

Motion of hydrogen bonds in diluted HDO/D₂O solutions: Direct probing with 150 fs resolution

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An experiment is described to study temporal variations of the hydrogen bond length in diluted HDO/D₂O solutions. The principles of this laser spectroscopic experiment are explained first. The construction of a laser source generating 150 fs pulses in the 2.5–4.5 μm spectral region at a 10 μJ power level is detailed next. The OH stretching band is reproduced for different excitation frequencies and different pump-probe delay times. A theory, based on statistical mechanics of nonlinear optical processes, is proposed to calculate the lowest two spectral moments. An effect is reported, the delay dependent vibrational solvatochromism. It is shown how this effect can be exploited to follow temporal variations of the OH...O bond length directly, in real time. The corresponding time scales are of the order of 700 fs. No bond oscillations are observed.

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I. INTRODUCTION

Direct observation of temporally varying molecular geometries during a chemical reaction represents an immense challenge for modern chemistry. Several techniques have been employed to reach this goal [1–3]. (i) Ultrafast laser spectroscopy, operating at pico- and femtosecond time scales, permits the detection of various short living species and the determination of their lifetimes. Unfortunately, it is difficult to convert spectral data into data on molecular geometry; the dependence of molecular dipole moments, or polarizabilities, on nuclear coordinates being poorly known, extra information is required for that purpose. (ii) Time-resolved x-ray diffraction allows a direct determination of structural changes, but this method is technically very demanding. Synchrotron x-ray sources have been employed to generate high flux beams with a well-defined pulse structure and polarization states. Other methods such as laser-plasma x-ray emission, time-resolved harmonic generation, Thomson scattering of laser pulses from relativistic electron beams, etc., have also been developed. However, the difficulties still forbid fs x-ray studies, although ns studies are practicable. (iii) Low-energy as well as small angle high-energy electron diffraction have been employed in studying dynamics of surface phase transformations and reactions at 10–100 ps scales. At the present time this technique is still in an early stage of development [4]. It is not surprising in these circumstances that real time observations of varying molecular geometries still remain rare; basic papers are given by Refs. [5–9]. Nevertheless, the intrinsic importance of the domain can hardly be overestimated: observing the first instants of a molecule's life is the very heart of chemistry.

The purpose of the present paper is to show how ultrafast infrared laser spectroscopy can be used to follow temporal variations of the hydrogen bond length in diluted HDO/D₂O solutions. Earlier work can be summarized as follows. (i) Midinfrared pump-probe experiments with tunable pulses were realized by Graener, Seifert, and Laubereau at 10 ps [10] and by Laenen, Rauscher, and Laubereau at 1 ps [11,12] time scales. Hole burning of the OH stretching band was

observed for the first time; a surprisingly short OH population relaxation time, as short as 1.5 ps, was reported. (ii) Much shorter pulses of 250 fs duration were used by Woutersen, Emmerichs, and Bakker [13] with polarization resolution. The orientational relaxation of HDO in D₂O was found to be biexponential with time constants of 0.7 and 13 ps; and characteristics of orientational motions were shown to vary with the pump frequency. Woutersen, Emmerichs, and Bakker also reported an anomalous temperature dependence of population relaxation time in ice and water [14]. (iii) Statistical theories using correlation function approach were employed by Bratos and Leicknam [15–17] to describe nonlinear pump-probe absorption in water. Three times were found to determine spectral behavior: the orientational relaxation time τ_0 as given by the second spherical harmonics, the vibrational population relaxation time τ_p , and the frequency shift correlation time τ_Ω . (iv) Computer simulation studies reported in recent years provide these basic quantities. The data on reorientational relaxation times τ_0 are particularly numerous; see, e.g., Refs. [18–22]. Typical values are of the order of 2 ps in pure H₂O and D₂O, but the HDO/D₂O mixture was not examined; polarization effects are surprisingly large. The frequency shift correlation function was determined by Diraison, Guissani, Leicknam, and Bratos [23] through a large scale semiclassical simulation. Its decay was found to be biexponential with time constants equal to 50 and 800 fs. Finally, the population relaxation time τ_p was estimated by Staib and Hynes [24] who combined the Fermi golden rule and the Lippincott-Schroeder potential. Calculated τ_p 's are of the order of 10 ps, too large by one order of magnitude. Moreover, a number of differently defined hydrogen bond lifetimes, τ_{HB} , were considered; see, e.g., Geiger *et al.* [25], and Marti, Padro, and Guardia [26]. They are all of the order of 1 ps, but their relation to the present problem is not obvious.

