# Direct vibrational relaxation of a molecule in a dense medium

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This note provides explicit, compact and useful theoretical expressions for the vibrational relaxation rate of a guest molecule in monoatomic and poly-atomic host solid matrices, which are valid throughout the entire temperature range.

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The fast developing experimental studies of medium-induced vibrational relaxation (VR) of a guest molecule in low temperature solids and in liquids [1–13] have triggered considerable theoretical activity in the field [14–20]. In particular, several recent studies [14, 16–18, 20] have considered the problem of direct VR without the participation of other intramolecular modes of the guest molecule. This theoretical problem, which pertains to the VR of a diatomic molecule and of the lowest frequency vibrational excitation of a polyatomic molecule, was handled in terms of a multiphonon process where the relevant coupling operator generates a shift in the momentum space [16, 20]. Following the common practice adopted in studies of a variety of multiphonon processes, such as electronic relaxation [21–24] in large molecules, electron transfer [25] and energy transfer, the general expression for the VR rate was reduced [20] to an explicit form in two limiting cases, both of which rest on the saddle-point approximation. At moderately low temperatures, below the characteristic Debye frequency of a monoatomic solid, the VR rate was found [20] to exhibit an exponential dependence on the (high order) multiphonon process, while in the high temperature (i.e. the strong coupling [22] situation) the common gaussian lineshape function [26–28] was derived [16, 20]. The purpose of the present note is twofold. First, we shall derive an explicit and useful expression for the rate VR in a monoatomic solid, which is valid throughout the entire temperature range, exhibiting a continuous ' transition ' from a temperature-independent rate at low temperatures to a gaussian type, activated rate, at high temperatures. Secondly, we shall extend this treatment providing some new results for the VR rate in a polyatomic solid with the participation of the host intramolecular vibrational modes. These theoretical results will be useful for the elucidation of the gross features of direct VR processes in a dense medium.

Invoking the conventional rotating wave and random-phase approximations the VR rate, $\gamma$, of a harmonic guest molecule in a harmonic medium is [20]

$$\gamma = D \exp{(G)} \int_{-\infty}^{\infty} dt \exp{(-i\omega t)} \exp{[G_+(t) + G_-(t)]}, \qquad (1.1)$$

$$G_+(t) = \int d\omega_\nu \, \rho(\omega_\nu)(\Delta_\nu{}^2/2)(v_\nu + 1) \exp{(i\omega_\nu t)}, \qquad (1.2)$$

$$G_-(t) = \int d\omega_\nu \, \rho(\omega_\nu)(\Delta_\nu^2/2)v_\nu \exp{(-i\omega_\nu t)}, \tag{1.3}$$

$$G = \int d\omega_\nu \, \rho(\omega_\nu)(\Delta_\nu^2/2)(2v_\nu+1), \tag{1.4}$$

$$v_\nu = [\exp{(\beta\hbar\omega_\nu)}-1]^{-1}; \quad \beta = (kT)^{-1}, \tag{1.5}$$

$$D = (2\hbar\mu\omega)^{-1}[1 - \exp{(-\beta\hbar\omega)}][Za \exp{(-\alpha X_j^0)}], \tag{1.6}$$

where $\mu$ and $\omega$ are the reduced mass and the vibrational frequency of the guest molecule, respectively, the medium phonons are specified in terms of the frequencies $\{\omega_\nu\}$, the effective molecule–medium coupling terms $\{\Delta_\nu\}$ and the density of states $\rho(\omega_\nu)$.  Finally, $z$ is the number of nearest neighbours, while $a \exp{(-\alpha X_i^0)}$ is the molecule–medium pair repulsion potential at the equilibrium configurations.   An alternative expression for the VR rate may be obtained by a power expansion of the exponential $\exp{[G_+(t)+G_-(t)]}$ in the integral, equation (1.1), in terms of a uniformly converging series

$$\gamma = D \exp{(G)} \sum_{r=0}^{\infty} (r\,!)^{-1} \int_{-\infty}^{\infty} dt \exp{(-i\omega t)}[G_+(t)+G_-(t)]^r. \tag{2}$$

Equation (2) corresponds to a sum of contributions of multiphonon processes of increasing order.

