Some features of vibrational relaxation of a diatomic molecule in a dense medium

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In this paper, we consider some experimental implications of a theory [Mol. Phys. **25**, 713 (1973)] of vibrational relaxation of a guest molecule in a host matrix induced by multiphonon processes. We have explored the dependence of the vibrational relaxation rate on the guest molecular frequency, on the temperature, on the gross features of the spectrum of a monatomic and a polyatomic host matrix, and on the presence of molecular impurities. The recent experimental results of Legay, Abouaf-Marguin, and Dubost on the vibrational relaxation of CO in solid rare gases and of the 970 cm^{-1} vibration of NH_3 in solid nitrogen are adequately interpreted in terms of the present theory.

I. INTRODUCTION

We have recently advanced[1] a theoretical model for the vibrational relaxation of a guest molecule in a dense medium, which rests on the following assumptions[1]:

(a) The guest molecule is located in an isolated trapping site.

(b) The nuclear motion of the guest molecule is harmonic.

(c) The medium is represented in terms of a phonon bath.

(d) The intramolecular vibrations are not coupled to each other via their interaction with the phonon bath, whereupon each molecular oscillator decays into its "own" phonon bath.

(e) The molecule–medium interaction is linear in the intramolecular displacements.

(f) The molecule–medium interaction is represented in terms of the rotating-wave approximation,[2] neglecting off-resonance contributions to the coupling.

(g) The medium retains its thermal equilibrium throughout the relaxation process.

(h) The equations of motion were linearized within the framework of the random phase approximation.[3]

Assumptions (a)–(c) are standard.[1] Assumptions (d) and (e) may be dangerous when applied to a polyatomic molecule. However, they are definitely applicable for two cases of physical interest: (1) relaxation of a diatomic molecule and (2) relaxation of the lowest frequency vibrational excitation of a polyatomic molecule. These two cases will be explicitly considered in the present paper. Assumptions (g) and (h) assert that dissipative processes in the medium, originating for example from anharmonic interactions, are fast on the relevant time scale of vibrational relaxation. Finally, assumptions (f) and (h), introduced for the sake of mathematical convenience, are common in a variety of applications of many-body theory.[2,3]

The Hamiltonian for the system can now be represented in the general form[1]

$$H=\hbar\omega a^{+}a+\sum_{\nu}\hbar\omega_{\nu}b_{\nu}^{+}b_{\nu}+\sum_{\nu}(G_{\nu}B_{\nu}a^{+}+G_{\nu}^{*}B_{\nu}^{+}a)\,, \tag{1}$$

where the molecular oscillator is characterized in terms of the frequency ω, the creation operator a^{+}, and the annihilation operator a. The medium is specified in terms of the phonon frequencies $\{\omega_{\nu}\}$ with the corresponding creation and annihilation operators $\{b_{\nu}^{+}\}$ and $\{b_{\nu}\}$, respectively, and the products $B_{\nu}=\prod_{\nu}b_{\nu}$ and $B_{\nu}^{+}=\prod_{\nu}b_{\nu}^{+}$. The molecule–medium coupling terms are denoted by G_{ν}. It is important to notice that Eq. (1) is general, being applicable to both single phonon and multiphonon decay. The medium phonons correspond either to low frequency optical and acoustic phonons in the case of a monoatomic solid, or to a superposition of low frequency phonons and high frequency intramolecular "vibrons"[1] in a solid consisting of polyatomic molecules.

The equations of motion for the molecule and for the medium operators in the Heisenberg picture are

$$\begin{aligned}\dot{a}&=-i\omega a-i\sum_{\nu}G_{\nu}B_{\nu}\,,\\ \dot{B}_{\nu}&=-i\omega_{\nu}B_{\nu}-in_{\nu}G_{\nu}^{*}a\,.\end{aligned} \tag{2}$$

The phonon states are denoted by $\nu=\{1, 2, \cdots, N\}$ and the frequency sum is

$$\omega_{\nu}=\sum_{\nu}\omega_{\nu}\,. \tag{3}$$

The thermally averaged commutator

$$n_{\nu}=\langle[B_{\nu}, B_{\nu}^{+}]\rangle_{T} \tag{4}$$

is expressed in terms of the thermally averaged Boson occupation numbers of the individual phonon (and vibron) modes

$$\langle n_{\nu}\rangle_{T}=[\exp(\beta\hbar\omega_{\nu})-1]^{-1}\,, \tag{5}$$

where $\beta=(kT)^{-1}$ and $\langle\ \rangle_{T}$ denotes thermal averaging.