The paper is organized in the following way. In Sec. II, the principle of the experiment is explained in qualitative terms. The subsequent Sec. III offers a technical description of the infrared laser source and of the experiment itself. The theory of the spectral moments of pump-probe absorption is detailed in Sec. IV. Finally, Sec. V refers to the results and to

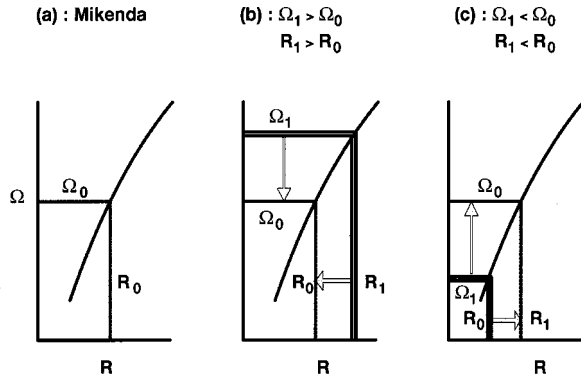


FIG. 1. Mikenda relation connecting the OH stretching frequency Ω and the OH...O bond length R in different hydrogen bonded systems (a): Ω_0 and R_0 denote the equilibrium values of Ω and R in a diluted HDO/D₂O solution. Principles of the experiment (b), (c): Ω_1 and R_1 represent the mean values of Ω and R in a coherently excited wave packet.

their discussion. For a preliminary account of the present research, see Refs. [27,28].

II. PRINCIPLE OF THE EXPERIMENT

Proposed by Bratos and Leicknam in 1995 [16,17], this experiment is based on the well known relationship linking the hydrogen stretching frequency Ω of an OH...O bond and its length R . The stronger the hydrogen bond, the softer the OH link and the lower is its frequency Ω : the covalent OH bond energy is lent to the OH...O bond and reinforces the latter. A number of empirical relationships were published, following the initial proposal of Rundle and Parasol [29–36]. The one adopted here is the recent relationship due to Mikenda [34]. It was obtained by compilation of spectroscopic and structural data of 61 solid hydrates containing more than 250 hydrogen bonds. Illustrated on Fig. 1(a), it is particularly suitable for the present purpose.

The experiment then goes as follows. An ultrafast pump pulse of frequency Ω_1 , belonging to the conventional OH stretching band of HDO, is used to excite OH vibrations; this excitation results in selecting OH...O bonds of a given bond length R_1 . A more precise statement is that a pump pulse, having a nonvanishing temporal and spectral width, generates a coherently excited wave packet with OH...O bonds contained in a small length interval around R_1 . Prepared in this way, the system relaxes back to equilibrium and is monitored by a probe pulse; the OH band is recorded for different time delays τ . Two choices exist for the pump frequency Ω_1 . First, let Ω_1 be larger than Ω_0 , the mean OH frequency of HDO in D₂O [Fig. 1(b)]; the laser selected OH...O bonds, initially longer than in equilibrium where their length is equal to R_0 , contract with time, and a low frequency shift of the OH band from Ω_1 to Ω_0 may be anticipated. The opposite behavior is expected if Ω_1 is smaller than Ω_0 [Fig. 1(c)]; the OH...O bonds, initially too short, expand on relaxing and a high frequency shift of the OH band is expected. No band shift should be observed if Ω_1 is equal to Ω_0 . Conversely, knowing the peak frequency $\Omega(\tau)$ of the signal at time τ and using the Mikenda relation between OH frequency and the OH...O length permits determination of this distance at time

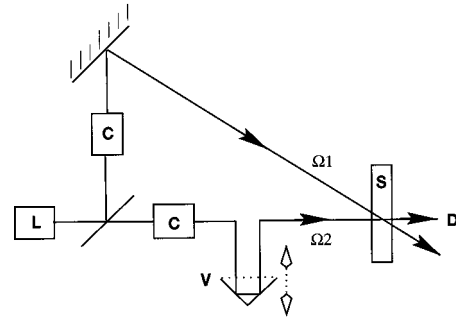


FIG. 2. Schematic representation of the experimental setup.

τ . A real-time study of H-bond dynamics is thus possible, in principle.

