Ultrafast Vibrational Population Dynamics of Water and Related Systems: A Theoretical Perspective

Rossend Rey,*,† Klaus B. Møller,*,‡ and James T. Hynes*,§

Departament de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, Campus Nord B4-B5, Barcelona 08034, Spain, Department of Chemistry, Building 207, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark, Département de Chimie, CNRS UMR 8640 PASTEUR, Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris Cedex 5, France, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

Contents

1. Introduction

For quite obvious reasons, which need not be recounted here, scientists have long been fascinated by liquid water, and accordingly, the quest for a microscopic understanding of this special and especially important liquid has a long and distinguished history.[1] The focus of the present review is on the rapid progress within about the past decade, both experimental and theoretical, on the vibrational aspects of liquid water, as probed by nonlinear ultrafast infrared and Raman spectroscopic methods of various sorts; discussions of some of the experimental techniques involved can be found, for ex-

ample, in the reviews by Elsaesser,[2] Bakker,[3] and Dlott.[4] In view of the qualifications of the authors, the underlying perspective is a theoretical one, but we attempt to always discuss theoretical issues in the context of experiments.

Vibrational dynamics in water can be approximately divided into two important categories. In this review, we focus on vibrational energy transfer aspects, that is, those features associated with the change of population of, for example, OH vibrational states. The second category is concerned with "dephasing" or spectral diffusion aspects, that is, those features associated with modulation of the OH frequency; we plan to address this in a separate review.

We need to begin with several important remarks defining the compass and character of our discussion. The first of these remarks is a caveat: in fact, much, though not all, of our discussion will concern the special aqueous system of HOD dilute in liquid D_2O, an aqueous system much studied experimentally in view of the very convenient isolated spectroscopic feature of the OH stretch in this system, discussed within. In fact, it is an abuse of language, albeit one frequently practiced, to call this system "water". As, for example, catalogued by Dlott and co-workers,[5] H_2O and D_2O and HOD in D_2O differ in many important ways: liquid D_2O is a poison, the bond stretches in the H_2O molecule are coupled, while those in HOD are not, and so on. These differences should always be kept in mind, and we draw attention to the most important of them at various points within. A second remark is that the hydrogen bond (H bond)[6] in which the probed molecule participates obviously lies at the core of our discussion (for an early model investigation of vibrational relaxation in a hydrogen-bonded system, see ref 7). Not only is the H bond capital for the properties of aqueous systems, it is key for fundamental chemical solution processes such as proton-transfer reactions (for a recent review about this connection, see ref 8) and is a pervasive aspect of many biochemical systems and processes.[9] A final remark we need to make is that the present brief review is constructed in the midst of very intense and rapidly evolving developments, and a number of key issues remain unsettled. Indeed, we fully expect that another review will be required in the not-too-distant future. Nonetheless, we hope that the present limited effort will not prove to be inutile.

* Address correspondence to any author. E-mail: R.R., rosendo.rey@upc.es; K.B.M., klaus.moller@kemi.dtu.dk; or J.T.H., casey.hynes@ens.fr.
† Universitat Politècnica de Catalunya.
‡ Technical University of Denmark.
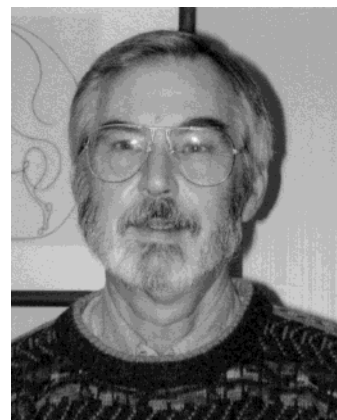§ Ecole Normale Supérieure and University of Colorado.

Rossend Rey Oriol obtained his Ph.D. degree from the University of Barcelona in 1992. After a postdoctoral fellowship at the University of Colorado in Boulder (1993), he joined the faculty of the Universitat Politècnica de Catalunya in Barcelona as an Associate Professor.

Klaus B. Møller obtained the M.Sc. and Ph.D. degrees from the Technical University of Denmark in 1993 and 1997, respectively, (he was a Research Assistant 1994–1995 at Harvard University). He has done postdoctoral work from 1997 to 2000 at the California Institute of Technology (partly as a Carlsberg Postdoctoral Fellow) and from 2001 to 2002 at Ecole Normale Supérieure in Paris, France (EC Postdoctoral Fellow). In 2002, he returned to the Technical University of Denmark, where he is now a Steno Research Assistant Professor.

James T. (Casey) Hynes obtained the B.A. degree from Catholic University in 1965 and the Ph.D. degree from Princeton University in 1969. He was then a NIH Postdoctoral Fellow at the Massachusetts Institute of Technology, before joining the faculty of the University of Colorado, Boulder, in 1971, where he is now Professor of Chemistry and Biochemistry. Since 1999, he has also been a CNRS Directeur de Recherche at the Ecole Normale Supérieure in Paris, France.

The outline of the remainder of this review is as follows. In section 2, we review the first experimental results for HOD in D_2O from the early 1990s to set the stage. In section 3, we consider an early suggestion that the OH population dynamics involved vibrational predissociation, that is, OH population decay involving breaking of a hydrogen bond between the HOD and D_2O. Section 4, which is the longest in the review, deals with energy transfer mechanisms directly involving vibrations other than the hydrogen bond, in particular the intramolecular HOD vibrations. A summary of the current picture for HOD in D_2O is given in section 5. Real water, H_2O, is considered briefly in section 6, while section 7 concludes with some thoughts about the future.

Previous reviews that deal in part with the topics of our discussion include those by Bakker,[3] Dlott,[4] Hynes and Rey,[10] and Heilweil.[11] Further, aspects of the formal theory of nonlinear vibrational spectroscopy can be found in the first two of these, as well as in the book of Mukamel;[12] our theoretical discussion focuses instead on the dynamic and mechanistic aspects of vibrational energy transfer for the OH stretch in aqueous systems. More generally, the book edited by Fayer[13] can be usefully consulted for discussions of dynamic infrared and Raman spectroscopy in various systems. Finally, although it is largely focused on diatomic molecules in relatively simple solvents, the classic review by Oxtoby[15] on the theory of intermolecular vibrational energy transfer in condensed phases, as well as several later reviews,[16−18] provides important background on theory and calculation methods.

2. Early Experimental Results

The population lifetime for an excited OH stretch, $\nu_{OH} = 1$, for HOD dilute in liquid D_2O was examined in two important initial contributions in 1991. In an infrared pump−probe study (Graener, Seifert, and Laubereau),[19] spectral hole burning by an intense IR pump pulse (duration 11 ± 2 ps with bandwidth 18 ± 2 cm^{-1} around 3400 cm^{-1}) was followed by a weak, independently tunable probe pulse; the induced transmission of the latter due to the presence of the pump was recorded as a function of the delay time between the two pulses. After a rapid increase/decrease (depending on the probe−pulse frequency) of the transmission, it relaxes with a time constant of 8 ± 2 ps, identified as the OH population lifetime. The same system was studied by Vodopyanov[20] employing a less direct method. Absorption of an intense IR pulse (duration 110 ± 10 ps, frequency either 3406 or 3580 cm^{-1}) was measured as a function of the laser intensity and the upper and lower boundary for T_1 was estimated by fitting experimental results to theoretical expressions for the absorption coefficient assuming a purely homogeneously or inhomogeneously broadened absorption line. Vodopyanov estimated this time to be between 0.3 and 0.6 ps, that is, an order of magnitude shorter than the Graener et al. results.

In later sections, we will review the conclusions of subsequent experiments about the magnitude of this time, although we do anticipate here that subsequent experiments infer a time in the range ~0.7−1 ps. At

this stage, one could ask whether any of these times is particularly remarkable. The answer is yes and no. Generally speaking, the population relaxation time T_1 for a high-frequency stretch in diatomic molecules is rather long, an especially striking example being that of liquid nitrogen[15,21] where the lifetime is 40–60 s, which is so slow that there is no vibration to translation pathway; the relaxation is instead radiative. This feature is understandable, for example, in terms of simple Landau–Teller ideas,[14,15] which indicate that, in a collision between the diatomic and a collision partner, only very infrequent high-energy collisions will provide interaction force Fourier components that match the high oscillator frequency. In this perspective, a short lifetime for the OH stretch is unexpected. On the other hand, a simple application of the ideas of the well-known isolated binary collision (IBC) theory, in which the gas-phase lifetime would be shortened due to an increased condensed-phase collision frequency with no other condensed-phase effects[22] gives an estimate of ~0.3 ps.[23] However, neither one of these two perspectives is appropriate for the HOD in D_2O problem. The first ignores the possible influence of the internal degrees of freedom of the HOD molecule, while the second invokes a picture of a sort of hard-sphere collision between the HOD and a D_2O molecule, which is quite implausible for a H-bonded liquid situation.[24] Thus, neither perspective is suitable for addressing the magnitude of the time and more especially the mechanism of the process involved. The authors of refs 19 and 20 did not propose a mechanism to explain their results, and an important part of our discussion below will deal with the central question of the mechanism for OH population relaxation.

3. Vibrational Predissociation

3.1. Theoretical Considerations

In the first theoretical commentary on the interpretation of the experimental OH lifetime results of ref 19, Staib and Hynes[25] suggested in a footnote the possibility that the accepting mode for the deposited OH energy might be the OOH bond, DOH···OD$_2$, in which the HOD is engaged, such that this H bond is broken, that is, there is vibrational predissociation. (Actually, this theoretical study was originally motivated by a different experiment in the Laubereau group on H-bonded ethanol molecules in liquid CCl$_4$, which were interpreted by the authors[26] in terms of H-bond breaking, an interpretation also supported in a more recent experimental study.[27])

To understand the issues involved in such vibrationally induced H bond breaking, it is helpful to very briefly recount here an important useful perspective for the spectroscopy of the OOH bond systems. This perspective is that of the Born–Oppenheimer (B–O) approximation, in which the high-frequency OH stretching mode is fast compared to the low-frequency OOH bond mode. There is a direct correspondence of such a treatment with the familiar classic B–O treatment of the electronic states of, for example, a diatomic molecule: the OH and OO modes play the analogous roles of the high-frequency elec-

trons and the low-frequency nuclear vibration, respectively. There is quite a long history of this perspective for H-bonded systems, continuing to the present.[28–30] Thus, one considers OH vibration states, for example, $\nu_{OH} = 0$ and $\nu_{OH} = 1$, as a function of the slow OO coordinate.