The time dependence of a is given by

$$a(t) = u(t)a + \sum_{\nu} v_{\nu}(t) B_{\nu} \tag{6}$$

with the coefficients

$$u(t) = \exp[-i(\omega + \delta\omega)t - \gamma t] , \tag{7}$$

$$v_{\nu}(t) = \frac{-iG_{\nu}}{i(\omega + \delta\omega - \omega_{\nu}) - \gamma} \times [\exp(-i\omega_{\nu}t) - \exp[-i(\omega + \delta\omega)t - \gamma t]] . \tag{8}$$

In Eqs. (7) and (8), we have defined the level shift

$$\delta\omega = PP\sum_{\nu} \frac{|G_{\nu}|^2 n_{\nu}}{\omega - \omega_{\nu}} \tag{9}$$

and the vibrational relaxation width

$$\gamma = \pi \sum_{\nu} |G_{\nu}|^2 n_{\nu} \delta(\omega - \omega_{\nu}) . \tag{10}$$

It will be useful to express this result incorporating explicitly the energy conservation implied by the delta function in (10), so that

$$\gamma = \pi \sum_{\{\nu\}} |G_{\{\nu\}}|^2 n_{\{\nu\}} \rho_{\{\nu\}} , \tag{11}$$

where $\rho_{\{\nu\}}$ is the compound many-phonon density of states

$$\rho_{\{\nu\}} = \int d\epsilon_1 \int d\epsilon_2 \ldots \int d\epsilon_{N-1} \rho_1(\omega - \epsilon_1)\rho_2(\epsilon_1 - \epsilon_2) \cdots \rho_N(\epsilon_{N-1}) , \tag{12}$$

which is expressed in terms of a convolution of single phonon densities of states $\{\rho_{\nu}(\epsilon)\}$. The phonon states $\{\nu\}$ in Eqs. (11) and (12) are given by these collections of phonon states, which obey the energy conservation law

$$\omega_{\{\nu\}} \equiv \sum_{\nu} \omega_{\nu} = \omega . \tag{13}$$

In a monatomic solid, $\{\nu\} = \{\mu\}$ where μ specifies the low frequency phonons, so that for this case

$$\omega = \sum_{\mu} \omega_{\mu} , \tag{13'}$$

while for a polyatomic solid we segregate the medium frequencies into low frequency $\{\mu\}$ modes and high frequency $\{\eta\}$ vibron modes, whereupon

$$\omega = \sum_{\mu} \omega_{\mu} + \sum_{\eta} \omega_{\eta} . \tag{13''}$$

The experimentally relevant observable for monitoring the nonradiative decay rate of a vibrationally excited state involves the time evolution $n(t)$ of the population of the molecular oscillator, which is given by[1]

$$n(t) = \exp(-2\gamma t)n(0) + [1 - \exp(-2\gamma t)]\langle n \rangle_T , \tag{14}$$

where $n(0)$ is a pure n state of the oscillator while the medium is in thermal equilibrium. In real life, such an experiment can be performed by optical ir excitation of a molecule embedded in a dense medium. The vibrationally excited level will decay by parallel infrared emission (characterized by the lifetime γ_{ir}^{-1}) and vibrational relaxation; the decay rate, $\tilde{\gamma}$, is given by

$$\tilde{\gamma} = \gamma_{ir} + \gamma . \tag{15}$$

We now proceed to consider some implications and applications of the general theory.

II. APPROXIMATE RELATIONS AND A CONJECTURE ON THE ENERGY GAP LAW FOR VIBRATIONAL RELAXATION

The general expression for the vibrational relaxation rate Eqs. (10) and (11) consists in general of a large number of terms corresponding to higher order multiphonon processes. The total number of phonons contributing to each of these terms is $N\{\nu\} = \sum_{\{\nu\}} 1$. The relative contributions of such terms are determined by the magnitude of the molecule–medium coupling terms. It is reasonable to assume that the $|G_{\{\nu\}}|^2$ terms decrease fast with increasing the order of the multiphonon process. As $G_{\{\nu\}}$ is expected to exhibit a very strong dependence on $N\{\nu\}$, we can select a single term in the sum (11) which provides the dominant contribution to the relaxation rate. This largest term is determined by the collection of phonon states $\{\bar{\nu}\} = 1, 2, \cdots, N$, where $N \equiv N\{\bar{\nu}\}$ is the smallest number of phonons that can result in a vibrational relaxation process subjected to the energy conservation (13). The approximate expression for the vibrational relaxation rate is now

$$\gamma \simeq \pi |G_{\{\bar{\nu}\}}|^2 \rho_{\{\bar{\nu}\}} n_{\{\bar{\nu}\}} . \tag{16}$$

