

## Femtosecond Dynamics of Hydrogen Bonds in Liquid Water: A Real Time Study

G. M. Gale, G. Gallot, F. Hache, and N. Lascoux

*Laboratoire d'Optique Quantique, Ecole Polytechnique, Route de Saclay, 91128 Palaiseau Cedex, France*

S. Bratos and J.-Cl. Leicknam

*Laboratoire de Physique Théorique des Liquides, Université Pierre et Marie Curie,  
Case courrier 121, 4 Place Jussieu, 75252 Paris Cedex 05, France*

(Received 22 September 1998)

A pump-probe experiment is described to study femtosecond dynamics of hydrogen bonds in liquid water. The key element of the experimental setup is a laser source emitting 150 fs pulses in the 2.5–4.4  $\mu\text{m}$  spectral region, at a 10  $\mu\text{J}$  power level. The OH-stretching band is recorded for different excitation frequencies and different pump-probe delay times. Time-dependent solvatochromic shifts are observed and are interpreted with the help of statistical mechanics of nonlinear optical processes. Using these spectral data, the OH $\cdots$ O motions are “photographed” in real time. [S0031-9007(98)08298-2]

PACS numbers: 82.20.Wt, 78.47.+p

Elementary chemical processes in gases and liquids take place on time scales ranging from 10 fs to 10 ps. It took ultrafast laser technology over 20 years to reach these scales. An important breakthrough was accomplished when Zewail and his colleagues, applying laser spectroscopic methods, succeeded in following the photochemical dissociation of gaseous iodine cyanide (ICN) in real time [1], producing in this way a “photographic” picture of the process. A number of related studies were published later; see, e.g., Refs. [2–4]. Although essential, this was only the first step; thermally activated chemical reactions in liquids necessitate further studies. They require the availability of femtosecond infrared sources, the knowledge of statistical mechanics of nonlinear optical processes, and that of large scale quantum molecular dynamics simulations.

Published work on femtosecond dynamics of thermally activated processes mainly refers to an isotopic variety of liquid water, the diluted solution HDO/D<sub>2</sub>O. The following directions of research were explored: (i) Pump-probe experiments were realized by Graener, Seifert, and Laubereau at 10 ps [5] and by Laenen, Rauscher, and Laubereau at 1 ps [6] time scales. Hole burning of the OH-stretching band was observed for the first time and a population relaxation time of 1.5 ps was inferred. (ii) Another midinfrared pump-probe study of HDO dissolved in D<sub>2</sub>O, realized with polarization resolution at 250 fs time scales, was published by Woutersen, Emmerichs, and Bakker [7]. The orientational relaxation of HDO was found to be biexponential, with time constants of 0.7 and 13 ps. (iii) Theoretical work on this subject, mainly due to Bratos and Leicknam [8,9], employed the correlation function approach of statistical mechanics of nonlinear optical processes. A method was proposed to study OH $\cdots$ O motions of water in real time.

The purpose of this paper is to realize the experiment suggested in Ref. [9], “photographing” H-bond motions in

this way. The principle of the experiment is as follows. Its key ingredient is the well-known relation between the OH-stretching frequency and the length of an H bond; it is described in Refs. [10,11] and is illustrated in Fig. 1. Pumping the HDO/D<sub>2</sub>O solution at a given frequency  $\Omega_1$  thus results in selecting the OH $\cdots$ O bonds of a specified length; an alternative statement is that the pump pulse generates a coherently excited wave packet, containing OH $\cdots$ O bonds with only a narrow length dispersion. This wave packet thermalizes gradually as time goes on; its evolution is monitored by a probe at time  $\tau$ . The pump-probe signal undergoes a  $\tau$ -dependent solvatochromic shift from  $\Omega_1$  to  $\Omega_0$ , the OH-stretching frequency of HDO in thermal equilibrium. This shift is towards lower frequencies if  $\Omega_1 > \Omega_0$  and towards higher frequencies if  $\Omega_1 < \Omega_0$ ; no frequency shift is expected if  $\Omega_1 = \Omega_0$ . Conversely, knowing the peak frequency  $\Omega(\tau)$  of the signal at time  $\tau$

