Vibrational spectroscopy of HOD in liquid D_2O. II. Infrared line shapes and vibrational Stokes shift

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We present semiclassical calculations of the infrared line shapes for the three intramolecular vibrations of dilute HOD in liquid D$_2$O. In these calculations the vibrations of HOD are treated quantum mechanically, and the rotations and translations of all the molecules are treated classically. The approach and model, which is based on earlier work of Oxtoby and of Rey and Hynes, was discussed in detail in Paper I, on vibrational energy relaxation in the same system, of this series. A novel feature of our approach is a self-consistent renormalization scheme for determining the system and bath Hamiltonians for a given vibrational state of the HOD molecule. Our results for the line shapes are in reasonable agreement with experiment. We also explore the extent to which the frequency fluctuations leading to the line shape are Gaussian. Finally, we calculate the vibrational Stokes shift for the OH stretch fundamental. Our result, which is nonzero only because the specification of the bath Hamiltonian depends on the vibrational state of the HOD molecule (as a result of the self-consistent renormalization scheme), is 57 cm^{-1}, in good agreement with the experimental number of 70 cm^{-1}. © *2002 American Institute of Physics.*
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I. INTRODUCTION

The vibrational frequencies of a molecule in a liquid are sensitive to the molecule's instantaneous environment. As this environment changes due to molecular dynamics these frequencies, therefore, fluctuate in time. Focusing on one particular vibrational mode, its average frequency is generally shifted from that of the isolated (gas-phase) molecule. This average frequency, which is the first moment of the infrared line shape, provides information about the average structure of the liquid. The linewidth, on the other hand, is in general sensitive to both the distribution and time scale of the frequency fluctuations, and as such can provide information about molecular dynamics.[1] This information is most readily available in systems where the magnitude of the fluctuations is small and/or where the fluctuations occur rapidly (the homogeneous limit).[2,3] When the opposite is true (the inhomogeneous limit), this dynamical information becomes buried amidst the broadening that results from the molecule's different environments.[2,3]

In this paper we focus on the mid-infrared (IR) vibrational spectrum of dilute HOD in liquid D$_2$O. This region of the spectrum arises from the three intramolecular vibrations of the HOD molecule: the bend, the OH stretch, and the OD stretch. The experimental line shapes for these three modes were first measured by Falk and Ford.[4] (Actually, only the first two can be clearly resolved in D$_2$O, while the third was measured in H$_2$O.) For each stretch, there is a large solvent shift (shift of the average frequency from the gas-phase frequency) and width associated with the line shape [for example, the OH stretch is redshifted by about 300 cm^{-1} and

the full width at half maximum (FWHM) is about 250 cm^{-1}]. This large shift shows that there are strong interactions with the environment (due to hydrogen bonding to D$_2$O molecules) and the large width shows that a specific molecule experiences a wide range of environments. The bend vibration is much less sensitive to interactions with the solvent, as evidenced by a much smaller shift and width (44 and 85 cm^{-1}, respectively).[4,5]

As is well known, the absorption line-shape function is the Fourier transform of the dipole–dipole time-correlation function (TCF).[6,7] One approach to calculating this TCF is with a classical molecular dynamics simulation using flexible molecules.[8–10] For water, the most popular flexible model is due to Toukan and Rahman.[8] Martí and co-workers calculated the vibrational spectrum of different isotopes of water using this approach, taking the Toukan/Rahman form for the intramolecular potential, but modifying the parameters to get good agreement with experiment.[11–13] A similar classical molecular dynamics approach was utilized by Ahlborn and co-workers,[14,15] except that in calculating the spectrum they included many-body polarization interactions. They also analyzed the results with an instantaneous normal mode approach. Silvestrelli, Bernasconi, and Parrinello[16] recently used *ab initio* molecular dynamics to calculate the dipole–dipole TCF, and hence the spectrum, thus considerably improving (at least in principle) upon the above more empirical approaches.

Despite the general success of these approaches, there are several reasons one might strive to do better. First, the vibrational frequencies of water (and HOD, in particular) are very high compared to kT (at least at room temperature), suggesting that one should really treat the vibrations quan-

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tum mechanically. In other words, in water the vibrational transitions occur between discrete quantum levels (the vibrational ground state and the first excited states of each mode), and so a classical treatment of the nuclear dynamics might be questionable. Second, it would be nice if the theoretical model was flexible and powerful enough to treat other related spectroscopic problems. One example is vibrational energy relaxation. While one could, in principle, perform a nonequilibrium classical molecular dynamics simulation to calculate this relaxation, in fact, quantum effects are likely to be even more important for this problem than they are for the line shape. Another example involves the vibrational Stokes shift: It is found that the average vibrational frequency of the OH fundamental shifts to the red by some 70 cm^{-1} when the molecule is in the excited vibrational state.[17] This means that the interaction of a given molecule with neighboring molecules depends on its vibrational quantum state. This effect clearly cannot be accounted for by classical models.

In this paper, we will use a semiclassical approach to calculate the absorption features for each of the three vibrations of dilute HOD in D_2O. In Paper I (Ref. 18) of this series we developed a general formalism, based on earlier work of Oxtoby[1] and of Rey and Hynes,[19] which can be used to calculate vibrational energy relaxation[20–26] [as in Paper I (Ref. 18)], vibrational line shapes and Stokes shifts (this paper), transient hole burning,[22,24] and frequency-dependent rotational anisotropy relaxation[27] [Paper III (Ref. 28)], and vibrational photon echoes[29,30] [Paper IV (Ref. 31)]. In this formulation, the vibrations of the HOD molecule are treated quantum mechanically, while the translations and rotations of all the molecules are treated classically. The Hamiltonian is partitioned into three terms: the ''system'' Hamiltonian describes the vibrations of the HOD molecule, the ''bath'' Hamiltonian includes contributions from the rotations and translations of all of the molecules, and the final term serves to couple the system and the bath. One novel feature of our approach is that we determine by an iterative procedure the system and bath Hamiltonians self-consistently, for a given vibrational state of the system.