For a monatomic lattice we can choose

$$N = \omega/\omega_A , \tag{17}$$

where ω_A is of the order of the Debye frequency. In fact, Eqs. (16) and (17) just correspond to the application of the Einstein model to the lattice spectrum. Numerical calculation of spectral line broadening via multiphonon processes[4] for impurity states in solids indicate that such a single frequency approximation is reasonably good.

In the case of a polyatomic solid, the minimum number N_{μ} of lattice phonons that can induce vibrational relaxation is given by

$$N_{\mu} = \frac{\omega - N_{\eta}\langle\omega_{\eta}\rangle}{\omega_A} , \tag{18}$$

where $\langle\omega_{\eta}\rangle$ is the average vibron frequency, and the most probable number of vibrons involved is determined from the relation

$$\frac{\omega}{\langle\omega_{\eta}\rangle} > N_{\eta} > \frac{\omega}{\langle\omega_{\eta}\rangle} - 1 . \tag{19}$$

No theory of the multiphonon coupling terms is available. On the basis of qualitative consideration, we propose that $G_{\{\bar{\nu}\}} \simeq A\delta^{N\{\bar{\nu}\}}$, where A is a constant and $0 < \delta \ll 1$. Such a relation together with Eq. (16) implies that (at constant T) $\gamma \propto \delta^{2N}$. Thus, for a monatomic lattice, we have from Eq. (17) $\ln\gamma \propto (2\omega/\omega_A)\ln\delta + \text{const}$. This qualitative result implies an energy gap law for vibrational relaxation. Different diatomic molecules in the same monatomic lattice will exhibit a linear dependence of $\ln\gamma$ on the molecular vibrational frequency. The relaxation will, of course, be more efficient for low frequency vibrations. Finally, we note that for a molecular host lattice, N_{μ}, Eq. (18) is relatively small and fast vibrational relaxation is expected, relative to that exhibited for the same molecule in a monatomic solid.

III. TEMPERATURE DEPENDENCE OF THE VIBRATIONAL RELAXATION

The vibrational relaxation rate should exhibit strong temperature dependence. Assuming that the coupling parameters $G_{\{\nu\}}$ are temperature independent, then the entire temperature dependence of γ originates from the thermally averaged commutator, Eq. (4). This can be expressed in one of the following alternative forms:

$$n_{\{\nu\}} = \sum_{\nu'} \langle n_1\rangle_T \langle n_2\rangle_T \cdots \langle n_{\nu'-1}\rangle_T (\langle n_{\nu'+1}\rangle_T + 1) \cdots (\langle n_N\rangle_T + 1), \quad (20)$$

or, as is easy to show by induction,

$$n_{\{\nu\}} = \prod_{\nu} (\langle n_\nu\rangle_T + 1) - \prod_{\nu} \langle n_\nu\rangle_T \ . \quad (21)$$

Finally, from Eqs. (5) and (21), we obtain the simple expression

$$n_{\{\nu\}} = \frac{\exp(\beta\hbar\sum_\nu \omega_\nu) - 1}{\prod_\nu [\exp(\beta\hbar\omega_\nu) - 1]} \ . \quad (22)$$

From Eqs. (11) and (22), the vibrational relaxation rate is

$$\gamma = \pi \sum_{\{\nu\}} |G_{\{\nu\}}|^2 \frac{\exp(\beta\hbar\omega) - 1}{\prod_\nu [\exp(\beta\hbar\omega_\nu) - 1]} \rho_{\{\nu\}} \ , \quad (23)$$

which incorporates the explicit form of the temperature dependence.

