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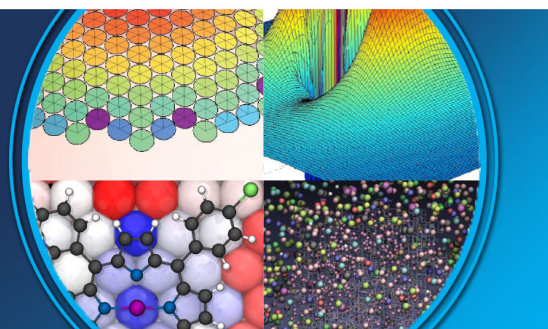
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**PERSPECTIVES**



## Dephasing of individual rotational states in liquids

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We continue our previous examination of the fate of individual rotational quantum states in liquids by an analysis of the rotational Raman spectrum of solutions of H<sub>2</sub> and D<sub>2</sub> in Ar(*l*). Rewriting the conventional Kubo treatment allows us to show how the character of the spectrum is an immediate consequence of the rotational friction felt by the solutes. On evaluating that friction via classical molecular dynamics we find that the spectra should consist of well-resolved, homogeneously broadened lines, reflecting the picosecond-long dephasing times. We find, in particular, that the rotational states in H<sub>2</sub> should relax predominantly by pure dephasing, whereas D<sub>2</sub>, with its smaller rotational quanta, should exhibit significant energy relaxation as well. The linewidths predicted for H<sub>2</sub> are nicely in accord with those computed by more involved nonadiabatic, mixed quantum-classical simulations. © 2000 American Institute of Physics. [S0021-9606(00)51448-2]

### I. INTRODUCTION

That nearly free-rotor rotational quantum states can exist in ordinary classical liquids, at least in some form, is clear. Not only do a number of the dissolved hydrides exhibit discrete rotational lines in their spectra, the lines often occur at frequencies remarkably close to those of their gas-phase counterparts.<sup>1–11</sup> The rotational Raman spectra of H<sub>2</sub> and D<sub>2</sub> in water,<sup>5,7,9</sup> and of H<sub>2</sub> in supercritical CO<sub>2</sub>,<sup>10</sup> make for some of the most intriguing examples, but HCl, DCl, and HF solutions in SF<sub>6</sub><sup>1–3</sup> also display much the same behavior.

The question we want to pose is the following: what liquid-state processes account for the relaxation of these rotational quantum states? In more concrete terms, we would like to understand how the rotational Raman lines end up being broadened by a liquid environment so much more than they end up being shifted. The prediction of various kinds of pure rotational spectra in liquids is, of course, a time-honored problem with considerable attention already having been devoted to both far-infrared and rotational Raman spectra.<sup>7–9,12–21</sup> In some cases these calculations are simply direct simulations of the appropriate linear-response correlation functions carried out with varying levels of sophistication in how the quantum and classical parts of the problem are mixed.<sup>7–9,12,13</sup> Other calculations, however, attempt to understand the ingredients in the spectra through formal line shape theories.<sup>7,14–21</sup> Such efforts can be quite informative in allowing us to discriminate between homogeneous (dynamical) and inhomogeneous (static) sources of line broadening<sup>22–25</sup> and in helping us partition the former into energy and phase relaxation components.<sup>23–25</sup> At the heart of all of these kinds of calculations, though, is a connection between the well-established formal theories and the key microscopic features of the liquid's dynamics—and it is here where much of the previous theoretical work on the spectroscopy of hydrides has had difficulties.

Some of the interpretation of the line broadening has been in terms of formal stochastic or quasiharmonic models,

approaches with only tenuous connections with the molecular details of liquid dynamics.<sup>17–21</sup> Other, more molecularly oriented efforts have focused on the liquid's density autocorrelation functions<sup>4,14,15</sup>—an approach that is correct but largely tautological. *All* of the liquid's motion leads to density fluctuations; the interesting question is which are the key fluctuations in the immediate vicinity of the solute. In fact, the literature of this field, viewed quite generally, is replete with references to the generic power spectra of liquids,<sup>16,26</sup> but there are few pointers as to which of the many different kinds of power spectra are best at capturing the essential solvent dynamics involved in molecular reorientation.

What we have emphasized in our own recent work<sup>27–29</sup> is that the critical quantity necessary to understand rotational dynamics in liquids is the *rotational friction*, which for a linear solute is given quite accurately by

$$\eta(t) = \langle \vec{N}(t) \cdot \vec{N}(0) \rangle / (2k_B T), \quad (1.1)$$

with  $\vec{N}$  the torque the solute would feel if it were held at a fixed orientation,  $T$  the temperature, and  $k_B$  Boltzmann's constant, and where the brackets denote an equilibrium average over all of the other degrees of freedom of the solution besides the orientation. Our first efforts showed that for the ordinary classical rotation that most molecules undergo in solution, this function was indeed the relevant friction in the classical sense of being the time-delayed drag on the angular velocity.<sup>27</sup> Instantaneous-normal-mode calculations of this  $\eta(t)$  then allowed us to uncover the detailed molecular origins of this kind of, fairly standard, rotational relaxation.<sup>27,28</sup> Subsequent work showed, however, that this same friction was also the key ingredient in understanding the energy relaxation of quantized rotational states in liquids.<sup>29</sup> The rates of energy relaxation turned out to obey a rotational Landau–Teller relation: the transition rate between rotational states in a liquid was shown to be proportional to the value of (the real part of) the classical frequency-dependent friction,

$$\hat{\eta}^R(\omega) = \int_0^\infty dt \cos \omega t \eta(t), \quad (1.2)$$

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evaluated at the frequency of the rotational transition. This particular power spectrum of the liquid—and therefore the limited band of frequencies available to the solution—was thus seen to be one of the main ingredients in determining the lifetime of rotational quantum states.<sup>29</sup>

Still missing from our analysis, though, is any measure of the time period over which quantized rotational motion should retain its phase memory—its pure dephasing time.<sup>30</sup> Since both energy and phase relaxation can, in principle, contribute to spectral line shapes,<sup>23–25</sup> we need to address the latter before we can begin to understand the actual spectra of hydrides. What we shall do in this paper is to show how a conventional Kubo treatment<sup>22,30–32</sup> of rotational Raman line shapes brings in this same classical rotational friction we have been discussing. The fact that pure dephasing ends up depending on the zero-frequency friction  $\hat{\eta}^R(0)$  (much as it does in vibrational spectroscopy)<sup>33–36</sup> means that our instantaneous-normal-mode methods cannot be used here,<sup>27–29,37</sup> but direct evaluation by classical molecular dynamics simulation is simple enough. With the aid of such simulations, we show how this formalism can be used to predict and study the spectra of H<sub>2</sub> and D<sub>2</sub> dissolved in Ar<sub>(*l*)</sub>.

