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# Dephasing and Decoherence in Vibrational and Electronic Line Shapes

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"bath" (in this case, the rotational and translational degrees of freedom of all the molecules in the liquid). If these degrees of freedom are treated classically, the broadening process is often known as dephasing. If, on the other hand, the bath degrees of freedom are instead treated quantum mechanically, there is additional broadening due to what is known in the chemical-physics literature as decoherence. The question addressed in this paper is the relative importance of decoherence (bath quantum effects) and dephasing. We present general developments of this subject for absorption and emission line shapes, discover several new relationships connecting



classical and quantum treatments of the bath, and also consider the Stokes shift (difference in peak frequencies in absorption and emission). We next draw some general conclusions by considering a model system whose transition-frequency time-correlation function has only one bath time scale. We then consider a realistic system of the vibrational OH stretch transition of dilute HOD in liquid  $D_2O$  at room temperature. For this system, we conclude that bath quantum effects are not very important, except for the Stokes shift. More generally, we argue that this is the case for many vibrational and most electronic transitions in room-temperature liquids.

# 1. INTRODUCTION

Vibrational and electronic spectroscopies have proven to be important techniques for probing the structure and dynamics of condensed matter. Herein, we focus on the absorption and emission line shapes for a transition between two vibronic states of a solute molecule in a liquid. These two quantum states are coupled to a thermal bath consisting of the rotational and translational degrees of freedom of all the molecules (including the solute). This coupling often results in broadening of the line shape in addition to the natural line width due to radiative relaxation. For example, the bath can induce additional population relaxation between the states through off-diagonal coupling; we discuss this process later in the Introduction, but it is not the focus of this paper. Rather, herein we consider the effect of diagonal coupling to the bath, which produces line broadening through phase relaxation.<sup>1–3</sup>

For a classical bath, this phase relaxation (which we simply call "dephasing") arises from time-dependent fluctuations of the energy gap,  $\hbar\omega$ , between the two quantum states, where  $\omega$  is the angular transition frequency. In 1969, Kubo laid out two important limiting cases, homogeneous and inhomogeneous dephasing, which are useful in understanding the effects of dephasing on line broadening.<sup>4</sup> Using Kubo's notation, where

 $\Delta$  is the root-mean-square (RMS) deviation of the transitionfrequency fluctuations, and  $\tau$  is the correlation time of the fluctuations, inhomogeneous dephasing corresponds to the limit  $\Delta \tau \gg 1$  and homogeneous dephasing corresponds to  $\Delta \tau \ll 1$ . In inhomogeneous dephasing, every member of the ensemble effectively has a different transition frequency. In this case, the line shape is typically Gaussian, with a line width proportional to  $\Delta$ . In the homogeneous dephasing limit, in effect each member of the ensemble has the same transition frequency (on the average), and the line shape is Lorentzian with a line width proportional to  $\Delta^2 \tau$ . Since in this limit  $\Delta^2 \tau < \Delta$ , one says that the line shape is "motionally narrowed". For more realistic baths, where the frequency time-correlation function decays on more than one time scale, the situation is more complex.<sup>5</sup>

Now suppose that the same bath is treated quantum mechanically. It turns out that the line broadening is enhanced

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from that for the classical bath, and the enhancement has come to be known in the chemical-physics literature as "decoherence".<sup>6-9</sup> Decoherence (bath quantum effects) by definition vanishes when the bath degrees of freedom are treated in the high-temperature (classical) limit. Note that the words decoherence and dephasing can have different meanings in the field of open quantum systems.<sup>10-15</sup> The following question arises, then: How important is decoherence in typical vibrational or electronic spectroscopy in liquids? In fact, decoherence is typically neglected completely, and so one would like to know if this is a good approximation or not. While formal approaches for including bath quantum effects in absorption spectra do exist,<sup>1,2,16,17</sup> they have only been applied to a few realistic systems. The earliest appears to have been by Kwac and Cho; in 2003, they calculated the absorption line shape, including bath quantum effects, for the amide I mode of N-methylacetamide in water.<sup>18</sup>

In 2005, Lawrence and Skinner<sup>19</sup> attempted to address the more general importance of bath quantum effects in line shapes by considering a simple model for the frequency timecorrelation function, characterized by the two parameters  $\Delta$ and  $\tau$  described above. Quantum effects of the bath were introduced through the harmonic quantum-correction factor (QCF),<sup>20–23</sup> which involves a third parameter, temperature T (or the time  $\hbar/kT \equiv \beta\hbar$ ). These three parameters lead to two independent dimensionless ratios. Within the Condon and second-cumulant approximations to the line shape, they then computed the magnitude of quantum effects as a function of these two ratios. They found that at low enough temperatures such that  $\beta\hbar > \tau$ , quantum effects could be significant. At room temperature (T = 295 K),  $\beta\hbar = 26$  fs.  $\tau$  depends on the liquid solvent, and the "fastest" common solvent is water, because of the light hydrogen atoms. In fact, in rigid water models the frequency time-correlation function decays on two time scales, and the shorter characteristic time is about 40 fs, in which case  $\beta\hbar/\tau = 0.65 < 1$ . From this, Lawrence and Skinner concluded that decoherence is typically not important for vibrational or electronic transitions in liquids. This conclusion was borne out by considering two realistic specific examples, one of which is the vibrational transition of the OH stretch of dilute HOD in liquid  $D_2O$ .

Another approach for including bath quantum effects comes from the closely related problem of bath-induced nonadiabatic transitions (population relaxation) between two vibronic states of a solute molecule in a liquid.<sup>24</sup> The theoretical formulation of this problem is similar to that of the line-shape problem, as the observable is written in terms of the Fourier transform of a similar time-correlation function. Bath quantum effects for both problems can be described by a decoherence function.<sup>6–9</sup> Even though the line shape and nonadiabatic transition timecorrelation functions involve different operators, the decoherence function is formally the same for both processes.<sup>6–9</sup>

Since the early 1990s, the decoherence function for nonadiabatic processes has usually been treated with the frozen Gaussian approximation (FGA) for wave packet evolution on the two potential surfaces.<sup>6,7,25–36</sup> If the multidimensional potential surface of the bath is harmonic when the system is in the ground state, and the surface in the excited state is identical but with a displaced minimum, the problem can be solved exactly quantum mechanically,<sup>1,27</sup> and it can be shown that the FGA is exact.<sup>27</sup> For realistic systems, this harmonic model is not realized exactly, but still the FGA is considered to be a good approximation. In 2006, Borgis,

Rossky, and Turi reconsidered the nonadiabatic transition problem and instead used the harmonic QCF, which for the harmonic model described above is also exact.<sup>22</sup> In fact, they showed that for the hydrated electron the decoherence functions from the FGA and QCF approximations were essentially the same.<sup>7,8,37</sup> In 2009, Turi et al.<sup>9</sup> used similar theoretical approaches to calculate the absorption spectrum of the hydrated electron, finding that decoherence was only of modest importance.

In 2016, Joutsuka, Thompson, and Laage<sup>38</sup> calculated the absorption spectrum for dilute HOD in liquid D<sub>2</sub>O, finding that quantum (decoherence) effects were substantial, increasing the line width by nearly a factor of 2. Unlike Lawrence and Skinner<sup>19</sup> and Turi et al.,<sup>9</sup> who used the harmonic QCF to introduce quantum effects into the line shape, Joutsuka et al.<sup>38</sup> used the FGA. Certainly, for the HOD/D<sub>2</sub>O system the surfaces are not harmonic; nonetheless, given the discussion above it is surprising that the results using the harmonic QCF<sup>19</sup> (quantum effects are negligible) and the FGA<sup>38</sup> (quantum effects are substantial) are so different. Moreover, the FGA result for HOD/D<sub>2</sub>O is in disagreement with the general conclusions of Lawrence and Skinner.<sup>19</sup> This motivated us to try to understand more deeply under what circumstances decoherence is expected to be important in lineshape problems.

