Nonperturbative approach to collisional dephasing: Application to vibrational dephasing in liquids

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(Received 17 June 1980; accepted 5 August 1980)

We develop a theory for the collisional dephasing of spectral lines in the binary collision approximation and in the Markovian (impact) limit of fast collisions. Making use of tetradic and dyadic scattering techniques we derive expressions for the line broadening which are nonperturbative in the potentials of interaction. We present some numerical applications corresponding to vibrational dephasing in liquids which show that for high temperatures, large masses, and short range interactions the nonperturbative corrections may be quite significant and may change the predictions of the binary collision models as to the variation of the dephasing rate with these parameters.

I. INTRODUCTION

Binary collision models are frequently used in the description of broadening of spectral lines.[1–5] Numerous experimental and theoretical works have been done on the problem of pressure broadening of spectral lines at low pressures, where the binary collision assumption is the most appropriate. In recent years binary collision models were also applied to the broadening of vibrational lines in the liquid phase.[6–19] Experimental data of this type exist mainly from coherent Raman techniques.[6,7,9]

The basic molecular model for line broadening (dephasing) consists of a two-level system coupled to a bath which does not interact directly with the radiation field and which induces the line broadening. The common theoretical treatments of vibrational dephasing in liquids[6,11–16] are perturbative in the system–bath interaction. It is our purpose in this paper to derive approximate expressions for dephasing rates which are nonperturbative and to apply them to the problem of vibrational dephasing. In Sec. II we present the necessary formal expressions for collisional dephasing. In Sec. III we consider colinear models and make use of methods of tetradic and dyadic scattering theory to derive simple nonperturbative expressions for the dephasing rates. Finally, in Sec. IV we make specific application to vibrational dephasing and present some numerical examples.

II. THE LINE SHAPE FUNCTION

We consider a two-level molecular system $|a\rangle$ and $|b\rangle$ which is coupled to a thermal bath. Within the binary collision model[1–5] we assume that the two-level system is fixed at the center of a macroscopic sphere with volume Ω. The bath consists of N perturber atoms which interact with the two-level system but not with each other. The total Hamiltonian for the system + bath is given by

$$H = |a\rangle [E_a + H_a(Q_B)]\langle a| + |b\rangle [E_b + H_b(Q_B)]\langle b| \ , \tag{1}$$

where

$$H_i(Q_B) = \sum_{\nu=1}^{N} \left[-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial Q_\nu^2} + G_i(Q_\nu) \right], \quad i = a, b \ . \tag{2}$$

Here $Q_B = \{Q_\nu\}$ is the collection of bath coordinates, E_a and E_b are the energies of the two levels, M is the reduced mass of the system and a bath molecule, and $G_a(Q_\nu)$ and $G_b(Q_\nu)$ are the adiabatic potentials of interaction of a bath molecule with the system. In our model Hamiltonian [Eqs. (1) and (2)] we have excluded T_1 processes (relaxation of population) in the system which are usually not important for vibrational line shapes in liquids.[6,12] The eigenstates of H_a and H_b, i.e., $|\alpha\rangle$ and $|\beta\rangle$, respectively, are given by products of single-particle states:

$$|\alpha\rangle = \prod_\nu |\alpha_\nu\rangle \ , \tag{3a}$$

$$|\beta\rangle = \prod_\nu |\beta_\nu\rangle \ , \tag{3b}$$

with eigenvalues

$$E_\alpha = \sum_\nu E_{\alpha\nu} \ , \tag{4a}$$

$$E_\beta = \sum_\nu E_{\beta\nu} \ . \tag{4b}$$

Each $|\alpha_\nu\rangle$ and $|\beta_\nu\rangle$ is assumed to be normalized in our spherical box so that

$$\langle\alpha|\alpha'\rangle = \delta_{\alpha,\alpha'} \ , \tag{5a}$$

$$\langle\beta|\beta'\rangle = \delta_{\beta,\beta'} \ . \tag{5b}$$

The *exact* solution for the absorption line shape of the system defined by the Hamiltonian H is given by[4]

$$I(\Delta) = \int_0^\infty d\tau \exp\left[-i\Delta\tau - \frac{N}{\Omega} g(\tau) \right] + \text{c.c} \ , \tag{6}$$

where

$$g(\tau) \equiv \Omega \sum_{\alpha,\beta} P(\alpha) |\langle\alpha|\beta\rangle|^2 [1 - \exp(i\omega_{\beta\alpha}\tau)] \tag{7}$$

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is the line-broadening function and

$$\Delta \equiv \omega_L + E_a - E_b \tag{8}$$

is the detuning of the incident light frequency (ω_L) from the two-level frequency. Also,

$$\omega_{\beta\alpha} = E_\beta - E_\alpha \ ,$$

and $P(\alpha)$ is the canonical distribution of α states

$$P(\alpha) = \exp(-E_\alpha/kT) \Big/ \sum_{\alpha'} \exp(-E_{\alpha'}/kT) \ . \tag{9}$$