Which is the pulse duration required by such an experiment? According to the basic principles of laser spectroscopy, it must correspond to time scales of the process under investigation; this process, in the present case, is the relaxation of initially compressed, or extended, hydrogen bonds. As there was no experimental evidence available, the data provided by molecular dynamics simulation of Ref. [23] were used. They showed that the relevant time scale of our experiment are of the order of 100 fs. The pulses required to probe the OH...O hydrogen bond dynamics in water are thus 100 fs pulses operating in the 2.5–4.5 μm region. It is worth noting that the OH covalent link dynamics are about two orders of magnitude faster than the OH...O dynamics; they are not attainable in the present stage of laser technology.

III. EXPERIMENT

The experiment envisaged to check the above conjecture is an ultrafast infrared pump-probe experiment, schematically presented on Fig. 2. Optical pulses generated by a laser L are separated into pump and probe pulses. After passage through the frequency converters C , they are directed on the liquid sample S . The transmitted fraction of the probe flux is measured by the detector D as a function of the pump-probe delay τ , the latter is generated by a variable path device V . This scheme is entirely classical, except for one point: generation of ultrafast midinfrared pulses is very difficult, and is not yet practicable routinely.

The following method was employed to overcome this difficulty [37–40]. The pump channel was driven by a 1 mJ, 130 fs pulse at 800 nm, provided by an amplified titanium:sapphire laser; the repetition rate was equal to 1 kHz. Using a small portion of this 800 nm pulse, weak broad-bandwidth radiation was produced in the near infrared by focusing into a glass plate. This near-infrared light was spectrally narrowed and increased in intensity by frequency-selective, high-gain parametric amplification in a β -barium borate crystal. Finally, this near-infrared radiation was difference frequency mixed with the 800 nm pulse in a potassium titanyl phosphate crystal to produce midinfrared at the 10 μJ level. Tunability was achieved by rotation of the crystals. These midinfrared pulses had a duration of 150 fs and a spectral width of 65 cm^{-1} ; they were tunable between 2300 and 4000 cm^{-1} . A second independent probe channel was constructed on the same basis as above, having similar spectral and temporal characteristics, but an energy of 1 μJ only.

The probe channel was automated under computer control to maintain pump-probe delay constant, independent of probe frequency.

The experiment was performed as follows: The pump and attenuated probe beams, polarized in the same direction, were focused at an angle of 15° into a 100 μm diameter spot. This spot was located on an 100 μm thick flow cell containing a 0.5% solution of HDO in D₂O at room temperature; the laser induced temperature variations were estimated to be 2 K. The pump partially saturated a portion of the $\nu=0 \rightarrow \nu=1$ OH stretching band, centered at 3420 cm⁻¹ and having a bandwidth of 260 cm⁻¹; this process is called hole burning. The time evolution of the hole was followed by measuring the spectrum with the probe pulse at different time delays. In order to obtain greater sensitivity, differential spectroscopy was performed. To this end, the pump beam was chopped at 500 Hz and probe transmission was measured with and without the pump for alternate shots. The observed differential spectra exhibited an induced transmission at the pump frequency; the intensity of this spectral feature decreased with increasing probe delay and moved towards the center of the OH band. Induced absorption was also observed at lower frequencies; it was assigned to the $\nu=1 \rightarrow \nu=2$ transition of the OH vibrator. The frequency shift was found equal to 270 cm⁻¹, and was ascribed to the anharmonicity of the OH band.

IV. THEORY

A. Expression of the signal

The process to be studied theoretically is the infrared pump-probe absorption of a dilute solution of HDO in D₂O. The notation is as follows: Ω_1 and Ω_2 designate the mean frequencies of the pump and probe fields, and τ the delay between them. The incident electric fields, coherent and polarized in the same direction, are denoted by E_1, E_2 , and the total electric field is E . The key quantity of the theory is the pump-probe signal $S(\Omega_1, \Omega_2, \tau)$, defined as the temporally integrated probe absorption $W(\Omega_1, \Omega_2, \tau)$ in the presence of the pump minus the probe absorption $W(\Omega_2)$ in the absence of the pump. It was calculated recently by Bratos and Leicknam [15]:

$$S(\Omega_1, \Omega_2, \tau) = \frac{2}{\hbar^3} \text{Im} \left\{ \int_{-\infty}^{\infty} \int_0^{\infty} \int_0^{\infty} \int_0^{\infty} dt d\tau_1 d\tau_2 d\tau_3 \right. \\ \times \langle \dot{E}_2(\mathbf{r}, t) E(\mathbf{r}, t - \tau_3) E(\mathbf{r}, t - \tau_3 - \tau_2) E(\mathbf{r}, t \\ - \tau_3 - \tau_2 - \tau_1) \rangle_E \langle M(0) [M(\tau_1), [M(\tau_1 \\ + \tau_2), M(\tau_1 + \tau_2 + \tau_3)]] \rangle_S \left. \right\}. \quad (1)$$