Specializing now to a monoatomic solid we neglect phonon dispresion, replacing the phonon frequencies in equations (1) and (2) by an average value $\langle\omega_\nu\rangle$.   Equation (2) now yields

$$\gamma = 2\pi D \exp{(S[2\langle v_\nu\rangle+1])} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{[S(\langle v_\nu\rangle+1)]^m [S\langle v_\nu\rangle]^n}{m\,!\ n\,!}$$
$$\times \delta[(m-n)\langle v_\nu\rangle - \omega]. \tag{3}$$

This result has been previously derived by Lin [16] where the phonon coupling strength is

$$S = \int d\omega_\nu \, \rho(\omega_\nu)(\Delta_\nu^2/2) \tag{4}$$

and the mean phonon (thermal) occupation being

$$\langle v_\nu\rangle = [\exp{(\beta\hbar\langle\omega_\nu\rangle)}-1]^{-1}. \tag{5}$$

In view of the ' Einstein type ' approximation inherent in equation (3), a ' coarse graining ' procedure has to be adopted, which amounts to integrating this expression over the energy range $\hbar\langle\omega_\nu\rangle$, corresponding to the lowest characteristic energy involved in the problem, whereupon

$$\gamma = \bar{D} \exp{(S[2\langle v_\nu\rangle+1])} \sum_{n=0}^{\infty} \frac{[S(\langle v_\nu\rangle+1)]^{n+N}[S\langle v_\nu\rangle]^n}{(n+N)\,!\ n\,!}, \tag{6}$$

where $\bar{D} = D/\hbar\langle\omega_\nu\rangle$ and the order of the multiphonon process is

$$N = \omega/\langle\omega_\nu\rangle. \tag{7}$$

We now invoke a mathematical technique originally introduced for the study of optical lineshapes [26] and polaron motion in solids [29].   Utilizing the definition of the modified Bessel function [30]

$$I_\mu(z) = (z/2)^\mu \sum_{L=0}^{\infty} (z/2)^{2L}/[(L+\mu)\,!\ L\,!]. \tag{8}$$

Equation (6) results in the relation

$$\gamma = \bar{D} \exp \left[ S(2\langle v_\nu \rangle + 1) \right] \left[ (\langle v_\nu \rangle + 1)/\langle v_\nu \rangle \right]^{N/2} I_N(2S[\langle v_\nu \rangle(\langle v_\nu \rangle + 1)]^{1/2}). \quad (9)$$

Equation (9) provides us with a new general result, which is applicable for the study of direct VR dominated by coupling with intermolecular phonon modes. This result is valid throughout the entire temperature range. Several limiting situations are of interest:

(A) Extremely low temperature limit, $kT \ll \hbar\langle\omega_\nu\rangle$. As $\langle v_\nu \rangle \to 0$ we can utilize the limiting form of equation (8), $I_\mu(z) \to (z/2)^\mu/\mu!$ for small values of $z$ which results in

$$\gamma(0) = \bar{D} \exp{(S)} S^N/N! \quad (10)$$

We note in passing that the low temperature ($T$ independent) VR rate is similar to the familiar form of the Franck–Condon vibrational overlap factor, except the positive exponent in the Debye–Weller factor.

(B) Onset of temperature dependence. When $kT \langle \hbar\langle\omega_\nu\rangle$ and $0 \ll v_\nu \rangle \ll 1$ we can utilize equation (8), retaining only the first two terms and set $\langle v_\nu \rangle = \exp(-\beta\hbar\langle\omega_\nu\rangle)$, whereupon equation (9) results in

$$\gamma = \gamma(0) \left[ 1 + \exp{(-\beta\hbar\langle\omega_\nu\rangle)} \left( N + \frac{S^2}{N+1} \right) \right]. \quad (11)$$

From this result we can provide a simple operational estimate of the temperature range where the VR starts increasing above $\gamma(0)$. The temperature $T_0$, where $\gamma$ increases by a factor of two relative to its $T = 0$ value, is given by

$$kT_0 = \hbar\langle\omega_\nu\rangle/\ln\left( N + \frac{S^2}{N+1} \right). \quad (12)$$