Since there have been few rotational Raman experiments published on these systems to date,<sup>38</sup> the most pertinent comparisons for this work certainly come from the Xiao and Coker seminal mixed quantum mechanical and classical simulation of the rotational Raman spectra of H<sub>2</sub> in Ar<sub>(*l*)</sub>.<sup>8</sup> While those authors neglected the possibility of transitions between distinct total angular momentum states *l* (an issue we shall return to later), they nonetheless successfully simulated the interconversion among the different angular momentum components *m* by viewing the process as a sequence of nonadiabatic transitions induced by the liquid. We will want to see if we find qualitatively, or even quantitatively, similar spectra and, in particular, if we find the same kind of nonmonotonic dependence of linewidth on *l* that Xiao and Coker do. More generally, we shall want to consider the extent to which such elaborate mixed quantum-classical simulations are really necessary to understand the behavior of a quantal solute in a classical liquid.<sup>39</sup>

The remainder of this paper will be organized as follows: In Sec. II we will summarize the molecular-level Kubo theory of rotational Raman spectroscopy and show how this theory can be recast into a form in which the dynamics of the liquid enters only through the rotational friction. We then turn to the specific cases of H<sub>2</sub> and D<sub>2</sub> in Ar<sub>(*l*)</sub>. Our choices for potentials and calculational approaches are detailed in Sec. III, and our numerical results are presented in Sec. IV. We conclude in Sec. V with a brief discussion of our findings.

## II. ROTATIONAL RAMAN SPECTROSCOPY AND ROTATIONAL FRICTION

### A. Microscopic Kubo theory

Within linear response theory, the rotational Raman spectrum of a molecule in a liquid can be written as the Fourier transform of the anisotropic polarizability autocorrelation function,<sup>7,13</sup>

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} C(t), \quad (2.1)$$

$$C(t) = \sum_{q=-2}^2 \langle \alpha_q(0) \alpha_q^\dagger(t) \rangle, \quad (2.2)$$

with  $\alpha_q$  the *q*th component of the second rank spherical polarizability tensor and  $\alpha_q^\dagger(t) = (-1)^q \alpha_{-q}(t)$  understood to be the adjoint of the polarizability operator in the Heisenberg representation,

$$\alpha_q^\dagger(t) = e^{itH/\hbar} \alpha_q^\dagger e^{-itH/\hbar} \quad (2.3)$$

(*H* being the solution's Hamiltonian).

For the weakly coupled linear solute such as H<sub>2</sub>, it is convenient to separate the anisotropic part of the solute–solvent interaction *V* from the rest of the Hamiltonian *H*<sub>0</sub>,

$$H = H_0 + V(\theta, \phi, \mathbf{R}), \quad (2.4a)$$

$$H_0 = H_{\text{rot}}(\dot{\theta}, \dot{\phi}, \theta, \phi) + H_B(\dot{\mathbf{R}}, \mathbf{R}), \quad (2.4b)$$

with  $\theta$  and  $\phi$  defining the orientation of the solute in the laboratory frame and the remaining coordinates, the center-of-mass coordinate of the solute  $\mathbf{r}_0$  and the coordinates of the *N* solvent molecules,  $\mathbf{R} = (\mathbf{r}_0, \dots, \mathbf{r}_N)$  comprising the bath degrees of freedom. Within this framework, the uncoupled reference Hamiltonian *H*<sub>0</sub> includes both *H*<sub>rot</sub>, the rotational Hamiltonian of the isolated solute, and *H*<sub>B</sub>, the reference part of the bath Hamiltonian. Note that the latter contains not only the solvent–solvent interaction but also the isotropic part of the solute–solvent potential.

If the rotor–bath coupling is sufficiently weak (as it is here),<sup>29</sup> it makes sense to work in a *Y*<sub>*lm*</sub> basis, the basis of eigenstates of *H*<sub>rot</sub>, which makes it possible to divide the spectrum into contributions from each *l*→*l'* transition

$$C(t) = \sum_{l,l'} C_{ll'}(t), \quad (2.5)$$

$$C_{ll'}(t) = \frac{P_l}{2l+1} \sum_{q=-2}^2 \sum_{m=-l}^l \sum_{m'=-l'}^{l'} \langle \langle lm | \alpha_q(0) | l'm' \rangle \rangle \times \langle \langle l'm' | \alpha_q^\dagger(t) | lm \rangle \rangle_B, \quad (2.6)$$

$$I_{ll'}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} C_{ll'}(t), \quad I(\omega) = \sum_{l,l'} I_{ll'}(\omega), \quad (2.7)$$

where the  $\langle \rangle_B$  brackets denote an equilibrium average over the bath degrees of freedom and *P*<sub>*l*</sub> is the equilibrium population of rotor states with the total angular momentum *l*.<sup>40,41</sup>

We can now take advantage of some standard operator manipulations.<sup>22,30,32</sup> By writing the anisotropic potential in the interaction representation

$$\bar{V}(t) = e^{-itH_0/\hbar} V e^{itH_0/\hbar}, \quad (2.8)$$

and introducing the notation that for any operators *A* and *B*

$$A^x B = [A, B],$$

we can express the time-dependent polarizability formally as

$$\alpha_q^+(t) = e^{itH_0/\hbar} \exp_+ \left( \frac{i}{\hbar} \int_0^t d\tau \bar{V}(\tau)^x \right) \alpha_q^\dagger e^{-itH_0/\hbar}, \quad (2.9)$$

where the notation  $\exp_+$  refers to a time ordered exponential.<sup>22,30</sup> But Eq. (2.9) means that the polarizability autocorrelation function, Eq. (2.6), can be rewritten as a product of a sinusoidal term oscillating at the frequency of the isolated-molecule transition

$$\Omega_{ll'} = (E_l - E_{l'})/\hbar, \quad (2.10)$$

and an average liquid-state modulation factor

$$C_{ll'}(t) = C_{ll'}(0) e^{-i\Omega_{ll'}t} \left\langle \exp_+ \left( \frac{i}{\hbar} \int_0^t d\tau \bar{V}(\tau)^x \right) \right\rangle_{ll'}, \quad (2.11)$$

with the brackets here defined so that for any operator  $X$ :

$$\langle X \rangle_{ll'} = \frac{\sum_q \sum_{m,m'} \langle \langle lm | \alpha_q | l'm' \rangle \langle l'm' | X \alpha_q^\dagger | lm \rangle \rangle_B}{\sum_q \sum_{m,m'} \langle \langle lm | \alpha_q | l'm' \rangle \langle l'm' | \alpha_q^\dagger | lm \rangle \rangle_B}.$$

Equation (2.11) is in precisely the form appropriate for a standard Kubo expansion.<sup>22,30,32</sup> Since in an isotropic liquid the first-order term will vanish by symmetry, we can write, through leading order in the fluctuations of the coupling,

$$C_{ll'}(t) = C_{ll'}(0) e^{-i\Omega_{ll'}t} \times \exp \left( -\frac{1}{\hbar^2} \int_0^t d\tau \int_0^\tau d\tau' \langle \bar{V}(\tau)^x \bar{V}(\tau')^x \rangle_{ll'} \right). \quad (2.12)$$

Thus, the basic structure of the polarizability autocorrelation function is

$$C_{ll'}(t) = C_{ll'}(0) e^{-i\Omega_{ll'}t} \exp[-g_{ll'}(t)], \quad (2.13a)$$

$$g_{ll'}(t) = \int_0^t d\tau \int_0^\tau d\tau' G_{ll'}(\tau, \tau'), \quad (2.13b)$$

with the liquid dynamics embodied in the second cumulant,

$$\hbar^2 G_{ll'}(\tau, \tau') \equiv \langle \bar{V}(\tau)^x \bar{V}(\tau')^x \rangle_{ll'}. \quad (2.14)$$