Applying this procedure to the ground vibrational state of HOD, the eigenvalues of the system Hamiltonian then lead to the average energies of vibrational transitions to the different fundamentals. In this way, the solvent shifts for the different transitions are determined quite naturally and directly, without introducing adjustable parameters. In addition, the Stokes shift can be calculated by repeating the entire procedure for the relevant excited vibrational state, and then determining the transition energy change. In order to calculate the absorption line shapes themselves, we use a Kubo-like approach, which involves the fluctuating frequency for a given vibrational transition.[1,32–35] This frequency is simply the difference in the diagonal matrix elements of the system–bath interaction for the two relevant vibrational states.[1,36] As mentioned above, this frequency fluctuates in time due to molecular dynamics.

The organization of this paper is as follows: In Sec. II we briefly review the Hamiltonian and self-consistent renormalization procedure developed in Paper I.[18] We also discuss the semiclassical line-shape formula and several approxima-

tions to it, including the second cumulant truncation result. In Sec. III we present results for the line shapes of the three fundamentals of HOD, and compare to experiment. We also discuss the validity of the several approximations. We find that the Gaussian approximation to the fluctuating frequencies, while not quantitative, is still reasonably good, at least for the line-shape calculations. We also find that there is significant motional narrowing of the bend line shape, while the stretches are closer to the inhomogeneous limit. The nearly Gaussian and inhomogeneous character of the OH stretch line shape has important implications in the description and analysis[28] of recent transient hole-burning experiments.[22,24] In Sec. IV we calculate the vibrational Stokes shift for the OH stretch fundamental, obtaining good agreement with experiment.[17] In Sec. V we conclude.

II. VIBRATIONAL LINE SHAPES

To calculate the vibrational line shapes we use the same Hamiltonian and self-consistent renormalization scheme as described in detail in Paper I.[18] Summarizing briefly, the Hamiltonian for the HOD chromophore interacting with the D_2O solvent is broken into three terms:

$$H = H_s + H_b + V. \tag{1}$$

H_s is the quantum-mechanical ''system'' Hamiltonian, which depends only on the three vibrational coordinates, $\mathbf{q}$, and their conjugate momenta, $\mathbf{p}$, of the HOD molecule. H_b is the classical ''bath'' Hamiltonian, which depends on the translations and rotations of all the molecules. V is the coupling between the system and the bath. The system and bath Hamiltonians are determined self-consistently, for a given vibrational state. This is accomplished with the following iterative procedure. The initial system Hamiltonian involves a very accurate and detailed potential surface, obtained by fitting the experimental gas-phase vibrational–rotation spectrum.[37] This Hamiltonian has a set of eigenvalues and eigenstates, labeled by index i. Diagonal matrix elements of the vibrational coordinates for the vibrational state of interest, say l, then define the average geometry of the HOD molecule, when it is in state l. This geometry is input into the bath Hamiltonian (since the latter involves the interaction of the HOD molecules with the D_2O solvent). The bath average of V is calculated from a classical molecular dynamics simulation, and then it is added to the initial system Hamiltonian and subtracted from V. This renormalized system Hamiltonian has a new set of eigenvalues and eigenstates, which leads to a new definition of the bath. Another molecular dynamics simulation is performed, and the entire process is repeated until convergence is obtained (that is, the system and bath Hamiltonians no longer change). Note that with this procedure the bath average of the perturbation V is zero.

For the calculation of the absorption spectrum the vibrational state of interest is the ground state. This is because at room temperature water is found (essentially) only in its ground vibrational state, and so before the absorption process occurs, the bath should be appropriate for that state. In this case, the system Hamiltonian has the set of eigenvalues and eigenstates

$$H_s|i\rangle = E_i|i\rangle, \quad i = 0,1,2,\dots. \tag{2}$$

The eigenvalue E_0, therefore, corresponds to the average energy of the HOD molecule in its ground vibrational state. On the other hand, the eigenvalue $E_l(l \neq 0)$ corresponds to the average energy of the HOD molecule in vibrational state l, but of course the average is with respect to the bath Hamiltonian appropriate for the ground vibrational state. This means that the average frequency for the transition from the ground state to vibrational state l is $\langle \omega \rangle = (E_l - E_0)/\hbar$.

The absorption line-shape function is given by the Fourier transform of the quantum-mechanical dipole TCF:[6,7]

$$I(\omega) \sim \int_{-\infty}^{\infty} dt\, e^{-i\omega t} Tr[e^{-\beta H} \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(t)], \tag{3}$$

where $\boldsymbol{\mu}$ is the quantum-mechanical dipole operator for the system, $\boldsymbol{\mu}(t)$ denotes the Heisenberg time evolution, and $\beta = 1/kT$. Within the usual semiclassical approximation the normalized line shape for the transition to vibrational state l is[1,32–35]

$$I(\Omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{-i\Omega t} \phi(t), \tag{4}$$

where

$$\phi(t) = e^{-|t|/T_1} \langle \hat{u}(0) \cdot \hat{u}(t) e^{i\int_0^t d\tau \Omega(\tau)} \rangle. \tag{5}$$

In the above $\Omega = \omega - \langle \omega \rangle$, $\hat{u}$ is the molecule-fixed transition dipole unit vector for the transition to state l, $\Omega(t)$ is the fluctuating frequency, given by $\Omega(t) = [V_{ll}(t) - V_{00}(t)]/\hbar$, and $V_{ii} = \langle i|V|i \rangle$. The brackets denote a classical equilibrium average Boltzmann weighted by the bath Hamiltonian. Note that since $\langle V \rangle = 0$, $\langle \Omega(t) \rangle = 0$. The effects of broadening due to population relaxation have been included phenomenologically. A simple derivation of this formula in the present content, which makes clear what approximations are involved, is presented in the Appendix.