From the general result, Eq. (23), we conclude that

(a) For a single phonon decay, γ is temperature independent. This result is compatible with Glauber's analysis of single phonon decay.[5]

(b) For multiphonon processes, the decay rate exhibits temperature dependence. In the low temperature limit when $T \to 0$ and $\beta\hbar\omega_\nu \gg 1$ for all the frequencies which contribute appreciably to $|G_{\{\nu\}}|^2$, the vibrational relaxation rate is finite. Now Eq. (22) results in $n_{\{\nu\}} = 1$, and Eq. (16) takes the form

$$\gamma(0) = \pi \sum_{\{\nu\}} |G_{\{\nu\}}|^2 \rho_{\{\nu\}} \ , \qquad T \to 0 \ , \quad (24)$$

and from the approximate relation (16) we have

$$\gamma(0) \simeq \pi |G_{\{\bar\nu\}}|^2 \rho_{\{\bar\nu\}} . \quad (24')$$

(c) In the high temperature limit,

$$\beta\hbar\omega_\nu \ll 1 \quad (25)$$

for all ν, whereupon kT exceeds all the low phonon frequencies in a monatomic solid and the high vibron frequencies in a polyatomic solid. Equation (22) is reduced to

$$n_{\{\nu\}} = \frac{\exp(\beta\hbar\omega) - 1}{\prod_{\{\nu\}} (\beta\hbar\omega_\nu)} \ , \quad (26)$$

so that

$$\gamma(T) = \pi \sum_{\{\nu\}} |G_{\{\nu\}}|^2 \rho_{\{\nu\}} \frac{\exp(\beta\hbar\omega) - 1}{\prod_{\{\nu\}} (\hbar\omega_\nu / k)} T^{N\{\nu\}} \ , \quad (27)$$

where $N\{\nu\}$ (see Sec. II) is the number of phonons contributing to the particular term in (25). Thus, in general, the high temperature limit results in a high power law in T, which is characteristic of multiphonon processes. It should be noted that condition (25) is oversimplified, as it is not expected to be realized for a molecular host matrix. Two separate cases have to be considered:

(c1) In the case of a monatomic solid, Eq. (21) is expected to be obeyed for all low frequency phonon modes $\{\omega_\mu\}$. Making use of the approximate expression, Eq. (16), we obtain

$$\gamma = \gamma(0) \frac{\exp(\beta\hbar\omega) - 1}{(\hbar\omega_A / k)^N} T^N \ , \quad (28)$$

where N is given by Eq. (17).

(c2) In the case of a polyatomic solid, it is reasonable to apply the high temperature condition only for the lattice modes. Making use of Eq. (16), we have

$$\gamma = \gamma(0) \left[\frac{\exp(\beta\hbar\omega) - 1}{\prod_{\eta=1}^{N_\eta} [\exp(\beta\hbar\omega_\eta) - 1] (\hbar\omega_A / k)^{N_\mu}} \right] T^{N_\mu} \ , \quad (29)$$

where N_μ is given by Eq. (18). As N_μ for a molecular lattice is considerably lower than N for a monatomic host, a weaker temperature dependence in the former case is expected.