We will proceed shortly with the explicit evaluation of the  $G_{ll'}$  cumulant, but it is clear what kind of terms will result. The cumulant will have both real and imaginary components, with the real (dephasing) terms leading to damping and the imaginary (oscillatory) terms contributing to frequency shifts. Moreover, each of these components will have both inelastic contributions, involving net energy transfer with the liquid, and energy-conserving, elastic, contributions. More specifically, we find that

$$g_{ll'}(t) = \int_0^t d\tau \frac{1}{T_2^{ll'}(\tau)} - i \int_0^t d\tau \Delta_{ll'}(\tau), \quad (2.15)$$

with the elastic and inelastic portions of the dephasing producing the pure-dephasing ( $T_2^*$ ) and population relaxation ( $T_1$ ) contributions, respectively,<sup>23–25</sup>

$$\frac{1}{T_2^{ll'}(t)} = \frac{1}{T_2^{*ll'}(t)} + \frac{1}{2T_1^{ll'}(t)}. \quad (2.16)$$

In much the same way, there will be elastic ( $\Delta_2^{*ll'}$ ) and inelastic ( $\Delta_1^{ll'}$ ) contributions to the frequency shift, which we can write as

$$\Delta_{ll'}(t) = \Delta_2^{*ll'}(t) + \frac{1}{2} \Delta_1^{ll'}(t). \quad (2.17)$$

Let us turn now to the molecular origins of each of these terms.

## B. The connection with rotational friction

Our basic approach to thinking about the rotational friction within the kind of weak coupling situation presented by the hydrides will be the same as we used previously in our treatment of rotational energy relaxation.<sup>29</sup> Unlike the strongly coupled isotropic portion of the solute–solvent interaction, we can safely expand the *anisotropic* part of the potential in orders of the anisotropy,

$$V(\theta, \phi, \mathbf{R}) = \sum_{J=1}^{\infty} \sum_{K=-J}^J A_{JK}(\mathbf{R}) Y_{JK}(\theta, \phi), \quad (2.18)$$

$$A_{JK}(\mathbf{R}) = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta V(\theta, \phi, \mathbf{R}) Y_{JK}^*(\theta, \phi),$$

meaning that the crucial quantities will be the correlation functions of the expansion coefficients,<sup>42</sup>

$$C_J(t) = \langle A_{J0}(t) A_{J0}(0) \rangle_B, \quad (2.19)$$

$$A_{J0}(t) \equiv e^{itH_B/\hbar} A_{J0} e^{-itH_B/\hbar},$$

where (in a slight switch from our previous notation)<sup>29</sup> this and all of the other correlation functions in this section are taken to be complex averages of time-dependent quantum mechanical operators. However, the complex rotational friction, Eq. (1.1), can also be expanded in orders of the anisotropy

$$\eta(t) = \sum_{J=1}^{\infty} \eta_J(t), \quad (2.20)$$

enabling us to make a connection between the two (within the weak coupling limit)<sup>29</sup>

$$\eta_J(t) = \frac{b_J}{2k_B T} C_J(t), \quad (2.21)$$

$$b_J \equiv \frac{J(J+1)(2J+1)}{4\pi}. \quad (2.22)$$

All of the key spectroscopic quantities, Eqs. (2.16) and (2.17), depend on the liquid dynamics solely through the  $C_J(t)$  correlation functions, and are therefore completely controlled by the components of the rotational friction. The technical details of evaluating these quantities are discussed elsewhere,<sup>43</sup> but we can summarize the steps easily enough. After some angular momentum algebra we find that the  $G_{ll'}$  cumulant can be written as

$$\begin{aligned} \hbar^2 G_{ll'}(t) = & \sum_{J=1}^{\infty} b_J [R_{ll'}(J) C_J^R(t) + iT_{ll'}(J) C_J^I(t)] \\ & + \sum_{J=1}^{\infty} b_J \left( \sum_{L \neq l'} F_{l'L}(J) e^{-i\Omega_{l'L}t} C_J^*(t) \right. \\ & \left. + \sum_{L \neq l} F_{lL}(J) e^{i\Omega_{lL}t} C_J(t) \right), \end{aligned} \quad (2.23)$$

where the superscripts  $R$  and  $I$  denote real and imaginary parts, and the various angular-momentum coupling coefficients are defined in terms of 3- $j$  and 6- $j$  symbols,<sup>44,45</sup>

$$\begin{aligned} F_{ll'}(J) &= \frac{2l'+1}{J(J+1)} \begin{pmatrix} lJl' \\ 000 \end{pmatrix}^2, \\ T_{ll'}(J) &= F_{ll}(J) - F_{l'l'}(J), \\ R_{ll'}(J) &= F_{ll}(J) + F_{l'l'}(J) - 2D_{ll'}(J), \end{aligned} \quad (2.24)$$

$$\begin{aligned} D_{ll'}(J) &= \frac{(2l+1)(2l'+1)}{J(J+1)} (-1)^J \\ &\times \begin{pmatrix} lJl \\ 000 \end{pmatrix} \begin{pmatrix} l'Jl' \\ 000 \end{pmatrix} \begin{Bmatrix} lJl \\ l'2l' \end{Bmatrix}. \end{aligned}$$

The form of Eq. (2.23) makes the basic behavior clear; while the first sum includes only elastic contributions, the second sum brings in inelastic transitions  $l, l' \rightarrow L$ . We can write these inelastic terms in a somewhat more transparent fashion, though, by introducing the complex, time-dependent ‘rate constants,’

$$\begin{aligned} k_{l \rightarrow L}(t) &= \frac{2}{\hbar^2} \sum_{J=1}^{\infty} b_J F_{lL}(J) \int_0^t d\tau e^{i\Omega_{lL}\tau} C_J(\tau) \\ &= \frac{4k_B T}{\hbar^2} \sum_{J=1}^{\infty} F_{lL}(J) \int_0^t d\tau e^{i\Omega_{lL}\tau} \eta_J(\tau). \end{aligned} \quad (2.25)$$

The real part of this rate constant,  $k_{l \rightarrow L}^R(t)$ , is, in fact, precisely the rate of  $l \rightarrow L$  transitions predicted by first-order time-dependent perturbation theory as a function of  $t$ , the time elapsed after populating a rotational state  $l$ . This expression may be a bit unfamiliar looking because it contains the full range of dynamics, starting from the earliest transients. However, the long-time limit is quite familiar; the asymptotic rate constant is nothing more than our previous Fermi’s Golden rule result<sup>29</sup> for the steady-state rate of population relaxation, written in terms of the Fourier transform of the friction, Eq. (1.2),

$$\begin{aligned} k_{l \rightarrow L} &= \lim_{t \rightarrow \infty} k_{l \rightarrow L}^R(t) \\ &= \frac{4k_B T}{\hbar^2} \sum_{J=1}^{\infty} F_{lL}(J) \\ &\times \int_0^{\infty} d\tau [\cos \Omega_{lL}\tau \eta_J^R(\tau) - \sin \Omega_{lL}\tau \eta_J^I(\tau)] \\ &= \frac{8k_B T}{\hbar^2} \frac{1}{1 + \exp(-\hbar\Omega_{lL}/\beta)} \sum_{J=1}^{\infty} F_{lL}(J) \hat{\eta}_J^R(\Omega_{lL}). \end{aligned} \quad (2.26)$$

Here  $\beta = (k_B T)^{-1}$  and we have made use of the identity<sup>46,47</sup> that for any quantum correlation function  $C(t) = \langle A(t)A(0) \rangle$ ,

$$\int_0^{\infty} dt \sin \omega t C^I(t) = -\tanh\left(\frac{\hbar\omega\beta}{2}\right) \int_0^{\infty} dt \cos \omega t C^R(t).$$

