internal coordinate Q . Thus our model Hamiltonian takes the form

$$H_{mL} = Q \sum_{j=1}^J a_j \exp(-\alpha_j X_j), \quad (\text{II. 1})$$

where a_j are constant coefficients and α_j denotes the characteristic inverse length for repulsive interactions,³⁰ while X_j represents the separation of the j th atom from the center of mass of the impurity molecule. Denoting the equilibrium atom–impurity separation by X_j^0 , we have $X_j = X_j^0 + x_j$, where x_j corresponds to the displacement of the j th nearest neighbor from its equilibrium position. Expanding the local coordinates x_j in terms of the (dimensionless) lattice normal modes

$$x_j = \sum_{\nu} q_{\nu} \beta_{\nu j}, \quad (\text{II. 2a})$$

where $\beta_{\nu j}$ are the appropriate expansion coefficients, Eq. (II. 1) takes the form³¹

$$H_{mL} = Q \sum_j a_j \exp(-\alpha_j X_j^0) \exp\left(-\sum_{\nu} q_{\nu} \beta_{\nu j} \alpha_j\right). \quad (\text{II. 2b})$$

Assuming that all the a_j and the α_j terms in Eq. (II. 1) are independent of j and defining the phonon coupling parameters $\Delta_{\nu} = \beta_{\nu j} \alpha_j$, we get a new model Hamiltonian for VR,

$$H_{mL} = CQ \exp\left(-\sum_{\nu} \Delta_{\nu} q_{\nu}\right), \quad (\text{II. 3})$$

where $C \cong Za \exp(-\alpha X_j^0)$, with Z being the number of nearest neighbors.

The following remarks are now in order:

(a) Equation (II. 3) is of the same functional form as Eq. (I. 1), with $F(\{q\}) = C \exp(-\sum_\nu \Delta_\nu q_\nu)$.

(b) A power expansion of the coupling term (II. 3) will result in terms of the form given by Eq. (I. 4). Thus, our new model Hamiltonian provides a generalization of the special product form (I. 4), with the advantage that the coupling terms in (I. 4) are now specified.

(c) The normal modes expansion (II. 2) which led to Eq. (II. 4) has to include all the modes of the lattice containing the impurity. The perturbations exerted by the impurity on the lattice spectrum may result in the appearance of resonances in the energy range of the pure lattice phonon spectrum or of localized modes outside it.³² The density of states of the pure crystal has to be accordingly modified to include delta function contributions for the local modes. For local modes, the expansion coefficients $\beta_{\nu j}$ in Eq. (II. 2) are large, of the order of the lattice constant d , so that³² $\Delta_\nu \approx \alpha d$ for these modes. On the other hand, for the lattice modes³² $\Delta_\nu \approx \alpha(\hbar/m\omega_\nu N_L)^{1/2}$, where N_L is the number of the atoms in the crystal.

Equation (II. 4) together with Eq. (II. 2) can now be utilized to derive explicit expression for the VR rate. The technical details are analogous to the treatment of other multiphonon processes such as optical line shapes in solids³³⁻³⁶ and transition probabilities for electronic relaxation.²²⁻²⁷ It is, however, important to emphasize that (II. 4) differs from the interstate coupling Hamiltonian for electronic relaxation. We shall dwell later on this point.

III. GENERATING FUNCTIONS FOR VIBRATIONAL RELAXATION

Following conventional procedures, we can readily recast Eq. (I. 2) together with Eq. (I. 4) in terms of a Fourier transform of a generating function,

$$\gamma = D \int_{-\infty}^{\infty} dt \exp(-i\omega t) \prod_\nu f_\nu(t), \quad (\text{III. 1a})$$

$$D = (2\hbar^2 B^2)^{-1} [1 - \exp(-\beta\hbar\omega)] C^2, \quad (\text{III. 1b})$$

while the generating function for a single lattice mode is

$$f_\nu(t) = \sum_{v_\nu} \sum_{v'_\nu} (Z_\nu)^{-1} \exp(-\beta\hbar v_\nu \omega_\nu) \times \langle v_\nu | \exp(-\Delta_\nu q_\nu) | v'_\nu \rangle^2 \exp[it(v'_\nu - v_\nu)\omega_\nu t]. \quad (\text{III. 2})$$