We begin by deriving some new results for the decoherence function and the decoherence time, and we discuss criteria for when quantum bath effects should be important (Section 2). We also discuss the analogous emission line shape (Section 3) and derive a new result for the Stokes shift (difference in absorption and emission peak frequencies) (Section 4). We illustrate this with a simple analytical model for the classical frequency time-correlation function (Section 5). We then reconsider the dilute HOD in D<sub>2</sub>O system discussed above, using our new results to determine if quantum effects should be important, and illustrate this by calculating absorption and emission line shapes (Section 6). Our conclusions agree with Lawrence and Skinner,<sup>19</sup> that quantum effects are not very important for the absorption line width of HOD/D<sub>2</sub>O. More generally, we conclude that quantum bath effects are not expected to be important for line shapes for nearly all electronic transitions, and many vibrational transitions, in room-temperature liquids.

# 2. ABSORPTION LINE SHAPE

In general, the absorption line shape of a quantum-mechanical system with Hamiltonian *H* and dipole operator  $\vec{\mu}$ , is given by

$$I(\omega) \sim Re\left\{\int_0^\infty dt \ e^{i\omega t} \langle \hat{\mathbf{e}} \cdot \vec{\mu}(t) \hat{\mathbf{e}} \cdot \vec{\mu}(0) \rangle\right\}$$
(1)

where  $\hat{\epsilon}$  is the polarization unit vector of the linearly polarized light,  $\vec{\mu}(t) = e^{iHt/\hbar}\vec{\mu}e^{-iHt/\hbar}$ , and  $\langle \cdots \rangle$  indicates a thermal quantum-mechanical average for Hamiltonian *H*.

As in ref 19, we immediately specialize this general situation by considering the transition between two vibronic quantum states of a solute molecule, where the ground state is  $|0\rangle$  and the excited state is  $|1\rangle$ . These two states are coupled to bath degrees of freedom. When the molecule is in its ground state, the bath Hamiltonian is  $H_0$ , and when the molecule is in the excited state, the bath Hamiltonian is  $H_1$ . Herein we neglect off-diagonal coupling to the bath. Thus, in the absence of the radiation field the full Hamiltonian is

$$H = H_0 |0\rangle \langle 0| + H_1 |1\rangle \langle 1| \tag{2}$$

Within this two-level approximation, the dipole operator is given by

$$\hat{\epsilon} \cdot \vec{\mu} = m\{|0\rangle\langle 1| + |1\rangle\langle 0|\}$$
(3)

where m is a bath operator. In the case where the excited vibronic state is not appreciably populated in thermal equilibrium, the line shape becomes

$$I(\omega) \sim Re\left\{\int_0^\infty dt \ e^{i\omega t} \langle m(t)e^{iH_0 t/\hbar}e^{-iH_1 t/\hbar}m(0)\rangle\right\}$$
(4)

where now  $m(t) = e^{iH_0t/\hbar}me^{-iH_0t/\hbar}$ , and the angular brackets indicate a thermal quantum average for the ground-state bath Hamiltonian  $H_0$ . Defining  $u = (H_1 - H_0)/\hbar$ ,  $u(t) = e^{iH_0t/\hbar}ue^{-iH_0t/\hbar}$ , and  $\delta u(t) = u(t) - \langle u \rangle$ , this can be written in terms of a time-ordered exponential:<sup>1,9,39</sup>

$$I(\omega) \sim Re\left\{\int_0^\infty \mathrm{d}t \, \mathrm{e}^{\mathrm{i}(\omega - \langle u \rangle)t} \left\langle m(t) \exp_+\left\{-\mathrm{i} \int_0^t \mathrm{d}t' \, \delta u(t')\right\} m(0) \right\rangle\right\}$$
(5)

where "+" orders the  $\delta u(t')$ 's in increasing time from right to left.

**2.1. Classical Limit.** In the classical limit, when m(t) and  $\delta u(t)$  become classical variables (whose order no longer matters), the line shape is

$$I(\omega) \sim Re\left\{\int_{0}^{\infty} dt \, e^{i(\omega - \langle u \rangle_{c})t} \left\langle m(t)m(0)\exp\left\{-i \int_{0}^{t} dt' \, \delta u(t')\right\} \right\rangle_{c}\right\}$$
(6)

The subscript c on the brackets explicitly indicates a classical average. One might assume that the transition dipole and frequency fluctuations are uncorrelated (although this is not necessarily a good approximation<sup>40</sup>), in which case

$$I(\omega) \sim Re\left\{\int_{0}^{\infty} \mathrm{d}t \, \mathrm{e}^{\mathrm{i}(\omega - \langle u \rangle_{c})t} \langle m(t)m(0) \rangle_{c} \left\langle \exp\left\{-\mathrm{i} \int_{0}^{t} \mathrm{d}t' \, \delta u(t')\right\} \right\rangle_{c}\right\}$$
(7)

The Condon approximation neglects the bath dependence of the transition dipole altogether, and so in this case

$$I(\omega) \sim Re\left\{\int_{0}^{\infty} dt \ e^{i(\omega - \langle u \rangle_{c})t} \left\langle \exp\left\{-i \int_{0}^{t} dt' \ \delta u(t')\right\} \right\rangle_{c}\right\}$$
(8)

From this, one can make the second-cumulant approximation by expanding the average of the exponential in cumulants and truncating after the second term to obtain<sup>1</sup>

$$I(\omega) \sim Re\left\{\int_0^\infty dt \ e^{i(\omega - \langle u \rangle_c)t} e^{-g_c(t)}\right\}$$
(9)

where

$$g_{\rm c}(t) = \int_0^t {\rm d}t' \int_0^{t'} {\rm d}t'' \ C_{\rm c}(t'')$$
(10)

and

$$C_{\rm c}(t) = \langle \delta u(t) \delta u(0) \rangle_{\rm c} \tag{11}$$

Article

is the classical frequency time-correlation function (FTCF). Note that  $C_c(t)$  is real and so is the "dephasing function"  $e^{-g_c(t)}$ . The time dependence of  $g_c(t)$  controls the broadening of the line shape.

Defining the mean-square frequency fluctuations by

$$\langle \delta u^2 \rangle_{\rm c} = C_{\rm c}(0) = \Delta^2 \tag{12}$$

at short times eq 10 becomes

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$$g_{\rm c}(t) \approx \Delta^2 t^2 / 2 \tag{13}$$

We also note that the correlation time  $\tau$  is defined by

$$\tau = \int_0^\infty \mathrm{d}t \ \bar{C}_{\rm c}(t) \tag{14}$$

where the normalized FTCF is

$$\overline{C}_{\rm c}(t) = C_{\rm c}(t)/\Delta^2 \tag{15}$$

In the inhomogeneous limit<sup>4</sup> where  $\Delta \tau \gg 1$ , the dephasing function is completely dominated by the short-time result in eq 13, in which case one can define a "dephasing time"  $\tau_{\rm p}$  by

$$g_{\rm c}(t) \approx \frac{t^2}{2\tau_{\rm p}^2} \tag{16}$$

since the dephasing function decays to zero on this time scale, and so  $\tau_{\rm p} = 1/\Delta$ .