Equation (1) involves two four-time correlation functions: the correlation function of the total and probe electric fields E and E_2 , and that of the electric dipole moment M of the system. The average $\langle \rangle_S$ is over the states of the nonperturbed liquid sample, and the average $\langle \rangle_E$ is over all possible realizations of the incident electric fields. The symbol $[,]$ denotes a commutator and the dot a time derivative. It should be noted that Eq. (1) represents an exact third-order pertur-

bation theory result; for a detailed derivation, see Ref. [41]. Earlier approximate formulas are due to Yan and co-workers [42,43].

A rapid and compact way of characterizing a spectral band consists in defining its moments. By definition, the moment $(M_n)_{\Omega_0}$ of a spectral band with respect to a frequency Ω_0 is

$$(M_n)_{\Omega_0} = \left[\lim_{\Omega_M \rightarrow \infty} \int_{-\Omega_M}^{\Omega_M} (\Omega - \Omega_0)^n I(\Omega) d\Omega \right] \\ \times \left[\lim_{\Omega_M \rightarrow \infty} \int_{-\Omega_M}^{\Omega_M} I(\Omega) d\Omega \right]^{-1}, \quad (2)$$

where $I(\Omega)$ is the spectral density. One notices that $(M_1)_{\Omega_0}$ defines the frequency of the band center. Moreover, if Ω_0 is identified with the latter, $(M_2)_{\Omega_0}$ gives indication about the bandwidth, $(M_3)_{\Omega_0}$ describes the asymmetry of the band contour, etc. In conventional, linear spectroscopies, $I(\Omega)$ is expressible as a Fourier transform of an appropriate two-time correlation function, and the calculation of the band moments is greatly simplified by introducing the δ function formalism.

The situation is much more complex in pump-probe spectroscopy. In this case, the signal appears under the form of a Fourier-Laplace transform of a product of two four-time correlation functions. Band moments can then be calculated by inserting Eq. (1) into Eq. (2) and integrating over Ω_2 :

$$(M_n)_{\Omega_0} = \left[\lim_{\Omega_M \rightarrow \infty} \int_{-\Omega_M}^{\Omega_M} (\Omega_2 - \Omega_{20})^n S(\Omega_1, \Omega_2, \tau) d\Omega_2 \right] \\ \times \left[\lim_{\Omega_M \rightarrow \infty} \int_{-\Omega_M}^{\Omega_M} S(\Omega_1, \Omega_2, \tau) d\Omega_2 \right]^{-1}. \quad (3)$$

This is the n th moment of the pump-probe absorption with respect to the probe frequency Ω_{20} . If the absorption consist of several separate bands, and this is usually the case, each of them is treated independently. The calculation is generally performed by inverting the order of frequency and time integrations and by calculating the limit $\Omega_M \rightarrow \infty$; the latter operation is always posterior to the integration. As expected, $(M_n)_{\Omega_0}$ generally depends on the pump frequency Ω_1 and on the delay τ . The problem is thus soluble in principle; for more details, see Ref. [17].

B. Model

The model employed hereafter to realize this study contains four basic assumptions. (i) The spectrally active OH vibrator of the HDO/D₂O mixture is assimilated to a three level quantum system perturbed by a stochastic solvent-solute interaction. (ii) The dipole moment M of the molecule is governed by the empirically modified Heisenberg equation

$$\frac{dM}{dt} = \frac{i}{\hbar} [H, M] - \Gamma M, \quad (4)$$

where H is an adiabatic Hamiltonian of the mixture and $\Gamma = \Gamma_p + \Gamma_o$ designates the total relaxation rate, due to the