Equation (III. 2) can be expressed in a more compact form,

$$f_\nu(t) = \langle \langle v_\nu | \exp(-\Delta_\nu q_\nu) \exp(iH_0 t) \times \exp(-\Delta_\nu q_\nu) \exp(-iH_0 t) | v_\nu \rangle \rangle_T, \quad (\text{III. 3})$$

where H_0 is the zero order Hamiltonian for the phonon bath, while $\langle \rangle_T$ again denotes thermal averaging. Utilizing standard operator techniques, Eq. (III. 3) takes the form

$$f_\nu(t) = \exp[\frac{1}{2} \Delta_\nu^2 (2\langle v_\nu \rangle_T + 1)] \exp[g_\nu^+(t) + g_\nu^-(t)], \quad (\text{III. 4})$$

where

$$g_\nu^+(t) = \langle \langle v_\nu \rangle_T + 1 \rangle (\Delta_\nu^2/2) \exp(i\omega_\nu t), \quad (\text{III. 5})$$

$$g_\nu^-(t) = \langle v_\nu \rangle_T (\Delta_\nu^2/2) \exp(-i\omega_\nu t). \quad (\text{III. 6})$$

$\langle v_\nu \rangle_T$ denotes the mean thermal population of the ν th mode

$$\langle v_\nu \rangle_T = [\exp(\beta\hbar\omega_\nu) - 1]^{-1}, \quad (\text{III. 7})$$

while Δ_ν is the effective coupling term for the ν th mode defined by Eqs. (II. 2b) and (II. 3).

The single mode generating function, Eq. (III. 4), which determines the VR rate, exhibits the same t dependence as the generating functions for electronic relaxation between two vertically displaced potential surfaces. It is important to notice that while in the latter case the Debye-Waller factor involves an exponential of a negative number, in our case the argument of the exponential is positive, which will contribute to a positive temperature dependence of γ at high temperatures. This difference originates from different forms of the single mode generating functions, which for vibrational relaxation [see Eq. (III. 3)] are

$$f_\nu(t) = \langle \langle v_\nu | \exp(-\delta_\nu q_\nu) \exp[-\delta_\nu q_\nu(t)] | v_\nu \rangle \rangle_T,$$

while for electronic relaxation the accepting mode generating functions take the form

$$f_\nu^{(ER)}(t) = \langle \langle v_\nu | \exp(i\bar{\delta}_\nu P_\nu) \exp[-i\bar{\delta}_\nu P_\nu(t)] | v_\nu \rangle \rangle_T,$$

where q_ν and P_ν correspond to the coordinates and to the conjugated momenta, while $q_\nu(t)$ and $P_\nu(t)$ denote these operators in the Heisenberg representation. Thus the coupling operator for electronic relaxation involves a Franck-Condon type coordinate displacement operator, while for the case of VR the coupling operator generates a shift in the momentum space. We thus conclude that the coupling responsible for VR cannot be represented in terms of a Franck-Condon coordinate displacement operator.

Equations (III. 1) and (III. 4) provide us with explicit expressions for the VR rate,

$$\gamma = D \exp(+G) \int \exp(-i\omega t) \exp[G_+(t) + G_-(t)] dt, \quad (\text{III. 8a})$$

$$G_+(t) = \sum_\nu \langle \langle v_\nu \rangle_T + 1 \rangle (\Delta_\nu^2/2) \exp(i\omega_\nu t), \quad (\text{III. 8b})$$

$$G_-(t) = \sum_\nu \langle v_\nu \rangle_T (\Delta_\nu^2/2) \exp(-i\omega_\nu t), \quad (\text{III. 8c})$$

$$G = G_+(0) + G_-(0) = \sum_\nu (2\langle v_\nu \rangle_T + 1) (\Delta_\nu^2/2). \quad (\text{III. 8d})$$

G , Eq. (III. 8d), can be considered as the phonon coupling strength for the VR process. The coupling coefficients can be expressed in terms of integrals over the density of phonon states $\rho(\omega_\nu)$ of the lattice perturbed by the impurity molecule; including, in principle, resonance and local impurity modes. Thus, we have

$$G_+(t) = \int d\omega_\nu \rho(\omega_\nu) (\Delta_\nu^2/2) \frac{\exp(\beta\hbar\omega_\nu)}{\exp(\beta\hbar\omega_\nu) - 1} \exp(i\omega_\nu t),$$

$$G_-(t) = \int d\omega_\nu \rho(\omega_\nu) (\Delta_\nu^2/2) [\exp(\beta\hbar\omega_\nu) - 1]^{-1} \exp(-i\omega_\nu t), \quad (\text{III. 9})$$

$$G = \int d\omega_\nu \rho(\omega_\nu) (\Delta_\nu^2/2) \coth(\beta\hbar\omega_\nu/2).$$