Equation (12) implies that for VR processes of high order (i.e. $N \gg 1$) or for strong molecule-medium coupling ($S \gg 1$) the onset of the temperature dependence of $\gamma$ occurs at temperatures which are considerably lower than the characteristic vibrational temperature to $\hbar\langle\omega_\nu\rangle/k$. For example, setting $N = 20$ and $S = 10$ leads to $kT_0 = 0.31 \, \hbar\langle\omega_\nu\rangle$, while for $N = 40$ and $S = 10$ one gets $kT_0 = 0.27 \, \hbar\langle\omega_\nu\rangle$. As expected, for high order multiphonon processes $T_0$ exhibits a weak dependence on $N$, slightly decreasing with increasing $N$.

(C) The high temperature limit, $kT \gg \hbar\langle\omega_\nu\rangle$. When $\langle v_\nu \rangle \gg 1$ an asymptotic expansion of the modified Bessel function, equations (8) and (9), $I_\mu(z) \to (2\pi z)^{-1/2} \exp{(z - \mu^2/2z)}$, for large values of $z$ results in the well-known gaussian lineshape function [16, 20]

$$\gamma = D(\pi\hbar\langle\omega_\nu\rangle kT)^{1/2} \exp{(4SkT/\hbar\langle\omega_\nu\rangle)} \exp\left[ \frac{\hbar(\omega - S\langle\omega_\nu\rangle)^2}{4S\langle\omega_\nu\rangle kT} \right]. \quad (13)$$

Equation (13), which corresponds to the 'strong coupling' situation, was previously systematically derived [20] by the application of the saddle-point integration followed by a truncation of the power series solution for the saddle point. The latter procedure is valid for $|(N/S) - 1|^2 \ll (2\langle v_\nu \rangle + 1)^2$ as borne out also by numerical calculations [31].

Equation (9) constitutes an explicit result for the direct VR rate of a guest molecule in a simple solid, which exhibits a smooth transition from a temperature-independent rate at low temperatures to a rate expression reminiscent of an

activated rate process at high temperatures. Furthermore, this expression holds (within the framework of the Einstein approximation) for any order of the multiphonon process, in contrast with our previous results [20] for $\gamma(0)$ which were valid only for large $N$. The following experimental implications of our results should be noted.

(1) Equation (10) provides a general energy gap law for simple direct VR processes in the low temperature limit. For low order processes, i.e. $N < S$ we expect that $\gamma(0)$ will increase with increasing $N$, for a class of guest molecules characterized by similar values of the coupling $S$. Such processes were not yet experimentally explored. On the other hand, in the case of high order multi-phonon VR processes we expect that for $N \gg S$, $\gamma(0)$ will decrease with increasing $N$, providing the conventional energy-gap law [20] for a (high order) multi-phonon process. For large values of $N$ application of the Stirling approximation results in

$$
\left.
\begin{aligned}
\gamma(0) &= A \exp(-fN), \\
f &= \ln(N/S) - 1, \\
A &= \bar{D} \exp(S).
\end{aligned}
\right\}
\tag{14}
$$

The exponential dependence of $\gamma(0)$ on $N (N \gg S)$ is borne by the available low temperature experimental data for the VR process, $v = 1 \to v = 0$ of $N_2$ in solid $N_2$[11], $C_2^-$ in solid Ar and $N_2$[10], and the lowest vibrational frequency of $NH_3$ in solid $N_2$[8]. The sparse experimental data [8, 10, 11] available at present obey equation (14) with the parameters $A = 1 \cdot 5 \times 10^{11}$ s$^{-1}$ and $f/\langle \omega_\nu \rangle = 1 \cdot 1 \times 10^{-2}$ cm. The latter parameter together with the reasonable estimate $\langle \omega_\nu \rangle = 50$ cm$^{-1}$ yields $f = 0 \cdot 54$ while the value $A = 1 \cdot 5 \times 10^{11}$ s$^{-1}$ is compatible with a recent theoretical estimate [20] $A = 10^{12}$ s$^{-1}$. On the basis of the foregoing analysis we conclude that for CO in solid Ar $\gamma(0) \simeq 1$ s$^{-1}$. This exceedingly low VR rate is consistent with the recent experimental work of Dubost and Charneau [12], who inferred that $\gamma(0) < 70$ s$^{-1}$, and the major channel for the decay of the $v = 1$ state involves infra-red emission.