In Eqs. (7)–(9) and from now on, $|\alpha\rangle \equiv |\alpha_\nu\rangle$ and $|\beta\rangle \equiv |\beta_\nu\rangle$ are *single particle bath states* and for convenience in the notation we omit the subscript ν. It should be noted that the sum in Eq. (7) is $0(1/\Omega)$ so that $g(\tau)$ is $0(1)$ and in the thermodynamic limit ($N \to \infty$, $\Omega \to \infty$, N/Ω finite), (N/Ω). $g(\tau)$ is simply proportional to the number density of perturbers N/Ω. In the Markovian (impact) limit the collisions are assumed to be fast (relative to the line broadening). In this case it is convenient to rewrite $g(\tau)$ in the form[20]:

$$g(\tau) = g'(0)\,\tau + \int_0^\tau d\tau_1 (\tau - \tau_1) g''(\tau_1) \ , \tag{10}$$

where

$$g''(\tau) \equiv \frac{d^2 g}{d\tau^2} = \Omega \sum_{\alpha\beta} P(\alpha) |\langle\alpha|\beta\rangle|^2 \omega_{\beta\alpha}^2 \exp(i\omega_{\beta\alpha}\tau) \ , \tag{11}$$

and $g'(\tau) = dg/d\tau$.

The Markovian limit is obtained mathematically by assuming that $g(\tau)$ (on a coarse-grained time scale) is linear in τ, i.e.,[20,5,4]

$$\frac{N}{\Omega} g(\tau) \to \frac{N}{\Omega}\left[g'(0)\,\tau + \tau \int_0^\infty d\tau_1 g''(\tau_1)\right] \equiv (\Gamma + i\tilde{\Delta})\,\tau \ . \tag{12}$$

Upon substitution of Eq. (11) in Eq. (12) we get

$$\Gamma = N \mathrm{Re} \int_0^\infty d\tau \sum_{\alpha\beta} P(\alpha) |\langle\alpha|\beta\rangle|^2 \omega_{\beta\alpha}^2 \exp(i\omega_{\beta\alpha}\tau)$$

$$= \pi N \sum_{\alpha\beta} P(\alpha) |\langle\alpha|\beta\rangle|^2 \omega_{\beta\alpha}^2 \delta(\omega_{\beta\alpha}) \tag{13a}$$

and

$$\tilde{\Delta} = -i \frac{N}{\Omega} g'(0)$$

$$+ N \mathrm{Im} \int_0^\infty d\tau \sum_{\alpha\beta} P(\alpha) |\langle\alpha|\beta\rangle|^2 \omega_{\beta\alpha}^2 \exp(i\omega_{\beta\alpha}\tau) = 0 \ . \tag{13b}$$

The line shape in the Markovian limit is obtained by substitution of Eq. (12) with Eq. (13) in Eq. (6), which results in the Lorentzian line shape

$$I(\Delta) = \frac{2\Gamma}{\Delta^2 + \Gamma^2} \ , \tag{14}$$

where Γ is the dephasing width given by Eq. (13a).

It is clear from Eqs. (1), (2), and (6) that $G_a - G_b$ is the perturbation responsible for the line broadening. In fact, when $G_a = G_b$ we have

$$g(\tau) = 0 \tag{15}$$

and

$$I(\Delta) = 2\pi\delta(\Delta) \ . \tag{16}$$

It is therefore convenient to partition H [Eqs. (1) and (2)] as follows:

$$H = H_s + \sum_\nu H_\nu(Q_\nu) \ , \tag{17a}$$

$$H_\nu = H_0^B + \lambda V \ , \tag{17b}$$

where

$$H_0^B = \left[-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial Q_\nu^2} + G^+(Q_\nu)\right](|a\rangle\langle a| + |b\rangle\langle b|) \ , \tag{17c}$$

$$H_s = |a\rangle E_a \langle a| + |b\rangle E_b \langle b| \ , \tag{17d}$$

and

$$V = G^-(Q_\nu)(|a\rangle\langle a| - |b\rangle\langle b|) \ , \tag{17e}$$

where

$$G^+(Q_\nu) \equiv [G_a(Q_\nu) + G_b(Q_\nu)]/2 \tag{18a}$$

and

$$G^-(Q_\nu) \equiv [G_a(Q_\nu) - G_b(Q_\nu)]/2 \ . \tag{18b}$$

Here λ is a smallness parameter introduced for bookkeeping purposes and at the end we set $\lambda = 1$. Using this partitioning we note that Eq. (13a), which is the exact expression for the dephasing rate Γ, is infinite order in λ. This may be clearly seen by a perturbative expansion of $|\alpha\rangle$ in terms of $|\beta\rangle$ by using $2\lambda G^-$ as the perturbation. The common treatments of dephasing in liquids are all perturbative in λ.[11–16] In order to obtain useful nonperturbative expressions for Γ we shall make use of two alternative expressions. The first is the expression of Fano[3,5,21] obtained using tetradic scattering theory in Liouville space, i.e. (to lowest order in bath density),