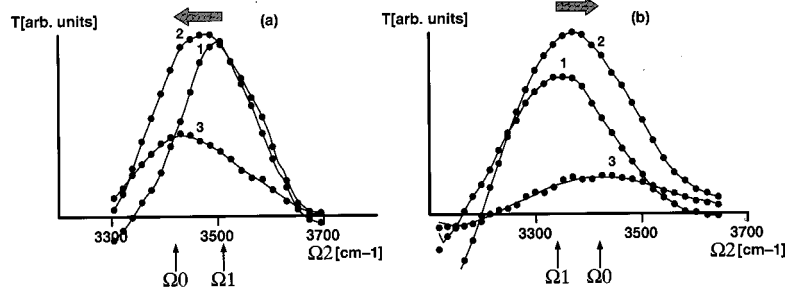


FIG. 3. Frequency-resolved pump-probe signal $T(\Omega_1, \Omega_2, \tau) = -S(\Omega_1, \Omega_2, \tau)$ of the $v=0 \rightarrow v=1$ OH band. (a) corresponds to excitation at 3510 cm^{-1} , and (b) to excitation at 3340 cm^{-1} . The spectra 0, 1, and 2 were recorded with a time delay τ of 0, 300, and 900 fs, respectively; the arrows indicate band shifts.

population and the orientational relaxation. (iii) The effect of permanent dipole moments is neglected, and only the elements M_{01} , M_{10} , M_{12} , and M_{21} of the dipole moment M are considered. (iv) The pump and probe fields are supposed to be coherent and to have Gaussian profiles of equal duration

$$E_1(\mathbf{r}, t) = \text{Re}[E_{10} e^{-\gamma t'^2} e^{i(\mathbf{k}_1 \cdot \mathbf{r} - \Omega_1 t)}]; \quad (5a)$$

$$E_2(\mathbf{r}, t) = \text{Re}[E_{20} e^{-\gamma t'^2} e^{i(\mathbf{k}_2 \cdot \mathbf{r} - \Omega_2 t)}], \quad (5b)$$

where $t' = t + \tau$, $\sqrt{\gamma} = \sqrt{2 \ln 2} / \tau_{\text{IR}}$, and τ_{IR} is the temporal half-width of incident infrared pulses. Assumptions of this kind are of current use in this field; and are not re-examined here.

C. Band moments

Detailed calculations are described in Ref. [17]; they can be sketched as follows. The dipole moment correlation function $\langle M(0)[M(\tau_1), [M(\tau_1 + \tau_2), M(\tau_1 + \tau_2 + \tau_3)]] \rangle_S$ was computed by (i) determining the time evolution of the matrix elements M_{01} , M_{10} , M_{12} , and M_{21} through Eq. (4), (ii) employing the cumulant expansion theorem, and (iii) noticing that the dephasing time τ_d , of the order of 15 fs, is short as compared with all other relaxation times. The resulting correlation function is composed of terms proportional to

$$C_{\pm}(\tau_1, \tau_2, \tau_3) = \exp\left[-\frac{1}{2}\beta\tau_1^2 - \frac{1}{2}\beta\tau_3^2 \pm \tau_1\tau_3\beta(\tau_1 + \tau_2)\right], \quad (6)$$

where $\beta(\tau) = \langle \omega(0)\omega(\tau) \rangle_c$ and $\beta = \beta(0)$, the subscript indicating the cumulants. This expression contains only two-time correlation functions of the solvent induced frequency shift $\omega(t)$. They may be calculated by using standard methods of statistical mechanics.

The electric field correlation function $\langle \dot{E}_2(\mathbf{r}, t)E(\mathbf{r}, t - \tau_3)E(\mathbf{r}, t - \tau_3 - \tau_2)E(\mathbf{r}, t - \tau_3 - \tau_2 - \tau_1) \rangle_E$ was computed in the slowly varying amplitude approximation by (i) decomposing E_1 and E_2 into individual exponentials and (ii) noticing that only those contributions survive the operation $\langle \rangle_E$ which exhibit no space oscillation over the sample S . The final result then appears as a sum of terms proportional to

$$D(t, \tau_1, \tau_2, \tau_3, \tau) = \exp[-\gamma(t_1^2 + t_2^2 + t_3^2 + t_4^2)], \quad (7)$$

where t_1, t_2, t_3 , and t_4 are various combinations of times $t, t - \tau_3, t - \tau_3 - \tau_2, t - \tau_3 - \tau_2 - \tau_1$, and $t' = t + \tau$. The assumption that the incident electric fields are coherent greatly simplifies the problem.