(d) The most interesting situation involves the inter-

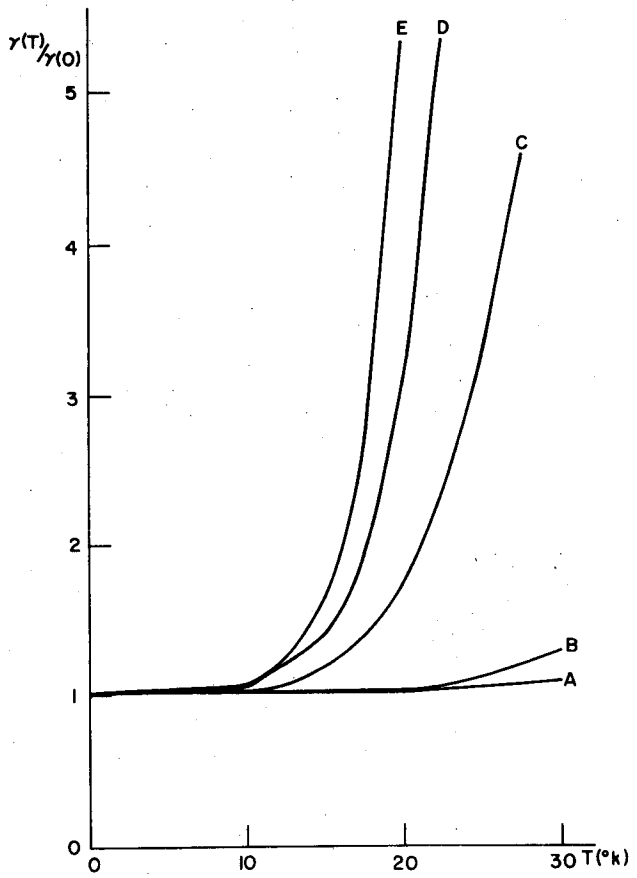

FIG. 1. Model calculations for the temperature dependence of the vibrational relaxation rate of a guest diatomic molecule in a monatomic lattice. A: $\omega = 1000\ \text{cm}^{-1}$, $\omega_A = 100\ \text{cm}^{-1}$; B: $\omega = 3000\ \text{cm}^{-1}$, $\omega_A = 100\ \text{cm}^{-1}$; C: $\omega = 1000\ \text{cm}^{-1}$, $\omega_A = 50\ \text{cm}^{-1}$; D: $\omega = 2000\ \text{cm}^{-1}$, $\omega_A = 50\ \text{cm}^{-1}$; E: $\omega = 3000\ \text{cm}^{-1}$, $\omega_A = 50\ \text{cm}^{-1}$.

mediate temperature range, where Eqs. (16) and (22) result in

$$\gamma/\gamma(0) = \frac{[\exp(\beta\hbar\omega) - 1]}{[\exp(\beta\hbar\omega_A) - 1]^{(\omega/\omega_A)}} \tag{30}$$

for a monatomic lattice and

$$\gamma/\gamma(0) = \frac{\exp(\beta\hbar\omega) - 1}{\prod_{\eta=1}^{N_\eta}[\exp(\beta\hbar\omega_\eta) - 1][\exp(\beta\hbar\omega_A) - 1]^{N_\mu}} \tag{31}$$

for a molecular lattice. Eq. (30) is of considerable interest, as for reasonable values of ω and ω_A it predicts (see Fig. 1) the onset of the temperature dependence for values appreciably lower than the Debye frequency (or of ω_A).

IV. A COMMENT ON IMPURITY ENHANCEMENT EFFECTS

Addition of diatomic or polyatomic molecular impurities to a monatomic host lattice may affect the vibrational relaxation rate of a guest molecule. Nearest-neighbor coupling between the guest molecule and the impurity will provide a localized high energy vibron, which together with the lattice phonons will result in an effective vibrational relaxation channel. Without performing any calculations, we can assert that nearest-neighbor coupling between the guest molecule and an impurity molecule in a monatomic lattice will reduce the order of the multiphonon process, thus resulting in an enhancement of the vibrational relaxation rate.

V. COMPARISON WITH EXPERIMENTAL RESULTS

The predictions of our theory can be summarized as follows:

1. The vibrational relaxation rate of a guest molecule in a host lattice depends crucially on the order of the multiphonon process.

2. For a monatomic rare gas lattice where $\omega_A \simeq 50$ cm^{-1}, then for typical values of molecular frequencies $\omega \simeq 1000-3000$ cm^{-1}, the vibrational relaxation rate will be low, as it is determined by a multiphonon process of the order of $N \simeq 20-60$. This qualitative conclusion concurs with the experimental results of Tinti and Robinson[6] for the vibrational relaxation of the $^3\Sigma_u$ state of N_2 in solid rare gases.

3. For a polyatomic host lattice, the order of the multiphonon process can be considerably reduced, whereupon the vibrational relaxation rate is considerably increased relative to that for a monatomic lattice.

4. Vibrational relaxation processes are expected to exhibit an energy gap law. For a monatomic lattice, we expect that $\ln\gamma = (\omega/\omega_A)\varphi + \epsilon$, while for a polyatomic host $\ln\gamma = (\omega - N_\eta\langle\omega_\eta\rangle/\omega_A)\varphi' + \epsilon'$ where φ, ϵ, φ', and ϵ' are temperature dependent constants. Thus, the dependence of the vibrational relaxation rate on the molecular frequency will be much more pronounced for a monatomic lattice.

5. Vibrational relaxation rates in a monatomic host are expected to exhibit a dramatic temperature dependence [see Eqs. (31) and (28)]. For typical values of $N \simeq 20-60$, the onset of the temperature effect will occur at low temperatures (~10 °K), where $\beta\hbar\omega \ll 1$, so that for Eq. (30) we have $\gamma(T) = \gamma(0)[1 - \exp(-\beta\hbar\omega_A)]^{-(\omega/\omega_A)}$. It is also important to notice that the onset of the temperature dependence and the temperature coefficient increases with the molecular frequency. Thus, low frequency vibrations characterized by a higher absolute relaxation rate will exhibit a weaker T dependence.