Equations (III. 8) and (III. 9) provide us with the final formal result for the VR rate. At first sight it may appear that we have transferred our ignorance concerning the nature of the molecule-medium coupling to the specification of the coupling terms, Δ_ν , which cannot be evaluated at present. However, our final result, Eq. (III. 8), will enable us to derive general relations and correlations for the VR problem.

Some general results for the VR rate can be obtained without referring to any further specific approximations. This may be accomplished following a procedure advanced by Lin and Bersohn²² and by Toyozawa³⁶ for the case of electronic relaxation, which rests on a power expansion of the integrand in Eq. (III. 8). Defining

$$\bar{\alpha}(t) = G^{-1} [G_+(t) + G_-(t)], \quad (\text{III. 10})$$

one can expand the exponential in the integral as a uniformly converging power series in G , and Eq. (III. 8) takes the form

$$\gamma = D \exp(G) \sum_{r=0}^{\infty} \frac{G^r}{r!} S_r, \quad (\text{III. 11})$$

$$S_r = \int_{-\infty}^{\infty} dt \exp(-i\omega t) [\bar{\alpha}(t)]^r. \quad (\text{III. 12})$$

The r th term in Eq. (III. 11) corresponds to a multiphonon process of the order r , which in turn is characterized by a (temperature dependent) Franck-Condon factor G and a weight S_r . For the limiting case of $T=0$, Eq. (III. 11) takes the transparent form

$$\gamma = 2\pi D \exp \left[\sum_{\nu} (\Delta_\nu^2/2) \right] \times \sum_{\nu_1} \sum_{\nu_2} \cdots \prod_{\mu} [(\frac{1}{2}\Delta_\mu^2)^{\nu_\mu} / (\nu_\mu)!] \delta \left(\sum_{\mu} \nu_\mu \omega_\mu - \omega \right) \quad (\text{III. 13})$$

reducing to products of (unnormalized) single mode Franck-Condon factors. Expansion in the $T > 0$ case is also possible.^{13b}

We now turn to the approximate evaluation of the integral (III. 8) which can be handled by the saddle point method.^{23-26,33} In the study of molecular electronic relaxation, Englman and Jortner²³ have distinguished between two limiting situations, the weak coupling limit $G \ll 1$ and the strong coupling situation $G \gg 1$. The same limiting cases are obviously applicable to the VR problem. The weak coupling limit was handled by saddle point integration, while the strong coupling limit was treated by a power expansion of the functions $G_+(t)$ and $G_-(t)$ in a power series of t , which to low order results in a Gaussian type generalized line shape for electronic relaxation. It should be pointed out that the latter procedure is fraught with some mathematical difficulties, as no quantitative criteria were established for the validity of the truncated series expansion in the strong coupling limit. In fact, the saddle point method is valid both for the weak and for the strong coupling situation.

The Gaussian line shape always provides a good approximation for the high temperature case, while in the low temperature limit it is obtained when the order of the multiphonon process is low compared to the coupling $\sum_{\nu} (\Delta_\nu^2/2)$. These results will be systematically derived in Sec. V.

Saddle point integration of Eq. (III. 8) results in³⁷

$$\gamma = D \exp(G) (2\pi)^{1/2} [-F''(t_s)]^{-1/2} \exp[F(t_s)], \quad (\text{III. 14})$$

where

$$F(t) = -i\omega t + [G_+(t) + G_-(t)] = -i\omega t + \int d\omega_\nu \rho(\omega_\nu) (\Delta_\nu^2/2) \times \{ [\langle \nu_\nu \rangle_T + 1] \exp(i\omega_\nu t) + \langle \nu_\nu \rangle_T \exp(-i\omega_\nu t) \} - i\omega t + \int d\omega_\nu \rho(\omega_\nu) (\Delta_\nu^2/2) \frac{\cos[(t - \frac{1}{2}i\beta\hbar)\omega_\nu]}{\sinh(\beta\hbar\omega_\nu/2)} \quad (\text{III. 15})$$

and the saddle point is given by the relation

$$F'(t_s) = 0. \quad (\text{III. 16})$$

The validity condition for the saddle point approximation is

$$\rho \equiv |F'''(t_s)| |F''(t_s)|^{-3/2} \ll 1. \quad (\text{III. 17})$$

The solution of Eqs. (III. 14)–(III. 17) will now be presented for two cases of physical interest. First, we shall consider the VR of a diatomic in a monoatomic solid at moderately low temperatures. Second, we shall consider the high temperature limit for VR.