(2) The onset of the temperature dependence of $\gamma$ is expected to occur around $kT_0 \simeq (0 \cdot 2 - 0 \cdot 3) \hbar \langle \omega_\nu \rangle / k$, i.e. at about $T \simeq 12$–$22$ K in simple molecular solids and $kT_0$ increases with the experimental observation of Dressler et al. [11] that $\gamma$ of $N_2$ in solid nitrogen (where $N = 40$–$50$) increases from $0 \cdot 9$ s$^{-1}$ at 4 K to $1 \cdot 8$ s$^{-1}$ at 18 K. On the other hand, Allamadola and Nibler [10] have reported that $\gamma$ for $C_2^-$ in solid Ar and $N_2$ is practically temperature independent in the range 14–24 K. As for the latter system, $N = 25$, the onset of the temperature dependence of $\gamma$ should occur at somewhat higher temperature than in the former case.

(3) The general temperature dependence of $\gamma$, as predicted by equation (9), was not yet subjected to an experimental study. Such results will emerge for VR studies of implicit molecules in ionic and covalent crystals.

Up to this point we have been concerned with direct vibrational energy dissipation into low frequency phonon modes of the host. In a polyatomic host solid the high frequency vibrational modes $\{\omega_c\}$ can be active as accepting modes for the VR process [17]. Then provided that $\omega > \omega_c$ these intramolecular vibrons can participate in the VR process. The theoretical methods developed

herein can be extended to handle this physical situation, which amounts to a drastic reduction of the order of the multiphonon process, resulting in a dramatic enhancement of $\gamma$, relative to the value exhibited in a simple solid. We consider again an exponential repulsive atom–atom interaction potential between the guest molecule and the polyatomic host. Expanding this intermolecular potential in the reciprocal of the interatomic separation and retaining first-order terms in the normal coordinates of the guest molecule results in an exponential perturbation hamiltonian, where the instantaneous displacement can be separated into a linear combination of the medium normal modes and of the intramolecular normal modes of the host. Invoking the Einstein approximation for both the lattice and for the intramolecular modes we characterize the former by the average frequency $\langle\omega_\nu\rangle$ and the latter by the average frequency $\langle\omega_c\rangle$. Two effective coupling parameters now enter into the problem, $S = \sum(\Delta_\nu^2/2)$ for the lattice modes, which is equivalent to equation (4), and $S_c = \sum_c(\Delta_c^2/2)$ for the coupling with the vibron modes. Expansion of the exponential function in the integrand of equation (1.1) results now in an expression for $\gamma$ which can be recast in terms of a convolution of two lineshape functions :

$$\gamma = \bar{D} \int d\Omega f_p(\omega - \Omega) f_c(\Omega), \tag{15}$$

$$f_p(\omega - \Omega) = \exp\left[S(2\langle v_\nu\rangle + 1)\right] \sum_{n=0}^{\infty} \frac{[S(\langle v_\nu\rangle + 1)]^{n+N-\Omega/\langle\omega_\nu\rangle}(S\langle v_\nu\rangle)^n}{(n+N-\Omega/\langle\omega_\nu\rangle)!\ n!} \tag{15.1}$$

$$f_c(\Omega) = {}'\exp\left[S_c(2\langle v_c\rangle + 1)\right] \sum_{m=0}^{\infty} \sum_{l=0}^{\infty} \frac{[S(\langle v_c\rangle + 1)]^m[S\langle v_c\rangle]^l}{m!\ l!}$$
$$\times \delta[\Omega + (l-m)\langle\omega_c\rangle], \tag{15.2}$$

where $\langle v_\nu\rangle$ is given by equation (1.5) while $\langle v_c\rangle = [\exp(\beta\hbar\langle\omega_c\rangle) - 1]^{-1}$. $f_p$ corresponds to the contributions of the intramolecular phonon modes, where ' coarse graining ' over these low frequency modes was again performed, while $f_c$ denotes the contribution of the intramolecular vibrons. Equation (15) can be recast in the compact form