6. In a polyatomic lattice, the onset of the temperature dependence will be higher and the temperature coefficient of γ will be appreciably lower than in a monatomic lattice.

7. Molecular impurities introduced into a monatomic lattice and characterized by frequencies lower than ω will result in an enhancement of the vibrational relaxation rate.

The best systems for which the present theory is applicable involve the vibrational relaxation of a diatomic molecule or the lowest vibrational frequency of a polyatomic molecule, where medium induced scrambling of intramolecular vibrations is not encountered. Recent experimental studies by Legay, Abouaf-Marguin, and Dubost[7-9] provide a conclusive test for the validity of the present theory. Legay *et al.* have studied the vibrational relaxation of CO in solid rare gases and of NH_3 in solid nitrogen in the temperature region 4 °K–20 °K. These experiments monitor the total decay rate of the $v=1$ level of CO[7,9] and of the $v=1$ state of the lowest $W=970$ cm^{-1} frequency of NH_3, which according to the present theory are given by Eq. (15). Utilizing the known radiative decay rates γ_{ir}, Legay *et al.* evaluated the vibrational relaxation rates. The experimental results of Legay *et al.*[7-9] can be summarized as follows

(a) The vibrational relaxation time of the 2170 cm^{-1} vibration of CO in solid Ar at 8 °K, which corresponds to the lowest temperature achieved, is $\gamma^{-1} = 13.6$ msec.

(b) The vibrational relaxation rate of the $\omega = 970$ cm^{-1} vibration of NH_3 in solid N_2 at 8 °K is $\gamma^{-1} = 2$ μsec.

(c) The vibrational relaxation rate of CO in solid Ar exhibits a strong temperature dependence at low temperatures (see Fig. 2) increasing by a factor of ~3 in the temperature range 8 °K–20 °K.

(d) The vibrational relaxation rate of the 970 cm^{-1} vibration of NH_3 at low temperatures exhibits a relatively weak temperature dependence.

(e) Addition of molecular impurities (i.e., O_2, CO_2, H_2O, NH_3) to CO/Ar mixtures enhances the vibrational relaxation rate of CO.

To confront these experimental results with theory, we first notice that for the relaxation experiment of NH_3 in solid N_2, the molecular frequency $\omega = 970$ cm^{-1} is considerably lower than the intramolecular frequency of the host N_2 molecules $\omega = 2360$ cm^{-1}, whereupon the intramolecular vibrons of this solid cannot participate in the vibrational relaxation. Thus, the NH_3/N_2 system studied by Legay *et al.* corresponds to vibrational relaxation in an effective monoatomic solid. The enhancement of the low temperature vibrational relaxation rate

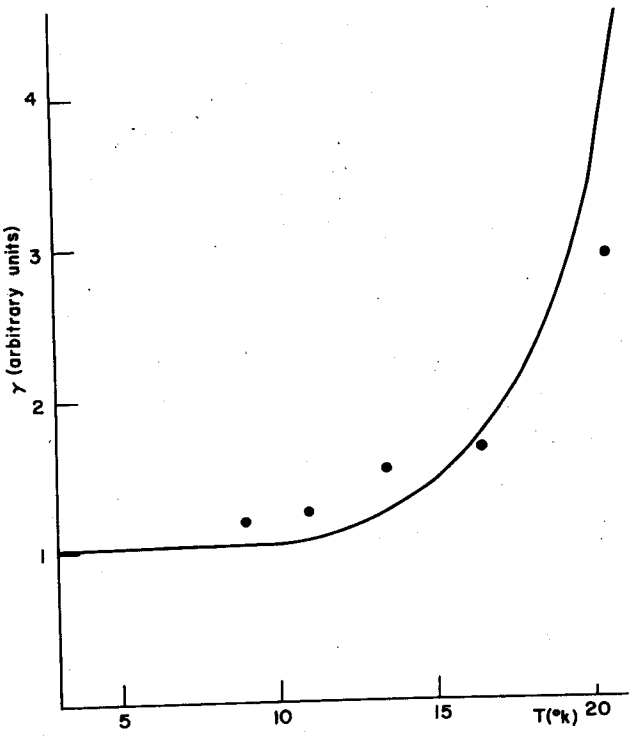

FIG. 2. The temperature dependence of the vibrational relaxation rate of CO in solid Ar. •: Experimental data of Legay, Abouaf-Marguin, and Dubost [Refs. (7–9)]. These relative values can be converted into absolute values taking $\gamma = 73$ sec^{-1} at $T = 9$°K; —: Theoretical curve from Eq. (30), with $\omega = 2170$ cm^{-1} and $\omega_A = 50$ cm^{-1}.