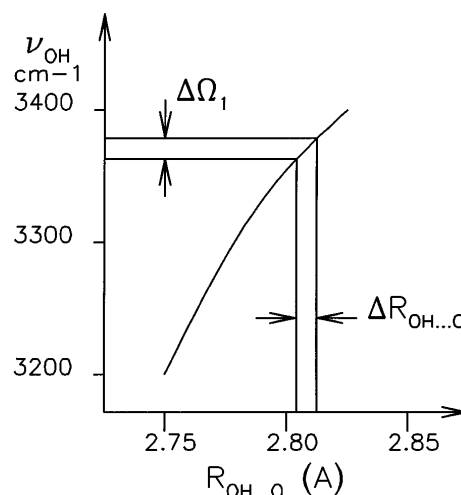


FIG. 1. Dependence of the OH stretching frequency on the H-bond length. This relation is one of the basic relations of the theory of hydrogen bonding.

and using the above-mentioned relation between the OH frequency and the  $\text{OH}\cdots\text{O}$  length, permits determination of this distance at time  $\tau$ . A real-time study of H-bond dynamics is thus possible, in principle.

The first requirement for a successful realization of the project concerns the laser pulse duration: It must be comparable to characteristic times of the process under investigation. As structural relaxation times of water were not known, semiclassical molecular dynamics simulations were realized by Diraison, Guissani, Leicknam, and Bratos [12]. The calculated frequency shift correlation function was found to be biexponential, decreasing monotonously with time constants of 50 and 800 fs. The laser device which is required should thus operate at 100 fs time scales in the 2.5–4.5  $\mu\text{m}$  spectral region.

A laser source having the above characteristics was constructed by Gale, Gallot, Hache, and Sander [13,14]. Its central element is a titanium:sapphire amplifier, generating 130 fs pulses at 800 nm with an energy of 1 mJ and a repetition rate of 1 kHz. The principle of the operation of the source is the parametric amplification of a quasicontinuum in the near infrared, which makes the source tunable, followed by a frequency mixing of the 800 nm and near-infrared beams, which produces mid-infrared light. The salient features of the experiment using this source are as follows. The pump beam had a duration of 150 fs and a spectral width of 65  $\text{cm}^{-1}$ , leading to a time-bandwidth product of 0.30. Tunability was between 2300 and 4000  $\text{cm}^{-1}$  with an energy superior to 10  $\mu\text{J}$  between 2800 and 3800  $\text{cm}^{-1}$ . The independently tunable probe beam had similar characteristics to those of the pump, but with a maximum energy of 1.5  $\mu\text{J}$ . The probe channel was automated, and spectra between 2700 and 3800  $\text{cm}^{-1}$  were recorded under computer control at fixed pump-probe delay. The sample cell was 100  $\mu\text{m}$  thick and contained a 0.5% solution of HDO in  $\text{D}_2\text{O}$  at room temperature. The sample was circulated to avoid problems due to the high repetition rate. Pump and (attenuated) probe beams were focused to a 100  $\mu\text{m}$  spot

on the sample cell. The angle between the pump and probe beams, polarized in the same direction, was 15°. The pump beam was chopped at 500 Hz (half the repetition rate) to obtain differential spectra, with and without excitation.

With the pump beam tuned to a fixed frequency inside the asymmetric OH stretching band of HDO, a selected subensemble of systems with a given  $\text{OH}\cdots\text{O}$  distance was excited. Time-resolved differential spectroscopy was then performed with the probe beam, at various pump-probe delays  $\tau$ , in order to follow the evolution of this subensemble. Induced transmission (bleaching) between  $\Omega_1$  and  $\Omega_0$  was examined; excited state absorption ( $\nu = 1 \rightarrow \nu = 2$ ), occurring at significantly lower frequencies, was also observed. In order to quantify more accurately the spectral shifts and for direct comparison with theory, the first moment  $M$  of the  $\nu = 0 \rightarrow \nu = 1$  band was calculated by making a minor correction for the tail of excited state absorption.