On substituting our full, time-dependent, complex rate constants, Eq. (2.25), into Eq. (2.23), and substituting that, in turn, into Eq. (2.13b) we find that we do indeed produce expressions of the form of Eqs. (2.15)–(2.17). The inelastic contributions to the dephasing and to the frequency shift are simply given by sums of these rate constants

$$\frac{1}{T_1^{ll'}(t)} = \sum_{L \neq l} k_{l \rightarrow L}^R(t) + \sum_{L \neq l'} k_{l' \rightarrow L}^R(t), \quad (2.27)$$

$$\Delta_1^{ll'}(t) = \sum_{L \neq l'} k_{l' \rightarrow L}^I(t) - \sum_{L \neq l} k_{l \rightarrow L}^I(t). \quad (2.28)$$

The elastic contributions, by contrast, stem from (what are essentially) the zero-frequency Fourier transforms of the friction

$$\frac{1}{T_2^{*ll'}(t)} = \frac{2k_B T}{\hbar^2} \sum_{J=1}^{\infty} R_{ll'}(J) \int_0^t d\tau \eta_J^R(\tau), \quad (2.29)$$

$$\Delta_2^{*ll'}(t) = -\frac{2k_B T}{\hbar^2} \sum_{J=1}^{\infty} T_{ll'}(J) \int_0^t d\tau \eta_J^I(\tau). \quad (2.30)$$

Equations (2.25) and (2.27)–(2.30), together with Eqs. (2.13a) and (2.15)–(2.17), constitute the principal results of this paper. If nothing else, these expressions make quite evident how direct the connections are between the rotational Raman spectrum and the (anisotropy-resolved) rotational friction. More than that, though, they indicate precisely how the friction enters the various features of the Raman line shapes.

### C. Line shapes and lifetimes

Though the details are specific to weakly coupled rotational states of a linear molecule dissolved in a liquid, the results obtained in the previous sections are of the classic Kubo form. As such, we know the basic range of possible outcomes.<sup>22</sup> As always, the critical comparison is between the steady-state dephasing time  $T_2 \equiv T_2(\infty)$  and the decay time,  $\tau_c$ , of some relevant correlation function. For  $H_2$  and  $D_2$ , in which a single value of  $J$  dominates, what we need to look at is the decay time for the  $J$ th-order rotational friction,

$$\tau_c(J) = \int_0^\infty dt \frac{\eta_J(t)}{\eta_J(0)}. \quad (2.31)$$

Should this friction decay very quickly for some  $l \rightarrow l'$  transition [ $\tau_c(J) \ll T_2^{ll'}$ ], the spectral peak would be in the *homogeneous* broadening limit: the polarizability autocorrelation function, Eqs. (2.13a) and (2.15), could be written with both the time-dependent dephasing rates and the time-dependent peak shifts replaced by their steady-state values [ $1/T_2^{ll'}$  and  $\Delta_{ll'} \equiv \Delta_{ll'}(\infty)$ , respectively],

$$C_{ll'}(t) = C_{ll'}(0) e^{-i(\Omega_{ll'} - \Delta_{ll'})t} e^{-t/T_2^{ll'}}, \quad (2.32)$$

rendering the peak itself, Eq. (2.7), perfectly Lorentzian,<sup>48</sup>

$$I_{ll'}(\omega) = \frac{C_{ll'}(0)}{\pi} \frac{1/T_2^{ll'}}{(1/T_2^{ll'})^2 + (\omega + \Omega_{ll'} - \Delta_{ll'})^2}, \quad (2.33)$$

with a half-width at half-maximum (HWHM) of  $1/T_2^{ll'}$ .

Were we in the opposite limit, with a very slowly decaying friction [ $\tau_c(J) \gg T_2^{ll'}$ ], the spectral peak would then be in the *inhomogeneous* broadening limit: the complex friction would be well approximated by its initial values:

$$\eta_J^R(t) \approx \eta_J^R(0), \quad \eta_J^I(t) \approx \eta_J^I(0) = 0,$$

leading to strongly oscillatory behavior of the complex rate constants, Eq. (2.25). So, as we could see by performing the integration, the energy transfer rates  $k_{l \rightarrow l'}(t)$  and thus the  $1/T_1$  terms, Eq. (2.27), would then be largely negligible, making the pure dephasing the sole source of the line width, Eq. (2.29),

$$\frac{1}{T_2^{*ll'}(t)} \approx \frac{2k_B T}{\hbar^2} \left( \sum_{J=1}^{\infty} R_{ll'}(J) \eta_J^R(0) \right) t \equiv \sigma_{ll'}^2 t. \quad (2.34)$$

Inelastic processes would contribute to a line shift, but after we integrate Eq. (2.25), neglect the imaginary part of the friction, and discard the highly oscillatory terms, Eq. (2.28) would leave us with

$$\Delta_1^{ll'}(t) \approx \Delta_{ih}^{ll'} \equiv -\frac{2k_B T}{\hbar^2} \sum_{J=1}^{\infty} \eta_J^R(0) \left( \sum_{L \neq l'} \frac{F_{lL}(J)}{\Omega_{lL}} - \sum_{L \neq l'} \frac{F_{l'L}(J)}{\Omega_{l'L}} \right). \quad (2.35)$$

Hence both the polarizability autocorrelation function

$$C_{ll'}(t) = C_{ll'}(0) e^{-i(\Omega_{ll'} - \Delta_{ih}^{ll'})t} e^{-\sigma_{ll'}^2 t^2/2}, \quad (2.36)$$

and the line shape itself<sup>48</sup>

$$I_{ll'}(\omega) = \frac{C_{ll'}(0)}{\sqrt{2\pi\sigma_{ll'}^2}} \exp\left(-\frac{(\omega + \Omega_{ll'} - \Delta_{ih}^{ll'})^2}{2\sigma_{ll'}^2}\right), \quad (2.37)$$

would be Gaussian, with the spectral line having a HWHM of  $\sqrt{2 \ln 2} \sigma_{ll'}$ .

Of course, our actual rotational Raman spectrum need not be in either of these textbook limits. However, we know that, barring unusual circumstances, vibrational lines do tend to be homogeneously broadened in liquids.<sup>25,49,50</sup> Since there

are strong similarities in the basic friction governing both rotational and vibrational dynamics in liquids,<sup>28,29</sup> it is natural to wonder if we should therefore expect to see largely homogeneous broadening of the rotational Raman lines for species such as H<sub>2</sub> and D<sub>2</sub>. Vibration and rotation are very different kinds of motion though, so the question before us is how quantitative is the parallelism between the solvent influences on these disparate degrees of freedom? To explore this issue, we turn to the numerical calculations.