In fact, it is not at all obvious a priori that energy flow from the high-frequency OH stretch into the low-frequency OO bond can be rapid; after all, the B–O approximation, which exploits this far off-resonance situation, would forbid that flow entirely. Staib and Hynes constructed a theoretical model for the vibrationally induced dissociation of an OOH bond system viewed as a nonadiabatic transition—that is, a breakdown of the adiabatic B–O approximation—between the vibrationally adiabatic states $\nu_{OH} = 1$ and $\nu_{OH} = 0$. Starting from a model Hamiltonian based on the formulation of Marechal and Witkowski[29] and a Lippincot–Schroeder potential representation for the OH···O system,[31] the nonadiabatic coupling allowing the predissociation was identified in terms of the derivative of the OH stretch frequency, ω_{OH}, with respect to the OO stretch coordinate, and the predissociation rate was calculated via a Fermi Golden Rule approach. The major result, in which the quantum character of the OOH bond played an important role, was that the lifetime, τ_{OH}, of the excited OH stretch with respect to vibrational predissociation could be represented via the power law

$$\tau_{OH} = \frac{const}{(\delta\omega_{OH})^{1.8}} \qquad (1)$$

(where const $\approx 7 \times 10^5$ ps/cm$^{1.8}$) in which ω_{OH} represents the OH absorption frequency. This result, which is close to that previously found to empirically hold for a variety of gas-phase H-bonded van der Waals complexes,[32] reflects the feature that, in comparing one complex to another, as the strength of the H bond increases (and the OH frequency decreases) the nonadiabatic coupling allowing the H bond rupture is enhanced and the predissociation lifetime shortens.

The discussion above made the point that the OH vibrational frequency ω_{OH} reflects the strength of the H bond: a stronger H bond results in an increasingly red-shifted OH frequency. It has long been known that when various different OH···O systems are compared, the experimental OH frequency is strongly correlated with assorted measures of the H bond strength. For example, the OH frequency increasingly red-shifts as a function of the OO bond length in the H-bonded system. This can be quite a large effect. As an extreme example, this red shift is 1800 cm^{-1} in solid oxalic acid.[33] For the OH stretch of HOD in D_2O, the red shift from the gas-phase value is much less but still significant: ~300 cm^{-1}.[34]

The theoretical derivation leading to eq 1 was based on a gas-phase three atom model of the H bond system without inclusion of OH fragment rotation, and it is important to stress that no aspects of a condensed-phase environment were included. Nonetheless, eq 1 involves the ω_{OH} frequency, and when
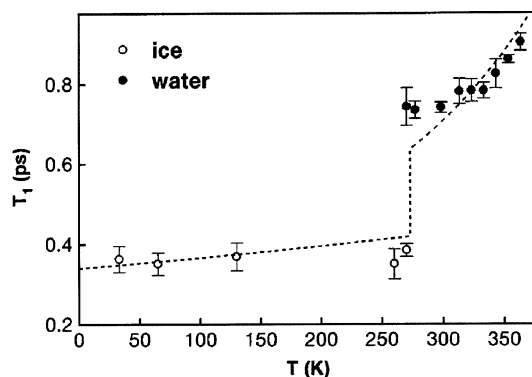
Figure 1. Population lifetime of the OH stretch of HOD in D_2O, measured in a two-color experiment by Bakker and co-workers.[35] The open and closed symbols denote results in solid and liquid phase, respectively. The dashed curve corresponds to the Staib−Hynes model[25] discussed in section 3.1. Reprinted with permission from ref 35a. Copyright (1998) by the American Physical Society.

the solution-phase value is inserted, a crude estimated lifetime of ∼20 ps results. (The actual argument in ref 25 was different but equivalent to this.) This result was used to suggest that perhaps vibrational predissociation of the H bond was involved in the Graener et al. experiments.

We remark that a simulation of the H bond vibrational predissociation in the liquid phase was not possible in 1993, essentially because of the need to deal with the quantum aspects of both the OH and OO vibrations. As will be seen below, such a calculation, which is now feasible, would be of considerable interest.

3.2. An Experimental Interlude

This vibrational predissociation suggestion was later investigated in 1998 by Bakker and co-workers[35] in connection with their IR pump (resonant with $0 \rightarrow 1$ in OH)−probe (resonant with $1 \rightarrow 2$ in OH) experiments on HOD in D_2O. These authors observed a relaxation of the $1 \rightarrow 2$ transition more rapid than the decay of the bleaching of the $0 \rightarrow 1$ transition, implying an intermediate state in which the OH vibration is in its ground state and other modes are excited, which influence the spectral response of the $0 \rightarrow 1$ transition. The transient intermediate state was observed to be blue-shifted compared with the linear $0 \rightarrow 1$ absorption. The room-temperature excited OH vibrational lifetime was ∼740 fs, that is, approximately an order of magnitude shorter than the 1991 estimate by Graener et al.[19] but not far from the 1991 Vodopyanov estimate[20] (see section 2). These authors also examined the lifetime as a function of temperature (T) for this system in the range 30−363 K with the transition from solid to liquid phase occurring at ∼270 K, see Figure 1. A striking feature of the results was a nearly constant value in the solid phase and an *increasing* value in the liquid phase by about 20% in the temperature range of the latter phase studied; ordinarily, one might expect relaxation times to decrease with increasing temperature.

Bakker and co-workers[35] inferred that both the transient blue shifting and the temperature results could be interpreted as indicating that the OOH bond

is the accepting mode and quite successfully fit the vibrational predissociation formula, eq 1 above, to their data, using as input the T-dependent OH frequency of the linear absorption OH spectrum. In this interpretation, the OH lifetime, for example, lengthens in the liquid phase due to the decrease of strength of the ground-state H bond with increasing T, which in the vibrational predissociation scenario (section 3.1) reduces the coupling allowing the predissociation.
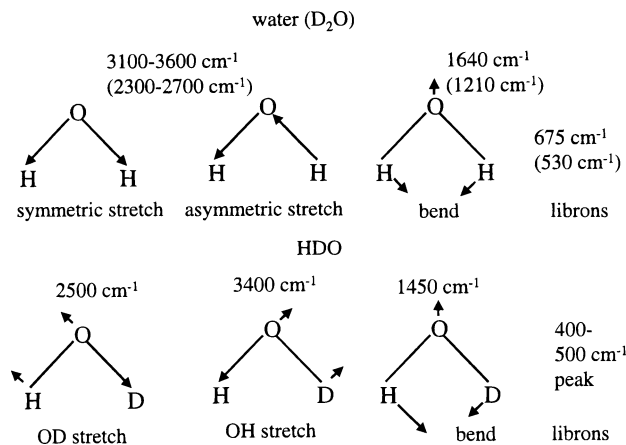
4. Intramolecular Energy Transfer Mechanisms

We use the title of this section as a convenient shorthand for energy transfer mechanisms directly involving the intramolecular HOD vibrations, and possibly those of a D_2O. This is a convenient designation to distinguish from vibrational predissociation, which is energy transfer to an intermolecular mode, the hydrogen bond. Certainly such mechanisms have long been known for H stretch relaxation in non-aqueous condensed-phase systems.[36]

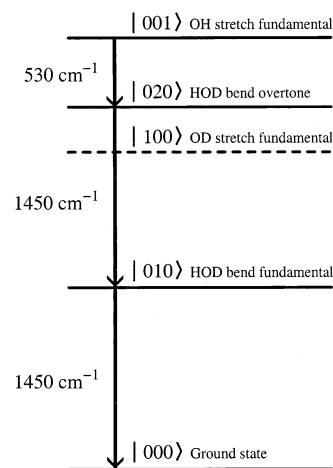## 4.1. Theoretical Considerations

An alternative possible mechanistic scenario is that the OH population lifetime is governed by energy flow from the OH into the bound intramolecular modes of the HOD molecule, for example the HOD bend, assisted by the D_2O solvent molecules. The intramolecular accepting mode(s) is thus bound, as opposed to the dissociative OOH bond in the vibrational predissociation route of section 3. As described below, the involvement of the bend is only one of a number of possibilities involving the bound modes of HOD; thus, for example, transfer to the OD stretch could be considered as well. Further, there is in principle the possibility that the excited OH vibrational energy is transferred to a bound mode of a D_2O solvent molecule, that is, intermolecular VV (vibration to vibration) transfer, or to translational motion of those D_2Os, that is, intermolecular VT (vibration to translation) transfer, and so on. There are also possibilities of Coriolis coupling involving the HOD rotational motions to consider. Further, the relaxation pathway all the way to the ground state of all vibrations involved must be explained. This litany of issues has been theoretically addressed in 1996 by Rey and Hynes (hereafter RH)[23] and in 2002−2003 in extensive work by Lawrence and Skinner[37,38] (hereafter LS), as now reviewed.