$$\Gamma = -\mathrm{Im} N \sum_{\gamma\gamma'} \langle\langle {}^{\gamma'\gamma'}_{ab} | \mathcal{T}(\omega_{ab}) | {}^{\gamma\gamma}_{ab} \rangle\rangle P(\gamma) \ , \tag{19}$$

where $\mathcal{T}(\omega)$ is the tetradic T matrix

$$\mathcal{T}(\omega) = \mathcal{V} + \mathcal{V} \frac{1}{\omega - L_s - L_\nu} \mathcal{V} \ . \tag{20}$$

$\omega_{ab} = E_a - E_b$, and L_ν, L_s, and $\mathcal{V}$ are the tetradic operators (commutators) corresponding to H_ν, H_s, and V, respectively, i.e.,

$$L_\nu \equiv [H_\nu, \quad], \text{ etc.} \tag{21}$$

$|\gamma\rangle$ and $|\gamma'\rangle$ are the eigenstates of H_0^B and they are normalized in the same way as $|\alpha\rangle$ and $|\beta\rangle$ [Eq. (5)]. Also, $P(\gamma)$ is given by Eq. (9) with the change of indexes. The second form is obtained by writing Eq. (19) in an alternative form using the dyadic T matrix,[5,21] i.e.,

$$\Gamma = \pi N \sum_{\gamma\gamma'} P(\gamma) |\langle a\gamma' | T(E_a + E_\gamma) | a\gamma\rangle$$

$$- \langle b\gamma' | T(E_b + E_\gamma) | b\gamma\rangle|^2 \delta(\omega_{\gamma\gamma'}) \ , \tag{22}$$

where

$$T(E) = V + V \frac{1}{E - H_s - H_\nu} V \ . \tag{23}$$

Equations (22) and (19) are identical if calculated exactly. However, they may yield quite different results once approximations are made. This will be shown in the next section.

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III. COLLINEAR EVALUATION OF THE DEPHASING RATES

Assuming spherically symmetric interaction potentials G_a and G_b, we have[4]

$$|\gamma\rangle = |\epsilon\rangle|lm\rangle \ ,$$

$$\langle r\theta\phi|\gamma\rangle = \frac{1}{r}\psi_{\epsilon l}(r)\, Y^{lm}(\theta,\phi) \ , \tag{24}$$

where $r\theta\phi$ are the spherical coordinates in our sphere of volume Ω, ϵ is the relative translational energy, and l, m are the angular momentum quantum numbers.

The rigorous evaluation of Γ thus involves a tedious calculation[4] and

$$\sum_{\gamma} \to \int d\epsilon\rho(\epsilon)\sum_{l,m} \ . \tag{25}$$

A simple colinear approximation to Eq. (19) or (22) may be obtained by taking only the $l=0$ term and replacing $\sum_{lm}$ by an effective cross section. For the sake of convenience we further adopt a δ-function normalization for our wave functions (instead of a box normalization), i.e.,

$$\langle\gamma|\gamma'\rangle = \delta(\epsilon-\epsilon')\,\delta_{ll'}\,\delta_{mm'} \tag{26a}$$

and

$$\rho(\epsilon) = 1 \ . \tag{26b}$$

We thus have

$$\Gamma = f\chi \ , \tag{27}$$

where [using Eq. (19)]

$$\chi \equiv -2\pi\,\mathrm{Im}\int d\epsilon\, P(\epsilon)\langle\langle {}^{\epsilon\epsilon}_{ab}|\mathcal{T}(\omega_{ab})|{}^{\epsilon\epsilon}_{ab}\rangle\rangle$$

$$\equiv -2\pi\,\mathrm{Im}\langle\mathcal{T}^{\epsilon\epsilon,\epsilon\epsilon}_{ab,ab}(\omega_{ab})\rangle \ , \tag{28}$$

or equivalently, using Eq. (22),

$$\chi = 2\pi^2\int d\epsilon\, P(\epsilon)\,|\langle a\epsilon|T(E_a+\epsilon)|a\epsilon\rangle - \langle b\epsilon|T(E_b+\epsilon)|b\epsilon\rangle|^2$$

$$\equiv 2\pi^2\langle|T^{\epsilon\epsilon}_{aa}(E_a+\epsilon) - T^{\epsilon\epsilon}_{bb}(E_b+\epsilon)|^2\rangle \ , \tag{29}$$

and the averaging $\langle\cdots\rangle$ is defined by

$$\langle A_\epsilon\rangle \equiv \frac{1}{kT}\int d\epsilon\,\exp(-\epsilon/kT)A_\epsilon \ . \tag{30}$$

Here χ is dimensionless and f has units of frequency. Since f is proportional to the bath number density N/Ω and to the effective cross section for collision, it may be interpreted as an effective collision frequency and χ is the dephasing effect of a single collision. We are now in a position to evaluate χ. To that purpose we use the following approximations.