$\hat{u}$ is obtained by taking the appropriate matrix element of the dipole operator for HOD, which follows from the charges assigned to the atoms, as discussed in Paper I.[18] Also, as discussed in Paper I, V is composed of several terms, each of which is expanded to third order in the normal coordinates and conjugate momenta of the HOD molecule. The diagonal matrix elements of V then lead to the fluctuating frequency. $\hat{u}(t)$ and $\Omega(t)$ are fluctuating bath variables, whose dynamics are obtained from a classical molecular dynamics simulation of rigid molecules, specified by the bath Hamiltonian.

In what follows we will calculate the line shapes using Eqs. (4) and (5). We will also be interested in several approximations to this result. First, if T_1 is sufficiently long then population relaxation can be ignored, so

$$\phi(t) = \langle \hat{u}(0) \cdot \hat{u}(t) e^{i\int_0^t d\tau \Omega(\tau)} \rangle. \tag{6}$$

In addition, one often assumes that the rotational time dependence of $\hat{u}$ is uncorrelated with the frequency fluctuations. Hence, $\phi(t)$ can be factored as

$$\phi(t) = \langle \hat{u}(0) \cdot \hat{u}(t) \rangle \langle e^{i\int_0^t d\tau \Omega(\tau)} \rangle. \tag{7}$$

TABLE I. Theoretical vibrational energy relaxation times for the three fundamental vibrations.

State	T_1 (ps)
Bend	0.22
OD stretch	18
OH stretch	2.7

In another common approximation one assumes that the rotations are sufficiently slow that the orientational dynamics can simply be ignored, yielding

$$\phi(t) = \langle e^{i\int_0^t d\tau \Omega(\tau)} \rangle. \tag{8}$$

If the frequency fluctuations are sufficiently slow then $\phi(t) \simeq \langle e^{i\Omega(0)t} \rangle$, in which case the line shape simply becomes the distribution of frequencies

$$P(\Omega) = \langle \delta(\Omega - \Omega(0)) \rangle. \tag{9}$$

One often performs a cumulant expansion of Eq. (8) and truncates at second order to give[2,32–35]

$$\phi(t) = \exp\left\{ -\int_0^t d\tau (t-\tau) C(\tau) \right\}, \tag{10}$$

where

$$C(t) \equiv \langle \Omega(0)\Omega(t) \rangle, \tag{11}$$

is the TCF of the fluctuating frequency. Truncating this expansion at this point is of particular interest because if the fluctuating frequency is Gaussian, then all higher cumulants would be zero and Eq. (10) would be equivalent to Eq. (8).

If $\Omega(t)$ describes a Gaussian process, a number of conditions must be satisfied.[7] One is simply that the distribution of frequencies is Gaussian. That is

$$P(\Omega) = \frac{1}{\sqrt{2\pi\langle\Omega^2\rangle}} e^{-\Omega^2/2\langle\Omega^2\rangle}. \tag{12}$$

A second property is that

$$C_4(t) \equiv \langle \Omega(t)^2\Omega(0)^2 \rangle = 2C(t)^2 + \langle\Omega^2\rangle^2. \tag{13}$$

Below we will calculate these two quantities to see to what extent the fluctuating frequencies are Gaussian (within our model).

III. RESULTS AND DISCUSSION

The details regarding the simulation are discussed in Paper I of this series.[18] After performing the iterative procedure for the ground-state surface described therein, a run of 10 ns at 300 K was performed during which the quantities of interest were calculated. Absorption line shapes were evaluated for the transitions to the first excited states of each of the three vibrational modes. The relaxation times used for Eq. (5) were calculated in Paper I and are given in Table I. The only relaxation time that has been measured experimentally for HOD in D_2O is that of the OH stretch fundamental, with a value of about 1 ps,[20,21,23,26] which is about a factor of 3 faster than our theoretical value. (While the relaxation time of the OD stretch of HOD has been measured in H_2O to be
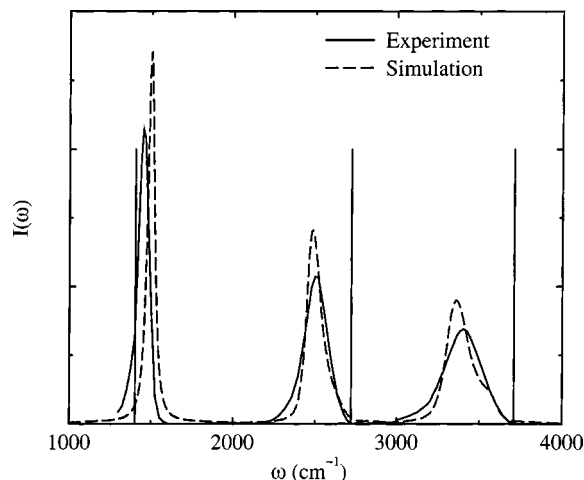
FIG. 1. Comparison of the vibrational line shapes from theory (dashed lines) and experiment (see Ref. 4) (solid lines). Vertical lines are gas-phase values.