To facilitate the discussion, we sketch in Figure 2 the approximate normal modes of HOD, together with their solution-phase frequencies; we will henceforth often label various HOD vibrational states in the fashion (001) for $\nu_{OH} = 1$, (010) for an excited HOD bend $\nu_{HOD} = 1$, (100) for the first excited OD stretch $\nu_{OD} = 1$, etc. There are two important points to make. The first, already implied by our notation, is that the OD and OH stretches have a *local mode* character due to the frequency mismatch, that is, the vibrations are largely those of the uncoupled individual bonds. This is in strong contrast to the situation for H_2O (see Figure 2), where the identical character of the two OH bonds results, after coupling,

water (D₂O)

water (D$_2$O)

3100-3600 cm^{-1}
(2300-2700 cm^{-1})

1640 cm^{-1}
(1210 cm^{-1})

675 cm^{-1}
(530 cm^{-1})

symmetric stretch   asymmetric stretch   bend   librons

HDO

2500 cm^{-1} 3400 cm^{-1} 1450 cm^{-1}

400-
500 cm^{-1}
peak

OD stretch   OH stretch   bend   librons

Figure 2. Normal modes of water, heavy water (D$_2$O frequencies in parentheses), and HOD. The "librons" entry refers to a characteristic frequency for librations (hindered rotations) in the given liquid. Reprinted from ref 5. Copyright 2000 American Chemical Society.

in the symmetric and antisymmetric vibrational stretching normal modes involving the motion of both bonds simultaneously. (Actually, in the condensed phase, asymmetric environments of a given water molecule can lead to local mode behavior, an aspect not yet much studied[39]). This stretching normal mode situation is of course the same in D$_2$O by symmetry, although the frequencies are less due to the heavier D atoms involved (Figure 2). The second point to make is that since none of the three HOD modes are close in frequency to each other, one needs to consider the possible involvement of excited vibrational states. Among these, the overtone state (020) of the HOD bend is of special interest, since its frequency, which is approximately double that of the HOD bend fundamental, is only ~530 cm^{-1} off-resonance with the $\nu = 1$ OH stretch state (001). The adjective "only" should be explained here. While this is obviously not a close resonance (Fermi resonance[25,40]), this frequency mismatch is the smallest among the panoply of possibilities starting with the $\nu_{OH} = 1$ stretch, and this energy mismatch could be taken up by solvent molecule motions. (We note parenthetically that, in H$_2$O, the bend overtone is much closer in frequency to the H$_2$O stretches). Figure 3 displays the situation in terms of possible transitions out of $\nu_{OH} = 1$ into HOD intramolecular modes. We also include in this figure, as a guideline for the discussion below, the dominant relaxation pathway originally found theoretically by RH, in which the energy flow is from the excited OH stretch $\nu_{OH} = 1$ state (001) to the overtone (020) of the HOD bend, $\nu_{HOD} = 2$, which then relaxes first to (010), that is, $\nu_{HOD} = 1$, and then finally to the ground state (000) where $\nu_{HOD} = 0$. We now turn to a description of the origin of these RH results and their interpretation; a description of the LS analysis and results, focusing on the similarities and differences with the RH results, will be interwoven with this discussion. In connection with the latter, since LS have treated the basic problem in two separate studies with somewhat different techniques and results, we will refer to their work as LS1[37] and LS2[38] when a distinction is necessary. As a general preliminary remark, the LS analyses represent definite

| 001 ⟩ OH stretch fundamental

530 cm^{-1}

| 020 ⟩ HOD bend overtone

| 100 ⟩ OD stretch fundamental

1450 cm^{-1}

| 010 ⟩ HOD bend fundamental

1450 cm^{-1}

| 000 ⟩ Ground state

Figure 3. Energy level diagram for the stretch fundamentals and bend modes of HOD in D$_2$O. (The frequency of the bend overtone has been estimated assuming that anharmonicity is negligible.[23]) The arrows indicate the dominating path for relaxation of the OH stretch found in refs 23 and 37, see eq 12.

improvements in the initial theoretical treatment of RH; the overall results of LS1 are however quite similar to those of RH, while important differences appear in LS2.

The first necessary ingredient is the intramolecular HOD potential, and as will become clear below, attention to anharmonicities is important here. RH employed the anharmonic potential for water, conveniently expressed in terms of the internal coordinates of the two bond stretches and the bending angle, proposed by Sceats and Rice,[41] which itself was based on a previous gas-phase model due to Smith and Overend.[42] The potential consists of quadratic, cubic, and quartic terms in the internal bond stretch coordinates, a quadratic term in the internal bend angle, and a mixed quadratic term in the bend angle and the bond stretch coordinates. When the potential is reexpressed in terms of dimensionless (harmonic) normal mode coordinates, q_i,[43] the potential consists of quadratic, cubic, and quartic terms

$$V/(hc) = \frac{1}{2}\sum_{i=1}^{3}\tilde{\nu}_i q_i^2 + \sum_{i \leq j \leq k} k_{ijk}q_i q_j q_k + \sum_{i \leq j \leq k \leq l} k_{ijkl}q_i q_j q_k q_l \quad (2)$$

The essential assumption for this potential is that on going from the gas phase to the condensed phase, there is no change in the anharmonic diagonal stretching terms; alternately stated, only the diagonal harmonic stretching force constant and the stretch−stretch interaction force constant are allowed to depend on hydrogen bonding. All in all, this is a semiempirical potential, adjusted to give the liquid-phase frequencies for HOD in D$_2$O. LS employ a more recent intramolecular potential, which is very accurate for gas-phase HOD; the effect of solvent distortions on that potential will be described below.

In an approach related to that of Berkowitz and Gerber[44] for energy transfer problems, RH decomposed the total Hamiltonian H as

$$H = H_{\text{HOD}} + H_{\text{coupling}} + H_{\text{bath}} \quad (3)$$

in which the vibrational HOD modes discussed above are described quantum mechanically with all other coordinates, for example translations and rotations of HOD, and all the degrees of freedom of the D_2O solvent molecules treated classically. H_{HOD} is the quantum mechanical anharmonic Hamiltonian of the HOD molecule, which includes the static effect of the solvent, and is expressed in terms of the normal modes of the HOD molecule *in solution* (and not in terms of the gas-phase HOD normal modes). The "bath" Hamiltonian is that of the D_2O solvent plus the translations and rotations of HOD. The nonequilibrium coupling between the HOD vibrational modes and the bath degrees of freedom is represented by

$$H_{\text{coupling}} = H_{\text{V-B}} + H_{\text{cor}} + H_{\text{cen}} \quad (4)$$

which contains the coupling $H_{\text{V-B}}$ of the HOD vibrational coordinates to the surrounding solvent molecules, as well as a Coriolis coupling, H_{cor}, between HOD normal modes and a contribution, H_{cen}, representing centrifugal coupling of the HOD vibrational modes and the HOD rotation. The inclusion of a Coriolis term[40,45] was motivated by classical arguments[40] indicating its importance in the water molecule; the centrifugal coupling, which has been occasionally discussed in vibrational energy transfer in solution problems,[46] was included for completeness. LS also include cross terms in their Hamiltonian, for example, Coriolis−bath.

The impact of the coupling $H_{\text{V-B}}$ was found by RH to be the most important with a not completely negligible contribution of H_{cor};[23] a related, though not identical, conclusion was reached by LS.[37,38] Accordingly, we focus most of the discussion on the influence of $H_{\text{V-B}}$, which was expressed in terms of the three solution-phase HOD (dimensionless) normal coordinates, q_i,[43] and the intermolecular forces F_i due to the solvent exerted on the coordinate q_i, evaluated at the equilibrium position of the latter:

$$H_{\text{V-B}} = -\sum_{i=1}^{3} q_i F_i \quad (5)$$

The feature that eq 5 is expressed in terms of the solution-phase HOD normal modes−rather than their gas-phase analogues, which would not include the expected important static distortions of the modes by the solvent−was used as a justification for truncation of $H_{\text{V-B}}$ at first order in the coordinates q_i. On the other hand, LS have included coupling terms up through third order. Finally, although we do not emphasize it further, the forces F_i in eq 5 are dominated by their electrostatic, Coulombic contributions.[10]

We conclude this description of the Hamiltonians used in the theoretical studies of RH and LS by briefly describing how LS deal with the distortion of their gas HOD vibrational Hamiltonian by the solvent. We first note that in RH the geometry of the HOD molecule is kept fixed at the mean value computed in a preliminary simulation of the liquid

with classical intramolecular potentials. The rationale is that this configuration should better represent the manifold of distorted configurations that (a quantal) HOD experiences in the liquid than by simply using the gas-phase mean geometry and hopefully should facilitate a more accurate sampling of the solvent configurations. It should be kept in mind, however, that whatever procedure is chosen, it will be necessarily ad hoc since one is actually forcing a nonphysical separation between classical and quantal degrees of freedom. In LS, this sort of approach is taken one step further. Basically, the mean HOD geometry for each vibrational state of interest in the liquid phase is estimated in a semiclassical iterative procedure. First, given a vibrational level of choice, the corresponding mean geometry of the molecule is computed from the gas-phase Hamiltonian. Fixing the HOD geometry at this configuration, a simulation of the liquid is run (either with fixed, ref LS1, or flexible, ref LS2, solvent molecules), during which the mean solute−solvent coupling, $\langle V \rangle$, over bath configurations is computed. This allows the definition of a new effective Hamiltonian for HOD in the liquid phase

$$H_s' = H_s + \langle V \rangle \quad (6)$$

because $\langle V \rangle$ is an operator in terms of HOD vibrational modes. This new Hamiltonian allows the computation of modified vibrational levels and corresponding mean geometries, which are in principle an improvement over the ones obtained with the bare gas Hamiltonian that served as a convenient starting point. It is clear that in this way an iterative process can be performed in which at each step one gets refined expressions for H_s' and mean molecular geometry. Finally, this process is repeated for each vibrational level of interest. In the end, one obtains an estimation of the mean (rigid) geometries for each HOD vibrational level in the liquid (and not a single one as in RH), which when used in the simulations will necessarily result in different solute−solvent interactions for each vibrational level. Moreover, one gets a set of corresponding effective vibrational Hamiltonians for HOD, which in the LS analysis play the role of the single semiempirical effective liquid-phase Hamiltonian of Sceats−Rice used by RH. The next step is to find the transition rate constants, k_{if}, between the HOD vibrational levels, that is, the anharmonic vibrational eigenstates of HOD in solution. RH employed a Landau−Teller approach, in which the Fermi Golden Rule expression for k_{if}, with the coupling eq 5, is converted to a rate expression following standard lines[15] with a slight variation to maintain the explicit time dependence of the vibrational coordinates,

$$k_{if} =$$
$$\gamma_{if} \text{Re} \sum_{s} \sum_{s'} \int_{-\infty}^{\infty} dt \, \langle i | \delta q_s | f \rangle \langle f | \delta q_{s'}(t) | i \rangle \langle \delta F_s \delta F_{s'}(t) \rangle$$
$$(7)$$

The same approach was followed in LS1. Here δF_s is the fluctuating solvent force on the coordinate q_s (the thermal average force is subtracted in its definition),

and $\delta q_s(t) = q_s(t) - \langle i|q_s|i\rangle$ involves the Heisenberg time-dependent operator $q_s(t)$ with dynamics governed by the full internal anharmonic molecular Hamiltonian. Finally, the prefactor γ_{if} used by RH is[15]

$$\gamma_{if} = \frac{2\hbar^{-2}}{1 + \exp(-\beta\hbar\omega_{if})} \qquad (8)$$

while different factors are used by LS, as later discussed.