IV. ENERGY GAP LAW FOR VIBRATIONAL RELAXATION

We shall now proceed to derive some approximate relations for the VR of a guest molecule in a monoatomic host lattice, where the molecular frequency ω considerably exceeds the lattice Debye frequency, so that the multiphonon process is of high order, i. e., $N \gg 1$. We shall at present limit ourselves to moderately low temperatures, i. e., $k_B T \lesssim \hbar\omega_D$. In this temperature range, an exact solution for Eq. (III. 16) cannot be obtained, and we have to rely on approximate methods, which were extensively discussed in the literature. The simplest approximation, which is quite safely applicable to the acoustic phonon spectrum of a monoatomic lattice, neglects phonon dispersion in Eq. (III. 15), replacing the phonon frequencies by an average value $\langle \omega_\nu \rangle$. This "Einstein type" approximation amounts to handling the integral in Eq. (III. 15) by the mean value theorem, setting

$$\int d\omega_\nu \rho(\omega_\nu) (\Delta_\nu^2/2) \frac{\cos[(t - i\beta\hbar/2)\omega_\nu]}{\sinh(\beta\hbar\omega_\nu/2)} = L_{(\nu)} \frac{\cos[(t - i\beta\hbar/2)\langle \omega_\nu \rangle]}{\sinh(\beta\hbar\langle \omega_\nu \rangle/2)}, \quad (\text{IV. 1a})$$

where

$$L_{(\nu)} = \int d\omega_\nu \rho(\omega_\nu) (\Delta_\nu^2/2) \quad (\text{IV. 1b})$$

is an average coupling strength, and the average frequency $\langle \omega_\nu \rangle$ is assumed to exhibit a weak temperature dependence. Equations (III. 14)–(III. 16) together with

Eq. (IV. 1) result in

$$\gamma = D \{ 2\pi\varphi / [\omega \langle \omega_\nu \rangle (1 + \varphi^2)^{1/2}] \}^{1/2} \exp(G) \\ \times \exp \left\{ -N \left[\ln(\varphi + \sqrt{1 + \varphi^2}) - (1 + \varphi^2)^{1/2} / \varphi - \frac{1}{2} \beta \hbar \langle \omega_\nu \rangle \right] \right\}, \quad (\text{IV. 2})$$

where

$$\varphi = N \sinh(\beta \hbar \langle \omega_\nu \rangle / 2) / L_{(\nu)}, \quad (\text{IV. 3})$$

and N , Eq. (I. 5), corresponds to the order of the multiphonon process. An expression analogous to Eq. (IV. 3), with the factor $\exp(-G)$ replacing $\exp(+G)$ in the latter equation, was derived by Diestler for the case of electronic relaxation. A considerable simplification of Eq. (IV. 3) is attained in the temperature range where

$$\varphi \gg 1. \quad (\text{IV. 4})$$

In the temperature range $k_B T \lesssim \hbar \langle \omega_\nu \rangle$ which is of interest for the present discussion,

$$\varphi \cong \frac{N}{2L_{(\nu)}} \exp\left(\frac{1}{2} \beta \hbar \langle \omega_\nu \rangle\right), \quad (\text{IV. 5})$$

and as $N \approx 10-40$ and $L_{(\nu)} \approx 1-10$, condition (IV. 4) definitely holds. We note in passing that in the high temperature range where $k_B T > \hbar \langle \omega_\nu \rangle$, we have $\varphi = \beta \hbar \omega / 2L_{(\nu)}$, and even then condition (IV. 4) may often be applicable. Making use of relation (IV. 4), Eq. (V. 2) reduces to the simple form