FIG. 2. Comparison of the several approximations to the line shape for the bend vibration.

1.8 ps,[38] this could well be quite different from that in D_2O, because of the very different vibrational frequencies of the solvent.) In our theoretical calculations we did not include the effects of solvent vibrations. We are now, however, repeating the T_1 calculations with flexible solvent molecules, which may well decrease the theoretical lifetimes.

Figure 1 displays the results for the vibrational line shapes calculated from Eqs. (4) and (5). We also show the experimental line shapes, which were obtained from the experimental transmittances[4] without correcting for the frequency dependence of the refractive index, as the latter would be fairly weak for this system.[39,40] As discussed in the Introduction, the line shape for the OD stretch was measured in H_2O, and so here the quantitative comparison with theory may not be as meaningful. The line shapes of the three vibrational modes from both theory and experiment are independently normalized. For reference, stick spectra of the gas-phase data are included in the figure.[41] One sees that the theoretical results are in good (but not quantitative) agreement with experiment. The features of the spectra are summarized in Table II. $\langle\omega\rangle$ are the average frequencies and Γ are the (FWHM) line widths. The experimental frequencies are actually the peaks of the absorption bands, but since they are quite symmetrical, in each case these are approximately the same as the average frequencies. We have also listed the experimental[41] and theoretical gas-phase frequencies ω_g for the three transitions, and the solvent shifts $\Delta\omega = \langle\omega\rangle - \omega_g$. In all three cases the experimental and theoretical gas-phase frequencies are in excellent agreement. For the two stretches

the theoretical solvent shifts are also in excellent agreement with experiment (both are redshifts), while for the bend, theory overestimates the blueshift by about a factor of 2. All theoretical linewidths are too small by 35% or 40%. Although the line shapes are not quantitatively correct, the qualitative features agree quite well. The directions of the shifts are reproduced, as are the relative magnitudes (in that the shift for the OH stretch is the largest and that of the bend is the smallest). The approximate ratio of 1:2:3 for the widths of the bend, OD stretch, and OH stretch is reproduced as well.

In Figs. 2–4 we compare the results obtained from several approximations to the line shapes for the bend, OD stretch, and OH stretch, respectively. The lines labeled "line shape" correspond to the most complete line-shape formula, using Eq. (5). When population relaxation is neglected [Eq. (6)] we obtain the long-dash lines. When, in addition, the rotational TCF is factored [Eq. (7)] we obtain the short-dash line. And when rotations are ignored altogether [Eq. (8)] we obtain the solid lines. Focusing on the bend vibration in Fig. 2, we see that since in this case T_1 is so short, it is important

TABLE II. Summary of the features of the experimental and theoretical line shapes. The experimental results listed for $\langle\omega\rangle$ are actually the peak frequencies. All results are in cm^{-1}.

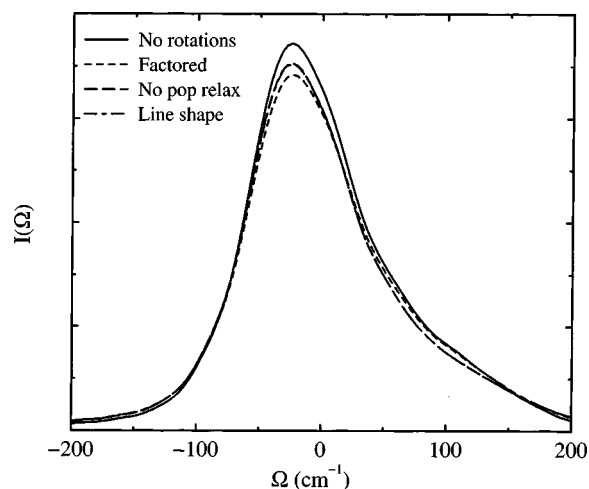|	Experiment				Theory			
	ω_g	$\langle\omega\rangle$	$\Delta\omega$	Γ	ω_g	$\langle\omega\rangle$	$\Delta\omega$	Γ
Bend	1403	1448	45	85	1404	1496	92	51
OD stretch	2724	2500	−224	160	2723	2510	−213	106
OH stretch	3707	3400	−307	255	3707	3395	−312	163

FIG. 3. Comparison of the several approximations to the line shape for the OD stretch.

FIG. 4. Comparison of the several approximations to the line shape for the OH stretch.
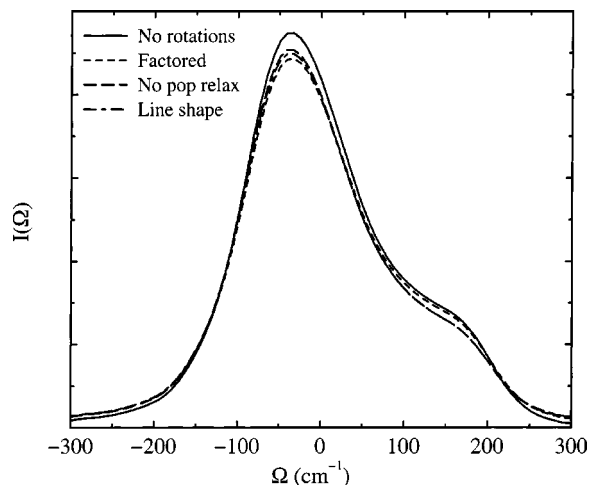
FIG. 6. Comparison of the distribution of frequencies and the line shape for the OD stretch.

to include this population relaxation contribution. Rotational dynamics also contributes a little to the broadening, and we see that the factorization approximation is only fair. In the case of the stretches (Figs. 3 and 4), since the linewidths are larger and the vibrational lifetimes are longer, neither population relaxation nor rotational dynamics is very important. As discussed in paper I, the theoretical relaxation times for these modes will presumably become smaller upon including solvent vibrations in the model, which could significantly affect the linewidths.