The last step of calculation consists in evaluating five-dimensional integrals over $t, \tau_1, \tau_2, \tau_3$, and Ω_2 ; compare with Eqs. (1) and (2). The integration over Ω_2 simplifies the situation, although not as much as in linear spectroscopies; though analytical work remains practicable if two-time correlation functions are all monoexponential. The zeroth moment $A(\tau)$ of the $v=0 \rightarrow v=1$ OH band, as well as its first moment $M(\tau)$, were calculated by proceeding in this way. The results

$$A(\tau) = \mathcal{C} \left\{ 1 + \text{erf} \left[\sqrt{\gamma} \left(\tau - \frac{1}{2\gamma\tau_1} \right) \right] \right\} \exp \left[-\frac{1}{\tau_1} \left(\tau - \frac{1}{4\gamma\tau_1} \right) \right] \quad (8a)$$

$$M(\tau) - \Omega_0 = \mathcal{C} \left\{ 1 + \text{erf} \left[\sqrt{\gamma} \left(\tau - \frac{1}{2\gamma\tau_2} \right) \right] \right\} \times \exp \left[-\frac{1}{\tau_2} \left(\tau - \frac{1}{4\gamma\tau_2} \right) \right] \frac{\Delta_1}{A(\tau)}, \quad (8b)$$

where $1/\tau_1 = 1/\tau_p + 1/\tau_0$ and $1/\tau_2 = 1/\tau_p + 1/\tau_0 + 1/\tau_\Omega$, $\Delta_1 = \Omega_1 - \Omega_0$ and \mathcal{C} is a constant. Note that the decay of A depends on τ_0 and τ_p , whereas τ_0, τ_p , and τ_Ω are required to determine M . If $\tau_p, \tau_0 \gg \tau_\Omega$, Eqs. (8a,b) reduce to Eqs. (13a,e) of Ref. [17], but this simplification cannot be taken for granted in the present context. Equations (8a,b) are the basis of interpretation of experimental data presented in the next section.

V. RESULTS AND DISCUSSION

A. Results

Five excitation frequencies Ω_1 were used, higher and lower than the mean frequency Ω_0 equal to 3420 cm^{-1} [10]. As the results are all comparable, only two of them are discussed here, one at 3520 cm^{-1} and another at 3340 cm^{-1} ; the following points merit attention. (i) Frequency resolved pump-probe signals $T(\Omega_1, \Omega_2, \tau) = -S(\Omega_1, \Omega_2, \tau)$ of the $v=0 \rightarrow v=1$ OH band, recorded for three different time delays τ , are illustrated in Figs. 3(a) and 3(b). A vibrational solvatochromic shift toward lower frequencies is observed in Fig. 3(a) where $\Omega_1 > \Omega_0$; and a high frequency shift is seen

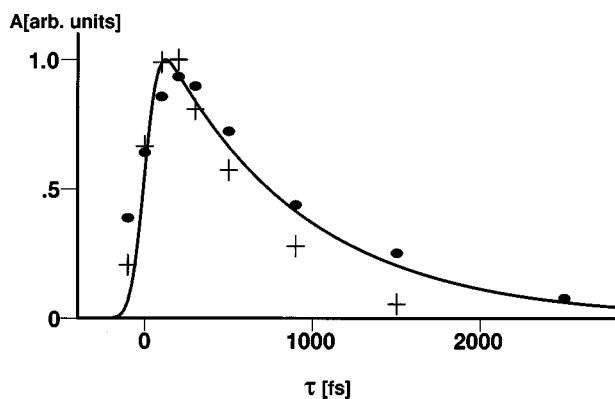


FIG. 4. Integrated intensity $A(\tau)$ of the $\nu=0 \rightarrow \nu=1$ OH band, expressed as a function of the time delay τ . The circles indicate experimental data obtained with excitation at 3510 cm^{-1} and the crosses those measured after excitation at 3340 cm^{-1} . The full lines correspond to Eq. (8a) where $\tau_p = 1.30 \text{ ps}$ and $\tau_o = 2.50 \text{ ps}$.

in Fig. 3(b) where $\Omega_1 < \Omega_0$. (ii) The $A(\tau)$ curves are centered around the zero time delay $\tau=0$. They vanish at large positive and negative τ 's (Fig. 4): the pump and probe absorption disappears in thermal equilibrium. Their rising part describes the buildup of the signal and thus depends on the pump pulse duration τ_{IR} and their decaying part expresses the effect of the population and orientational relaxation and is thus determined by τ_p, τ_o . As $\tau_{\text{IR}} \ll \tau_p, \tau_o$, the $A(\tau)$ curves are distinctly asymmetrical. (iii) The $M(\tau)$ curves evolve from the pump frequency Ω_1 to a frequency identifiable, within the experimental error, with the mean frequency Ω_0 . They are monotonously decreasing if $\Omega_1 > \Omega_0$ [Fig. 5(a)], and increasing if $\Omega_1 < \Omega_0$ [Fig. 5(b)]. The error bars, below 10 cm^{-1} , always remain small as compared to the overall solvatochromic shift, of the order of 100 cm^{-1} . The effect is thus very large, and its existence cannot reasonably be questioned. (iv) The OH...O fs dynamics were studied in real time by converting Figs. 5(a) and 5(b) into diagrams displaying the relationship between $R(\tau)$ and τ . The inter-