### III. CALCULATIONAL DETAILS

The model we consider is the same as that employed in our previous work:<sup>29</sup> a single H<sub>2</sub> or D<sub>2</sub> solute, with a bond length fixed at 0.77 Å, together with 107 Ar solvent atoms. The H<sub>2</sub>-Ar interaction potential is taken to be the one proposed by Leroy and Hutson,<sup>51</sup> though we use the Xiao and Coker numerically equivalent Lennard-Jones parametrization to represent the isotropic part of this potential ( $\sigma = 3.1375$  Å,  $\epsilon/k_B = 59.145$  K)<sup>8</sup> (with identical potentials used for the D<sub>2</sub>-Ar interaction). Lennard-Jones potentials are assumed as well for the Ar-Ar interactions ( $\sigma = 3.405$  Å,  $\epsilon/k_B = 119.8$  K).<sup>52</sup> All of the calculations reported here were carried out at a single high-density, supercritical thermodynamic state ( $\rho\sigma^3 = 0.95$ ,  $k_B T/\epsilon = 2.5$ ), the same conditions used by Xiao and Coker.<sup>8</sup>

As we outlined in our earlier work,<sup>29</sup> our semiclassical approach identifies the real part of the rotational friction  $\sum_J \eta_J^R(t)$  with the classical limit of Eq. (1.1). Since the anisotropic part of the Leroy-Hutson potential has only a  $J = 2$  term in its spherical harmonic expansion, Eq. (2.18), all we needed to compute the friction was the classical  $\eta_2(t)$  function, which we obtained via Eq. (2.21) from the classical  $C_2(t) = \langle A_{20}(t)A_{20}(0) \rangle$  correlation function. This correlation function, in turn, was evaluated by performing a molecular dynamics simulation on the reference system we introduced in our previous paper (in which the solute is taken to be a sphere whose interactions with the solvent are solely through the isotropic part of the solute-solvent potential).<sup>53</sup> The equations of motion of this, effectively atomic, mixture were then solved by a velocity-Verlet algorithm<sup>54</sup> using a time step of 2.16 fs with the resulting time evolution used to propagate the  $A_{20}$  coefficients. When the imaginary part of the friction was called for, we computed it via the exact relation

$$\eta_J^I(t) = \frac{2}{\pi} \int_0^\infty d\omega \sin \omega t \tanh\left(\frac{\hbar \omega \beta}{2}\right) \int_0^\infty dt' \cos \omega t' \eta_J^R(t'), \quad (3.1)$$

the inverse of the relationship used in Sec. II.

The only other ingredients needed for computing the rotational Raman spectrum, Eqs. (2.6) and (2.7), are the equilibrium populations of the rotational states  $P_l$ , which we take to be given by the isolated-molecule result<sup>55</sup>

$$P_l = \frac{(2l+1)g_l^{ns} e^{-\beta E_l}}{\sum_{l=0}^{\infty} (2l+1)g_l^{ns} e^{-\beta E_l}}, \quad E_l = \frac{\hbar^2}{2I} l(l+1), \quad (3.2)$$

with  $I$  the solute moment of inertia and  $g_l^{ns}$  the nuclear-spin degeneracy of each angular momentum state

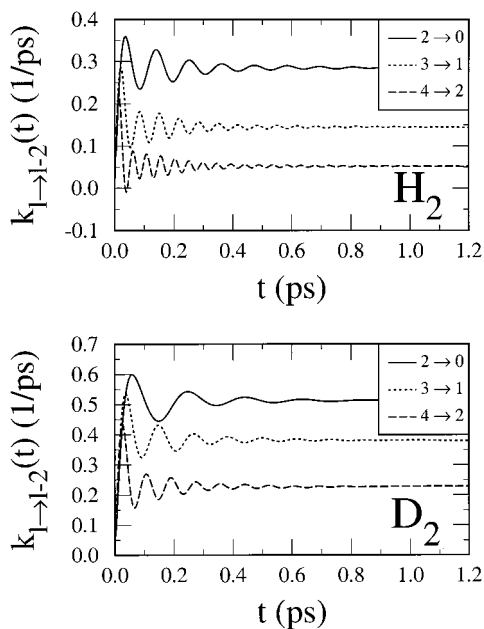


FIG. 1. The time-dependent rates for transitions from rotational states with total angular momentum  $l$  to states with total angular momentum  $l-2$ . Shown here are the real parts of the complex rates for several transitions of  $\text{H}_2$  and  $\text{D}_2$  dissolved in high-density supercritical Ar. The asymptotic values are the steady-state rates for energy transfer to the solvent.

$$g_l^{\text{ns}}(\text{H}_2) = \begin{cases} 3 & (\text{odd } l) \\ 1 & (\text{even } l) \end{cases}, \quad g_l^{\text{ns}}(\text{D}_2) = \begin{cases} 3 & (\text{odd } l) \\ 6 & (\text{even } l) \end{cases}, \quad (3.3)$$

and the angular momentum coupling coefficients, Eq. (2.24). The requisite  $3-j$  symbols for these coefficients were evaluated from the analytical formula given in Edmonds<sup>44</sup> and the  $6-j$  symbols were calculated using the numerical routine provided by Zare.<sup>45</sup>

Integral over trigonometric functions, when needed, were evaluated via numerical fast Fourier transforms.<sup>56</sup>

## IV. NUMERICAL RESULTS

### A. Preliminaries

We begin our presentation by making a few connections with our study of the rotational energy relaxation of  $\text{H}_2$  and  $\text{D}_2$  in Ar.<sup>29</sup> The main objects of interest there were the  $k_{l \rightarrow l'}$ , the steady-state transition rates between rotational states  $l$  and  $l'$ , Eq. (2.26). We found that we could understand how the populations of these states equilibrated by noting that, aside from the  $F_{ll'}(2)$  angular momentum coupling factors (which constrained the transitions to  $\Delta l = \pm 2$ ), these transition rates were largely controlled by the size of the real part of the friction evaluated at the transition frequency  $\Omega_{ll'}$ . The rates, in particular, were therefore found to decrease monotonically with the energy gap  $\hbar\Omega_{ll'} = E_l - E_{l'}$ .

What we point out in the present paper is that in order to understand rotational Raman spectra, we need to understand the quantum dynamics of rotational transitions in a little more detail. Knowing the steady-state rate constants no longer suffices; we have to generalize to a (complex) time-dependent rate, Eq. (2.25), the real part of which we illustrate in Fig. 1. What is evident from the figure, though, is that the

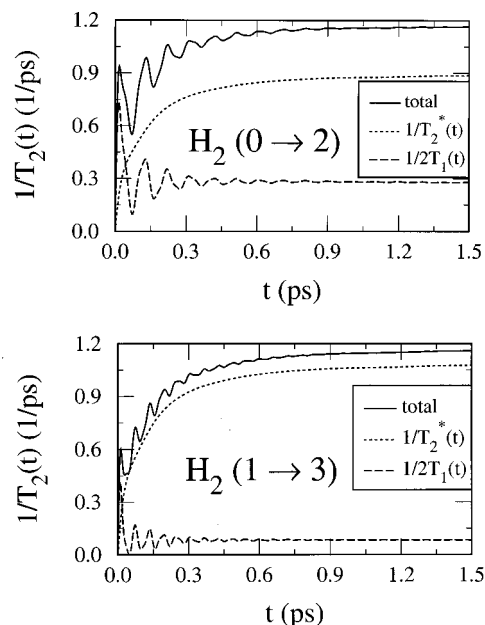


FIG. 2. The time-dependent dephasing rates for two different rotational-Raman transitions of  $\text{H}_2$  dissolved in high-density supercritical Ar. In each panel we compare the total dephasing rate  $1/T_2(t)$  with its constituent parts, the pure dephasing rate  $1/T_2^*(t)$ , and the component arising from energy relaxation,  $1/[2T_1(t)]$ .

rates for all of the transitions have substantially converged to their steady-state values within 750 fs or so, with these asymptotic rates precisely the values we arrived at in our earlier work (values, which do, in fact, become progressively smaller as  $\Omega_{ll'}$  increases).<sup>29</sup> The only difference from what we had before is that we now see the transient coherent behavior, a sharp rise within 50–100 fs followed by rapidly damped oscillations with frequency  $\Omega_{ll'}$ .