A. FOBA (first order Born approximation)

This is the perturbative approach commonly used for dephasing in liquids. We set $T \cong V$. Using Eq. (17e), we have

$$\langle a\epsilon|V|a\epsilon\rangle = -\langle b\epsilon|V|b\epsilon\rangle = \langle\epsilon|G^-|\epsilon\rangle \equiv G_\epsilon \ , \tag{31}$$

so that we have

$$\chi^{(\mathrm{FOBA})} = 8\pi^2\langle G_\epsilon^2\rangle \ . \tag{32}$$

B. FODK (first order dyadic K matrix)

The dyadic T matrix may be written in the form[22]

$$T(E) = K - i\pi K\,\delta(E-H_0)\,T \ , \tag{33}$$

where K is the K matrix (reaction operator) given by

$$K = V + V\left(PP\,\frac{1}{E-H_0}\right)K \ . \tag{34}$$

PP is the principal part, and we write $H_0 = H_s + H_0^B$. The equivalence of Eqs. (33) and (34) to Eq. (23) may be easily verified by a simple substitution.

The FODK is given by taking Eq. (34) to first order in V, i.e.,

$$K \cong V \ , \tag{35}$$

which results in

$$T(E) = V - i\pi V\delta(E-H_0)T \ . \tag{36}$$

The required matrix elements are

$$T^{\epsilon\epsilon}_{aa}(E_a+\epsilon) = \langle a\epsilon|V|a\epsilon\rangle - i\pi\langle a\epsilon|V|a\epsilon\rangle\, T^{\epsilon\epsilon}_{aa}(E_a+\epsilon) \tag{37}$$

and similarly for $T^{\epsilon\epsilon}_{bb}(E_b+\epsilon)$. Solving Eq. (37) for $T^{\epsilon\epsilon}_{aa}$ and substituting in Eq. (29), we get

$$\chi^{(\mathrm{FODK})} = 8\pi^2\left\langle\frac{G_\epsilon^2}{(1+\pi^2G_\epsilon^2)^2}\right\rangle \ . \tag{38}$$

C. FOTK (first order tetradic K matrix)

We may write equations analogous to Eqs. (33) and (34) by replacing V, T, H_0, and K by their tetradic analogs[3]

$$\mathcal{T} = \mathcal{K} - i\pi\mathcal{K}\delta(\omega-L_0)\mathcal{T} \ , \tag{39}$$

$$\mathcal{K} = \mathcal{V} + \mathcal{V}\left(PP\,\frac{1}{\omega-L_0}\right)\mathcal{K} \ . \tag{40}$$

The first order tetradic $\mathcal{K}$ is

$$\mathcal{K} \cong \mathcal{V} \ , \tag{41}$$

which results in

$$\mathcal{T}(\omega) = \mathcal{V} - i\pi\mathcal{V}\delta(\omega-L_0)\mathcal{T}(\omega) \ . \tag{42}$$

We need the matrix element

$$\mathcal{T}^{\epsilon\epsilon\epsilon\epsilon}_{abab}(\omega_{ab}) = \mathcal{V}^{\epsilon\epsilon\epsilon\epsilon}_{abab} - i\pi\mathcal{V}^{\epsilon\epsilon\epsilon\epsilon}_{abab}\,\mathcal{T}^{\epsilon\epsilon\epsilon\epsilon}_{abab}(\omega_{ab}) \ , \tag{43}$$

where

$$\mathcal{V}^{\epsilon\epsilon\epsilon\epsilon}_{abab} = \langle a\epsilon|V|a\epsilon\rangle - \langle b\epsilon|V|b\epsilon\rangle = 2G_\epsilon \ . \tag{44}$$

[Nondiagonal matrix elements of the type $\mathcal{T}^{\epsilon\epsilon\epsilon'\epsilon'}_{abab}$ $(\epsilon\neq\epsilon')$ are zero.] Solving Eq. (43) for $\mathcal{T}_{ab,ab}$ and substitution in Eq. (28) finally results in

$$\chi^{(\mathrm{FOTK})} = 8\pi^2\left\langle\frac{G_\epsilon^2}{1+4\pi^2G_\epsilon^2}\right\rangle \ . \tag{45}$$