It is interesting to ascertain from these theoretical results the extent of motional narrowing; that is, how much narrower is the line shape than the distribution of frequencies?[2,3] To this end, in Figs. 5–7, comparisons are made between the distributions of frequencies from Eq. (9) and the line shapes obtained from Eq. (8). Here, rotations and population relaxation have been excluded in order to focus solely on motional narrowing. While all three line shapes exhibit narrowing, that of the bend vibration is the greatest.

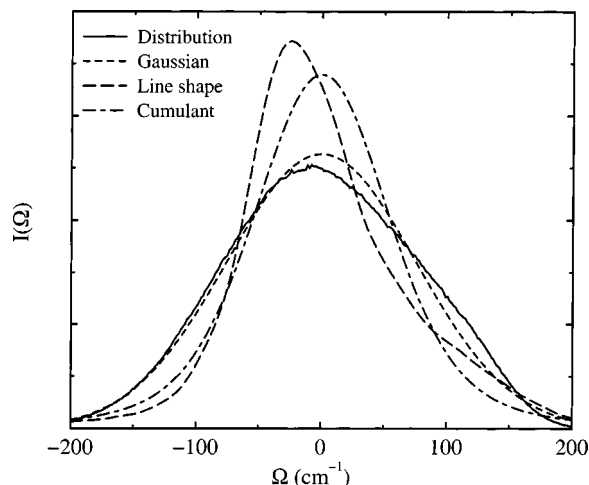In these same figures we compare the truncated cumulant expansion results for the distribution of frequencies

[from Eq. (12), and labeled Gaussian in Figs. 5–7] and for the line shape [Eq. (10), labeled cumulant]. In all cases, the Gaussian approximation to the distribution is reasonably accurate, although there is some asymmetry in a shoulder that appears on the red (blue) side for the bend (stretches). In the case of the line shapes, there is good agreement between the truncated cumulant and exact (within the model) results for the bend vibration, but the agreement is less good for the stretches. The feature that is most obviously lacking in the truncated cumulant results is the shoulder mentioned in regard to the distributions of frequencies. As will be shown in Paper III, at least in the case of the OH stretch, this shoulder is due to instances in which the H of HOD does not form a hydrogen bond.[28] Overall, however, from these figures one would conclude that the Gaussian approximation is quite reasonable for this system.

Within the second cumulant approximation, one can understand the extent of motional narrowing by considering, for a given transition,

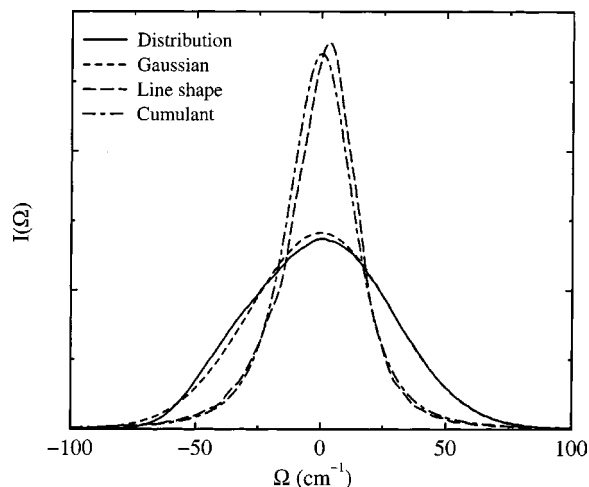$$\Delta^2 \equiv \langle \Omega^2 \rangle, \tag{14}$$

FIG. 5. Comparison of the distribution of frequencies and the line shape for the bend vibration.
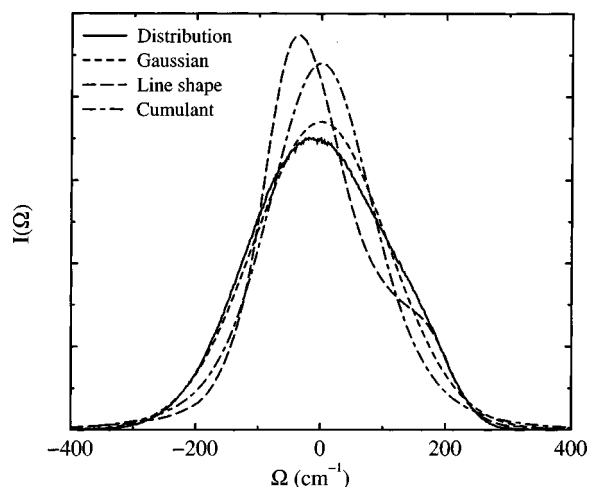

FIG. 7. Comparison of the distribution of frequencies and the line shape for the OH stretch.
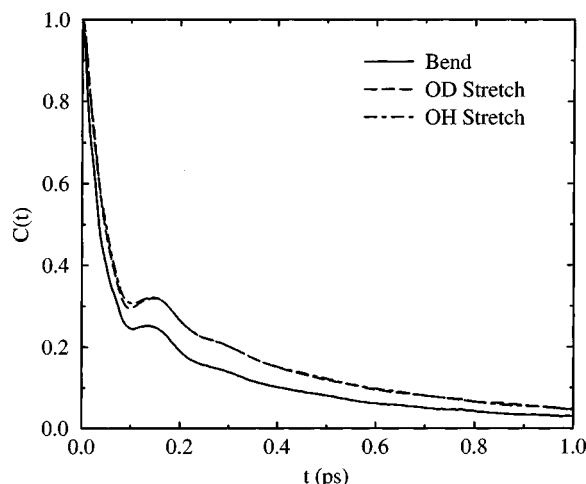
FIG. 8. Normalized frequency time-correlation functions for the three vibrational modes.