Much the same behavior shows up in the time-dependent dephasing rates themselves, Fig. 2. Both the energy-relaxation,  $1/[2T_1(t)]$ , and the pure dephasing rates,  $1/T_2^*(t)$ , also converge to their asymptotic values within 750 fs. However, since pure dephasing relies on just the zero-frequency dynamics, and thus involves only elastic transitions, its rate converges monotonically. Moreover, the coherences one sees in the remaining portion, the energy relaxation, are now superpositions of different frequencies. Equation (2.27) tells us that the rate of energy relaxation between a state  $l$  and a state  $l'$  can be written as the average of rates associated with each state<sup>24,30</sup>

$$\frac{1}{2T_1^{ll'}(t)} = \frac{1}{2} \left( \frac{1}{T_1^l(t)} + \frac{1}{T_1^{l'}(t)} \right), \quad (4.1)$$

$$\frac{1}{T_1^l(t)} = \sum_{L \neq l} k_{l \rightarrow L}^R(t), \quad \frac{1}{T_1^{l'}(t)} = \sum_{L \neq l'} k_{l' \rightarrow L}^R(t).$$

Since the  $l_1 \rightarrow l_2$  rate constants are nonzero for any  $|l_1 - l_2| = 2$ , we see coherent oscillations not only at the frequency of the actual spectroscopic transition but at the frequencies of the neighboring transitions as well. Similar transient behav-

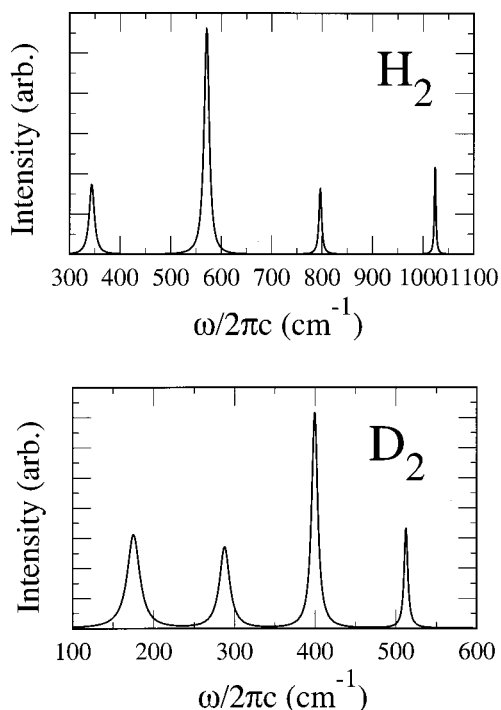


FIG. 3. The predicted rotational Raman spectra for  $\text{H}_2$  and  $\text{D}_2$  dissolved in high-density supercritical Ar. The four transitions shown here (from left to right:  $0 \rightarrow 2$ ,  $1 \rightarrow 3$ ,  $2 \rightarrow 4$ , and  $3 \rightarrow 5$ ) are broadened compared to their gas-phase counterparts, but have a barely noticeable shift on this scale.

ior, and similar convergence to the asymptotic values, are seen for the time-dependent peak shifts  $\Delta_1^{ll'}(t)$  and  $\Delta_2^{*ll'}(t)$  (not shown).

## B. Rotational Raman spectra

With the aid of these dephasing rates, and the analogous results for the peak shifts, we can assemble the full rotational Raman spectra from Eqs. (2.7), (2.13a), and (2.15). The results are shown in Fig. 3. For reference, we provide the steady-state values of the dephasing rates and the peak shifts in Tables I and II.

So what do these spectra tell us? To answer this question we need to know where the line shapes fit in the continuum between the extreme homogeneous and inhomogeneous limits. When the exact spectra are plotted on the same graphs as the limiting spectra, Fig. 4, the answer becomes apparent: the spectral lines for both  $\text{H}_2$  and  $\text{D}_2$  are almost perfect Lorentzians and can therefore be described nearly quantitatively as

TABLE I. Steady-state dephasing lifetimes (in ps) for rotational Raman transitions of  $\text{H}_2$  and  $\text{D}_2$  dissolved in Ar.<sup>a</sup>

Transition	$\text{H}_2$			$\text{D}_2$		
	$T_2$	$T_2^*$	$T_1$	$T_2$	$T_2^*$	$T_1$
$(l \rightarrow l')$						
$(0 \rightarrow 2)$	0.9	1.1	1.8	0.6	1.1	0.6
$(1 \rightarrow 3)$	0.9	0.9	6.0	0.7	0.9	1.6
$(2 \rightarrow 4)$	1.6	2.3	3.0	1.2	2.2	1.3
$(3 \rightarrow 5)$	3.0	4.1	6.2	1.9	3.9	2.0

<sup>a</sup>Total dephasing ( $T_2$ ), pure dephasing ( $T_2^*$ ), and energy relaxation ( $T_1$ ) lifetimes for Ar solutions.

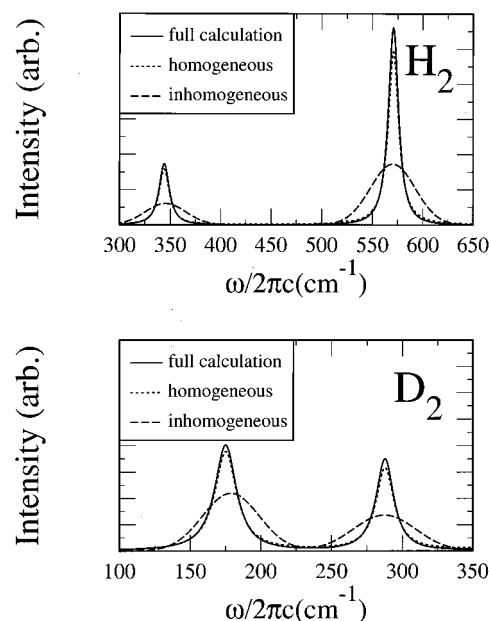


FIG. 4. A comparison of our full calculation of the rotational Raman spectra of  $\text{H}_2$  and  $\text{D}_2$  dissolved in high-density supercritical Ar with the extreme homogeneous and inhomogeneous limits of the spectra.

homogeneously broadened. We can understand this observation quite simply by noticing how short the decay time is for the rotational friction, Eq. (2.31):  $\tau_c = 62$  fs for  $\text{H}_2$  and 65 fs for  $\text{D}_2$ , values an order of magnitude smaller than even the smallest dephasing times in Table I.