**2.2.** Quantum Cumulant Approximation. Returning to the fully quantum situation described by eq 5 and applying the Condon and second-cumulant approximations, one obtains<sup>1</sup>

$$I(\omega) \sim Re\left\{\int_0^\infty dt \ e^{i(\omega - \langle u \rangle)t} e^{-g(t)}\right\}$$
(17)

where

$$g(t) = \int_0^t dt' \int_0^{t'} dt'' C(t'')$$
(18)

and

$$C(t) = \langle \delta u(t) \delta u(0) \rangle \tag{19}$$

where now C(t) is the quantum FTCF. Note that since C(t) is complex, g(t) is as well. With the definition of the decoherence function  $e^{-g_d(t)}$  by<sup>6-9</sup>

$$e^{-g_d(t)} = \frac{e^{-g(t)}}{e^{-g_c(t)}}$$
 (20)

clearly

$$g_{\rm d}(t) = g(t) - g_{\rm c}(t) = \int_0^t {\rm d}t' \int_0^{t'} {\rm d}t'' \left[ C(t'') - C_{\rm c}(t'') \right]$$
(21)

 $g_{\rm d}(t)$  results solely from the quantum effects of the bath, and of course,  $g(t) = g_{\rm c}(t) + g_{\rm d}(t)$ . Thus, the line shape is determined by both dephasing and decoherence. The real part of  $g_{\rm d}(t)$  causes additional line broadening over and above the classical broadening, and the imaginary part produces an additional line shift and possibly line-shape distortion (since the classical line shape is symmetric within the second-cumulant approximation). In the short-time limit  $g_{\rm d}(t)$  is given approximately by<sup>9</sup>

$$g_{\rm d}(t) \approx [C(0) - C_{\rm c}(0)]t^2/2$$
 (22)

2.3. Evaluating the Decoherence Function. The goal of this Article is to calculate  $g_d(t)$  and assess its importance. To this end, the strategy herein is to start with a particular classical model, defined by its classical FTCF  $C_c(t)$ , and then determine  $g_d(t)$ . To do this we need to obtain the quantum FTCF C(t)from a knowledge only of its classical counterpart  $C_c(t)$ . One approach is through the QCF discussed in the Introduction.<sup>22</sup> Quantum FTCFs obey certain time symmetries,<sup>22</sup> which impose specific restrictions on the form of acceptable QCFs. Nonetheless, there are still an infinite number of different QCFs that lead to the correct symmetry properties. The one we choose here is called the harmonic QCF, because if the system is harmonic, and the FTCF involves a linear combination of the coordinates, then the harmonic QCF is exact.<sup>22</sup> And indeed, this is the case with the harmonic model described in the Introduction. To the extent to which localized or collective modes of the bath are approximately harmonic, the harmonic QCF should be a good approximation.<sup>41</sup>

Defining the Fourier transforms

$$\hat{C}_{c}(\omega) = \int_{-\infty}^{\infty} dt \ e^{i\omega t} C_{c}(t) = 2 \int_{0}^{\infty} dt \ \cos(\omega t) C_{c}(t)$$
(23)

(since  $C_c(t)$  is even in time), and

$$\hat{C}(\omega) = \int_{-\infty}^{\infty} dt \ e^{i\omega t} C(t)$$
(24)

the multiplicative frequency-domain QCFs  $Q(\omega)$  are defined by<sup>22</sup>

$$\hat{C}(\omega) = Q(\omega)\hat{C}_{c}(\omega)$$
(25)

and the harmonic QCF is  $^{20-23}$ 

$$Q(\omega) = \frac{\beta \hbar \omega}{1 - e^{-\beta \hbar \omega}}$$
(26)

As mentioned in the Introduction,  $\beta\hbar$  has units of time and will be an important parameter in what follows.

One way to proceed is to start with the classical FTCF  $C_c(t)$ and calculate  $g_c(t)$  from eq 10. Then Fourier transform  $C_c(t)$ to get  $\hat{C}_c(\omega)$ , obtain  $\hat{C}(\omega)$  using the QCF in eqs 25 and 26, and then Fourier transform back using

$$C(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \ e^{-i\omega t} \hat{C}(\omega)$$
(27)

to obtain C(t). From this, one can obtain g(t) with eq 18 and get  $g_d(t)$  from g(t) and  $g_c(t)$  (see eq 21). This was essentially the approach we took in ref 19. On the other hand, note that the classical limit follows as T gets large and hence  $\beta\hbar\omega$  tends toward 0. Indeed, in this limit, Q(0) = 1,  $\hat{C}(\omega) = C_c(\omega)$ , and  $C(t) = C_c(t)$ . Therefore, if one is interested in quantum corrections to the classical result, one can obtain these by expanding the QCF in eq 26 in powers of  $\beta\hbar\omega$ , which gives

$$Q(\omega) = 1 + \frac{\beta \hbar \omega}{2} + \frac{(\beta \hbar \omega)^2}{12} + \cdots$$
(28)

Then using eq 25 and inverse Fourier transforming gives

$$C(t) = C_{\rm c}(t) + i\frac{\beta\hbar}{2}\dot{C}_{\rm c}(t) - \frac{(\beta\hbar)^2}{12}\ddot{C}_{\rm c}(t) + \dots$$
(29)

Using eq 21 and the fact that since  $C_c(t)$  is analytic and even,  $\dot{C}_c(0) = 0$ , this yields

$$g_{\rm d}(t) = -i\frac{\beta\hbar\Delta}{2}\Delta\int_{0}^{t}dt'[1-\bar{C}_{\rm c}(t')] + \frac{(\beta\hbar\Delta)^{2}}{12}[1-\bar{C}_{\rm c}(t)] + \cdots$$
(30)

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The first term, which is imaginary, was found by Lawrence and Skinner,<sup>19</sup> and in earlier work by Mukamel,<sup>1</sup> but the second term, which is real (and hence controls the decoherence contribution to line broadening), is new to the best of our knowledge. This is a central result of this work, which allows one to understand under what circumstances decoherence is important.

We now consider the short-time behavior of the decoherence function, which may be important when  $\Delta \tau \gg$  1. As mentioned above, the classical FTCF is even, so it must be quadratic at short time. Defining the time  $\tau_s$  ("s" signifies "short") by

$$\overline{C}_{\rm c}(t) \equiv 1 - \frac{t^2}{2\tau_{\rm s}^2} + \cdots$$
(31)

we immediately see from eq 30 that at short times

$$g_{\rm d}(t) = \frac{(\beta\hbar\Delta)^2 t^2}{24\tau_{\rm s}^2} - i\frac{\beta\hbar\Delta^2 t^3}{12\tau_{\rm s}^2} + \cdots$$
(32)

From this, one can define a "decoherence time"  $\tau_d$  by

$$\operatorname{Re}\{g_{\mathrm{d}}(t)\} \equiv \frac{t^{2}}{2\tau_{\mathrm{d}}^{2}}$$
(33)

in which case

$$\tau_{\rm d} = \frac{2\sqrt{3}\,\tau_{\rm s}}{\beta\hbar\Delta}\tag{34}$$

We believe that this is also a new result. Since, as discussed before,  $\tau_p = 1/\Delta$ , this gives the interesting result that the ratio of decoherence to dephasing times is

$$\frac{\tau_{\rm d}}{\tau_{\rm p}} = \frac{2\sqrt{3}\,\tau_{\rm s}}{\beta\hbar} \tag{35}$$