FIG. 9. Comparison of $C_4(t)$ to $2C(t)^2 + \langle \Omega^2 \rangle^2$ for the three vibrations. The functions are plotted in ascending order: bend, OD stretch, and OH stretch, each normalized by $C_4(0)$.

and

$$\tau \equiv \int_0^\infty dt\, C(t)/C(0). \tag{15}$$

The inhomogeneous and homogeneous (motionally narrowed) limits are given by $\Delta\tau \gg 1$ and $\Delta\tau \ll 1$, respectively.[3] Plots of the normalized frequency TCFs are shown in Fig. 8. The three TCFs are similar, all showing a fast decay with a time constant of about 70 fs, an oscillation with a period of about 140 fs, and a slower decay of about 500 fs. These results are similar to earlier results of Diraison et al.,[42] except that these authors did not see an oscillation. The oscillation can be identified as arising from the hindered translations (hydrogen-bond stretching) of the HOD and a D_2O molecule.[18,43–45] For each transition values for Δ and τ, and their product, are given in Table III. As Fig. 8 would suggest, the τ for the stretches are almost identical, and there is also not too much difference between these times and that of the bend. However, the distributions of frequencies show that there is a large difference in Δ for these vibrational modes. For the bend $\Delta\tau = 0.77$, indicating substantial motional narrowing, consistent with Fig. 2. For the stretches, where $\Delta\tau$ is 3 or 4, experience with the simple Kubo model (involving an exponentially decaying TCF), would suggest there is little motional narrowing.[3] The figures, however, still show quite a bit. This indicates that conclusions from the Kubo model, involving a single decay time of the TCF, may not be applicable to more realistic situations (like in Fig. 8), which involve TCFs with two or more disparate time scales.

As a final look at the Gaussian nature of the fluctuating vibrational frequencies, we consider the two- and four-point correlation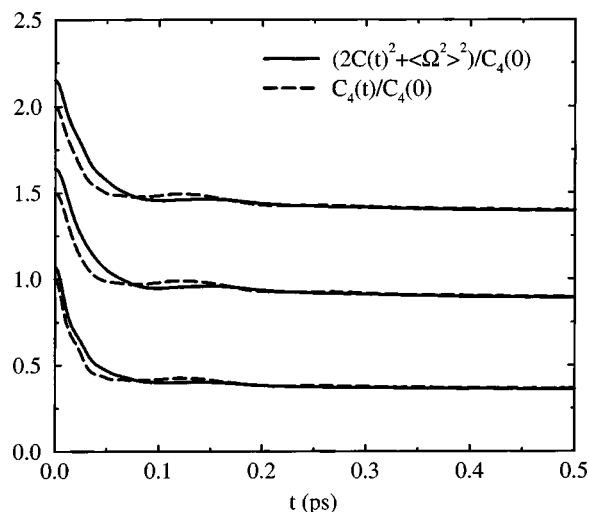 functions, $C(t)$ and $C_4(t)$. Figure 9 shows a comparison of $C_4(t)$ to $2C(t)^2 + \langle \Omega^2 \rangle^2$, which would be equal if $\Omega(t)$ were Gaussian, for the three modes. Both functions are normalized by $C_4(0)$, and the results are shifted in Fig. 9 by 0.5 for clarity. While these two functions are certainly not equal in each case, the deviations are not all that great. This leads us to the conclusion that while $\Omega(t)$ is not Gaussian, this approximation could still lead to fairly accurate results.

IV. VIBRATIONAL STOKES SHIFT

The vibrational Stokes shift for state l is the difference between the average frequency for the transition from the ground state to state l and that for the transition from l to the ground state. In general, these two frequencies are different because the interactions of the HOD with surrounding solvent molecules depend on the vibrational state of the HOD. While this effect has not been included previously in any theoretical treatment of vibrational spectroscopy (as far as we know), it is present in our treatment since the bath depends on the vibrational state of the HOD through the self-consistent renormalization procedure.

For the OH stretch the average frequency for the transition from the ground state is (from the theory) 3395 cm^{-1} (see Table II). To obtain the average frequency for the transition from the excited state, the entire calculation must be repeated, determining the appropriate bath for the first excited state of the stretch, and then running a new simulation for this different bath. In fact, precisely this calculation was performed in Paper I in a different context. Therein we were interested in vibrational energy relaxation from the OH stretch fundamental, and as such needed to have the bath defined for that initial state. It was also important to determine vibrational frequencies for that bath, since the frequency differences were needed in order to calculate vibrational lifetimes. In any case, we found that the average frequency for the fundamental transition when the OH

TABLE III. Δ, τ, and their product for each of the transitions.