We have several times alluded above to the importance of anharmonicity and several crucial aspects of this can be pointed out in connection with eq 7. Each of the molecular vibration factors in eq 7 is a type of molecular time correlation function for the internal vibrational dynamics. In the harmonic approximation, $|i\rangle$ and $|f\rangle$ would reduce to the harmonic vibrational eigenstates and the q_s would be the actual molecular normal modes. In that special circumstance, one has the simplification

$$\mathrm{Re}\langle i|\delta q_s|f\rangle\langle f|\delta q_{s'}(t)|i\rangle \propto \cos(\omega_{if}^0 t) \qquad (9)$$

where ω_{if}^0 are the harmonic frequencies, and in the case of the harmonic OH stretch state, only transitions $1 \rightarrow 0$ occur in this mode, since the VB Hamiltonian eq 5 induces no intramode mixing of the harmonic normal modes. But in the presence of anharmonicity, this is no longer true. The H_{V-B} derived vibrational coupling factors, δq_s, couple the anharmonic vibrational eigenstates $|i\rangle$ and $|f\rangle$ with two important consequences. First, transitions formerly forbidden are now allowed, for example, as will be seen below, the transition to the bend overtone ((001) → (020)) is now possible: a Fourier factor, $\exp(i\omega_{if}t)$, will appear at the corresponding frequency gap, ω_{if}, and the Fourier component of the corresponding force time correlation function (tcf) at this much lower frequency can be effective in the relaxation. Second, even formerly allowed transitions will have their rates altered because of both the anharmonic shift in the OH frequency and the coupling to the remaining internal modes. In short, the central point is that the vibrational eigenstates and modes in the absence of H_{V-B} are *not* the harmonic ones, due to the internal molecular anharmonicities. Therefore, as already noted above, the states $|i\rangle$ and $|f\rangle$ in eq 7 refer to the *anharmonic* vibrational eigenstates of the HOD molecule and not to their harmonic approximation.

Finally, the ingredients necessary for the transition rate calculations can be more explicitly exposed by rewriting eq 7 such that the Fourier transforms appear explicitly

$$k_{if} = \gamma_{if}\int_{-\infty}^{\infty} dt\, e^{i\omega_{if}t} \sum_{s,s'}^{3} \langle i|q_s|f\rangle\langle f|q_{s'}|i\rangle\langle F_s F_{s'}(t)\rangle$$

$$= \gamma_{if}\sum_{s,s'}^{3} \langle i|q_s|f\rangle\langle f|q_{s'}|i\rangle\langle F_s \hat{F}_{s'}(\omega_{if})\rangle \qquad (10)$$

that is, one must calculate quantum matrix elements

such as $\langle i|q_s|f\rangle$ and the Fourier transforms at the appropriate frequencies ω_{if} of the classical (generally mixed) tcf's of the forces F_s. The total rate constant k_i for depletion of state $|i\rangle$ is just the sum $k_i = \sum_f k_{if}$ over all possible final states $|f\rangle$. The force tcf's can be calculated with classical molecular dynamics simulation methods;[47] for this purpose, RH used a flexible model of the solvent D_2O molecules due to Toukan and Rahman[48] (and similar results were obtained[10] with an improved flexible (SPC) model due to Martí et al.[49]), while a rigid D_2O model due to Jorgensen et al.[50] was used in LS1. Finally, LS2 used a flexible D_2O model based upon the rigid model used in LS1 (see also ref 51), developed using methodology similar to that of Martí et al. for their flexible SPC model.

The computation of the matrix elements and frequencies requires the calculation of the eigenenergies and eigenfunctions of the HOD Hamiltonian, H_{HOD}. For the potential used in RH described above, this was accomplished via first-order perturbation theory in both the cubic and quartic parts of the potential. For the potential used by LS, this was accomplished via full diagonalization. The key point for the energy transfer problem is that due to the anharmonicity of the HOD potentials, there is a very strong mixing of harmonic states; thus, in the RH treatment each one of the anharmonic eigenstates is a superposition of more than 40 harmonic eigenstates.

Before we proceed, it is important to stress that this sort of Golden Rule, Landau−Teller (LT) approach has its advantages and drawbacks. It is a time-dependent perturbation theory approach, where the perturbation is the coupling term inducing the vibrational transitions, that coupling itself taken, in the simplest case (RH), to be linear or, in more detailed treatments (LS), higher order in the deviation of the HOD vibrational coordinates from their equilibrium positions. As a result, the force time correlation functions appearing in eqs 7 and 10 are evaluated with the HOD vibrational modes *fixed* in their equilibrium positions. Thus molecular dynamics computer simulations need only evaluate such equilibrium force time correlation functions for the *non-vibrating* HOD molecule. This feature is the source of the advantage and drawback, which are one and the same: the quantum dynamics of the actual vibrational energy flow is calculated, that is, is not followed in time. Such a direct simulation, while obviously to be desired, is a difficult technical proposition due to its quantum aspects; the LT formula only requires that classical dynamics of the solvent be computed. We will return several times to this important point below.

4.2. Theoretical Predictions

### 4.2.1. First Step: OH Stretch to HOD Bend Overtone (RH/LS1)

We begin the discussion by focusing on the very first step of the energy transfer process in the RH results, which sets the basic time scale for the OH relaxation; this same basic conclusion is reached in LS1. The rate constant k_{001} for transitions out of the anharmonic excited OH stretch state, while composed

of many contributions arising from the aharmonicity in the HOD force field (see eqs 2 and 10), is dominated by the contribution $k_{001,020}$ arising from the transition (001) → (020) to the HOD bend overtone

$$k_{001} \approx k_{001,020} \approx$$
$$\gamma_{001,020} \langle 001|q_{HOD}|020 \rangle^2 \langle F_{HOD} \hat{F}_{HOD}(\omega_{001-020}) \rangle \quad (11)$$

the dominance of which arises largely via the Fourier component factor; recall our discussion above about this transition at the frequency $\omega_{001-020} \approx 530$ cm^{-1} being characterized by the smallest frequency mismatch for the $\nu_{OH} = 1$ stretch. The associated relaxation time is 9.4 ps, which is reduced to 7.7 ps when Coriolis effects are taken into account. There are two important remarks to make about this result. The first is that the anharmonicity is critical; if only the harmonic portion of the HOD force field is employed, $k_{001,020}$ vanishes and instead k_{001} is given by the term corresponding to the only allowed transition directly to the ground state, (001) → (000), with a relaxation time of ~3 ns. The anharmonicity thus results in a complete change of mechanism and a reduction in the time scale by almost 3 orders of magnitude. The second remark concerns the role of the solvent in the transition. The $\omega_{001-020} \approx 530$ cm^{-1} frequency mismatch of the excited OH stretch and the bend overtone indicates that this is not an especially effective Fermi resonance if these vibrational states were viewed in isolation. But the D$_2$O solvent can assist the transition, and in the formulation eq 11, that assistance enters through the Fourier component at the frequency $\omega_{001-020}$ of the correlation function of the solvent force component acting on the HOD bend. This Fourier component is large, and indeed the calculated Fourier transform is large in a region in a frequency range around this key frequency as shown in Figure 4. For the same D$_2$O model, Martí et al.[49] found that the D$_2$O librational (hindered rotational) spectrum is peaked at ~400 cm^{-1} with a fwhm of ~300 cm^{-1}. Altogether, these features indicate that the dominant motions in the bend force spectrum at $\omega_{001-020} \approx 530$ cm^{-1} responsible for the relaxation are the D$_2$O solvent librations. One could also say that the energy mismatch in the transition has been taken up by the solvent librations. However, the basic feature of the LT approach emphasized earlier has to be stressed again: the simulations are used to calculate the Fourier components of the force correlations, and those forces are those exerted on a nonvibrating HOD molecule. The dynamic event of the energy flow out of the OH stretch is not directly calculated, and neither is any energy flow into the D$_2$O librations. As mentioned above, the LS1 analysis comes to the same basic conclusions concerning the (001) → (020) transition with one important difference: the LS1 self-consistent Hamiltonian approach reduces $\omega_{001-020}$ to 343 cm^{-1}, which reduces the associated time to ~4.1 ps.[37]

RH also found a minor contribution to the first step from the transition to the OD stretch of HOD, (001) → (100) (time scale of ~360 ps compared to ~7.5 ps for (001) → (020)). This transition is disfavored by the larger frequency gap, $\omega_{001,100} \approx 900$ cm^{-1}, and
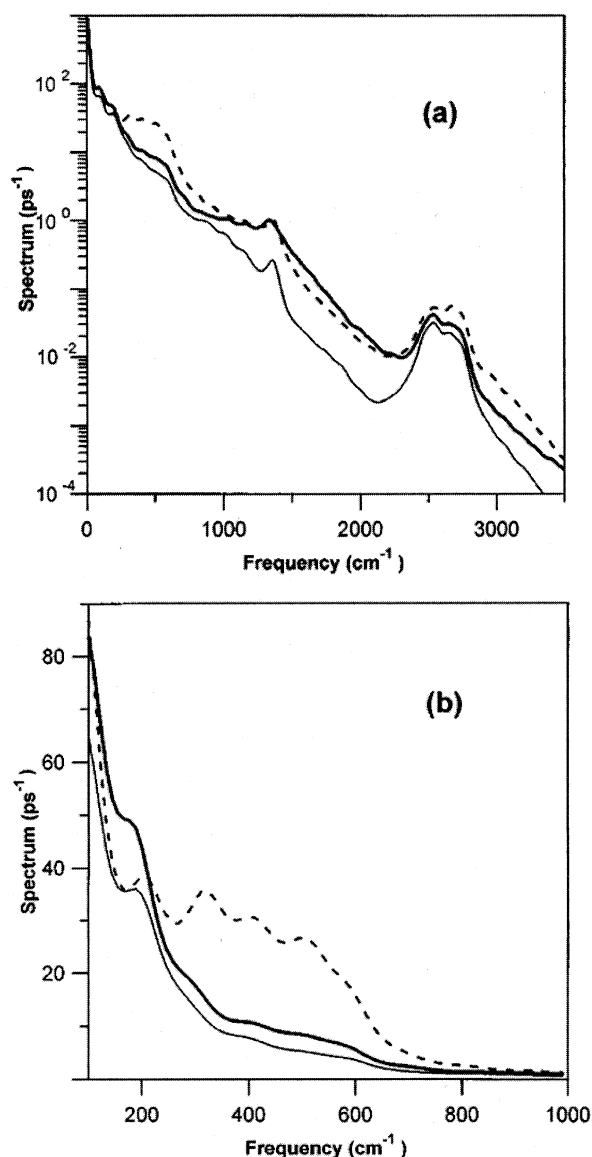
Figure 4. Power spectrum for various force time correlation functions computed by Rey and Hynes:[23] OH stretch (thick solid curve); OD stretch (thin solid curve); HOD bend (dashed curve). Only the HOD bend curve is relevant for the discussion of the OH to HOD overtone transition in the text. Reprinted with permission from ref 23. Copyright (1996) by the American Institute of Physics.

the weak coupling between the OH and OD stretches in the nearly local mode HOD molecule. Its contribution is more important, but still minor, in the LS1 treatment with a time scale of ~30 ps compared to 4 ps for the transition to the bend overtone. LS1 find the transition to the bend fundamental, (001) → (010), to be the second most dominant with a time scale of 14 ps.