What this assignment means is that these line shapes do carry interesting information about the rotational dynamics in the liquid. For example, how important is energy exchange between the solute and the solvent in determining the spectra? A comparison between the exact spectra and spectra in which the inelastic contributions ( $T_1$  and  $\Delta_1$ ) have been neglected, Fig. 5, reveals that energy transfer is virtually negligible with  $\text{H}_2$ ; the rotational energy spacing is too large compared to the natural frequency range of the solvent to permit significant energy relaxation.<sup>29</sup> In  $\text{D}_2$  (with energy-level spacings half as big), energy relaxation plays a much more vital role. In particular, as we can see from Table II, since the solvent-induced frequency shifts stem largely from inelastic processes, the peak shifts from the isolated-

TABLE II. Steady-state frequency shifts (in  $\text{cm}^{-1}$ ) for rotational Raman transitions of  $\text{H}_2$  and  $\text{D}_2$  dissolved in Ar.<sup>a</sup>

Transition	$\text{H}_2$			$\text{D}_2$		
	$\Delta$	$\Delta_2^*$	$\frac{1}{2} \Delta_1$	$\Delta$	$\Delta_2^*$	$\frac{1}{2} \Delta_1$
$(l \rightarrow l')$						
$(0 \rightarrow 2)$	2.8	-0.8	3.6	4.4	-0.9	5.3
$(1 \rightarrow 3)$	2.0	0.4	1.6	3.3	0.4	2.9
$(2 \rightarrow 4)$	0.4	0.1	0.3	1.3	0.1	1.2
$(3 \rightarrow 5)$	-0.05	0.03	-0.08	0.33	0.03	0.30

<sup>a</sup>Solvent-induced shifts from the isolated-molecule transition frequencies. The total frequency shift ( $\Delta$ ) is divided into elastic ( $\Delta_2^*$ ) and inelastic ( $\frac{1}{2} \Delta_1$ ) contributions.



TABLE III. Linewidths (in  $\text{cm}^{-1}$ ) for rotational Raman transitions of  $\text{H}_2$  dissolved in Ar.<sup>a</sup>

Transition	Predicted <sup>b</sup>	Homogeneous <sup>c</sup>	Inhomogeneous <sup>c</sup>	Elastic <sup>d</sup>	Xiao–Coker <sup>e</sup>
(0→2)	6.0	6.2	23.7	4.6	4.2
(1→3)	6.0	6.2	26.1	5.6	5.1
(2→4)	3.1	3.2	16.4	2.3	2.1
(3→5)	1.7	1.8	12.4	1.3	1.3

<sup>a</sup>Reported as half-widths at half-maxima (HWHM).<sup>b</sup>Linewidths resulting from our complete calculation.<sup>c</sup>Linewidths predicted in the extreme homogeneous and inhomogeneous limits of our calculation.<sup>d</sup>Linewidths computed neglecting all inelastic ( $T_1$ ) contributions.<sup>e</sup>Linewidths predicted by the nonadiabatic, mixed quantum/classical simulations of Xiao and Coker (Ref. 8).

molecule positions are more noticeable with  $\text{D}_2$  than with  $\text{H}_2$ .

Still, in an absolute sense, neither solute has shifts all that large, so perhaps a more revealing view of the situation is provided by the linewidths, Tables III and IV. As we would expect, both for  $\text{H}_2$  and  $\text{D}_2$ , the homogeneous-limit predictions for the linewidths are in quantitative accord with the exact results. For  $\text{H}_2$ , though, assuming that pure dephasing is the sole relaxation process would lead to respectable estimates for the width. The same assumption for  $\text{D}_2$  would underestimate the width by a factor of 2.

Since there are no experiments on  $\text{H}_2$  or  $\text{D}_2$  in Ar to compare with, it is difficult to make definitive statements about the accuracy of our basic theoretical approach. Nonetheless, it is informative to compare with the nonadiabatic simulation predictions of Xiao and Coker for the rotational Raman spectrum of  $\text{H}_2$  in Ar (Table III).<sup>8</sup> Our linewidths are in reasonably good agreement with the more elaborate calculations of Xiao and Coker, both in terms of magnitudes and trends. If we remember though, that those authors' non-

adiabatic simulations did not allow the solvent to induce transitions between different  $l$  states, we realize that the proper comparison is not with our overall width, but with the widths we would predict in the absence of inelastic processes.<sup>57</sup> When we make that comparison we find that the agreement becomes amazingly good, with the two calculations within 10% of one another.

A particularly intriguing feature is that when (and only when) we limit ourselves to the pure-dephasing-induced broadening in this fashion, we reproduce the Xiao and Coker finding that the  $1 \rightarrow 3$  line ought to be the broadest.<sup>8</sup> Those authors suggested that their results reflect the way in which a liquid environment splits the degeneracy of the  $m$  sublevels of each  $l$  level — and an  $l=1$  state, they argued, ought to have the maximum amount of inhomogeneous broadening caused by such splitting. However, we would analyze this linewidth rather differently. Because we are considering only pure dephasing, Eq. (2.29) tells us that an  $l \rightarrow l'$  linewidth will depend on  $l$  only through the angular momentum coupling factor  $R_{ll'}(2)$  — and this,  $m$  independent, purely kinematic, factor is at its largest for  $l=1$ . From the perspective of our work, then, the breadth of the  $1 \rightarrow 3$  line arises from purely dynamical considerations.

## V. CONCLUDING REMARKS

For nearly free rotors such as  $\text{H}_2$  and  $\text{D}_2$  in Ar, the pivotal role played by the rotational friction in defining the rotational spectroscopy ought to be abundantly clear. It is the nearly Markovian character of the friction (the 60 fs decay time) that ensures that the rotational Raman spectrum is homogeneously broadened; it is the limited frequency range of the friction that severely limits the efficiency of rotational energy transfer to the solvent; and it is the zero-frequency

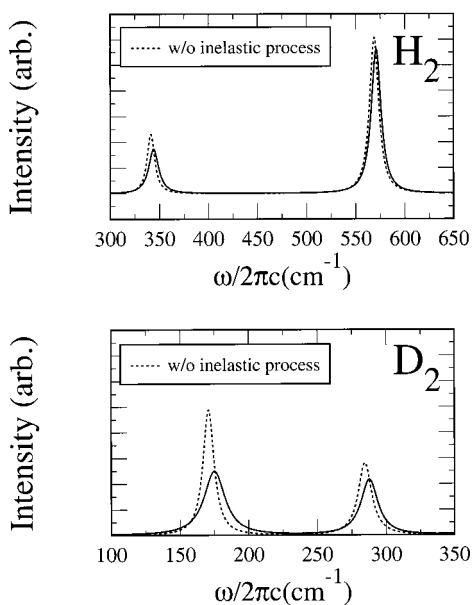


FIG. 5. The role of solute–solvent energy transfer (inelastic) processes in shaping the rotational Raman spectra of  $\text{H}_2$  and  $\text{D}_2$  dissolved in high-density supercritical Ar. The full calculation (solid line) is compared with a calculation completely neglecting energy-transfer effects (dotted line). While the  $\text{H}_2$  spectrum is affected only modestly, the  $\text{D}_2$  spectrum shows how inelastic processes lead to both broadening and shifting of the observed peaks.

TABLE IV. Linewidths (in  $\text{cm}^{-1}$ ) for rotational Raman transitions of  $\text{D}_2$  dissolved in Ar.<sup>a</sup>

Transition	Predicted <sup>b</sup>	Homogeneous <sup>c</sup>	Inhomogeneous <sup>c</sup>	Elastic <sup>d</sup>
(0→2)	9.2	9.3	23.7	4.8
(1→3)	7.4	7.7	26.1	5.8
(2→4)	4.5	4.6	16.4	2.4
(3→5)	2.7	2.8	12.4	1.4

<sup>a</sup>Reported as half-widths at half-maxima (HWHM).<sup>b</sup>Linewidths resulting from our complete calculation.<sup>c</sup>Linewidths predicted in the extreme homogeneous and inhomogeneous limits of our calculation.<sup>d</sup>Linewidths computed neglecting all inelastic ( $T_1$ ) contributions.

value of the friction that sets the scale of the pure dephasing processes that account for half of the spectral width for D<sub>2</sub>, and for 75%–90% of the width for H<sub>2</sub>.