by a factor of 5000 for NH_3 relative to CO is consistent with the energy gap law for vibrational relaxation. In the case of solid Ar, we take $\omega = 50$ cm^{-1} (slightly lower than the Debye frequency $\omega_A = 65$ cm^{-1}), while for solid N_2, $\omega = 100$ cm^{-1}.[10] Thus, $N \simeq 43$ for CO/Ar and $N \simeq 10$ for NH_3/N_2, resulting in a dramatic increase of γ for the latter case. The strong temperature dependence of γ for the CO/Ar system is adequately accounted for in terms of our theory. In Fig. 2, we present the analysis of the experimental results of Legay *et al.*[9] in terms of Eq. (30); the fit of the theory to the experimental data is as good as may be expected. The weak temperature dependence of γ for the NH_3/N_2 system at low temperatures is compatible with the relatively low $N \simeq 10$ value for this system. Finally, we note that the effect of addition of molecular impurities characterized by frequencies $\omega_\eta \lesssim \omega$ to the CO/Ar system concurs with our qualitative considerations regarding impurity enhancement effects.

VI. DISCUSSION

It is gratifying that our theory provides a semiquantitative description of a variety of interesting experimental data. At present, our ignorance of the explicit form of the multiphonon coupling constants $G_{\{\nu\}}$ prohibits us from obtaining detailed theoretical information regarding the absolute values of the vibrational relaxation rates. Extension of the present theory for the explicit evaluation of the molecule–medium coupling will be of interest for the elucidation of the details of vibrational relaxation in a dense medium, medium-induced intramolecular vibrational energy redistribution in polyatomic molecules, and coupled electronic–vibrational relaxation processes in large molecules.

The physical picture for vibrational relaxation advanced herein rests on the dissipation of the internal vibrational energy of a harmonic oscillator into N medium phonons, providing an example for a multiphonon relaxation process. Another important class of multiphonon relaxation phenomena involves electronic radiationless transitions between electronically excited states of a large "statistical" molecule[11–15] or of an impurity center (i.e., an ion or an F center in solids.[16–19] Such radiationless processes correspond to the dissipation of electronic energy into a manifold of "phonon levels" of a lower electronic configuration. For a large statistical molecule[11–15] these phonon levels correspond to a quasicontinuum of intramolecular vibrational states, while for an impurity center these are just the lattice phonons.[16–19] The latter case bears a close analogy to the vibrational relaxation problem as far as the dissipative phonon channel is considered. Electronic relaxation in a two electronic levels system, which is characterized by displaced adiabatic potential surfaces,[13–16,18–20] can be specified in terms of the Hamiltonian[16,20]

$$H = \Delta E d^\dagger d + \sum_\mu \hbar\omega_\mu b_\mu^\dagger b_\mu + \left\{ \sum_\kappa C_{ab}^\kappa d \prod_\mu \exp\left[-\frac{\Delta_\mu}{\sqrt{2}} (b_\mu^\dagger - b_\mu) \right] \frac{i}{\sqrt{2}} (b_\kappa^\dagger - b_\kappa) + hc \right\}, \quad (32)$$

where ΔE is the electronic energy gap between the origins of the electronic states $|a\rangle$ and $|b\rangle$, $d^\dagger$ and d correspond to the electronic creation and annihilation operators, i.e., $d^\dagger|a\rangle = |b\rangle$, $d|b\rangle = |a\rangle$ and $d^\dagger|b\rangle = d|a\rangle = 0$. The index μ specifies all the phonon modes, while the index κ corresponds to the subset of promoting phonon modes. C_{ab}^κ is the interstate electronic coupling matrix element induced by the κ mode. Finally, Δ_μ represents the reduced displacement of the two adiabatic potential surfaces for the μth mode, and for simplicity, we have taken $\Delta_\kappa = 0$ for all κ. It is important to notice that the exponential Franck–Condon displacement operator[16,20] $\exp[-(\Delta_\mu/\sqrt{2})(b_\mu^\dagger - b_\mu)]$ in Eq. (32) involves all multiphonon processes for electronic relaxation.