$$\gamma = \bar{D} \exp\left[S(2\langle v_\nu\rangle + 1) + S_c(2\langle v_c\rangle + 1)\right] \sum_{m=-\infty}^{\infty} [(\langle v_\nu\rangle + 1)/\langle v_\nu\rangle]^{p(m)/2}$$
$$\times [(\langle v_c\rangle + 1)/\langle v_c\rangle]^{m/2} I_{|p(m)|}(2S[\langle v_\nu\rangle(\langle v_\nu\rangle + 1)]^{1/2}) I_{|m|}$$
$$\times (2S_c[\langle v_c\rangle(\langle v_c\rangle + 1)]^{1/2}), \tag{16}$$

where $p(m) = N - (m\langle\omega_c\rangle/\langle\omega_\nu\rangle)$ is taken as the integer closest to the value of $p(m)$.

We have thus derived a general result for direct VR relaxation in a complex polyatomic host medium, which is valid throughout the entire temperature range. In the extreme low temperature limit, i.e. $kT \ll \hbar\langle\omega_\nu\rangle \ll \hbar\langle\omega_c\rangle$, equation (16) can be recast in the form

$$\gamma = \bar{D} \exp(S + S_c) \sum_{m=0}^{\infty} \frac{S^{p(m)} S_c^m}{[p(m)]!\ m!}, \tag{17}$$

providing a low temperature $T$ independent VR rate, which constitutes of a sum where each term consists of a product of two Poissonian type distributions. The $m = 0$ term in equation (17) is (apart for a proportionality constant) identical

with $\gamma(0)$, equation (10); however, higher $(m > 0)$ terms will lead to a large contribution. It is apparent that the low temperature VR rate in a polyatomic solid (or an aggregate of the guest with a polyatomic impurity) is considerably enhanced. The onset of the $T$ dependence of $\gamma$ can now be obtained by considering the situation whence $0 \ll \langle v_\nu \rangle \ll 1$ while $\langle v_e \rangle \to 0$. In this case

$$\gamma = \bar{D} \exp{(S + S_c)} \sum_{m=0}^{\infty} \frac{S^{p(m)} S_c{}^m}{[p(m)]! \; m!} \left[ 1 + \langle v_\nu \rangle \left( p(m) + \frac{S^2}{p(m) + 1} \right) \right]. \quad (18)$$

The dominating contribution to the sum in equation (18) will result from $m > 0$ terms, i.e. for $p(m) < N$. Thus the onset of the $T$ dependence of $\gamma$ in a polyatomic solid will be exhibited at temperatures higher than for the simple monoatomic solid. Next, we consider the situation when effective thermal excitation of the medium modes prevails while the vibron modes are still frozen, i.e., $\hbar \langle \omega_\nu \rangle \ll kT \ll \hbar \langle \omega_c \rangle$; the former modes are treated classically while the latter correspond to the low temperature case, whereupon

$$\gamma = D(\pi \hbar / \langle v_\nu \rangle S k T)^{1/2} \exp{(4 S k T / \hbar \langle \omega_\nu \rangle)}$$

$$\sum_{m=0}^{\infty} \exp \left[ \frac{\hbar(\omega - S \langle \omega_\nu \rangle - m \langle \omega_c \rangle)^2}{4 S \langle \omega_\nu \rangle k T} \right] (S^m / m!). \quad (19)$$

The transition probability consists of a sum of products each involving gaussian and poissonian terms. We could have easily proceeded to consider the higher temperature limit of equation (16), which will result in a (single) gaussian contribution to the lineshape function, involving both intermolecular and intramolecular contributions. This situation is hardly accessible in real life, as usually $\hbar \langle \omega_c \rangle \gg kT$.

The present study provides a general quantitative approach for the elucidation of the features of direct VR processes in monoatomic and polyatomic host solids. The only serious sin of omission inherent in the present treatment involves the neglecting of coupling between vibrational and rotational modes. Such effects may be important for the cases when the matrix-isolated guest molecule does exhibit rotational motion in the solid.

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