D. FOES (first order exponential S matrix)

We write the ordinary S matrix

$$S = 1 - 2\pi i\delta(E-H_0)T \tag{46}$$

as[22,23]

$$S = \exp(iA) \ . \tag{47}$$

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Upon expansion of Eqs. (46) and (47) in V and comparing term by term, we get

$$S = \exp[-2\pi i\delta(E - H_0)V + 0(V^2)] \ . \tag{48}$$

The FOES is

$$S = \exp[-2\pi i\delta(E - H_0)V] \ . \tag{49}$$

[The tetradic analog of Eq. (49) will yield the same result.] Upon taking matrix elements of Eq. (49), we get our approximation for χ:

$$\langle a\epsilon|S(E_a+\epsilon)|a\epsilon\rangle = \exp(-2\pi i G_\epsilon) \ ,$$

$$\langle b\epsilon|S(E_b+\epsilon)|b\epsilon\rangle = \exp(2\pi i G_\epsilon) \ ,$$

and

$$\chi = \frac{1}{2}\int d\epsilon\, P(\epsilon)\left|\langle a\epsilon|S(E_a+\epsilon)|a\epsilon\rangle - \langle b\epsilon|S(E_b+\epsilon)|b\epsilon\rangle\right|^2 \ , \tag{50}$$

i.e.,

$$\chi^{(\mathrm{FOES})} = 2\langle \sin^2(2\pi G_\epsilon)\rangle \ . \tag{51}$$

Equations (38), (45), and (51) provide three nonperturbative expressions for dephasing rates. In the perturbative limit $G_\epsilon \ll 1$ they all reduce to the FOBA result [Eq. (32)], but otherwise they are different. The difference arises since these approximations are the results of a partial resummation of the perturbative series of Γ with respect to λ. Each resummation includes some of the terms in the series to infinite order. The evaluation of the dephasing rate thus reduces to the calculation of the matrix element G_ϵ and performing the thermal average over ϵ. In the theories of dephasing in liquids it is common also to use classical mechanics.[6,11,12] The classical limit of G_ϵ may be easily obtained using the WKB approximation for the wave function

$$\langle Q|\epsilon\rangle = \sqrt{\frac{2M}{\pi k_\epsilon(Q)}}\cos\left[\int_{Q_\epsilon}^{Q} k_\epsilon(Q')\,dQ' + \frac{\pi}{4}\right] , \tag{52}$$

where

$$k_\epsilon = 2M[\epsilon - G^+(Q)]^{1/2} \tag{53}$$

is the momentum and Q_ϵ is the classical turning point.

Substitution of Eq. (52) in Eq. (31) results in the semiclassical matrix element:

$$G_\epsilon = \frac{M}{\pi}\int_{Q_\epsilon}^{\infty} dQ\,\frac{G^-(Q)}{k_\epsilon}\left\{1 + \cos\left[2\int_{Q_\epsilon}^{Q} k_\epsilon(Q')\,dQ' + \frac{\pi}{4}\right]\right\} . \tag{54}$$

In the classical limit we neglect the oscillatory cosine term in Eq. (54) and get the classical expression for G_ϵ:

$$G_\epsilon = \frac{M}{\pi}\int_{Q_\epsilon}^{\infty} dQ\,\frac{G^-(Q)}{k_\epsilon(Q)} . \tag{55}$$

Upon defining the new time variable

$$t = M\int_{Q_\epsilon}^{Q} dQ'\,\frac{1}{k_\epsilon(Q')} , \tag{56}$$

we get

$$G_\epsilon = \frac{1}{\pi}\int_0^\infty dt\, G^-(Q(t)) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, G^-(t) \ , \tag{57}$$

where $t = 0$ is the time at the turning point and $G^-(t)$ is the classical perturbation. We then have

$$G_\epsilon^2 = \frac{1}{2\pi^2}\int_0^\infty d\tau\int_{-\infty}^{\infty} dt\, G^-(t)\,G^-(t+\tau) \ . \tag{58}$$

We have thus shown the equivalence of G_ϵ^2 to a classical correlation function.

IV. APPLICATION TO VIBRATIONAL DEPHASING—THE EXPONENTIAL REPULSIVE POTENTIAL

We shall now apply the results of Sec. III to the problem of vibrational dephasing. To that aim we assume an exponential repulsive interaction between a harmonic oscillator (the system) and an atom (the collider)[11-13]

$$V(Q,R) = W\exp(\gamma_B R/L - Q/L) \ . \tag{59}$$

Here R is the oscillator coordinate and Q is the distance between the perturber C and the center of mass of the AB oscillator. W and L are parameters characterizing the interaction and

$$\gamma_B = \frac{m_A}{m_A + m_B} . \tag{60}$$

In Eq. (59) we assume that the perturber approaches the B side of the AB oscillator. For the other approach we should replace γ_B by $\gamma_A = 1 - \gamma_B$. R may be expressed in terms of the oscillator creation and annihilation operators as