$$\gamma = D(2\pi / [\omega \langle \omega_\nu \rangle])^{1/2} \exp[L_{(\nu)}(2 \langle v_{(\nu)} \rangle_T + 1)] \\ \times \exp \left\{ -N \left[\ln \frac{N}{L_{(\nu)} \langle v_{(\nu)} \rangle_T + 1} - 1 \right] \right\}, \quad (\text{IV. 6})$$

where $\langle v_{(\nu)} \rangle_T = [\exp(\beta \hbar \langle \omega_\nu \rangle) - 1]^{-1}$ is the thermally averaged population of the frequency averaged mode. The analogous equation to (IV. 6) for electronic relaxation was derived by Englman and Jortner.²³ To conclude these simple mathematical manipulations we consider the validity condition, Eq. (III. 7), for the applicability of the saddle point integration method. The parameter ρ , defined by Eq. (III. 17), is

$$\rho = N^{-1/2} (1 + \varphi^{-2})^{-3/4}. \quad (\text{IV. 7})$$

Thus, for high order multiphonon processes, which are of interest to us, $\rho \ll 1$ and the saddle point integration method can be safely applied.

It would be useful to summarize the assumptions and approximations involved in the derivation of Eq. (IV. 6). First, Eq. (III. 8) is valid under the conventional conditions of weak coupling, rotating wave, and random phase approximations. Second, the mean frequency approximation for the medium phonon spectrum is introduced. Third, the validity of the saddle point approximation implies that $\rho \ll 1$. Fourth, for the sake of convenience we require that $\varphi \gg 1$, considering the moderately low temperature range $\hbar \langle \omega_\nu \rangle \gtrsim k_B T$. Under these conditions, the VR rate, Eq. (IV. 6), is valid and can be recast in the final compact form

$$\gamma = \gamma(0)F(T), \quad (\text{IV. 8a})$$

where $\gamma(0)$ corresponds to the relaxation rate at $T = 0$

$$\gamma(0) = A \exp(-fN), \quad (\text{IV. 8b})$$

where the preexponential factor is

$$A = (2\pi \hbar^2 B^2)^{-1} C^2 [2\pi / (\omega \langle \omega_\nu \rangle)]^{1/2} \exp(L_{(\nu)}) \quad (\text{IV. 8c})$$

and the coefficient in the exponent is given by

$$f = \ln(N/L_{(\nu)}) - 1. \quad (\text{IV. 8d})$$

The temperature coefficient of the VR rate is

$$F(T) = [1 - \exp(-\beta \hbar \omega)] [1 + \langle v_{(\nu)} \rangle_T]^N \\ \times \exp[2L_{(\nu)} \langle v_{(\nu)} \rangle_T]. \quad (\text{IV. 8e})$$

These results provide us with the following gross features of VR of a diatomic molecule in a monoatomic host lattice in the moderately low temperature range:

a. The energy gap law. The VR rate exhibits an exponential, or rather super exponential, dependence on the order $N = \omega / \langle \omega_\nu \rangle$ of the multiphonon process. In view of the weak logarithmic dependence of f on N , we expect that for a class of molecules in a given solid [or even in several monoatomic solids characterized by close values of $\langle \omega_\nu \rangle$], a relation of the general form (I. 6) is obeyed, which constitutes the EGL for VR.

We note in passing that the zero temperature VR rate constant, Eq. (III. 8b), can be derived from the exact relation Eq. (III. 13), which together with the average frequency approximation results in

$$\gamma(0) \propto \exp(L_{(\nu)}) [L_{(\nu)}]^N / \Gamma(N+1), \quad (\text{IV. 9})$$

where Γ is the Γ function and $\Gamma(N+1) = N!$ for an integer N . Applications of the Stirling approximation to Eq. (IV. 9) will result in Eq. (IV. 8b) for $\gamma(0)$. Equation (IV. 9) provides an alternative expression for the EGL.