4.2.2. Energy Transfer from the HOD Bend Overtone (RH/LS1)

In the RH analysis, the remainder of the dominant relaxation pathway is that displayed in Figure 2, that is, (001) → (020) → (010) → (000), that is, the bend overtone relaxes relatively quickly through its fundamental to the ground state. The associated times for the last two steps are 1.1 and 1.6 ps, respectively.

An interesting feature of the $(020) \rightarrow (010)$ transition is that this was found to be the dominant relaxation route for the bend overtone despite the fact that its frequency gap, $\omega_{020,010} \approx 1450$ cm^{-1}, is much larger than that, $\omega_{020,100} \approx 350$ cm^{-1}, for the transition to the excited OD stretch state, $(020) \rightarrow (100)$. This result indicates that while energy difference considerations may dominate for transitions between different modes (which would be forbidden in an harmonic approximation), this need not apply to transitions in which the molecule relaxes to a lower state of the same mode, due to the larger coupling (present even in an harmonic approximation), which results in a larger prefactor of the Fourier transform. LS1 find faster rates for the two transitions taking the bend overtone to the ground state, (due to a difference in the multiplicative prefactors γ in eq 8, in a fashion similar to that discussed in section 4.2.4). The numbers are 0.10 ps (0.24 ps) for $(020) \rightarrow (010)$ and 0.22 ps (0.38 ps) for $(010) \rightarrow (000)$, where the two different values for each transition are due to different computational methods[37,38]—the numbers reported first correspond to the LT approach in LS1 whereas the numbers in parentheses are obtained by solving the Schrödinger equation. The corrected RH results, employing the corrected prefactor ratio $15/2 = 7.5$, are 0.14 ps for the bend overtone and 0.21 ps for the bend fundamental. This type of correction is discussed in more detail in section 4.2.4.

4.2.3. OD Fundamental Relaxation (RH/LS1)

As noted above, the excited OD stretch state (100) was found to be involved in only a minor way in both the RH and LS1 analyses and does not influence the overall OH relaxation rate. However both groups analyzed the relaxation of this state with somewhat different conclusions. In RH, the relaxation is dominated by the transition to the ground state, $(100) \rightarrow (000)$, with a substantial contribution also from the transition to the first excited HOD bend, $(100) \rightarrow (010)$, with a net time scale of $\sim$24 ps, while LS1 find that the latter transition is dominant with a similar time scale of $\sim$18 ps. As we will see, though not important in either of the RH or LS1 results, the excited OD stretch will reemerge in our subsequent discussion.

In summary, the RH and LS1 analyses paint the same dominant mechanistic picture

$$(001) \rightarrow (020) \rightarrow (010) \rightarrow (000) \qquad (12)$$

for the HOD relaxation with the first step setting the basic time scale for the $\nu_{OH} = 1$ lifetime. When transitions are taken into account, RH estimate an excited OH lifetime of 7.5 ps, while LS1 estimate a time of 2.7 ps, the shorter LS1 time largely due to the faster transition to the bend overtone, as discussed above. The RH time was in fact close to the only available direct estimate of Graener et al., 8 ± 2 ps,[19] at the time, though longer than the indirect estimate of Vodopyanov.[20] However, RH gave a strong caution about the force fields used in their study. As discussed further below, current experimental estimates of the OH population lifetime are

in the range 0.7$-$1 ps, so the LS1 estimate is certainly closer to those results.

4.2.4. Comparison of Methodologies (RH/LS1/LS2)

Finally, in LS2, the D$_2$O solvent was treated as flexible (as opposed to rigid in LS1), a feature already incorporated in RH. Again a Landau$-$Teller approach is employed, the validity of which for the OH relaxation, as well as for all fundamentals and the bend overtone, was confirmed by a direct integration of the time-dependent Schrödinger equation following an approach of Sibert and Rey.[52] An important difference between RH and LS2 is that while RH employed the multiplicative prefactors, eq 8, in the state-to-state Landau$-$Teller rate constant, k_{if}, expressions, LS2 employ *different* prefactors (here called γ_{if}^{LS}), which are supposed to deal more adequately with the quantum mechanical character of the energy transfer process.[53] Briefly, the issue concerns the proper way to introduce a correction factor γ_{if} such that classical time correlation functions can be used to predict the rate of a quantum process $i \rightarrow f$, a topic of quite longstanding discussion continuing to the present.[15,46,53$-$59] To date, there is no known solution to this problem, although there are many proposed correction factors. Here we only draw attention to a few contributions in the context of vibrational energy transfer in solution, although several of these certainly have antecedents in the earlier solid-state literature. The "standard approach" was introduced by Oxtoby[15] and at least guarantees that detailed balance is satisfied; these are the factors of eq 8 used by RH. It is fair to say that for liquid-state vibrational relaxation the interest in the issue was spurred by the work of Bader and Berne,[56] who noted that for a fully harmonic system an exact relation exists between quantum and classical tcf's and that the mixed quantum-classical expression of Oxtoby underestimates the rate. There are in fact very many suggestions in the literature for the correction factor;[15,46,53$-$59] perhaps the most sophisticated and practical prescriptions available at the moment are those of Skinner and Park,[53] which we have labeled γ_{if}^{LS} above for convenience in the ensuing discussion. For purposes of the present discussion, the key point is that the general impact of these different prefactors γ_{if}^{LS} is that they increase k_{if} by 1 or 2 orders of magnitude if the transition frequency, ω_{if}, is large, and this has two consequences, as now discussed.

The first consequence is that the dominance of the relaxation pathway, eq 12, is somewhat softened; nonetheless, LS2 conclude that for $(001) \rightarrow (000)$, the pathway eq 12 is still dominant; thus, for example, only 8% of the relaxation involves $\nu_{OD} = 1$.

The second impact of the γ_{if}^{LS} factors concerns the transition out of $\nu_{OD} = 1$ to the ν_{OD} ground state with a transition frequency of 2482 cm^{-1}. While this transition is evidently not important in the predicted overall OH relaxation, there is a large effect for the transition itself. In contrast to LS1, the $\nu_{OD} = 1$ relaxation pathway is now found to be completely dominated by $(100) \rightarrow (000)$, as in RH, with an interpetation in terms of VV energy transfer to
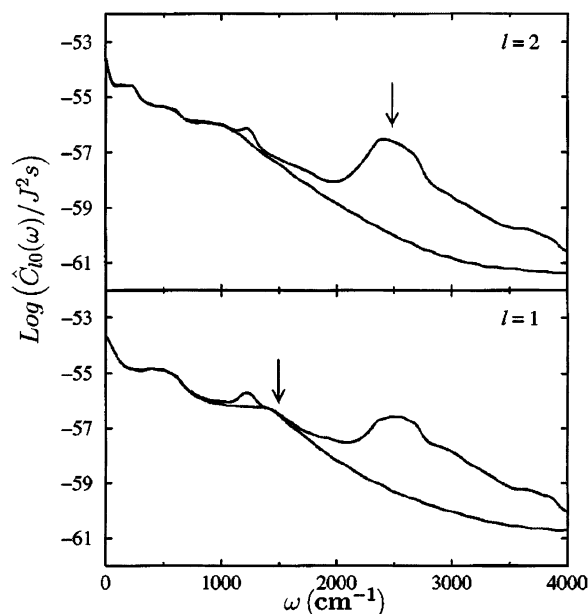
Figure 5. Power spectra computed by Lawrence and Skinner[38] with rigid (lower curve of each pair) and flexible (upper curve of each pair) solvent molecules for the transitions to the ground state from the OD stretch ($l = 2$) and the bend ($l = 1$) fundamentals. Arrows indicate the transition frequency from state l to 0. Reprinted with permission from ref 38. Copyright (2003) by the American Institute of Physics.

solvent D_2O stretch vibrations. It should be emphasized that in both RH and LS2 (but not LS1), the D_2O is flexible and thus such VV transfer is possible. However, in LS2, this (100) → (000) transition is considerably accelerated (0.4 ps) compared to that in LS1 (18 ps) and RH (24 ps). For LS2 compared to LS1, the difference is due strictly to the absence of DOD vibrations (Figure 5 illustrates the difference between power spectra computed with rigid and flexible solvent molecules and the impact on the transition rates for two important transitions). For RH compared to LS2, the difference has two sources. The first is that the ratio of γ_{if}^{LS} to eq 8 for this transition ≈ 6, and from this source, the RH estimate would be reduced to ~4 ps. A second difference is that the D_2O SPCE potential used in RH overestimates the D_2O stretch frequencies, such that there was not a good resonance with the OD stretch in HOD. A recalculation[10] was done to address this with a better D_2O potential,[49] which exhibits a much closer resonance. (A similar problem was dealt with in LS2 by adjusting a flexible TIP4P model). This recalculation produced no effect on the overall OH relaxation time, but the RH OD relaxation time was not recalculated at that time. A recalculation of this review indicates that, with the improved resonance, there is a further drop by a factor of 4 in the OD relaxation time to give ~1 ps, only about twice the LS2 result. Finally, LS2 find the OH lifetime to be 2.3 ps, slightly shorter than the LS1 estimate of 2.7 ps.