**2.4. Decoherence Function from \hat{C}\_{c}(\omega).** Alternatively, one can obtain a quantum result for  $g_{d}(t)$  that is valid for *all* temperatures (within the Condon, cumulant, and harmonic QCF approximations) by working in the frequency domain. We begin by using eqs 25–27 to write C(t) in terms of  $\hat{C}_{c}(\omega)$ :<sup>8</sup>

$$C(t) = \frac{\beta\hbar}{2\pi} \int_0^\infty d\omega \ \omega \hat{C}_c(\omega) \{ \coth(\beta\hbar\omega/2)\cos(\omega t) - i\sin(\omega t) \}$$
(36)

Then, doing the time integrals in eq 18, one finds that

$$g(t) = \frac{\beta\hbar}{2\pi} \int_0^\infty d\omega \, \frac{\hat{C}_c(\omega)}{\omega} \{ \coth(\beta\hbar\omega/2)[1 - \cos(\omega t)] + i[\sin(\omega t) - \omega t] \}$$
(37)

This formula is identical to that in ref 8 and similar to those in refs 1 and 2.

To compute  $g_d(t)$  we need to subtract the classical limit of g(t). To that end, the hyperbolic cotangent can be expanded for small  $\beta\hbar\omega$  (high temperature); keeping the first term, and

since in this limit the real part dominates the imaginary part, this becomes the classical line-shape function

$$g_{\rm c}(t) = \frac{1}{\pi} \int_0^\infty \mathrm{d}\omega \frac{\hat{C}_{\rm c}(\omega)}{\omega^2} [1 - \cos(\omega t)]$$
(38)

which is equal to eq 10.

Using this, from eq 21 the decoherence function can be written as

$$g_{d}(t) = \frac{\beta\hbar}{2\pi} \int_{0}^{\infty} d\omega \frac{\hat{C}_{c}(\omega)}{\omega} \left\{ \left[ \coth(\beta\hbar\omega/2) - \frac{2}{\beta\hbar\omega} \right] [1 - \cos(\omega t)] + i[\sin(\omega t) - \omega t] \right\}$$
(39)

Now keeping the first *two* terms in the expansion of the hyperbolic cotangent yields

$$g_{\rm d}(t) \approx \frac{\beta\hbar}{2\pi} \int_0^\infty d\omega \frac{\hat{C}_{\rm c}(\omega)}{\omega} \left\{ \frac{\beta\hbar\omega}{6} [1 - \cos(\omega t)] + i[\sin(\omega t) - \omega t] \right\}$$
(40)

which one can show is precisely equal to eq 30 (as it should be, since these are both high-temperature expansions). Expanding this for short time gives

$$g_{\rm d}(t) \approx \frac{\beta \hbar t^2}{12\pi} \left[ \frac{\beta \hbar}{2} - \mathrm{i}t \right] \int_0^\infty \mathrm{d}\omega \ \hat{C}_{\rm c}(\omega) \omega^2 \tag{41}$$

Since the integral is  $\pi\Delta^2/\tau_s^2$  (from eqs 15, 23, and 31), this agrees exactly with eq 32. We note that one can also obtain the  $t^2$  term in eq 41 directly from eq 22 and the expansion of the hyperbolic cotangent in eq 36.<sup>8</sup>

**2.5. When Is Decoherence Important?** Now that we have some expressions for  $g_d(t)$ , our next task is to determine when quantum effects are important. This basically entails comparing  $g_d(t)$  to the classical function  $g_c(t)$ . In the simple case where the short-time approximations to both  $g_c(t)$  and  $g_d(t)$  (eqs 16 and 33) are valid, then quantum effects will be substantial if  $\tau_d < \tau_p$  (since then  $g_d(t) > g_c(t)$ , producing over a factor of 2 increase in the line width). From eq 35, this will be true if  $\tau_s < \beta\hbar/2\sqrt{3}$ .

More generally, in comparing these two functions we need to see which is larger at the "relevant" times, those when the dephasing function  $e^{-g_c(t)}$  is changing from 1 to 0. In particular, the relevant times are those when  $g_c(t)$  is about 1 (since then  $e^{-g_c} = 1/e$ ), so defining  $t^*$  by  $g_c(t^*) = 1$ , decoherence will not be important if  $Re\{g_d(t^*)\} \ll 1$ , but it will be significant when  $Re\{g_d(t^*)\} \simeq 1$ . To this end, let us consider the perturbative (in powers of  $\beta\hbar\Delta$ ) expression for  $g_d(t)$  in eq 30.

Since  $1 - \overline{C}_{c}(t^{*})$  is bounded from above by 1, certainly it is true that if

$$(\beta\hbar\Delta)^2 \ll 12\tag{42}$$

then  $Re\{g_d(t^*)\} \ll 1$ , independent of  $t^*$ , which means that in this case decoherence will not be important. Note that when  $(\beta\hbar\Delta)^2 > 12$ , this does *not* imply that decoherence is always important (see Section 5).

Regarding quantum effects on the peak frequency and shape of the absorption spectrum, these will not be important if  $|Im\{g_d(t^*)\}| \ll 1$  (that is, the phase of the decoherence

function  $e^{-g_d(t)}$  does not change too much over the relevant time  $t^*$ ), which from eq 30 will certainly be true if

$$\frac{\beta\hbar\Delta^2 t^*}{2} \ll 1 \tag{43}$$

If one is in the inhomogeneous limit for classical dephasing such that only the short-time behavior of  $g_c(t)$  is important, then from eq 13  $t^* = \sqrt{2}/\Delta$ , in which case the inequality becomes

$$\beta \hbar \Delta \ll \sqrt{2} \tag{44}$$

which is similar to the result for the real part in eq 42.

More generally still, one should use the full eq 30 to evaluate  $g_d(t^*)$ , or better yet, either of the equivalent nonperturbative expressions in eqs 21 or 39 to determine when  $Re\{g_d(t^*)\}$ ,  $|Im\{g_d(t^*)\}| \ll 1$ .

## 3. EMISSION LINE SHAPE

It turns out that a discussion of the emission spectrum is also quite illuminating, and so in this section we present some theory for the emission line shape. In relaxed emission, the system is equilibrated on the excited-state surface. The theory of the line shape, then, is very similar to that for absorption, except the roles of ground and excited states are reversed. If a particular transition in absorption is significantly shifted from its gas-phase value, and broadened considerably, this indicates that the two potential surfaces of the bath (when the molecule is in its ground or excited state) are significantly different. In this case, equilibration on the two different surfaces may produce significantly different absorption and emission line shapes (and of course they are shifted from one another by what is called the Stokes shift). If the system-bath coupling (difference between the two surfaces) is weak, then in the classical limit the Stokes shift is simply related to the meansquare transition-frequency fluctuations for either surface.<sup>1</sup> If it is not weak, then this formula can be generalized.<sup>42</sup> For all these reasons, then, it is also of interest to consider quantum effects in emission.