b. Temperature effects. The temperature dependence Eq. (IV. 8e) for the VR rate contains three factors. The first term originates from the Bose-Einstein statistics of the multilevel harmonic oscillator and, as in most cases of interest $\beta \hbar \omega \gg 1$, this contribution can be disregarded. The second contribution $[1 + \langle v_{(\nu)} \rangle_T]^N$ accounts for the spontaneous and stimulated phonon emission process of order N . The temperature dependence of the VR rate utilizing the model Hamiltonian (I. 4) just includes the product of these two terms. The model Hamiltonian, Eq. (II. 3), results in an additional contribution to the temperature dependence of the form $\exp[2L_{(\nu)} \langle v_{(\nu)} \rangle_T]$. This positive exponential Debye-Waller type factor results in an enhancement of the VR rate at higher temperature, in contrast to the conventional negative exponential Debye-Waller factor which contributes to the reduction of the electronic relaxation rate. The temperature dependence predicted herein differs dramatically from that expected for electronic relaxation processes. At sufficiently low temperatures, when $\langle v_{(\nu)} \rangle_T \ll 1$, the temperature coefficient takes the simple form

$$F(T) = 1 + (N + 2L_{(\nu)}) \exp(-\beta \hbar \langle \omega_\nu \rangle), \quad (\text{IV. 10})$$

whereupon both the model Hamiltonians (I. 4) and (II. 3) exhibit the same functional temperature dependence in that region.

c. Isotope effects. The energy gap law implies the existence of a large intramolecular isotope effect on the VR rate. The occurrence of an appreciable isotope ef-

fect was noted by Diestler.¹⁶ When two diatomic molecules which differ in their isotopic composition are studied in the same host matrix, we can safely assume that the repulsive molecule-medium coupling is invariant. Denoting the relaxation rates by $\gamma_1(T)$ for the molecule characterized by frequency ω_1 and by an exponential coefficient [Eq. (IV. 8d)] f_1 and $\gamma_2(T)$ for the molecule specified by the frequency ω_2 and by the exponential coefficient f_2 , the isotope effect at $T=0$ is

$$\frac{\gamma_1(0)}{\gamma_2(0)} = \left(\frac{\omega_2}{\omega_1}\right)^{3/2} \exp\left[\frac{f_2\omega_2 - f_1\omega_1}{\langle\omega_\nu\rangle}\right]. \quad (\text{IV. 11a})$$

Taking a mean value \bar{f} for the f_1 and f_2 parameters, a procedure which is valid for all cases excluding that of the (large) deuterium isotope effect, we have

$$\frac{\gamma_1(0)}{\gamma_2(0)} \approx \exp\left[\bar{f}N\left(\frac{\omega_2 - \omega_1}{\omega_1}\right)\right]. \quad (\text{IV. 11b})$$

For the reasonable value $(\omega_2 - \omega_1)/\omega_1 \approx 1/N$, the isotope effect is $\exp(\bar{f})$ and can assume a value in the range $2-10^2$. At finite temperatures, the isotope effect is

$$\frac{\gamma_1(T)}{\gamma_2(T)} = \exp\left[\frac{f_2\omega_2 - f_1\omega_1}{\langle\omega_\nu\rangle}\right] (1 + \langle v_{\nu} \rangle_T)^{(\omega_1 - \omega_2)/\omega_1} \quad (\text{IV. 11c})$$

decreasing somewhat at higher temperatures.

d. Relaxation of individual vibrational levels. The cooling process of a harmonic oscillator initially excited to the state $n(t=0) = v$ at $T=0$ is determined by a Bernoulli type distribution. The decay rate of the initially excited v state in the temperature range $\beta\hbar\omega \ll 1$ is given by

$$k_v(T) = v\gamma(T). \quad (\text{IV. 12})$$

e. Relaxation of an anharmonic oscillator. The energy gap law can be utilized to provide semiquantitative expressions for the VR of an anharmonic diatomic molecule in the low temperature range. Nitzan and Silbey¹⁵ have shown that the relaxation rate of an harmonic oscillator and a two-level system, both induced by the same coupling Hamiltonian, converge to the same value in the low temperature limit when $\beta\hbar\omega \ll 1$. Thus, in the temperature range $\beta\hbar\omega \ll 1$ which is relevant for us, we can handle the relaxation in the multilevel system of the anharmonic oscillator as a sequence of two-level relaxation processes. Adopting again the model Hamiltonian Eq. (II. 3), the VR rate constant for the $v \rightarrow v-1$ transition of the anharmonic oscillator can be expressed in terms of the modified energy gap

$$N_v = N + \frac{2v x_e \omega}{\langle\omega_\nu\rangle}, \quad (\text{IV. 13})$$

where $x_e \omega$ is the anharmonicity constant. Multiphonon relaxation theory now results in the following modified approximate expression:

$$k_v(T) = Av \exp(-f_v N_v) (1 + \langle v_{\nu} \rangle_T)^{N_v} \exp(2L_{\langle\nu\rangle} \langle v_{\nu} \rangle_T), \quad (\text{IV. 14})$$

where f_v is given by Eq. (IV. 8d) with N_v replacing N , while the constant A is still reasonably well approximated by the harmonic oscillator expression Eq. (IV. 8c).