Typical results are collected in Figs. 2 and 3, illustrating the observed spectra and their first moment  $M$ . In Figs. 2(a) and 3(a), the pump frequency  $\Omega_1$  taken at 3510  $\text{cm}^{-1}$  is 90  $\text{cm}^{-1}$  above the OH band center  $\Omega_0$  at 3420  $\text{cm}^{-1}$ ; low frequency shifts are observed in this case. An opposite behavior is shown in Figs. 2(b) and 3(b), where the excitation is at 3340  $\text{cm}^{-1}$ , 80  $\text{cm}^{-1}$  below the band center. Note that the spectral intensities decrease with increasing  $\tau$ , due to the thermalization of the pump prepared wave packet.  $M$  is initially close to the pump frequency and subsequently decays smoothly to  $\Omega_0$ . The initial decay to 50% of the total displacement occurs in 400 fs, which justifies the use of short pulses. These findings, in agreement with the predictions of Ref. [9], prove the existence of a new spectral effect, not yet reported in the literature. Its presence is conjectured in all hydrogen bonded liquids.

The theory of the processes just described is based on statistical mechanics of nonlinear optical processes. Its key ingredient is an expression for the pump-probe signal  $S(\Omega_1, \Omega_2, \tau)$ , recently proposed by Bratos and

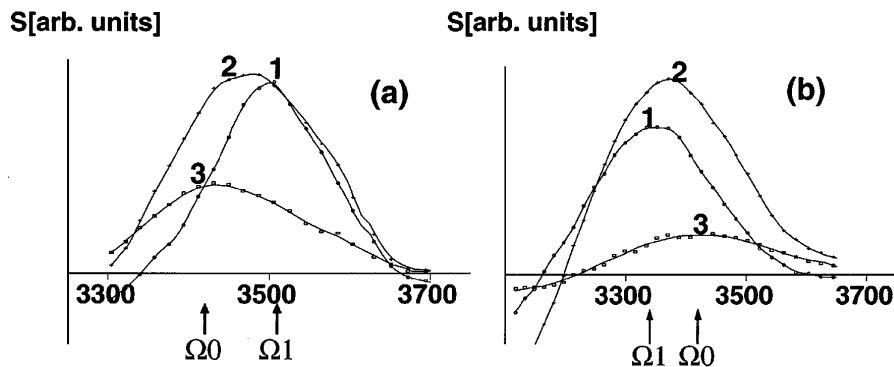


FIG. 2. Pump-probe signal  $S(\Omega_1, \Omega_2, \tau) = -S(\Omega_1, \Omega_2, \tau)$  of the OH band expressed as a function of the time delay  $\tau$ . (a) This corresponds to the excitation at 3510  $\text{cm}^{-1}$ , and to time delays equal to 0 (1), 300 (2), and 900 fs (3). In (b), the excitation is at 3340  $\text{cm}^{-1}$  and the time delays are 0 (1), 300 (2), and 900 fs (3).

Leicknam [8]:

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

It involves two 4-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 non-perturbed liquid system, 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 perturbation theory result; earlier (approximate) formulas are due to Mukamel *et al.* [15,16].

Equation (1) was applied to the present problem under the following conditions. The system under consideration contains a single HDO and a large number of D<sub>2</sub>O molecules. It is modeled by a three-level quantum system, representing the three low energy OH-stretching levels of HDO. This system is subjected to a random perturbation, expressing molecular interactions; it is quantum mechanical in the vibrational degree of freedom, and classical elsewhere. Two quantities were calculated as a function of  $\tau$ , the integrated intensity  $A$  of the  $\nu = 0 \rightarrow \nu = 1$  band, as well as its first moment  $M$ . Because band moments are much easier to calculate than complete spectral shapes, the calculation was performed under excellent conditions with the following results:

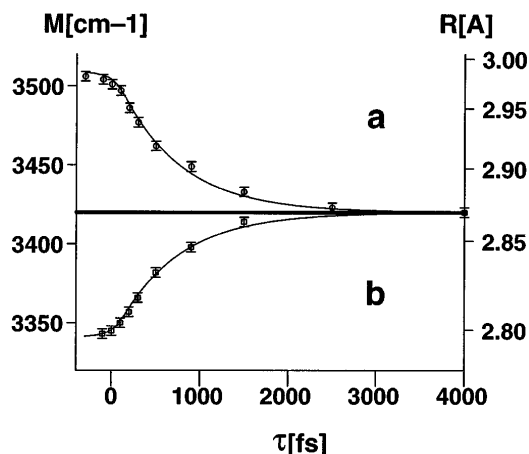


FIG. 3. First moment  $M(\tau)$  of the OH band expressed as a function of the pump-probe delay  $\tau$ . (a) This corresponds to the excitation at  $3510 \text{ cm}^{-1}$  and (b) to that at  $3340 \text{ cm}^{-1}$ . The same figure illustrates the evolution of the OH $\cdots$ O bond length  $R$  as a function of the real time  $\tau$ . The initial OH $\cdots$ O bond length is equal to  $2.99 \text{ \AA}$  in (a), and to  $2.80 \text{ \AA}$  in (b). The solid curves are theoretical curves [Eq. (3)].

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

$$M(\tau) - \Omega_0 = C \left\{ 1 + \text{erf} \left[ \sqrt{\gamma} \left( \tau - \frac{1}{2\gamma\tau_2} \right) \right] \right\} \\ \times \exp \left[ -\frac{1}{\tau_2} \left( \tau - \frac{1}{4\gamma\tau_2} \right) \right] \frac{\Delta_1}{A(\tau)}, \quad (3)$$

where  $\sqrt{\gamma} = 2\sqrt{\ln 2}/\tau_{\text{IR}}$ ,  $\tau_{\text{IR}}$  being the temporal half width of incident infrared pulses;  $1/\tau_1 = 1/\tau_p + 1/\tau_o$  and  $1/\tau_2 = 1/\tau_p + 1/\tau_o + 1/\tau_\Omega$ ;  $\tau_p$  and  $\tau_o$  are the population and the orientational relaxation times, respectively, and  $\tau_\Omega$  is the frequency shift correlation time,  $\Delta_1 = \Omega_1 - \Omega_0$ , and  $C$  is a constant. Note that the decay of  $A$  depends on  $\tau_o$  and  $\tau_p$ , whereas  $\tau_o$ ,  $\tau_p$ , and  $\tau_\Omega$  are needed to determine  $M$ . If  $\tau_p, \tau_o \gg \tau_\Omega$ , Eq. (3) reduces to Eqs. 13a and 13e of Ref. [9], but this simplification is not justified in the present case.

Theory (solid lines) and experiment (points) are compared in Figs. 3(a) and 3(b); they agree very well with each other. The optimized values of the parameters, obtained by adopting for  $\tau_o$  the value of 2.5 ps [17], are  $\tau_p = 1.3$  ps and  $\tau_\Omega = 0.7$  ps. This value for  $\tau_p$  compares favorably with the value of  $1.5 \pm 0.5$  ps, reported by Laenen *et al.* [6]. Moreover, a  $\tau_\Omega$  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 [12]. Its fast mode decays with a time constant of 50 fs; it is too short to be detectable by the present experiment.

Finally, Figs. 3(a) and 3(b) are converted in diagrams displaying the relationship between  $R_{\text{OH}\cdots\text{O}}$  and  $\tau$ . This may be done by using the Mikenda empirical relation between the OH-stretching frequency and the H-bond length [11] and replacing the  $M$  axis by the  $R_{\text{OH}\cdots\text{O}}$  axis. The measured OH $\cdots$ O length is, in fact, the mean OH $\cdots$ O length in the wave packet; the scatter is due to the finite width of the exciting pulse. Femtosecond dynamics of H-bonds in water have thus been “photographed” in real time. The contraction of initially stretched hydrogen bonds is illustrated in Fig. 3(a), whereas Fig. 3(b) pictures the extension of bonds which are initially compressed. No hydrogen bridge oscillations are “seen” experimentally, a

result in agreement with molecular dynamics simulations [12]. The present experiment thus permits, as did the early Zewail experiment, a direct observation of temporally varying molecular geometries on femtosecond time scales. This domain will certainly be given much attention in the future.

The authors gratefully acknowledge the support of the GDR 1017 of the CNRS during this work. The Laboratoire d'Optique Quantique is a "Unité Mixte de Recherche" No. 7645 of the CNRS and the Laboratoire de Physique Théorique des Liquides is a "Unité Mixte de Recherche" No. 7600 of the CNRS.

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