The general formula for the emission line shape can be derived from Fermi's golden rule in much the same way as the usual derivation of the absorption line shape. The roles of the two surfaces are reversed, however, since in this case the transition begins on the equilibrated excited surface, the dynamics occurs on the excited state surface, and the system emits rather than absorbs a photon. For our two-state model, the analogue to eq 4 for emission is

$$I_{\rm l}(\omega) \sim Re \left\{ \int_0^\infty \mathrm{d}t \ \mathrm{e}^{-\mathrm{i}\omega t} \langle m_{\rm l}(t) \mathrm{e}^{\mathrm{i}H_{\rm l}t/\hbar} \mathrm{e}^{-\mathrm{i}H_{\rm 0}t/\hbar} m_{\rm l}(0) \rangle_{\rm l} \right\}$$
(45)

where now  $m_1(t) = e^{iH_1t/\hbar}me^{-iH_1t/\hbar}$ , and the subscript 1 on the brackets indicates a thermal quantum average for the excitedstate bath Hamiltonian  $H_1$ . Note that the sign in  $e^{-i\omega t}$  is correct and differs from that in absorption, because in this case the photon is being emitted and so the other delta function in Fermi's golden rule is operative. Again defining  $u = (H_1 - H_0)/\hbar$  (exactly as before), but now  $u_1(t) = e^{iH_1t/\hbar}ue^{-iH_1t/\hbar}$ ,  $\delta u_1(t) = u_1(t) - \langle u \rangle_1$ , and the analogue of eq 5 is

$$I_{1}(\omega) \sim Re\left\{\int_{0}^{\infty} dt \ e^{-i(\omega - \langle u \rangle_{1})t} \left\langle m_{1}(t) \exp_{+}\left\{i \int_{0}^{t} dt' \ \delta u_{1}(t')\right\} m_{1}(0) \right\rangle_{1}\right\}$$

$$(46)$$

The classical results analogous to eqs 6, 8, and 9 become

$$I_{l}(\omega) \sim Re\left\{\int_{0}^{\infty} dt \ e^{i(\omega-\langle u\rangle_{lc})t} \left\langle m_{1}(t)m_{1}(0)\exp\left\{-i\int_{0}^{t} dt' \ \delta u_{1}(t')\right\} \right\rangle_{lc}\right\}$$

$$(47)$$

for the classical non-Condon result

$$I_{\rm l}(\omega) \sim Re \left\{ \int_0^\infty {\rm d}t \, e^{{\rm i}(\omega - \langle u \rangle_{\rm lc})t} \left\langle \exp \left\{ -{\rm i} \int_0^t {\rm d}t' \, \delta u_{\rm l}(t') \right\} \right\rangle_{\rm lc} \right\}$$

$$\tag{48}$$

for the Condon approximation, and

$$I_{\rm l}(\omega) \sim Re \left\{ \int_0^\infty dt \ e^{i(\omega - \langle u \rangle_{\rm lc})t} e^{-g_{\rm lc}(t)} \right\}$$
(49)

for the cumulant approximation. Thus, these are completely analogous to absorption, except the classical averages are with respect to the excited-state surface, and the fluctuating quantities are propagated on the excited-state surface. This introduces new parameters for the excited-state surface such as  $\Delta_1$ , the RMS frequency fluctuation on this surface.

For the quantum cumulant result, however, because  $g_1(t)$  is complex, the result analogous to eq 17 is

$$I(\omega) \sim Re\left\{\int_0^\infty dt \ e^{i(\omega - \langle u \rangle_1)t} e^{-g_1(t)^*}\right\}$$
(50)

Since the imaginary part of  $g_1(t)^*$  will now have the opposite sign as in absorption, it means that the line shift due to quantum effects will go in the other direction compared to absorption. On the other hand, all the formulas for  $g_1(t)$  in emission are identical to g(t) in absorption, as long as C(t) is replaced by  $C_1(t) = \langle \delta u_1(t) \delta u_1(0) \rangle_1$ .

## 4. STOKES SHIFT

The Stokes shift is the difference between the peak frequencies in absorption and emission. Within the quantum theories at the level of Condon and cumulant approximations (see eqs 17 and 50), this difference comes from two sources: the difference in their average frequencies ( $\langle u \rangle$  and  $\langle u \rangle_1$ ), and additional differences having to do with line-shape distortions and shifts coming from the imaginary parts of g(t) and  $g_1(t)^*$ . Traditionally, theorists usually consider only the former to be the Stokes shift, and so we will adopt that same convention in this section. Denoting the Stokes shift as  $\omega_{S}$ , we then have

$$\omega_{\rm S} = \langle u \rangle - \langle u \rangle_1 \tag{51}$$

This can be rewritten as

$$\omega_{\rm S} = \frac{1}{2} [\langle \delta u_1 \rangle - \langle \delta u \rangle_1] \tag{52}$$

where, as before,  $\delta u = u - \langle u \rangle$  and  $\delta u_1 = u - \langle u \rangle_1$ .

Considering the first term and recalling that  $\hbar u \equiv H_1 - H_0$ , we have

$$\begin{aligned} \langle \delta u_1 \rangle &= \frac{\mathrm{Tr}[\delta u_1 \mathrm{e}^{-\beta H_0}]}{\mathrm{Tr}[\mathrm{e}^{-\beta H_0}]} = \frac{\mathrm{Tr}[\delta u_1 \mathrm{e}^{-\beta (H_1 - \hbar u)}]}{\mathrm{Tr}[\mathrm{e}^{-\beta (H_1 - \hbar u_1)}]} \\ &= \frac{\mathrm{Tr}[\delta u_1 \mathrm{e}^{-\beta (H_1 - \hbar \delta u_1)}]}{\mathrm{Tr}[\mathrm{e}^{-\beta (H_1 - \hbar \delta u_1)}]} \end{aligned}$$
(53)

Article

where Tr is the trace over all bath quantum states. Using a general quantum operator identity for parameter  $\beta$  and (noncommuting) operators A and B,<sup>1,43</sup> to lowest order in B

$$e^{-\beta[A+B]} \approx e^{-\beta A} \left[ 1 - \int_0^\beta d\lambda \ e^{\lambda A} B e^{-\lambda A} \right]$$
 (54)

Eq 53 then becomes

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$$\langle \delta u_1 \rangle \sim \beta \hbar \langle \tilde{\delta} u_1 \delta u_1 \rangle_1 \tag{55}$$

where  $\delta u_1$  is the Kubo transform of  $\delta u_1$ :<sup>44</sup>

$$\tilde{\delta}u_1 = \frac{1}{\beta} \int_0^\beta d\lambda \ e^{\lambda H_1} \delta u_1 e^{-\lambda H_1}$$
(56)

This can also be written as

$$\langle \delta u_1 \rangle \approx \hbar \int_0^\beta d\lambda \ C_1(-i\hbar\lambda)$$
 (57)

A similar calculation shows that

$$\langle \delta u \rangle_1 \approx -\hbar \int_0^\beta \mathrm{d}\lambda \ C(-\mathrm{i}\hbar\lambda)$$
 (58)

Thus, we arrive at

$$\omega_{\rm S} = \frac{\hbar}{2} \int_0^\beta d\lambda [C_1(-i\hbar\lambda) + C(-i\hbar\lambda)]$$
(59)

We believe that this result, which is valid for any general Hamiltonians  $H_0$  and  $H_1$ , is new. In the classical limit as  $\beta$  goes to 0, the Stokes shift is

$$\omega_{\rm S} = \frac{\beta\hbar}{2} [C_{\rm 1c}(0) + C_{\rm c}(0)] = \frac{\beta\hbar}{2} [\Delta_1^2 + \Delta^2]$$
(60)

which agrees with our previous result.<sup>42</sup> If the coupling to the bath is sufficiently weak, or in the linearly coupled harmonicoscillator model, the mean-square frequency fluctuations on the two surfaces are the same, and so we obtain the familiar result<sup>1,45</sup> from linear response theory that

$$\omega_{\rm S} = \beta \hbar \Delta^2 \tag{61}$$

# 5. MODEL CLASSICAL FREQUENCY TIME-CORRELATION FUNCTION

Before we consider a realistic system, we can profitably explore quantum effects by considering a model classical FTCF. We choose to revisit the model considered earlier by Lawrence and Skinner:<sup>19</sup>

$$C_{\rm c}(t) = \Delta^2 \operatorname{sech}(\pi t/2\tau) \tag{62}$$

As described above,  $\Delta$  is the RMS frequency fluctuation, and  $\tau$  is the correlation time defined by eq 14. Note that this model is more physical than the exponential Kubo model,<sup>4</sup> since the short-time dynamics is quadratic; in fact, for this model  $\tau_s = 2\tau/\pi$  (see eq 31). Thus, this model has (essentially) a single characteristic relaxation time.