4.3. Experiment

We have already discussed the 1991 experiments by Graener, Seifert, and Laubereau[19] and by Vodopyanov[20] in section 2 and the 1998−1999 experimental
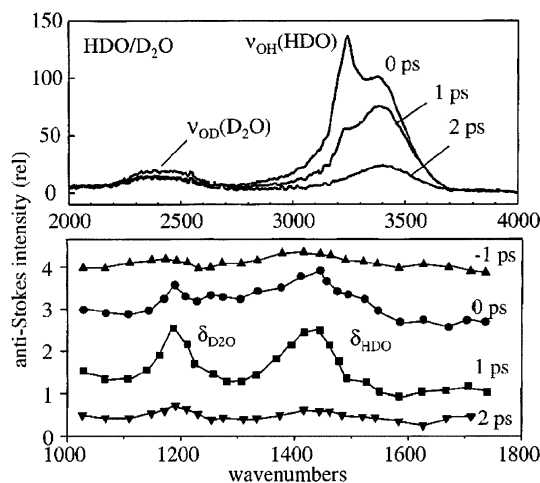
Figure 6. Anti-Stokes Raman transients for HOD in D_2O with pumping of the OH stretch fundamental, obtained by Deàk et al.[5] Reprinted from ref 5. Copyright 2000 American Chemical Society.

results of the Bakker group[35] in section 3.2. Here, we turn to subsequent results.

In 2000, Dlott and co-workers,[5] hereafter D1, reported the results of an IR (pump)/Raman (probe) experiment on HOD dilute in D_2O. An important feature of this technique is that the anti-Stokes probing involved is sensitive only to vibrationally excited states. The pulse duration was 1.5 ps. Figure 6 shows some of the D1 data for the OH vibration and bend vibrations.

D1 found the $\nu_{OH} = 1$ lifetime to be ~1 ps, slightly longer than that in ref 35. They observed (a) the rise of both HOD bend and (solvent) DOD bend on the same time scale and with the same intensity (the estimated quantum yield for each of the bends was larger than 0.6, and no HOD bend overtone in the HOD was seen) and (b) the generation of OD stretch motion in the D_2O solvent with a smaller quantum yield larger than 0.1. No OD stretch activity in the HOD was seen. A lifetime of the HOD bend fundamental (010) was estimated to be between 0.6 and 1.2 ps. D1 conclude that the primary mode of $\nu_{OH} = 1$ stretching relaxation is via the generation of a *pair* of bending vibrations (see item a above), implicating intermolecular energy transfer to the solvent D_2O in the process; the possibility that a fraction of OH stretching decay might have involved H bond excitation (as in the predissociation mechanism, section 3) is not ruled out but is restricted by D1 to be less than 40%.

5. The Current Picture

Here we attempt to portray the current situation for HOD in D_2O, focusing on the key views of theory and experiment, starting with the vibrational energy transfer pathway of section 4.

5.1. Vibrational Energy Transfer Pathway

First, the current best theoretical estimate of the ν_{OH} lifetime by such a route, by LS, is 2.7 (LS1) or 2.3 ps (LS2), compared to the experimental estimates of 0.74[35] and 1.0 ps.[5] As we noted early on in section

1, of the original experimental estimates, only that of Vodopyanov,[20] $\sim$0.3–0.6 ps, would be close to these. Whether this overall theoretical/experimental discrepancy might be due to the operation of the different predissociation mechanism or reflects remaining difficulties in the treatment of the VET pathway, issues of the correction factors for quantum effects, or, more trivially, is due to defects in the potentials employed is not currently known. For other times in the relaxation process estimated experimentally by D1, the D1 estimate of the HOD bend fundamental (010) lifetime of 0.6–1.2 ps can be compared with the RH estimate (1.6 ps) and the LS2 estimate (0.38 ps).

Second, concerning the dominant relaxation pathway, both RH and LS2 identify the dominant OH relaxation pathway as (001) → (020) → (010) → (000), that is, eq 12, with only minor involvement of the OD stretch in the HOD. Experimentally, D1 do not see the bend overtone (020), and this represents a significant source of disagreement. One possibility here is that the (020) lifetime is too short in comparison to the D1 time resolution for it to be seen.

Third, concerning the generation of OD stretch in D_2O, in a commentary[10] on the RH analysis, the authors noted that the minor energy transfer to the OD stretch in HOD that was found could decay by near-resonant transfer to an OD stretch in the solvent. LS2 definitely implicate such transfer from OD to solvent D_2O stretches. D1 say that if this process is to be significant, the $\nu_{OD} = 1$ (HOD) must be a short-lived intermediate because it is not seen in the experiment.

Fourth, the generation of D_2O bends in D1 presents another theoretical puzzle. D1 state that this cannot be solely generated by D_2O stretches and propose two possible mechanisms for direct intermolecular VV transfer following energy flow out of the OH stretch: (a) from the HOD bend overtone to the solvent bend overtone and (b) from the HOD bend fundamental to the solvent bend fundamental. Both mechanisms are in principle included in RH but were not found to be important, a conclusion shared by LS2. What other possibilities are there? One such is that in a fast relaxation from the HOD bend overtone, the combination of HOD bend fundamental and solvent D_2O bend fundamental are produced, followed by decay to the ground state. This pathway would be viable provided the HOD bend overtone decayed rapidly enough to be invisible on the D1 time resolution window of $\sim$1.2 ps and is in principle present in both the RH and LS2 studies, where the D_2O solvent is flexible. However, LS2 find that the (020) relaxation rate is the same for both rigid and flexible D_2O solvent, apparently ruling out such a mechanism. LS2 favors the D_2O stretches (see the third item above) as the source of the solvent D_2O bends, but this contradicts the D1 assertion that these stretches cannot be exclusively the source of this bend activity. The picture remains unclear.

5.2. Vibrational Predissociation

Turning to the vibrational predissociation pathway, as noted above, D1 assign a maximum of 40%

contribution to this route. What then of the agreement found by Bakker and co-workers[35] with the vibrational predissociation formula eq 1 matching the experimental temperature dependence? As was discussed in section 3.2, the ultimate source of the increasing lifetime with increasing T is the weakening of the H bond between the OH in HOD and a D_2O. But as noted by Møller et al.,[60] the key step, (001) → (020), in the energy transfer route should also be slowed with increasing T because of the increasing gap $\omega_{001,020}$ for the OH stretch and the HOD bend overtone occasioned by the weakened H bond.[61,62] Lawrence and Skinner[63] follow a different perspective and analyze the T dependence of the OH lifetime by keeping the transition frequencies *fixed* at their 300 K values and using the time correlation functions, for example, of the forces, at different temperatures; they conclude that approximately one-half of the T dependence of the lifetime can be accounted for in this way, though the experimental T dependence is certainly weaker than is their theoretical one. Thus, the experimental temperature dependence remains to be fully clarified.

To conclude on the vibrational predissociation route, it currently appears that it could contribute together with energy transfer pathways. As noted in section 3.1, the original Staib–Hynes paper remains the only theoretical work on this route, and that was not even a condensed-phase treatment. It would seem to be timely to address this route theoretically. This would not only be critical for the HOD in D_2O problem but could be of use in a variety of other condensed-phase problems where vibrational predissociation is believed to occur.[64]

6. Water, H₂O in H₂O

As of yet, there are no theoretical studies of the OH vibrational dynamics, either predissociational or intramolecular, in real water, although RH make a few remarks, to which we will return below. We do however give a very brief summary of the current experimental situation, focusing solely on the OH relaxation time. We first recall that in the H_2O molecule the OH stretches are internally coupled to produce the symmetric and antisymmetric stretch normal modes. In the experiments to be discussed below, no distinction is made between the symmetric and antisymmetric stretches.

In 2002, Lock and Bakker[62] estimated the OH lifetime as 0.26 ps in an IR pump–probe experiment monitoring the $\nu_{OH} = 1 \rightarrow 2$ transition; an additional tail of 0.55 ps was measured, which was interpreted as a daughter process, probably the bend overtone relaxation. These authors give a Golden Rule argument in support of a OH stretch to H_2O bend overtone mechanism. Earlier, in 2000, Deàk et al. in D1 using their infrared–Raman technique estimate 1 ps for this time, a factor of 4 disagreement, which has generated a certain amount of discussion.[65] On the basis of their data, which involves the observation that there is more than one quantum of excitation in the bend per OH stretch decay, D1 conclude that at least one of the two mechanisms, OH stretch to bend overtone or OH stretch to two bend fundamen-

tals, is probably in competition with OH stretch to bend fundamental with any excess energy being dissipated into the solvent.

There is one theoretical consideration, given by RH, which can give at least some limited perspective on the OH lifetime. RH note, within the energy transfer picture involving the pathway in which the rate is dominated by transfer to a bend overtone, that the librational spectrum of liquid H_2O peaks very near 600 cm^{-1}, which is the gap for OH stretch relaxation into the H_2O bend overtone. This is a much better overlap, and thus solvent assistance, than that for the D_2O librations and the OH fundamental−HOD overtone gap, and RH suggested that a shorter OH lifetime in H_2O compared to HOD in D_2O would be expected. It may also be of relevance to note that, in the gas phase, experiments indicate an OH relaxation pathway via transfer to the bend overtone.[66] However, very recent measurements[67] of the quantum yield for OH stretch to the bend give 0.33; such a low value would imply that the bend may not play such a substantial role in the decay of the OH stretch in water.

It is interesting to note that, as discussed in RH and mentioned in section 2, the well-known isolated binary collision picture,[22] which expresses the solution energy transfer time in terms of the gas-phase value and the density of the solvent−in the image that the solute rate is altered from the gas-phase rate solely by the difference in collision frequency−gives a value for T_1 of 0.34 ps;[23] this is not far from current experimental estimates of the lifetime! RH noted, however, that the IBC picture was hardly plausibly in a H-bonded system (e.g., see ref 24). Temperature-dependent studies for H_2O analogous to those of Bakker and co-workers[35] for HOD in D_2O (see section 3.2) could be quite useful in assessing the situation. The IBC theory would predict a dependence of T_1 on (density)$^{-1/3}$, which is in principle also qualitatively consistent with the trend of increasing T_1 with increasing T. However, the evaluated IBC prediction is almost flat in the experimental T range. If the T-dependent studies for H_2O reveal a behavior similar to that for HOD/D_2O, the IBC theory could be eliminated on experimental grounds as a description for HOD in D_2O.