The energy gap law, the temperature dependence and the isotope effects for VR processes, provide a specific example of the general characteristics of multiphonon relaxation phenomena. What is new in the present approach is the utilization of an explicit model Hamiltonian, which enabled us to elucidate the detailed features of VR process.

The general relations and correlations for VR processes have to be supplemented by numerical estimates of the VR rate. However, at present, the latter are very difficult to obtain in a reliable manner. Let us first attempt to estimate the coupling energy parameter C in Eq. (II. 3), which is given by $C = ZR_0 a$, where $R_0 a$ corresponds to the repulsive interaction at the nuclear equilibrium configuration. Thus Eq. (IV. 8c) is

$$A = Z^2 R_0^2 a^2 [\sqrt{2\pi} \hbar^2 B^2 (\omega \langle\omega_\nu\rangle)^{1/2}]^{-1}. \quad (\text{IV. 15})$$

The rms zero energy displacement B^{-1} is of the order of $0.01X_0$. Taking typical values $R_0 a \approx (4/X_0) \times 10^{-1}$ eV/cm, which corresponds to the repulsion of two Ar atoms, $Z=6$, $\hbar\omega=0.2$ eV, and $N=40$, we estimate $A = 2 \times 10^{12}$ sec⁻¹, and the zero temperature VR rate is $\gamma(0) \approx 10^{12} \times \exp(-fN)$ sec⁻¹. The phonon coupling function $L_{\langle\nu\rangle}$ can presumably assume values in the range $L_{\langle\nu\rangle} = 1-10$ so that the exponential factor, Eq. (IV. 8c), takes values in the range $f = 0.5-3$.

The sparse experimental data available at present^{6-10,38} on the features of type B VR processes of diatomic molecules in inert solid matrices are compatible with our rough numerical estimates. The VR rates of CO in solid Ar,^{7,10,38} $\gamma(0) < 10^{-2}$ sec⁻¹, and of N₂ in solid N₂,¹⁰ $\gamma(0) \sim 1$ sec⁻¹, together with the reasonable values $\langle\omega_\nu\rangle = 50$ cm⁻¹ and $N \approx 40$ for both cases, imply that $f \approx 0.7$ for these systems. Invoking the dangerous assumption that the preexponential factor is a slowly varying function, we estimate $\gamma(0) = 10^6$ sec⁻¹ for the VR of the 970 cm⁻¹ vibration of NH₃ in solid N₂, which is in fortuitous good agreement with the experimental value $\gamma(0) = 2 \times 10^6$ sec⁻¹ for this system.

V. HIGH TEMPERATURES LIMIT AND STRONG COUPLING

An obvious disadvantage of the treatment presented in Sec. IV involves the mean frequency approximation for the phonon spectrum of the host lattice. In view of our ignorance of the energy dependence of the individual mode coupling terms, Eq. (III. 7), we were forced to introduce that "coarse graining" procedure in the moderately low temperature range $\beta\hbar\langle\omega_\nu\rangle \ll 1$, where the (thermal) phonon occupation numbers are small, i. e., $\langle v_\nu \rangle_T \ll 1$ for all ν . In the temperature range above the characteristic phonon frequency, we may adopt an alternative approach which is applicable in the high temperature limit without involving the mean frequency approximation.

In the limit $G \gg 1$, where G is given by Eq. (III. 8d), we encounter the strong coupling situation,²³ which can be realized under two conditions³⁴:

(1) large phonon coupling strength at low temperatures, i. e.,

$$L_{\nu} = \int d\omega_{\nu} \rho(\omega_{\nu}) (\Delta_{\nu}^2/2) \gg 1, \quad (\text{V. 1})$$

(2) the high temperature limit, i. e.,

$$\langle v_{\nu} \rangle_T \gg 1 \quad (\text{V. 2})$$

for all ν .