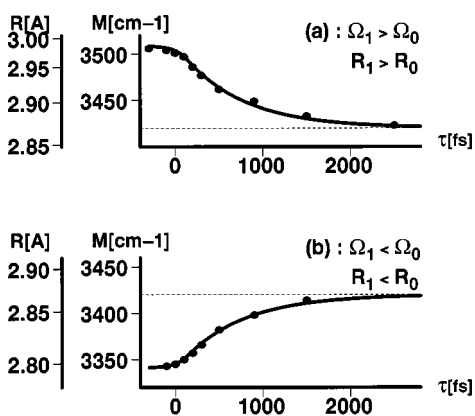


FIG. 5. Observing OH...O motions in real time: First moment $M(\tau)$ of the OH band and the length $R(\tau)$ of the OH...O bond expressed as a function of the time τ . (a) corresponds to excitation at 3510 cm^{-1} and (b) to 3340 cm^{-1} ; the initial OH...O bond length is 2.99 \AA in (a) and 2.80 \AA in (b). The points represent experimental data; the full curves are given by the theory where $\tau_p = 1.30 \text{ ps}$, $\tau_o = 2.50 \text{ ps}$, and $\tau_\Omega = 0.70 \text{ ps}$.

pretation is as follows. In Fig. 5(a), the excitation Ω_1 is at 3510 cm^{-1} ; the length of the pump selected hydrogen bonds is $R_1 = 2.99 \text{ \AA}$, longer than $R_0 = 2.86 \text{ \AA}$. Fig. 5(a) thus illustrates the contraction of initially elongated hydrogen bonds. In Fig. 5(b), the excitation Ω_1 is at 3340 cm^{-1} ; here the length of the pump selected hydrogen bonds is $R_1 = 2.80 \text{ \AA}$, smaller than $R_0 = 2.86 \text{ \AA}$. Figure 5(b) thus illustrates the extension of initially compressed hydrogen bonds. Each point represents an experimentally measured bond length: the OH...O dynamics were thus studied in real time, and the bonds were ‘‘photographed’’ during their evolution in the liquid sample. As there is some spread in the OH...O length due to the finite duration of incident pulses, the observed bond distances, in fact, represent an average over the pump-prepared wave packet; this explains the absence of Brownian noise in Fig. 5. It is interesting to notice that the release of the initial constraint generates monotonic motions, and no oscillations appear in Figs. 5(a) and 5(b). This behavior, suggesting a strong damping, was expected, but it is to the best of our knowledge, the first time that it was ‘‘seen’’ directly.

An additional experiment was realized to check whether the hydrogen bond stretching and contracting mechanism just described is the only mechanism generating vibrational solvatochromic shifts. For example, can the frequency-dependent population relaxation produce a similar effect? The simplest way to answer this question is to eliminate the hydrogen bond stretching and contracting mechanism by choosing $\Omega_1 = \Omega_0$. It was then found that, in between the limits of experimental accuracy, solvatochromic shifts disappear altogether. It can thus safely be concluded that the hydrogen bond stretching and contracting mechanism dominates the spectral behavior.

Theory (solid lines) and experiment (points) are compared in Figs. 4 and 5; they agree very well with each other, except for large τ 's in Fig. 4; the origin of this discrepancy is not clearly understood. The optimized values of parameters, obtained by adopting for τ_o the value of 2.5 ps [44], are $\tau_p = 1.3 \text{ ps}$ and $\tau_\Omega = 0.7 \text{ ps}$. This value for τ_p compares favorably with the value of $1.5 \pm 0.5 \text{ ps}$, reported by Laenen, Rauscher, and Laubereau [11]. Moreover, a τ_Ω of 0.7 ps is close to the decay time of 0.8 ps predicted by molecular dynamics simulation for the slow mode of the frequency shift correlation function [23]. Its fast mode, decaying with a time constant of 50 fs , is too short to be detectable by the present experiment.