Lawrence and Skinner<sup>19</sup> investigated quantum effects by calculating the quantum-corrected line shape numerically as a

function of the two dimensionless ratios  $\Delta \tau$  and  $\beta \hbar / \tau$ . They showed percent deviations from the classical line width and shift as a function of these parameters in contour plots. Armed with our new analytical result in eq 30, in this paper we calculate  $t^*$  defined by  $g_c(t^*) = 1$  (from eq 10), and then the real and imaginary parts of  $g_d(t^*)$  (from eq 30), as described above. These plots as a function of  $\Delta \tau$  and  $\beta \hbar / \tau$  are shown in Figures 1 and 2. As seen, they are very similar to the plots in ref



**Figure 1.**  $\log[Re\{g_d(t^*)\}]$  as a function of  $\log[\Delta \tau]$  and  $\log[\beta \hbar/\tau]$ . The white line corresponds to  $Re\{g_d(t^*)\} = 0.1$ .



**Figure 2.**  $\log[IIm\{g_d(t^*)\}]$  as a function of  $\log[\Delta \tau]$  and  $\log[\beta \hbar/\tau]$ . The white line corresponds to  $IIm\{g_d(t^*)\}\} = 0.1$ .

19, and in fact, the contours when the logs are -1 (white lines) are very similar to the 10% deviation contours from that paper. From this we conclude that when the (magnitudes of the) real and imaginary parts of  $g_d(t^*)$  are 0.1 or smaller, quantum effects will not be very important (as discussed in Section 2.5).

Our new analytic results in eq 30 show an explicit dependence on the dimensionless product  $\beta\hbar\Delta$ . This, with the realization that the parts of eq 30 involving the classical FTCF involve only the dimensionless product  $\Delta\tau$ , leads to the conclusion that it may be more meaningful to consider  $\beta\hbar\Delta$ and  $\Delta\tau$  as the two independent dimensionless quantities. To that end, for the above simple model classical FTCF we have calculated  $t^*$  as a function of  $\Delta\tau$ , and then the log of the real and imaginary parts of  $g_d(t^*)$  as a function of these two dimensionless parameters. As above, regions where the log of these quantities is less than -1 indicate parameter values where quantum effects on the line shape will not be important.

The results for Log[ $Re\{g_d(t^*)\}$ ] are shown in Figure 3. The log is less than -1 for  $\beta\hbar\Delta < 1$ , which is consistent with the general argument in eq 42 that  $Re\{g_d(t^*)\} \ll 1$  when  $(\beta\hbar\Delta)^2 \ll 12$ . The results for Log[ $IIm\{g_d(t^*)\}I$ ] are shown in Figure 4. Here, we see that, for  $\beta\hbar\Delta < 1$ , and  $\Delta\tau > 1$ , the contours are less than -1, and so quantum effects should not be important for the line shift (and shape distortion). This is consistent with



**Figure 3.** Log[ $Re\{g_d(t^*)\}$ ] as a function of Log[ $\Delta \tau$ ] and Log[ $\beta \hbar \Delta$ ]. The white line corresponds to  $Re\{g_d(t^*)\} = 0.1$ .



**Figure 4.**  $\text{Log}[|Im\{g_d(t^*)\}|]$  as a function of  $\text{Log}[\Delta \tau]$  and  $\text{Log}[\beta \hbar \Delta]$ . The white line corresponds to  $|Im\{g_d(t^*)\}| = 0.1$ .

the general argument above that quantum effects for the line shift are not important if (classically) one is in the inhomogeneous limit ( $\Delta \tau > 1$ ), and  $\beta \hbar \Delta \ll \sqrt{2}$ . So, quite generally, we see that for this simple model quantum effects for both the line width and shift will not be important when  $\Delta \tau >$ 1 and  $\beta \hbar \Delta < 1$ . However, also note from these figures that if  $\Delta \tau > 1$ , as long as  $\Delta \tau > \beta \hbar \Delta$ ,  $\beta \hbar \Delta$  itself can get arbitrarily large and quantum effects will still not be important. This is all consistent with the requirement that if  $\beta \hbar / \tau < 1$ , quantum effects will not be important, as noted previously<sup>19</sup> and shown in Figures 1 and 2 herein.

## 6. EXAMPLE: DILUTE HOD IN LIQUID D<sub>2</sub>O

In this section we consider a simple example of a dilute vibrational chromophore in a liquid: the OH stretch of dilute HOD in liquid  $D_2O$ . The isotope substitution allows one to study an isolated chromophore and avoids the significant complications of OH stretch vibrational coupling in neat water.<sup>46,47</sup> Thus, this is a useful, well-studied, and representative system. Lawrence and Skinner considered this problem in their 2005 paper<sup>19</sup> by performing a molecular-dynamics simulation of rigid  $SPC/E^{48}$  water and used a frequency map to determine the OH stretch frequency for a given configuration. They then calculated the classical FTCF from the simulation, and from that calculated the classical absorption spectrum within the Condon and cumulant approximations. They then used the harmonic QCF to calculate the quantum-corrected FTCF and absorption line shape. Due to space limitations, the actual line shapes were not shown in the paper. The imaginary part of C(t) is negative, which led to a red-shift in the absorption spectrum of 14 cm<sup>--</sup> or about 5% of the classical line width. The quantum correction to the line width was negligible. From these results they concluded that quantum effects were small for this system.

In this Article our goal is to confirm these previous results and then extend them in the following ways: (1) to present actual results for the line shapes themselves; (2) to compare classical spectra at three levels of approximation (exact, Condon approximation, and cumulant approximation), to make the case that our conclusions within the cumulant approximation are qualitatively correct; (3) to explore whether the criteria discussed above regarding  $g_d(t^*)$  for the importance of quantum effects are useful and correct; and (4) to consider the emission line shape and Stokes shift.

6.1. Simulation and Spectroscopy Protocols. In order to calculate absorption spectra of HOD in D<sub>2</sub>O, the groundstate molecular-dynamics simulations are performed using the LAMMPS<sup>49</sup> program. The simulation box contains 216 SPC/E<sup>48</sup> water molecules at the experimental density of liquid H<sub>2</sub>O at 298 K (0.997 g/mL<sup>50</sup>). Three-dimensional periodic boundary conditions are applied, and electrostatic interactions are calculated using the particle-particle particle-mesh summation.<sup>51</sup> The cutoff for Lennard-Jones interactions is 0.9 nm. The equations of motion are integrated with a 1 fs time step using the velocity Verlet integrator and SHAKE<sup>52</sup> algorithm for constraints. The Nosé-Hoover<sup>53,54</sup> algorithm with damping parameter of 0.1 ps is used to maintain the system at a constant temperature of 298 K during an equilibration run of 1 ns. This is followed by a production run at constant energy, during which the coordinates of all atoms are saved every 10 fs for spectroscopy calculations.