Provided that condition (V. 2) is satisfied, we can seek a good approximation for the solution of the saddle point equation (III. 16), by a power series expansion of the exponentials $\exp(\pm i\omega_{\nu}t)$ in Eq. (III. 15),

$$F'(t) = -i\omega + i\{L\omega_{\nu}\} \\ - \{L\omega_{\nu}^2 \coth(\frac{1}{2}\beta\hbar\omega_{\nu})\} t + \frac{1}{2}i\{L\omega_{\nu}^3\} t^2 - \dots, \quad (\text{V. 3})$$

where we have defined

$$\{L f(\omega_{\nu})\} = \int d\omega_{\nu} \rho(\omega_{\nu}) (\Delta_{\nu}^2/2) f(\omega_{\nu}) \quad (\text{V. 4})$$

for any function of the phonon frequencies. In the high temperature limit, when Eq. (V. 2) is satisfied, we may neglect terms of the order $O(t^2)$ in Eq. (V. 3) and obtain the simple result

$$t_s = i(\omega - \{L\omega_{\nu}\}) / \{L\omega_{\nu}^2 \coth(\frac{1}{2}\beta\hbar\omega_{\nu})\} \quad (\text{V. 5})$$

for the saddle point. Equation (V. 5) together with a power expansion of Eq. (III. 14) up to $O(t^2)$ immediately result in the Gaussian line shape function for the relaxation rate

$$\gamma(T) = \tilde{B} \exp \left[- \frac{(\omega - \{L\omega_{\nu}\})^2}{2\{L\omega_{\nu}^2 \coth(\frac{1}{2}\beta\hbar\omega_{\nu})\}} \right] \exp(2G), \\ \tilde{B} = D \left[\frac{4\pi}{2\{L\omega_{\nu}^2 \coth(\frac{1}{2}\beta\hbar\omega_{\nu})\}} \right]^{1/2}. \quad (\text{V. 6})$$

Equation (V. 6) is expected to hold provided that

$$\left| \frac{(\omega - \{L\omega_{\nu}\})\{L\omega_{\nu}^3\}}{\{L\omega_{\nu}^2 \coth(\frac{1}{2}\beta\hbar\omega_{\nu})\}^2} \right| \ll 1. \quad (\text{V. 7a})$$

Adopting for the moment the mean frequency approximation, Eq. (V. 7) reduces to

$$\left| \frac{N}{L_{\nu}} - 1 \right| \ll \coth^2(\frac{1}{2}\beta\hbar\langle\omega_{\nu}\rangle). \quad (\text{V. 7b})$$

Equation (V. 7b) provides us with the general validity condition for the applicability of the "strong coupling" situation. We note that this limit prevails provided that either $L_{\nu} \sim N \gg 1$ or, alternatively, in the high temperature case when $\beta\hbar\langle\omega_{\nu}\rangle \gg 1$. The high temperature case is pertinent for the present discussion, and Eq. (V. 6) then takes the form

$$\gamma(T) = \tilde{B} \exp(uT) \exp(-E_A/k_B T), \\ u = 4\{L(\hbar\omega_{\nu})^{-1}\} k_B, \\ E_A = \frac{\hbar(\omega - \{L\omega_{\nu}\})^2}{4\{L\omega_{\nu}\}}. \quad (\text{V. 8})$$

We thus obtain an activated rate constant modified by a temperature dependent factor $\exp(uT)$. For $L_{\nu} \gg 1$, the contribution of the latter term may be appreciable. At present, no experimental data are available for VR processes of class B in the high temperature limit.

Such results may be obtained from the studies of VR of impurity molecules in ionic and covalent crystals.

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³⁸The preliminary observations of Legay *et al.* on the time resolved infrared emission of CO in solid Ar (Refs. 8 and 9) seemed to indicate a vibrational relaxation time of 13.6 msec at 0°K increasing by a factor of ~3 in the temperature range 8°--20°K. These unpublished results were quoted in Refs. 14 and 16. Further experimental work⁹ on the CO/Ar system revealed the effects of temperature dependent vibrational ener-

gy transfer between different isotopic species. These experiments now provide a lower limit for the VR time $t_{VR} > 10$ msec for CO in solid Ar at low temperatures. t_{VR} in this system is too long relative to the spontaneous infrared radiative decay time to yield the temperature dependence of the VR rate. It should be noted that this new experimental development does not reflect on the validity of the theoretical analysis of Ref. 14, which is correct.