$$R = \frac{1}{\sqrt{2m\omega}}(a + a^*) \ , \tag{61}$$

where

$$m = \frac{m_A m_B}{m_A + m_B} \tag{62}$$

is the reduced mass of the oscillator. Assuming that the two relevant states of the oscillator for the line shape are $|a\rangle = |0\rangle$ and $|b\rangle = |1\rangle$, then $\omega = \omega_{ba}$ and we have

$$G_i(Q) = W\langle i|\exp(\gamma_B R/L)|i\rangle\exp(-Q/L) \ , \quad i = 0, 1 \ . \tag{63}$$

To lowest order in $\gamma_B/L\sqrt{2m\omega}$ we thus get

$$G_i(Q) = W\left[1 + \frac{1}{2}\frac{\gamma_B^2}{(L\sqrt{2m\omega})^2}(\delta_{i,0} + 3\delta_{i,1})\right]\cdot\exp(-Q/L) \ . \tag{64}$$

Substitution of Eq. (64) in Eq. (18) results in

$$G^+(Q) = W\left[1 + \frac{\gamma_B^2}{(L\sqrt{2m\omega})^2}\right]\exp(-Q/L) \ , \tag{65}$$

$$G^-(Q) = -\frac{1}{2}W\frac{\gamma_B^2}{(L\sqrt{2m\omega})^2}\exp(-Q/L) \ .$$

The eigenstates of H_0^B as well as the matrix elements of $\exp(-Q/L)$ were solved by Jackson and Mott,[24] i.e.,

$$\langle\epsilon|G^-|\epsilon'\rangle = -\frac{1}{2}\left(\frac{\gamma_B}{L\sqrt{2m\omega}}\right)^2 ML^2 S(\epsilon,\epsilon') \ , \tag{66}$$

$$S(\epsilon,\epsilon') = \frac{[\sinh(2\pi L\sqrt{2M\epsilon'})\sinh(2\pi L\sqrt{2M\epsilon})]^{1/2}}{\sinh[\pi L(\sqrt{2M\epsilon} + \sqrt{2M\epsilon'})]} \times \frac{\epsilon' - \epsilon}{\sinh[\pi L(\sqrt{2M\epsilon'} - \sqrt{2M\epsilon})]} \ . \tag{67}$$

M, the reduced mass of the colliding pair, is

$$M = \frac{(m_A + m_B)m_C}{m_A + m_B + m_C} . \tag{68}$$

$S(\epsilon,\epsilon')$ is required for the evaluation of the general line

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shape function. In the Markovian limit we need only the diagonal elements of G^-, i.e.,

$$G_\epsilon = \langle \epsilon | G^- | \epsilon \rangle = -\frac{1}{2\pi}\left(\frac{\gamma_B}{L\sqrt{2m\omega}}\right)^2 \sqrt{2\epsilon M L^2} \,. \tag{69}$$

The FOBA for χ may now be evaluated utilizing Eqs. (32), (30), and (69) resulting in[13]

$$\chi^{(\mathrm{FOBA})} = \frac{M\gamma_B^4}{L^2 m^2 \omega^2}\, kT \,. \tag{70}$$

It is interesting to note that the quantum result (70) is identical in this case to the classical result obtained by substitution of

$$G^-(t) = -\tfrac{1}{2}\epsilon\left(\frac{\gamma_B}{L\sqrt{2m\omega}}\right)^2 \exp[-Q(t)/L]$$

$$= -\tfrac{1}{2}\epsilon\left(\frac{\gamma_B}{L\sqrt{2m\omega}}\right)^2 \operatorname{sech}^2 \sqrt{\frac{\epsilon}{2ML^2}}\, t \tag{71}$$

in Eq. (58) and performing the integration. We see that, for this particular choice of the potential [Eq. (59)], the fully quantum and the semiclassical descriptions of the colinear binary collision give to second order in V, the same pure dephasing rate.

In order to illustrate the significance of our nonperturbative expressions for the dimensionless dephasing rate χ we have performed some numerical calculations. We chose parameters corresponding to several vibrations of cyclohexane which were studied experimentally recently by Jonas and co-workers[8] using spontaneous Raman techniques. We have also calculated χ for the CH stretch of trichloroethane CH_3CCl_3. The homogeneous dephasing rate for this molecule was studied by Laubereau and Kaiser using picosecond coherent Raman techniques.[6] $\chi^{(i)}$ for our four different approximations i = FOBA, FODK, FOTK, and FOES was evaluated using Eqs. (32), (38), (45), and (51), respectively, and G_ϵ is given by Eq. (69) (exponential repulsive interaction). The reduced mass of the colliding pair M is taken to be one half of the molecular mass. γ_B is replaced by $\gamma_B = \gamma\cos\theta$, where θ is the angle between the "axis" of the oscillator corresponding to the normal mode considered and the incident direction of the collider. We then average the resulting χ function over all directions of incident perturbers, i.e.,