The detailed form of the Hamiltonians (1) and (32) specifying vibrational and electronic relaxation, respectively, differs in two important aspects: (a) The operators $d^\dagger$ and d in (32) span a two level system, while the operators $a^\dagger$ and a in Eq. (1) define an infinite discrete spectrum. (b) The perturbation Hamiltonian, i.e., the third term in Eqs. (1) and (32) is, of course, different. It is interesting to compare the general features characteristic of electronic and vibrational multiphonon relaxation processes, although the physical models and consequently the detailed form of the Hamiltonians are different. First, we notice that the heuristic expression for the phonon coupling $G\{\nu\} = A\delta^{N\{\nu\}}$ in Sec. II, which results in the energy gap law for vibrational relaxation,

is analogous to the energy gap law for electronic radiationless processes.[13–15,17–19] Second, it will be useful to consider the temperature dependence of the two classes of multiphonon relaxation processes, which will bring up an interesting difference resulting from the level structure of the zero order Hamiltonians. The temperature dependence of the electronic relaxation probability, $W(T)$, in low order can be recast by applying the generating function method to the "Golden Rule" rate expression and handling the resulting Fourier integral by the steepest descent approximation. This treatment results in the approximate relation[13–15,18]

$$W(T) = W(0)(1 + \langle n_m \rangle_T)^p \exp(-B\langle n_m \rangle_T) , \tag{33}$$

where the index m specifies an effective mode of frequency ω_m and degeneracy L_m, which probably lies close to the maximum phonon frequency, $\langle n_m \rangle_T$ is the thermally averaged occupation number of this mode [see Eq. (5)], $p = \Delta E/\hbar\omega_m$ corresponds to the normalized electronic energy gap, while $B = L_m(\Delta_m^2/2)$ represents the effective electron–phonon coupling. The temperature effect in Eq. (33) originates from two contributions, a spontaneous and stimulated process involving the emission of p phonons resulting in $(1 + \langle n_m \rangle_T)^p$ and the exponential term $\exp(-B\langle n_m \rangle_T)$, which involves the usual Debye–Weller factor.[13–15,18] For a weak electron–phonon coupling situation, $B \ll 1$ and the first contribution dominates the temperature dependence. Indeed, an early simplified treatment[17] utilized the expression $W(T)/W(0) = (1 + \langle n_m \rangle_T)^p$ for a proper fit of the temperature dependence of electronic relaxation of rare earth ions in ionic crystals. Now, for vibrational relaxation in a monatomic lattice, assuming the role of a single phonon mode ω_A, we have from Eq. (21)

$$\gamma(T) = \gamma(0)\{(1 + \langle n_A \rangle_T)^N - \langle n_A \rangle^N\} . \tag{34}$$

Only at moderately low temperatures (i.e., $\langle n_A \rangle_T$, $\langle n_m \rangle_T \ll 1$) and for large p and N, Eqs. (33) and (34) exhibit identical formal temperature dependence,

$$W(T)/W(0) = 1 + (p - B)\exp(-\beta\hbar\omega_m) ,$$

and

$$\gamma(T)/\gamma(0) = 1 + N\exp(-\beta\hbar\omega_A), \quad N \gg 1 ,$$

while at higher temperatures the qualitative features of the two multiphonon relaxation processes with regard to the temperature dependence are different. In particular, we note the appearance of the negative contribution $\langle n_A \rangle^N$ due to a phonon absorption process in Eq. (34) that is absent from Eq. (33). To consider an interesting special case, the single phonon $p = 1$ electronic relaxation process exhibits temperature dependence (although the approximations underlying calculations such as the saddle point integration that lead to Eq. (33) are somewhat doubtful in this case), while the single phonon vibrational relaxation $N = 1$ probability is temperature independent. Our result for the $N = 1$ vibrational relaxation is compatible with the study of the harmonic oscillator paradox.[21] The interaction of a harmonic oscillator with a phonon bath results both in excitation and deactivation of the internal degrees of freedom. The vibrational relaxation problem corresponds to a multilevel molecular system with equidistant level spacing rather than to a two internal levels system encountered in the basic model for electronic relaxation. This basic difference results in the different dependence of these two multiphonon processes on the equilibrium population of the phonon field. This is also the reason that second order perturbation theory is adequate for the study of electronic relaxation, while the vibrational relaxation problem was handled[1] by a many body method.

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