	Δ (cm^{-1})	τ (ps)	$\Delta\tau$
Bend	28.2	0.146	0.77
OD stretch	75.8	0.212	3.0
OH stretch	107.9	0.206	4.2

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stretch is excited is 3338 cm^{-1}, leading to a calculated Stokes shift of 57 cm^{-1}. This is close to the experimental value of approximately 70 cm^{-1}.[17]

If one is in the weak-coupling limit the Stokes shift can actually be calculated simply from[33]

$$\omega_s = \beta\hbar\Delta^2, \tag{16}$$

or the presumably more accurate result[35]

$$\omega_s = \frac{\beta\hbar}{2}(\Delta^2 + \Delta_1^2), \tag{17}$$

where Δ_1^2 is the variance of the frequency distribution when HOD is in its excited state. Δ is given in Table III as 107.9 cm^{-1}, and Δ_1 is found to be 109.1 cm^{-1}. Therefore, either of the above two formulas lead to a Stokes shift of 56 cm^{-1}, in excellent agreement with the above.

For completeness we also give results for the vibrational Stokes shifts for the other two modes (which have not been measured experimentally). From the theoretical results in Table II of this paper and Tables V and VI of Paper I,[18] we find Stokes shifts of 28 and 2 cm^{-1} for the OD stretch and the bend, respectively.

V. CONCLUDING REMARKS

In this paper we have presented theoretical results for the vibrational absorption line shapes and Stokes shifts of HOD in liquid D$_2$O. While there is still room for improvement, the overall agreement with experiment is quite good. We have discussed the merits of several approximations to the line shapes and have explored the Gaussian nature of the fluctuating frequencies. The inclusion of orientational dynamics and population relaxation significantly broadens the bend line shape, but is not very important for the stretches. While the fluctuating vibrational frequencies are not strictly Gaussian, the deviations are not great.

There are two major motivations for performing these calculations. The first is that previous works on the vibrational spectroscopy of liquid water have treated the nuclear motions classically, whereas a quantum-mechanical treatment (of at least the HOD nuclear degrees of freedom) such as ours seems more appropriate. The second and perhaps more important motivation is that, as mentioned in the Introduction, vibrational spectroscopy can, in principle, provide information about molecular dynamics. In the case of the OH stretch of HOD in D$_2$O, however, we have seen that the line shape is to a large extent inhomogeneously broadened. This means that from a line-shape analysis it would be very difficult to obtain dynamical information, such as, for example, the frequency TCF. On the other hand, very recent ultrafast vibrational transient-hole-burning[22,24] and photon-echo experiments[29,30] have directly measured the frequency TCF. Any model that can describe these experiments must also be able to describe the linear spectroscopy. The fact that we get acceptable agreement with the line shape and Stokes shift experiments, suggests that our model is indeed reasonable, providing some confidence that our description and analysis of the nonlinear experiments will be meaningful. Papers III and IV in this series compare theory to hole-burning and echo experiments, respectively, and help us understand precisely what these experiments are telling us about molecular dynamics in liquid water.

APPENDIX

The (at this point, fully quantum-mechanical) Hamiltonian is given in Eq. (1), and the system Hamiltonian has eigenstates and eigenvalues as in Eq. (2). As noted in Sec. II for the absorption problem, the bath is appropriate for the ground vibrational state. To proceed, we write the Hamiltonian in terms of the eigenstates of H_s:

$$H = \sum_i H_i |i\rangle\langle i|, \tag{A1}$$

where $H_i = E_i + V_{ii} + H_b$. In the above, we have neglected the off-diagonal terms, as population relaxation will be added phenomenologically. Assuming that only the ground state is populated in thermal equilibrium, and focusing on the transition to vibrational state l, the absorption line-shape formula Eq. (4) becomes

$$I(\omega) \sim \int_{-\infty}^{\infty} dt\, e^{-i\omega t} Tr_b [e^{-\beta H_0}\hat{u} \cdot e^{iH_l t/\hbar}\hat{u}e^{-iH_0 t/\hbar}], \tag{A2}$$

where the trace is over the bath states and $\hat{u} \sim \langle 0|\boldsymbol{\mu}|l\rangle$ is the transition dipole unit vector operator for the transition from the ground state to state l. This can be rewritten as

$$I(\omega) \sim \int_{-\infty}^{\infty} dt\, e^{-i\omega t} Tr_b \left[e^{-\beta H_0}\hat{u}\, \exp_T\left(\frac{i}{\hbar}\int_0^t d\tau e^{iH_0\tau/\hbar}\right.\right.$$
$$\left.\left. \times (H_l - H_0)e^{-iH_0\tau/\hbar}\right) e^{iH_0 t/\hbar}\hat{u}e^{-iH_0 t/\hbar} \right], \tag{A3}$$

where T is the appropriate time-ordering operator.[33,46,47] Next, we make two approximations. First, we assume that H_0 can be replaced by $H_b + E_0$ (we neglect V_{00}) in both the Boltzmann factor and the time-evolution operators. To this end, we note that within our self-consistent renormalization scheme to a large extent the system–bath coupling is already included in H_s, and also that the bath average of V is 0. Second, we take the classical limit for all bath variables, in which case since all operators commute the time-ordering operator becomes irrelevant, and we obtain

$$I(\omega) \sim \int_{-\infty}^{\infty} dt\, e^{-i(\omega - \langle\omega\rangle)t} \left\langle \hat{u}(0)\cdot\hat{u}(t) \right.$$
$$\left. \times \exp\left(\frac{i}{\hbar}\int_0^t d\tau[V_{ll}(\tau) - V_{00}(\tau)]\right) \right\rangle, \tag{A4}$$

where now the brackets correspond to a classical equilibrium average with respect to the bath Hamiltonian, and the (classical) time evolution is propagated with the same Hamiltonian.

[1] D. W. Oxtoby, D. Levesque, and J.-J. Weis, J. Chem. Phys. **68**, 5528 (1978).