In concluding this brief section on H_2O, one can ask what is the impact of the short 0.26 or 1 ps excited OH lifetime, here denoted T_1, on the intermolecular VV transfer of OH excitation in liquid water? With such a short T_1, such VV transfer would have to be quite fast to be important; otherwise, the OH excitation in a single molecule would decay locally rather than being transferred to other molecules (note that of course the VV transfer leaves the excited OH population unaffected). This has been addressed in pump−probe experiments by Woutersen and Bakker (WB)[68,69] in which the rotational anisotropy $R(t)$ is measured for a polarized pump pulse. Briefly, $R(t)$ is not affected by the time dependence of the OH population relaxation but is affected both by reorientation of the water molecules and by the VV transfer. WB infer that VV in H_2O takes place extraordinarily rapidly, indeed more rapidly than the

experimental time resolution of ∼100 fs. The authors point to the probable importance of the proximity of the OH groups to each other in water and to anharmonic coupling of OH groups in different water molecules via hydrogen bonding. This extremely short time scale is also less than one would estimate using a Förster (point) dipole−dipole interaction mechanism,[70] the parameters necessary for this comparison (T_1 for OH and a characteristic length, "the Förster radius") having been determined by WB via an analysis of $R(t)$ measurements in connection with the slower VV transfer between HOD molecules at different dilutions in D_2O. As noted by WB, the difficulty with the Förster analysis for the H_2O case is that, for example, the point dipole approximation can hardly be expected to apply at the intermolecular separation in water.

The issue of such rapid VV transfer in H_2O has been very recently addressed, for ice and for small water clusters, in an interesting first theoretical calculation by Poulsen, Nyman, and Nordholm.[71] These authors have developed a completely *harmonic* approach in which a bilinear coupling, proportional to $x_1 x_2$, allows energy transfer between two harmonic OH local modes x_1 and x_2 (but not between harmonic normal modes, since such a coupling itself generates the normal modes.[72]). These authors compute for, for example, a H_2O cluster the harmonic normal modes via high-level ab initio quantum chemistry. With these in hand, one OH stretch local mode is extended and the composition of this in terms of the system normal modes is ascertained. This "wave packet" then can be propagated analytically. Application of this sort of procedure for the modeled liquid H_2O gives times in the 80−250 fs range. While this formulation does not allow any anharmonic effects either within or between water molecules or any transitions to bend overtones or to two bends in separate molecules, it is an interesting beginning, which is consistent with very fast VV transfer in liquid H_2O.

7. Concluding Remarks

We begin these concluding remarks with a brief commentary on the HOD in D_2O situation. As has been extensively discussed in sections 4 and 5, the two theoretical treatments of the intramolecular energy transfer route for the OH population relaxation by Rey and Hynes (RH)[23] and by Lawrence and Skinner (LS2)[38] both treat the D_2O solvent molecules as flexible, but the latter has improved potentials and improved quantum correction factors for the rates. When these types of corrections (sometimes substantial) are made to RH, both treatments are essentially in agreement, both with respect to the mechanism and time scales. There is a disagreement with experimental estimates of the OH population lifetime[5,35] by about a factor of 3. However, it is certainly not clear what this signifies, because an outstanding issue remaining to be resolved is the relative contributions of the intramolecular vibrational energy transfer and the vibrational predissociation (IR-induced hydrogen bond breaking) routes for the OH population decay. Surveying the situation on the

theoretical side, we can identify several avenues where progress is required. A full theoretical treatment for the vibrational predissociation process for the HOD/D_2O system is needed; as noted in section 3.1, this should now be possible. We also believe that a more direct approach to VV processes (e.g, the participation of D_2O librations in assisting in the excited OH to HOD bend overtone transition, the energy transfer from the OD in HOD to solvent D_2O vibrations, etc.), a point that two of us have emphasized before with a suggested approach, is needed.[10] Further, the issue of the proper quantum correction factors (section 4.2.4) deserves ongoing investigation. Finally, there is an obvious need for a theoretical treatment of the OH population dynamics of water, H_2O, itself.

The considerations of the present review should prove useful—but will no doubt require extension to account for new important phenomena—when one considers OH population dynamics in other more complex aqueous systems. Some such systems of obvious interest here are ionic solutions,[73] the water–air interface,[39] and micelles.[74] Even more complex aqueous systems of biochemical interest could also be mentioned: membranes[75] and water near protein surfaces.[76]

We close this list of potential future applications, and this review, with an example that we mentioned in the Introduction: proton transfer (PT) reactions in solution. If one wishes to consider the possibility of driving PT reactions in solution by IR absorption of a H stretch,[77] then clearly the population relaxation of that H stretch via the processes we have reviewed is in competition with the desired photoinduced chemistry and needs to be understood. Further, and perhaps less obviously, the second major theme for OH dynamics in water and related systems identified in the Introduction, spectral diffusion/dephasing, will also require examination, since, for example, this is related to the dynamics of the H bond coordinate in which the H stretch is involved. (A similar remark could be made for the various applications listed in the paragraph preceding this one). Such spectral diffusion dynamics for HOD in D_2O have seen extensive recent experimental[5,78–81,84] and theoretical[60,82–84] scrutiny, and some important themes have begun to emerge. But this is the subject for a separate review.

8. Acknowledgments

9. References

(1) Eisenberg, D.; Kauzmann, W. *The Structures and Properties of Water*; Oxford University Press: New York, 1969. *Water: a Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1972.
(2) Elseasser, T. In *Ultrafast Hydrogen Bonding Dynamics and Proton Transfer Processes in the Condensed Phase*; Elseasser, T., Bakker, H. J., Eds.; Kluver Academic Publishers: Dordrecht, The Netherlands, 2002.
(3) Bakker, H. J. In *Ultrafast Hydrogen Bonding Dynamics and Proton Transfer Processes in the Condensed Phase*; Elseasser, T., Bakker, H. J., Eds.; Kluver Academic Publishers: Dordrecht, The Netherlands, 2002.
(4) Dlott, D. D. *Chem. Phys.* **2001**, *266*, 149.
(5) Deàk, J. C.; Rhea, S. T.; Iwaki, L. K.; Dlott, D. D. *J. Phys. Chem. A* **2000**, *104*, 4866.
(6) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; Freeman: San Francisco, CA, 1960. *Hydrogen Bonding*; Hadzi, D., Ed.; Pergamon Press: Oxford, U.K., 1959.
(7) Bruel, H.; Hynes, J. T. *Chem. Phys.* **1993**, *175*, 205.
(8) Keifer, P.; Hynes, J. T. In *Ultrafast Hydrogen Bonding Dynamics and Proton Transfer Processes in the Condensed Phase*; Elseasser, T., Bakker, H. J., Eds.; Kluver Academic Publishers: Dordrecht, The Netherlands, 2002.
(9) See, for example: Fersht, A. *Enzyme Structure and Mechanism*, 2nd ed.; W. H. Freeman and Co.: New York, 1985. Creighton, T. E. *Proteins*; W. H. Freeman and Co.: New York, 1984. *Nucleic Acids in Chemistry and Biology*, 2nd ed.; Blackburn, G. M., Gait, M. J., Eds.; Oxford University Press: Oxford, U.K., 1996.
(10) Hynes, J. T.; Rey, R. In *Ultrafast Infrared and Raman Spectroscopy*; Fayer, M. D., Ed.; Marcel Dekker: New York, 2001.
(11) Heilweil, E. J. *Science* **1999**, *283*, 1467.
(12) Mukamel, S. *Nonlinear Optical Spectroscopy*; Oxford University Press: New York, 1995.
(13) *Ultrafast Infrared and Raman Spectroscopy*; Fayer, M. D., Ed.; Marcel Dekker: New York, 2001.
(14) Oxtoby, D. W. *Adv. Chem. Phys.* **1979**, *40*, 1.
(15) Oxtoby, D. W. *Adv. Chem. Phys.* **1981**, *47*, 487.
(16) Stratt, R. M.; Maroncelli, M. *J. Phys. Chem.* **1996**, *100*, 12981.
(17) Voth, G. A.; Hochstrasser, R. M. *J. Phys. Chem.* **1996**, *100*, 13034.
(18) Owrutsky, J. C.; Raftery, D.; Hochstrasser, R. M. *Annu. Rev. Phys. Chem.* **1994**, *45*, 519.
(19) Graener, H.; Seifert, G.; Laubereau, A. *Phys. Rev. Lett.* **1991**, *66*, 2092.
(20) Vodopyanov, K. L. *J. Chem. Phys.* **1991**, *94*, 5389.
(21) Everitt, K. F.; Skinner, J. L.; Ladanyi, B. M. *J. Chem. Phys.* **2002**, *116*, 179.
(22) Madigosky, W. M.; Litovitz, T. A. *J. Chem. Phys.* **1961**, *34*, 489. Chesnoy, J.; Gale, G. M. *Adv. Chem. Phys.* **1988**, *70*, 297.
(23) Rey, R.; Hynes, J. T. *J. Chem. Phys.* **1996**, *104*, 2356.
(24) Whitnell, R. M.; Wilson, K. R.; Hynes, J. T. *J. Phys. Chem.* **1990**, *94*, 8625; *J. Chem. Phys.* **1992**, *96*, 5354.
(25) Staib, A.; Hynes, J. T. *Chem. Phys. Lett.* **1993**, *204*, 197.
(26) Graener, H.; Ye, T. Q.; Laubereau, A. *J. Chem. Phys.* **1989**, *90*, 3413; *J. Chem. Phys.* **1989**, *91*, 1034.
(27) Woutersen, S.; Emmerichs, U.; Bakker, H. J. *J. Chem. Phys.* **1997**, *107*, 1483.
(28) Henri-Rousseau, O.; Blaise, P. *Adv. Chem. Phys.* **1998**, *103*, 1.
(29) Witkowski, A. *J. Chem. Phys.* **1967**, *47*, 3645. Marechal, Y.; Witkowski, A. *J. Chem. Phys.* **1968**, *48*, 3697; *Theor. Chim. Acta* **1976**, *9*, 116.
(30) Bratos, S.; Leicknam, J.-C.; Gallot, G.; Ratajczak, H. In *Ultrafast Hydrogen Bonding Dynamics and Proton Transfer Processes in the Condensed Phase*; Elseasser, T., Bakker, H. J., Eds.; Kluver Academic Publishers: Dordrecht, The Netherlands, 2002.
(31) Lippincott, E. R. *J. Chem. Phys.* **1953**, *21*, 2070. Lippincott, E. R.; Schroeder, R. *J. Chem. Phys.* **1955**, *23*, 1099.
(32) Miller, R. *Science* **1988**, *240*, 447.
(33) Lord, R. C.; Merrifield, R. E. *J. Chem. Phys.* **1953**, *21*, 166.
(34) Falk, M.; Ford, T. *Can. J. Chem.* **1966**, *44*, 1699.
(35) (a) Woutersen, S.; Emmerichs, U.; Nienhuys, H.-K.; Bakker, H. J. *Phys. Rev. Lett.* **1998**, *81*, 1106. (b) Nienhuys, H.-K.; Woutersen, S.; van Santen, R. A.; Bakker, H. J. *J. Chem. Phys.* **1999**, *111*, 1494.
(36) Laubereau A.; Kaiser, W. *Annu. Rev. Phys. Chem.* **1975**, *26*, 83. Laubereau, A.; Fischer, S. F.; Spanner, K.; Kaiser, W. *Chem. Phys.* **1978**, *31*, 335.
(37) Lawrence, C. P.; Skinner, J. L. *J. Chem. Phys.* **2002**, *117*, 5827.
(38) Lawrence, C. P.; Skinner, J. L. *J. Chem. Phys.* **2003**, *119*, 1623.
(39) Morita, A.; Hynes, J. T. *Chem. Phys.* **2000**, *259*, 371.
(40) Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand: Princeton, NJ, 1968.
(41) Sceats, M. G.; Rice, S. A. *J. Chem. Phys.* **1979**, *71*, 973.
(42) Smith, D. F.; Overend, J. *Spectrochim. Acta* **1972**, *28A*, 471.
(43) Kuchitsu, K.; Morino, Y. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 814.
(44) Berkowitz, M.; Gerber, R. B. *Chem. Phys.* **1979**, *37*, 269.
(45) Velsko, S.; Oxtoby, D. W. *Chem. Phys. Lett.* **1980**, *69*, 462.
(46) Berne, B. J.; Gordon, R. G.; Jortner, J. *J. Chem. Phys.* **1967**, *47*, 1600. Berne, B. J.; Gordon, R. G.; Sears, V. F. *J. Chem. Phys.* **1968**, *49*, 475.
(47) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon Press: Oxford, U.K., 1989.
(48) Toukan, K.; Rahman, A. *Phys. Rev. B* **1985**, *31*, 2643.
(49) Martí, J.; Padró, J. A.; Guàrdia, E. *Mol. Simul.* **1993**, *11*, 321.
(50) Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. *J. Chem. Phys.* **1983**, *79*, 926.
(51) Lawrence, C. P.; Skinner, J. L. *Chem. Phys. Lett.* **2003**, *372*, 842.
(52) Sibert, E. L., III; Rey, R. *J. Chem. Phys.* **2002**, *116*, 237.
(53) Skinner, J. L.; Park, K. *J. Phys. Chem. B* **2001**, *105*, 6716.