B. Discussion

The first major result reached by the present study is the observation of vibrational solvatochromic shifts. They represent the counterpart of the well known electronic solvatochromic shifts, currently observed in time-resolved fluorescence [45–50]. Although predicted theoretically [16,17], they have never, to the best of our knowledge, been observed before and thus make up a new spectral effect. It should be stressed that the full four-time correlation function theory is required to study them. The usual approximation, which consists in replacing the solvatochromic response function $S(\tau) = [M(0) - M(\tau)] / [M(0) - M(\infty)]$ by the normalized two-time frequency shift correlation function $C(\tau)$

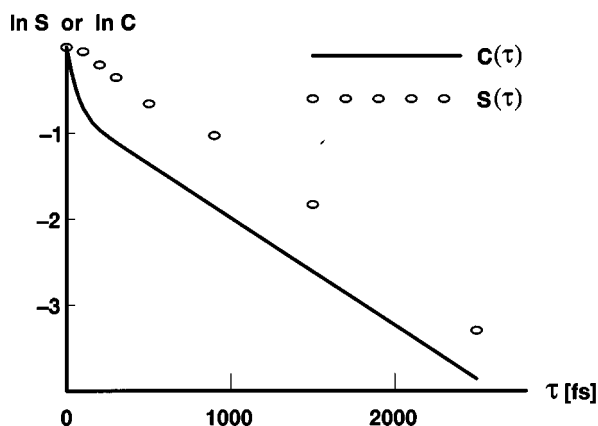


FIG. 6. Comparison between the experimentally determined solvatochromic response function $S(\tau)$ and the computed frequency shift correlation function $C(\tau)$. They disagree at short times.

$=\langle\Delta\omega(0)\Delta\omega(\tau)\rangle/\langle\Delta\omega(0)\Delta\omega(0)\rangle$ is not satisfactory at the short times considered here. This is illustrated on Fig. 6 obtained by comparing our experimental and our computer simulation data.

The second important result is the real time detection of fs dynamics of OH...O bonds in diluted HDO/D₂O solutions. In this respect, our experiment is closely related to the very important Zewail experiment on photodissociation of the iodine cyanide molecule [5]. The two experiments permit the observation of temporally varying molecular geometries during a chemical process. It is worth emphasizing that extra information had to be supplied to both of them to pass from time-resolved spectra to time-resolved molecular geometries. In Zewail's experiment, this extra knowledge concerns the potential energy surfaces of two low lying excited electronic states of iodine cyanide (ICN), whereas in ours the relation between the OH stretching frequency and OH...O bond length is required. The main difference is that one of the two papers concerns a photochemical process in a gas, whereas the other treats a thermal process in a liquid.

The hydrogen bond dynamics were also examined by Laubereau and co-workers [10–12]. The system under investigation is the same, a diluted solution of HDO in D₂O. The difference is in the pulse duration: 1–10 ps in Laubereau's experiments and 150 fs in ours. These authors thus mainly

focused their attention on the study of structural properties of liquid water; the total OH band of the transient spectrum was decomposed into three major constituents with different spectral and dynamical properties. Our research, on the contrary, mainly concerns fs dynamics of OH...O bonds; this objective requires short enough pulses. It should be noted that population relaxation times, measured by these two groups of researchers, are largely consistent with each other.

The hydrogen bonds lifetimes τ_{HB} , as introduced and calculated by Geiger *et al.* [25] and Marti, Padro, and Guardia [26], also merit comments. According to these authors, an OH...O system is considered as a hydrogen bond if the OH...O length R is shorter than a limiting length R_0 and if the



angle α is close enough to 180°. Alternatively, the energy criteria can be employed; an OH...O system is declared hydrogen bonded, if the interaction energy E exceeds a cutoff value E_{HB} . Calculated on this basis, τ_{HB} was found to be of the order of 1 ps. τ_{HB} is comparable to τ_{Ω} , the frequency shift correlation time: $\Delta\Omega$ becomes very small if $R > R_0$ and $\alpha \neq 180^\circ$, or if $E < E_{\text{HB}}$. In no case should it be assimilated to τ_p , lifetime of the excited vibrational state.

The present discussion may be closed by pointing out that a number of authors have recently studied fs real-time clocking of chemical reactions in liquid solutions; see, e.g., Refs. [51–54]. Several problems have been investigated in this frame: solvent dependence of the wave packet motion, caging and geminate recombination, dissociation, predissociation and impulsive dissociation, symmetry breaking, etc. However, no attempt was made to convert spectral data into data on molecular geometry. These studies thus differ from the present one in many essential aspects.

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