$$\chi = \int_0^{\pi/2} d\theta \sin\theta\, \chi^{(i)} \,. \tag{72}$$

Figures 1(a), 1(b), and 1(c) present our calculations for cyclohexane which correspond to three typical normal modes, namely, a CH stretch ($\omega = 2938$ cm^{-1}), a CH_2 bending ($\omega = 1465$ cm^{-1}), and a C–C stretch ($\omega = 802$ cm^{-1}). L, the range of interaction, is given a reasonable value of 0.20 Å.[25] Values of the force constants $k_F = m\omega^2$ are taken from Ref. 26.

For trichloroethane we have chosen the high frequency stretching vibration CH ($\omega = 2939$ cm^{-1}) studied experimentally by Laubereau and Kaiser. We present three sets of curves for three values of the range of interaction $L = 0.16$, 0.20, and 0.24 Å [Figs. 2(a), 2(b), and 2(c), respectively].

The effect of the nonperturbative corrections of the

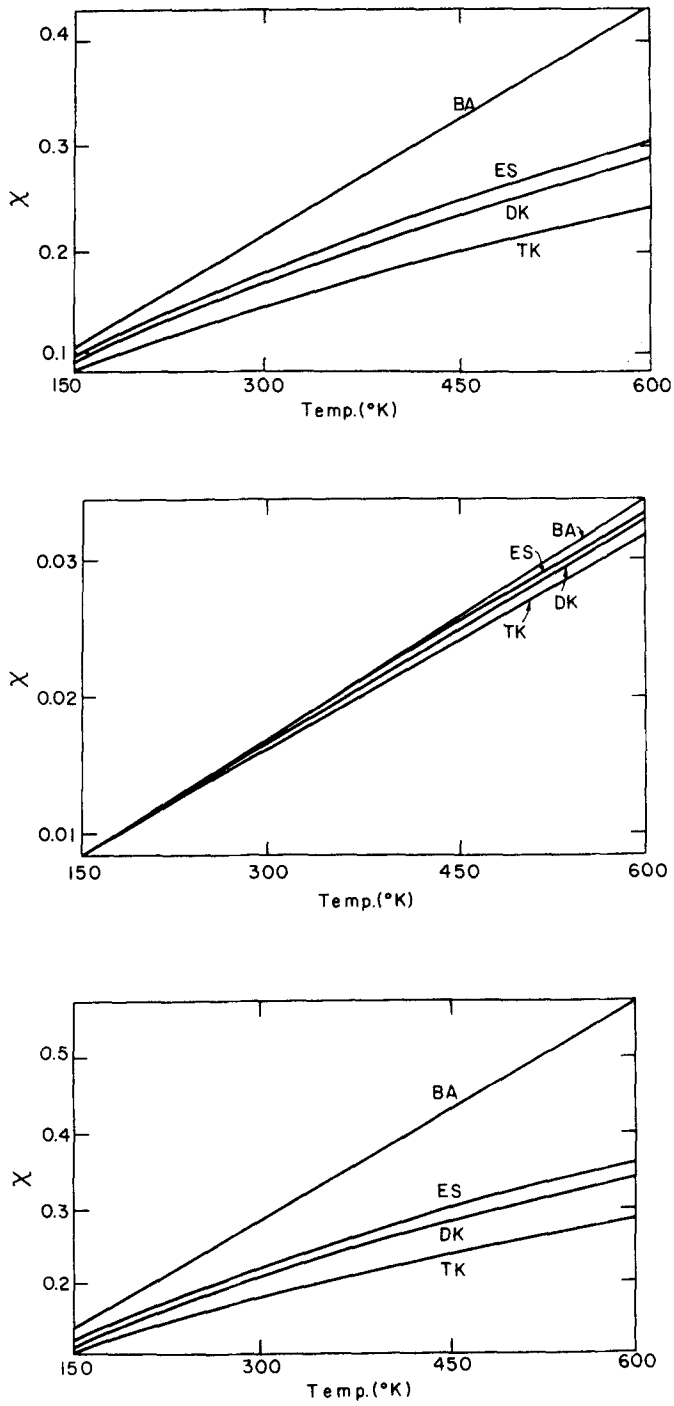

FIG. 1. The dimensionless dephasing rate χ as a function of temperature for three normal modes of cyclohexane. Each figure contains the results of the FOBA, FODK, FOTK, and FOES approximations denoted by BA, DK, TK, and ES, respectively. $L = 0.20$ Å, $M = 42$ g. (a) CH stretch, $\omega = 2938$ cm^{-1}, $k_F = 4.554\times10^5$ dyne/cm, $\gamma = 1$; (b) CC stretch, $\omega = 802$ cm^{-1}, $k_F = 4.38\times10^5$ dyne/cm, $\gamma = 1$; (c) CH_2 bending, $\omega = 1465$ cm^{-1}, $k_F = 0.49\times10^5$ dyne/cm, $\gamma = 0.5$.