(54) Schofield, P. *Phys. Rev. Lett.* **1960**, *4*, 39. Egelstaff, P. A. *Adv. Phys.* **1962**, *11*, 203. Guissani, Y.; Bratos, S.; Leicknam, J.-C. *C. R. Acad. Sci. Paris* **1969**, *269*, 137. Berne, B. J. In *Physical Chemistry: An Advanced Treatise*; Henderson, D., Ed.; Academic Press: New York, 1971; Vol. 8B.

(55) Berens, P. H.; White, S. R.; Wilson, K. R. J. *J. Chem. Phys.* **1981**, *75*, 515. Borysow, J.; Moraldi, M.; Frommhold, L. *Mol. Phys.* **1985**, *56*, 913. White, J. A.; Velasco, S.; Hernandez, A. C.; Luis, D. *Phys. Lett. A* **1988**, *130*, 237. Frommhold, L. *Collision-induced Absorption in Gases*; Cambridge University Press: Cambridge, England, 1993; Vol. 2.

(56) Bader, J. S.; Berne, B. J. *J. Chem. Phys.* **1994**, *100*, 8359. Egorov, S. A.; Rabani, E.; Berne, B. J. *J. Phys. Chem. B* **1999**, *103*, 10978. Egorov, S. A.; Berne, B. J. *J. Chem. Phys.* **1997**, *107*, 6050.

(57) Rostkier-Edelstein, D.; Graf, P.; Nitzan, A. *J. Chem. Phys.* **1997**, *107*, 10470.

(58) Egorov, S. A.; Skinner, J. L. *J. Chem. Phys.* **1996**, *105*, 10153. Skinner, J. L. *J. Chem. Phys.* **1997**, *107*, 8717. Egorov, S. A.; Skinner, J. L. *Chem. Phys. Lett.* **1998**, *293*, 469. Egorov, S. A.; Everitt, K. F.; Skinner, J. L. *J. Phys. Chem. A* **1999**, *103*, 9494.

(59) Kim, H.; Rossky, P. J. *J. Phys. Chem. B* **2002**, *106*, 8240.

(60) Møller, K. B.; Rey, R.; Hynes, J. T. *J. Phys. Chem. A* **2004**, *108*, 1275.

(61) Gale, G. M.; Gallot, G.; Lascoux, N. *Chem. Phys. Lett.* **1999**, *311*, 123.

(62) Lock, A. J.; Bakker, H. J. *J. Chem. Phys.* **2002**, *117*, 1708.

(63) Lawrence, C. P.; Skinner, J. L. *J. Chem. Phys.* **2003**, *119*, 3840.

(64) Arrivo, S. M.; Heilweil, E. J. *J. Phys. Chem.* **1996**, *100*, 11975. Audibert, M.-M.; Palange, E. *Chem. Phys. Lett.* **1983**, *101*, 407. Giebels, I. A. M. E.; van den Broek, M. A. F. H.; Kropman, M. F.; Bakker, H. J. *J. Chem. Phys.* **2000**, *112*, 5127. Grubbs, W. T.; Dougherty, T. P.; Heilweil, E. J. *J. Phys. Chem.* **1995**, *99*, 10716. Levinger, N. E.; Davis, P. H.; Fayer, M. D. *J. Chem. Phys.* **2001**, *115*, 9352. van den Broek, M. A. F. H. Ph.D. Thesis, University of Amsterdam, Amsterdam, The Netherlands, 2002.

(65) Pakoulev, A.; Wang, Z.; Dlott, D. D. *Chem. Phys. Lett.* **2003**, *371*, 594. Bakker, H. J.; Lock, A. J.; Madsen, D. *Chem. Phys. Lett.* **2004**, *385*, 329.

(66) Zittel, R. M.; Masturzo, D. E. *J. Chem. Phys.* **1989**, *90*, 977.

(67) Pakoulev, A.; Wang, Z.; Pang, Y.; Dlott, D. D. *Chem. Phys. Lett.* **2003**, *380*, 404.

(68) Woutersen, S.; Bakker, H. J. *Nature* **1999**, *402*, 507.

(69) Nitzan, A. *Nature* **1999**, *402*, 472.

(70) Förster, T. In *Modern Quantum Chemistry*; Sinanoglu, O., Ed.; Academic: New York, 1965; Vol. III. Eisental, K. B. *Chem. Phys. Lett.* **1970**, *6*, 155.

(71) Poulsen, J. A.; Nyman, G.; Nordholm, S. *J. Phys. Chem. A* **2003**, *107*, 8420.

(72) See, for example: Rapp, D. *Quantum Mechanics*; Holt, Rinehart and Winston: New York, 1971, Chapter 13.

(73) Kropman, M. F.; Bakker, H. J. *Science* **2001**, *291*, 2118. Kropman, M. F.; Bakker, H. J. *J. Chem. Phys.* **2001**, *115*, 8942. Kropman, M. F.; Bakker, H. J. *Chem. Phys. Lett.* **2002**, *262*, 349. Nienhuys, H.-K.; Lock, A. J.; van Santen, R. A.; Bakker, H. J. *J. Chem. Phys.* **2002**, *117*, 8021.

(74) Patzlaff, T.; Janich, M.; Seifert, G.; Graener, H. *Chem. Phys.* **2000**, *261*, 381. Seifert, G.; Patzlaff, T.; Graener, H. *Phys. Rev. Lett.* **2002**, *88*, 7402.

(75) Busing, H.; Ouw, D.; Kundu, S.; Vohringer, P. *Phys. Chem. Chem. Phys.* **2002**, *3*, 2378. Bursing, H.; Kundu, S.; Vohringer, P. *J. Phys. Chem. B* **2003**, *107*, 2404.

(76) Pal, S. K.; Peon, J.; Bagchi, B.; Zewail, A. H. *J. Phys. Chem B* **2002**, *106*, 12376. Bizzari A. R.; Cannistaro, S. *J. Phys. Chem. B* **2002**, *106*, 6617.

(77) Kim, H. J.; Staib, A.; Hynes, J. T. In *Femtochemistry and Femtobiology*; Sundström, V., Ed.; Imperial College Press: London, 1998.

(78) Laenen, R.; Rauscher, C.; Laubereau, A. *Phys. Rev. Lett.* **1998**, *80*, 2622. Laenen, R.; Rauscher, C.; Laubereau, A. *J. Phys. Chem. B* **1998**, *102*, 9304.

(79) Woutersen, S.; Bakker, H. J. *Phys. Rev. Lett.* **1999**, *83*, 2077. Bakker, H. J.; Nienhuys, H.-K.; Gallot, G.; Lascoux, N.; Gale, G. M.; Leicknam, J.-C.; Bratos, S. *J. Chem. Phys.* **2002**, *116*, 2592.

(80) Gale, G. M.; Gallot, G.; Hache, F.; Lascoux, N.; Bratos, S.; Leicknam, J.-C *Phys. Rev. Lett.* **1999**, *82*, 1068. Bratos, S.; Gale, G. M.; Gallot, G.; Hache, F.; Lascoux, N.; Leicknam, J.-C. *Phys. Rev. E* **2000**, *61*, 5211.

(81) Stenger, J.; Madsen, D.; Hamm, P.; Nibbering, E. T. J.; Elsaesser, T. *Phys. Rev. Lett.* **2001**, *87*, 027401. Stenger, J.; Madsen, D.; Hamm, P.; Nibbering, E. T. J.; Elsaesser, T. *J. Phys. Chem. A* **2002**, *106*, 2341.

(82) Rey, R.; Møller, K. B.; Hynes, J. T. *J. Phys. Chem. A* **2002**, *106*, 11993.

(83) Lawrence, P.; Skinner, J. L. *J. Chem. Phys.* **2003**, *118*, 264; *Chem. Phys. Lett.* **2003**, *369*, 472.

(84) Fecko, C. J.; Eaves, J. D.; Loparo, J. J.; Tokmakoff, A.; Geissler, P. L. *Science* **2003**, *301*, 1698.