[2] R. Kubo, in *Fluctuation, Relaxation, and Resonance in Magnetic Systems*, edited by D. Ter-Haar (Oliver and Boyd, Edinburgh, 1962).

[3] R. Kubo, Adv. Chem. Phys. **15**, 101 (1969).

[4] M. Falk and T. A. Ford, Can. J. Chem. **44**, 1699 (1966).

[5] D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford University Press, New York, 1969).

[6] R. G. Gordon, Adv. Magn. Reson. **3**, 1 (1968).

[7] D. A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1976).

[8] K. Toukan and A. Rahman, Phys. Rev. B **31**, 2643 (1985).

[9] R. Bansil, T. Berger, K. Toukan, M. A. Ricci, and S. H. Chen, Chem. Phys. Lett. **132**, 165 (1986).

[10] A. Wallqvist and O. Teleman, Mol. Phys. **74**, 515 (1991).

[11] J. Martí, J. A. Padró, and E. Guàrdia, J. Mol. Liq. **62**, 17 (1994).

[12] J. Martí, E. Guàrdia, and J. A. Padró, J. Chem. Phys. **101**, 10883 (1994).

[13] J. Martí, J. A. Padró, and E. Guàrdia, J. Chem. Phys. **105**, 639 (1996).

[14] H. Ahlborn, X. Ji, B. Space, and P. B. Moore, J. Chem. Phys. **111**, 10622 (1999).

[15] H. Ahlborn, B. Space, and P. B. Moore, J. Chem. Phys. **112**, 8083 (2000).

[16] P. L. Silvestrelli, M. Bernasconi, and M. Parrinello, Chem. Phys. Lett. **277**, 478 (1997).

[17] S. Woutersen and H. J. Bakker, Phys. Rev. Lett. **83**, 2077 (1999).

[18] C. P. Lawrence and J. L. Skinner, J. Chem. Phys. **117**, 5827 (2002).

[19] R. Rey and J. T. Hynes, J. Chem. Phys. **104**, 2356 (1996).

[20] S. Woutersen, U. Emmerichs, H.-K. Nienhuys, and H. J. Bakker, Phys. Rev. Lett. **81**, 1106 (1998).

[21] H.-K. Nienhuys, S. Woutersen, R. A. van Santen, and H. J. Bakker, J. Chem. Phys. **111**, 1494 (1999).

[22] G. M. Gale, G. Gallot, F. Hache, N. Lascoux, S. Bratos, and J.-Cl. Leicknam, Phys. Rev. Lett. **82**, 1068 (1999).

[23] G. M. Gale, G. Gallot, and N. Lascoux, Chem. Phys. Lett. **311**, 123 (1999).

[24] R. Laenen, C. Rauscher, and A. Laubereau, Phys. Rev. Lett. **80**, 2622 (1998).

[25] R. Laenen, C. Rauscher, and A. Laubereau, J. Phys. Chem. B **102**, 9304 (1998).

[26] J. C. Deàk, S. T. Rhea, L. K. Iwaki, and D. D. Dlott, J. Phys. Chem. A **104**, 4866 (2000).

[27] S. Woutersen, U. Emmerichs, and H. J. Bakker, Science **278**, 658 (1997).

[28] C. P. Lawrence and J. L. Skinner, J. Chem. Phys. (to be published).

[29] J. Stenger, D. Madsen, P. Hamm, E. T. J. Nibbering, and T. Elsaesser, Phys. Rev. Lett. **87**, 027401 (2001).

[30] J. Stenger, D. Madsen, P. Hamm, E. T. J. Nibbering, and T. Elsaesser, J. Phys. Chem. A **106**, 2341 (2002).

[31] A. Piryatinski, C. P. Lawrence, and J. Skinner, J. Chem. Phys. (to be published).

[32] L. E. Fried and S. Mukamel, Adv. Chem. Phys. **84**, 435 (1993).

[33] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995).

[34] J. G. Saven and J. L. Skinner, J. Chem. Phys. **99**, 4391 (1993).

[35] M. D. Stephens, J. G. Saven, and J. L. Skinner, J. Chem. Phys. **106**, 2129 (1997).

[36] K. F. Everitt and J. L. Skinner, J. Chem. Phys. **115**, 8531 (2001).

[37] O. L. Polyansky, P. Jensen, and J. Tennyson, J. Chem. Phys. **105**, 6490 (1996).

[38] M. F. Kropman, H.-K. Nienhuys, S. Woutersen, and H. J. Bakker, J. Phys. Chem. A **105**, 4622 (2001).

[39] J. E. Bertie, M. K. Ahmed, and H. H. Eysel, J. Phys. Chem. **93**, 2210 (1989).

[40] A. Morita and J. T. Hynes, J. Phys. Chem. B **106**, 673 (2002).

[41] W. S. Benedict, N. Gailar, and E. K. Plyler, J. Chem. Phys. **24**, 1139 (1956).

[42] M. Diraison, Y. Guissani, J.-Cl. Leicknam, and S. Bratos, Chem. Phys. Lett. **258**, 348 (1996).

[43] E. W. Castner, Jr., Y. J. Chang, Y. C. Chu, and G. E. Walrafen, J. Chem. Phys. **102**, 653 (1995).

[44] J. T. Kindt and C. A. Schmuttenmaer, J. Chem. Phys. **106**, 4389 (1997).

[45] D. M. Carey and G. M. Korenowski, J. Chem. Phys. **108**, 2669 (1998).

[46] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many Particle Systems* (McGraw-Hill, New York, 1971).

[47] D. Hsu and J. L. Skinner, J. Chem. Phys. **81**, 1604 (1984).