FODK, FOTK, and FOES increases as G_ϵ [Eq. (69)] increases. We thus expect it to increase with M, kT, and γ and to decrease with L and $\sqrt{m\omega}$. This is clearly demonstrated in Figs. 1 and 2, which show corrections of about a factor of 2. We should also bear in mind that

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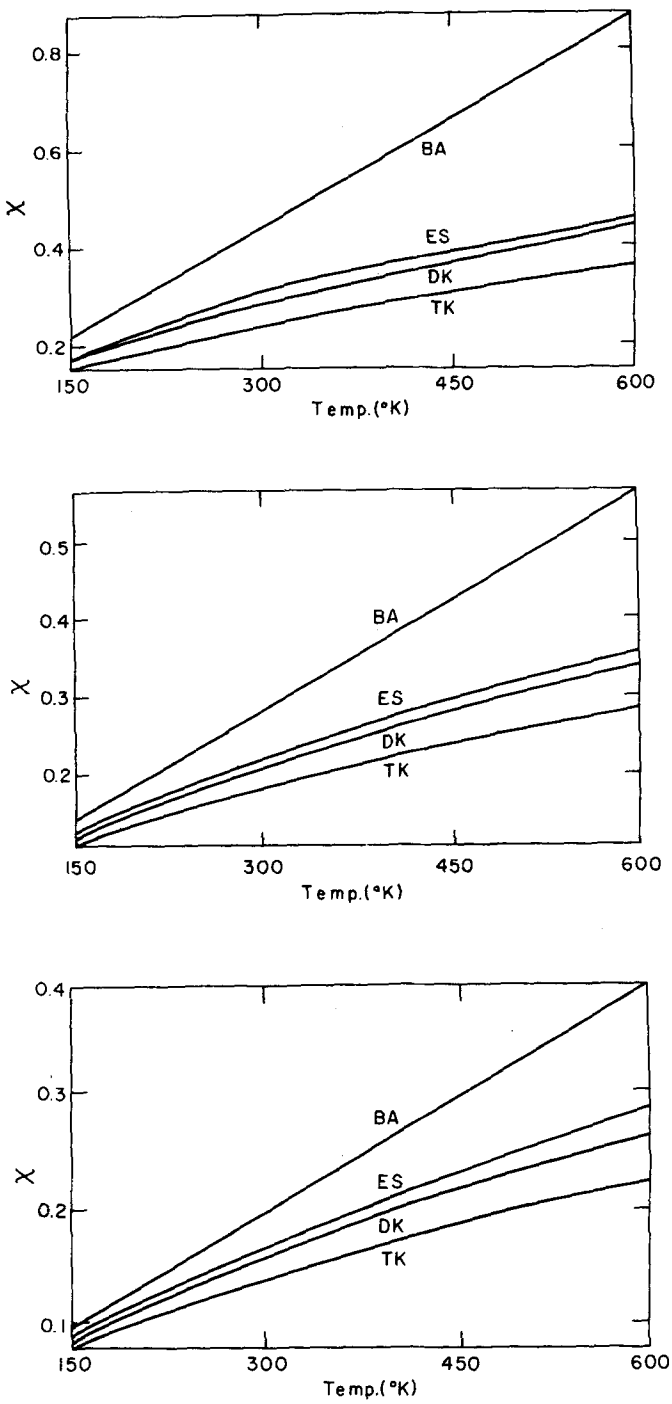

FIG. 2. The dimensionless dephasing rate χ as a function of temperature for the CH stretch of CH_3CCl_3. $\omega = 2939\ cm^{-1}$, $k_F = 5.0\times10^5$ dyne/cm, $M = 66.75$ g, $\gamma = 1$. (a) $L = 0.16$ Å; (b) $L = 0.20$ Å; (c) $L = 0.24$ Å.

the nonperturbative expressions will exhibit a different dependence on the various parameters such as mass or temperature compared to the FOBA expression. Recent deviations of experimental results from the predictions of Eq. (70) regarding the mass dependence of χ were attributed by Harris and co-workers[9] to the breakdown of the binary collision approximation. The present expressions which are within the binary collision approximation may account for these discrepancies since they exhibit a dependence on M which is different from Eq. (70).

ACKNOWLEDGMENTS

The support of the National Science Foundation and the Educational Foundation of Research Corporation is gratefully acknowledged.

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