The dilute HOD in D<sub>2</sub>O system consists of isolated OH stretch chromophores, since the frequency mismatch with OD stretches renders any vibrational coupling ineffective. To model this system with our pure H2O simulation, for the purpose of spectroscopy calculations, 215 H<sub>2</sub>O molecules are implicitly treated as D2O molecules, one randomly chosen H<sub>2</sub>O molecule is chosen as the HOD molecule, and one of the OH stretches is chosen as the OH stretch chromophore. As in previous work we use spectroscopic maps to determine the frequency and transition dipole moment for an OH stretch chromophore in any D<sub>2</sub>O environment. In this case, we use the maps for the frequency from ref 55, and for the matrix element and transition dipole from ref 56. Note that these simulations and spectroscopic calculations are not precisely the same as those performed in refs 19 and 57. Moreover, there are more accurate simulation models<sup>58</sup> and frequency maps<sup>56</sup> now available for this problem if one is primarily interested in a comparison with experimental results, but that is not our aim here. The population relaxation contribution to the line shape was included phenomenologically by multiplying integrands in the line-shape expressions by the exponential factor  $\exp(-t/2T_1)$ , where the lifetime,  $T_1$ , of the vibrationally excited state is taken to be 700 fs,<sup>59–62</sup> which corresponds to a natural line width of 8 cm<sup>-1</sup>. Since line shapes of liquid water are much broader than that, lifetime broadening does not have a significant effect on the line shapes reported in this work.

The OH-stretch emission spectrum of dilute HOD in D<sub>2</sub>O involves molecular-dynamics simulation with the excited-state Hamiltonian  $H_1 = H_0 + \hbar u$ . Thus, while the ground-state simulations relevant for absorption have atomic forces derived only from  $H_0$  (in this case the SPC/E force field), for the emission spectrum one needs to include the forces from u. According to the spectroscopic maps we use, u is a function of the electric field at the relevant H atom.<sup>55</sup> Since the electric

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field is a function of all the nuclear coordinates, one can derive the atomic forces due to the vibrationally excited OH stretch. This excited-state force field was implemented in LAMMPS and is available on GitHub.<sup>63</sup> Note, however, that when running on the ground-state surface, one can, in parallel, treat each OH stretch as the special one, since the dynamics is independent of which one you choose, but for the excited-state simulation one has to run the dynamics for a specific choice of which H atom is the special one, and so the statistics are much worse. Hence, much more simulation time is required.

**6.2. Classical Line-Shape Results.** The classical FTCFs for simulation on the ground and excited state surfaces,  $C_c(t)$  and  $C_{1c}(t)$  (for absorption and emission, respectively), are shown in Figure 5. While the initial values are different (that is,



**Figure 5.** Classical FTCFs  $C_c(t)$  and  $C_{1c}(t)$  for absorption and emission, respectively, as a function of time *t* (for HOD/D<sub>2</sub>O).

 $\Delta_1 > \Delta$ ), they both have a recurrence at about 130 fs due to the hydrogen-bond stretch,<sup>64</sup> and they both decay to zero in 1 or 2 ps. The parameters obtained from fitting these two FTCFs ( $\Delta$  from eq 12,  $\tau_s$  from eq 31, and  $\tau$  from eq 14) are given in Table 1. Note that for emission the parameter labels should each be subscripted with 1, but for ease of presentation we have suppressed that notation.

Table 1. Values of the Parameters for the Classical FTCFs for Absorption and Emission (for  $HOD/D_2O$ )

	$\Delta (ps^{-1})$	$\tau_{\rm s}~({\rm ps})$	$\tau$ (ps)
absorption	27.9	0.019	0.34
emission	32.3	0.019	0.35

The area-normalized classical line shapes for absorption and emission, with no approximation (from eqs 6 and 47), with the Condon approximation (from eqs 8 and 48), and with the Condon and cumulant approximations (from eqs 9 and 49), are shown in Figure 6. Note that the angular frequencies have been converted to cm<sup>-1</sup> by  $\tilde{\nu} = \omega/2\pi c$ . First, considering the "exact" line shapes (in this context exact means without making the Condon or cumulant approximations), one sees a significant Stokes shift from absorption to emission. As is wellunderstood, the Condon approximation line shapes are blueshifted from the exact line shapes, since the transition dipole is much stronger on the red side of the line. Both Condon approximation line shapes have shoulders above 3600 cm<sup>-1</sup> due to non-hydrogen-bonded OH groups. These shoulders do not show up in the exact line shapes because their transition dipoles are very weak. The cumulant line shapes are not significantly different from the Condon ones, except they are necessarily symmetric (the peak frequency equals the average frequency), and so the blue shoulders have disappeared. The peak frequencies and FWHM values of these line shapes are



**Figure 6.** Absorption and emission line shapes at three different levels of approximation (for HOD/D<sub>2</sub>O).

shown in Table 2, as well as the Stokes shifts for the three levels of approximation. On the whole, the three levels of

Table 2. Parameters of the Absorption and Emission Line Shapes at Three Levels of Approximation  $(for HOD/D_2O)^a$ 

		FWHM (cm <sup>-1</sup> )	$\omega_{\rm p}~({\rm cm^{-1}})$	$\omega_{\rm S}~({\rm cm}^{-1})$
exact	absorption	284	3396	124
	emission	327	3272	
condon	absorption	359	3430	106
	emission	325	3324	
cumulant	absorption	297	3458	127
	emission	340	3331	

<sup>*a*</sup>FWHM is the full-width at half maximum,  $\omega_p$  is the peak frequency, and  $\omega_S$  is the Stokes shift (see text for details).

approximation give qualitatively similar absorption and emission spectra, and especially the Stokes shift does not change too much. This gives us some confidence that the conclusions we draw from the cumulant line shapes will carry over to the exact line shapes.

Note that in this section the Stokes shift is the difference in the actual peak frequencies in absorption and emission. Only in the case of the cumulant approximation is this the same as the difference between the average frequencies (as in eq 51). We can compare the value of the cumulant Stokes shift from Table 2, 127 cm<sup>-1</sup>, with that from eq 60 (the values of  $\Delta$  and  $\Delta_1$  come from Table 1), which is 125 cm<sup>-1</sup>. The agreement is excellent, and significantly better than with the result from using eq 61, 107 cm<sup>-1</sup>, which shows that this problem is not in the weak-coupling limit, and the shifted harmonic-oscillator model does not apply.

**6.3. Quantum Line-Shape Results.** Next we consider quantum effects on these line shapes (that is, the importance of decoherence). We begin by examining  $g_d(t^*)$ , as discussed earlier. We calculate  $t^*$  in absorption and emission from  $g_c(t^*) = 1$ , and then evaluate  $g_d(t^*)$  from eq 30 and its analogue for emission. The results are shown in Table 3. Since in both cases  $Re\{g_d(t^*)\} \ll 1$ , we do not expect that quantum effects will be important for the line width.  $|Im\{g_d(t^*)\}|$  is on the order of 0.1,

Table 3.  $t^*$  and the Real and Imaginary Parts of  $g_d(t^*)$ , for Absorption and Emission (for HOD/D<sub>2</sub>O)

	<i>t</i> * (ps)	$Re[g_d(t^*)]$	$Im[g_d(t^*)]$
absorption	0.056	0.021	-0.11
emission	0.048	0.031	-0.11

Article

and so we expect modest quantum effects on line shift and shape.