Interestingly, every one of these statements could have been made about the solution-phase spectroscopy of most vibrational transitions.<sup>25,49,58,59</sup> Vibrational lines themselves are normally homogeneously broadened in liquids and the purely elastic phase relaxation of vibrational modes is normally much faster than their energy relaxation. Despite the numerous differences between rotational and vibrational dynamics, then, the liquid-state relaxation of discrete quantum states seems to be fairly universal, probably because the friction itself is more a function of the solution's dynamics than it is of the particulars of the spectroscopically active degrees of freedom. In fact, some of this behavior is actually fairly clear from an instantaneous-normal-mode perspective.<sup>60</sup> The high-frequency part of the dynamics, the energy relaxation, seems to be dominated by strongly repulsive solvent–solute interactions operating between individual atoms (even when one has molecular solutes and solvents).<sup>29,61</sup> Whether a solute atom is involved in a rotation or a vibration is therefore reasonably irrelevant. The commonalities seen in the lower-frequency portion of the friction, the part that accounts for the pure dephasing, are less obvious, however. Instantaneous-normal-mode theories are necessarily silent on such matters.<sup>62</sup>

Of course, the other point we have had to be silent on during the course of our investigation of individual rotational states in liquids is whether our reliance on classical dynamics to understand quantum dynamical events is really justified. While we found that our particular approach had no difficulty in matching the results of a mixed quantum/classical simulation, it is not obvious that another semiclassical prescription would not have worked just as well,<sup>63</sup> nor is it clear that the Raman linewidths in our example made for as stringent a test as, say, the energy relaxation rates. Especially now that we have managed to develop a reasonable level of insight into the classical features of this problem, it would be intriguing to see what legitimate quantum dynamical calculations would have to say about rotational relaxation in liquids.

## ACKNOWLEDGMENTS

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<sup>39</sup>A similar nonadiabatic perspective on vibrational relaxation has been suggested by J. K. Rudra and M. F. Herman, J. Mol. Liq. **39**, 233 (1988).

<sup>40</sup>Our basic assumption is that both the *l* and *m* quantum numbers remain well enough defined in the liquid to serve as labels for spectroscopic transitions, but the *m* states are spectroscopically unresolvable. Consistent

with this ansatz, Eqs. (2.5)–(2.7) assume that the equilibrium density matrix can be factored into isolated-rotor,  $\exp(-\beta H_{\text{rot}})$ , and pure-bath,  $\exp(-\beta H_B)$ , parts. This kind of factoring is tantamount to assuming that the  $m$  states retain their isolated-molecule  $(2l+1)$ -fold degeneracy. The equilibrium probabilities  $P_{lm}$  are thus just equal to  $P_l/(2l+1)$  with  $P_l$  prescribed by the simple gas-phase expression, Eq. (3.2).

<sup>41</sup>We do note that the  $m$ -level degeneracy is actually split by the instantaneous asymmetry of the solvent (Refs. 7–9). Exactly why our weak coupling approach (which takes into account the individual  $m$  states only in an average sense), should lead to results so similar to those of Ref. 8—which looks specifically at the  $m$ -state splitting—is not entirely clear.

<sup>42</sup>Because of the isotropy of a liquid we need only consider the  $J=K$ ,  $M=M'=0$  elements of any correlation functions of the form  $\langle A_{JM}(t)A_{KM'}(0) \rangle$ . See Ref. 7.

<sup>43</sup>Note that, consistent with our basic assumption that there are identifiable  $l \rightarrow l'$  spectral transitions, we keep only  $(l, l')$  matrix elements of the  $\alpha_q$  operators. See Ref. 30. This assumption makes the  $G_{ll'}$  cumulant time translation invariant:  $G_{ll'}(t, t') = G_{ll'}(|t - t'|)$ . A systematic presentation of the entire development is given in J. Jang, Ph.D. thesis, Brown University, 2000.

<sup>44</sup>A. R. Edmonds, *Angular Momentum in Quantum Mechanics*, 2nd ed. (Princeton University Press, Princeton, 1974). Eqs. (3.7.8), (3.7.17), (4.6.3), and (5.4.1).

<sup>45</sup>R. N. Zare, *Angular Momentum* (Wiley-Interscience, New York, 1988). Equation (4.13) and the Appendix.

<sup>46</sup>B. J. Berne, J. Jortner, and R. Gordon, *J. Chem. Phys.* **47**, 1600 (1967); J. Borysow, M. Moraldi, and L. Frommhold, *Mol. Phys.* **56**, 913 (1985).

<sup>47</sup>D. W. Oxtoby, *Adv. Chem. Phys.* **47** (part 2), 487 (1981).

<sup>48</sup>Note that by virtue of our definition in Eq. (2.10), the transition frequency  $\Omega_{ll'}$  is *negative* for  $l \rightarrow l+2$  spectral transitions we study.

<sup>49</sup>R. M. Stratt and M. Maroncelli, *J. Phys. Chem.* **100**, 12 981 (1996).

<sup>50</sup>S. J. V. Frankland and M. Maroncelli, *J. Chem. Phys.* **110**, 1687 (1999).

<sup>51</sup>R. J. LeRoy and J. M. Hutson, *J. Chem. Phys.* **86**, 837 (1987).

<sup>52</sup>M. F. Pas and B. J. Zwolinski, *Mol. Phys.* **73**, 471 (1991).

<sup>53</sup>The use of this reference system is, in fact, precisely what is required by the bath average in Eq. (2.19). However, we showed in Ref. 29 that it also provides a numerically accurate way to compute the full friction.

<sup>54</sup>M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1989), pp. 81, 82.

<sup>55</sup>D. A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976), Secs. 6.4 and 6.5.

<sup>56</sup>W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in Fortran*, 2nd ed. (Cambridge University Press, Cambridge, 1992), Chap. 12.

<sup>57</sup>In the context of this paper, “the absence of inelastic processes” means that there are no solvent-induced changes in the total angular momentum quantum number  $l$ .

<sup>58</sup>J. C. Owrtzky, D. Raftery, and R. M. Hochstrasser, *Annu. Rev. Phys. Chem.* **45**, 519 (1994).

<sup>59</sup>The connection between the rotational dynamics seen in fluids and rovibrational spectra is discussed by A. I. Burshtein and S. I. Temkin, *Spectroscopy of Molecular Rotation in Gases and Liquids* (Cambridge University Press, Cambridge, 1994).

<sup>60</sup>R. E. Larsen, E. F. David, G. Goodyear, and R. M. Stratt, *J. Chem. Phys.* **107**, 524 (1997).

<sup>61</sup>R. E. Larsen and R. M. Stratt, *J. Chem. Phys.* **110**, 1036 (1999); B. M. Ladanyi and R. M. Stratt (unpublished).

<sup>62</sup>However, generalizations of INM theory have been suggested that may not turn out to be as limited. T. Keyes, *J. Chem. Phys.* **104**, 9349 (1996).

<sup>63</sup>J. Borysow *et al.* (in Ref. 46); S. A. Egorov, K. F. Everitt, and J. L. Skinner, *J. Phys. Chem. A* **103**, 9494 (1999).