Numerical results for the quantum-corrected line shapes are obtained from the full (nonperturbative) results for the linebroadening function g(t) in eq 37 (and its analogue in emission). Note that in calculating quantum line shapes from eqs 17 and 50 we replace  $\langle u \rangle$  and  $\langle u \rangle_1$  by  $\langle u \rangle_c$  and  $\langle u \rangle_{1c}$ , as it is difficult to calculate the former. The area-normalized results are shown in Figure 7. One sees very small changes in the line



**Figure 7.** Quantum-corrected (including decoherence) and classical cumulant line shapes in absorption and emission (for HOD/D<sub>2</sub>O).

widths, and modest red- and blue-shifts in absorption and emission, respectively, as discussed earlier. The changes (quantum-corrected minus classical) in widths and peak frequencies are shown in Table 4. Thus, the conclusions

Table 4. Quantum Effects on Absorption and Emission Line Shapes (for HOD/ $D_2O$ ), as Indicated by Changes in the FWHM, Peak Frequency, and Stokes Shift

	$\delta$ FWHM (cm <sup>-1</sup> )	$\delta\omega_{ m p}~({ m cm}^{-1})$	$\delta\omega_{ m S}~( m cm^{-1})$
absorption	2.5	-17	-40
emission	4.3	23	

from our  $g_d(t^*)$  analysis are borne out by our numerical calculations, and we confirm our previous conclusion that quantum effects are really quite modest for this system. We also note that for absorption the width and shift changes (2.5 and  $-17 \text{ cm}^{-1}$ , respectively), agree well with what we obtained previously ( $\approx 0$  and  $-14 \text{ cm}^{-1}$ , respectively).<sup>19</sup> Finally, we note that a decade ago Paesani, Xantheas, and Voth<sup>65</sup> calculated bath quantum effects on the OD frequency distribution of dilute HOD in H<sub>2</sub>O and found results very similar to the absorption spectra shown in Figure 7.

It is interesting that since frequency shifts due to bath quantum effects for absorption and emission are in opposite directions, the change in the Stokes shift due to quantum effects is significant (40 cm<sup>-1</sup>, see Table 4), and so including these quantum effects in this model predicts a Stokes shift of (127 - 40) cm<sup>-1</sup> = 87 cm<sup>-1</sup>. The experimental situation regarding the vibrational Stokes shift for HOD/D<sub>2</sub>O is, regrettably, unclear; earlier work reported a value of 70 cm<sup>-1,66</sup> while more recent work found that values were widely scattered, depending on time delay and pump frequency.<sup>67</sup>

# 7. DISCUSSION AND CONCLUSION

The results of the last section show that within this model for the OH-stretch vibrational fundamental transition of dilute HOD in liquid  $D_2O$  bath quantum effects have only a modest effect on the absorption line shape. Our approach, of course, involves a number of approximations: (1) the approximate classical modeling of the ground-state Hamiltonian (SPC/E water force field), (2) the bath dependence of the transition frequency (through a frequency map), (3) the harmonic QCF to approximate the bath quantum effects in the FTCF, (4) the Condon approximation, and (5) the cumulant approximation. The first two approximations have been validated by water spectroscopy in a number of circumstances.<sup>47</sup> The harmonic QCF, while certainly an uncontrolled approximation, is the only reasonable choice of QCF for absorption spectroscopy,<sup>9,19</sup> and since the localized and collective modes of a liquid bath are actually quite harmonic,<sup>41</sup> this may be a good approximation. Furthermore, this QCF is exact for the popular spectroscopic model of shifted harmonic oscillators.<sup>22</sup> The Condon and cumulant approximations are also uncontrolled, but we have demonstrated herein that our results are not qualitatively different if we make these approximations.

We have one more general argument suggesting that bath quantum effects are not important for this system. Others have observed that the magnitude of the decoherence function,  $e^{-Re\{g_d(t)\}}$ , is Gaussian,<sup>7,8,38</sup> and indeed we find that under certain circumstances this is the case (see eqs 32–34). If this is so, and assuming that the classical dephasing is more or less in the inhomogeneous limit, quantum effects will be significant if  $\tau_s < \beta \hbar/2\sqrt{3}$  (see Section 2.5). Recall that  $\tau_s$  is the time constant for the short-time dynamics of the classical FTCF, as in eq 31. At room temperature,  $\beta \hbar = 26$  fs, and so this inequality is  $\tau_s \leq 7$  fs. This is not possible for the bath (rotational and translational) degrees of freedom in water, as these nuclear motions are on longer time scales.<sup>47,64</sup>

Joutsuka et al.<sup>38</sup> have considered the same HOD in D<sub>2</sub>O system and reached a different conclusion: that quantum bath effects are quite significant, as described by a Gaussian decoherence function, leading to an increase of a factor of almost 2 in the line width. Their starting point for the line shape is exactly the same as ours, but their theoretical approach is quite different. They calculate directly quantum dynamics on the two relevant potential surfaces using the FGA. As mentioned earlier, this method can be shown to be exact for the model of shifted harmonic potential surfaces.<sup>27,28</sup> For more realistic models for the classical dynamics, the FGA makes uncontrolled approximations. Even so, in their study of nonadiabatic transition rates for the solvated electron in water and methanol, Borgis, Turi, and Rossky<sup>7,8,37</sup> compared the FGA with a QCF approach similar to the one presented in this Article and found the corresponding decoherence times to be nearly the same. We do not understand the discrepancy between the results of the two methods for  $HOD/D_2O$ , although perhaps it is due to the neglect of librational motions in the FGA, as noted by Joutsuka et al.<sup>38</sup>

Turning now to a discussion of the importance of quantum effects for general electronic and vibrational absorption spectra, it is difficult to make precise comments without microscopic calculations for specific systems. On the other hand, we do have general results for a model FTCF (see Section 5); however, this model has only one characteristic time, whereas realistic systems usually have at least two characteristic times. Typically, the FTCF decays to less than half of its initial value within several tens of femtoseconds, and this time is more important than the longer characteristic time for controlling the spectroscopy. Therefore, we will proceed by using the model calculations, and taking  $\tau = 26$  fs (the time scale of the initial drop; see, for example, Figure 1 of ref 9). At room

temperature this gives  $\beta\hbar/\tau = 1$ , and  $\text{Log}[\beta\hbar/\tau] = 0$ . From Figure 1 we see that in this case *any* value of  $\Delta$  will lead to insignificant effects on line broadening. In Figure 2 we see that if  $\text{Log}[\Delta\tau] > 0$ , there will be insignificant quantum effects on the line position and distortion. This corresponds to  $\Delta\tau > 1$ , or taking  $\tau = 26$  fs,  $\Delta > 38$  ps<sup>-1</sup>, which corresponds to  $\Delta > 200$  cm<sup>-1</sup>. Thus, for virtually all electronic transitions (which typically have significantly larger values of  $\Delta$ ), and many vibrational transitions, we expect quantum effects to be minimal, with the only exceptions being for relatively narrow lines not in the inhomogeneous limit.

Theoretical calculations of vibrational and electronic line shapes can complement and support experimental results. The results reported herein suggest that, with realistic potential models, classical molecular-dynamics simulations can be profitably used to calculate such line shapes. In the presumably rare instances that quantum effects are needed, it is quite straightforward to incorporate them with the harmonic QCF, as demonstrated herein.

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## Notes

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