Dynamics of Local Substructures in Water Observed by Ultrafast Infrared Hole Burning

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Transient hole burning in the OH-stretching region of HDO dissolved in D_2O is investigated by two-color pump-probe spectroscopy in the temperature range 273–343 K. Spectral holes are observed with widths of 45 cm^{-1} and a lifetime of $\approx$1 ps. The total OH band in the transient spectrum may be decomposed into three major constituents with different spectral and dynamical properties that are traced over the full temperature range. From the measured cross relaxation among the spectral components a structural relaxation time of 1.5 ± 0.5 ps (273 K) to 0.8 ± 0.4 ps (343 K) is inferred. [S0031-9007(98)05648-8]

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Because of its outstanding role in nature, the investigation of the structural and dynamical properties of water [1] has a long tradition in science. This liquid consists of one of the smallest kinds of molecules with specific intermolecular interaction via hydrogen bonds. The latter are known to play an important role for numerous chemical and biological processes and structures like protein folding and the structure of the DNA. Raman [2] and conventional IR-spectroscopic data of water [3] suggest discrete spectral species underlying the broad OH-stretching band(s) and corresponding structural components, as the OH mode acts as a local probe for the strength of the hydrogen bonding of the hydroxilic group determining its frequency position [4]. These ideas, discussed for several decades, were substantiated by time-resolved spectroscopy in the infrared with independently tunable pump and probe pulses of 11 ps duration [5]. Changes of the transient OH band shape as a function of the frequency position of the excitation pulse provided evidence for the "inhomogeneous" character of the OH band of water (HDO in D_2O) at 298 K. Three major spectral components were inferred from the data and assigned to different environments [5]. The time resolution of the investigation, however, did not allow one to observe a spectral hole and determine the structural relaxation dynamics. It was surmised that a lifetime of a few picoseconds of the spectral components was consistent with the observations [5]. The latter conclusion was doubted by other authors [6], who presented a profound theoretical analysis of the spectroscopic method and showed that a solvent relaxation time (frequency shift correlation time) of 200 fs accounted for basic features of the measured transient spectra. From NMR experiments [7], Rayleigh [8], and neutron scattering [9] structural relaxation of water is supposed to proceed on a picosecond time scale. A common disadvantage of these studies is the averaging over all possible structural components contributing to the dynamics and the uncertainty in interpreting a measured time constant in terms of structural dynamics.

The present investigation is aimed at overcoming such difficulties using two-color pump-probe spectroscopy in the IR with notably shorter pulses of 1–2 ps. The narrow bandwidth of these pulses allows one for the first time to observe spectral holes in the OH stretching band of liquid systems [10]. Similar features are reported in the following for water.

Our experimental system was described recently [11]. The pulses are derived from parametric oscillator-amplifier devices with durations of 1 ps (2 ps), spectral width 16 cm^{-1} (8 cm^{-1}) and a typical energy of $\approx$10 nJ (10 μJ) in the range 1600 to 3700 cm^{-1} (2800 to 3700 cm^{-1}; numbers in brackets refer to the pump). The energy transmission $T(\nu)$ of the probing pulse through the excited sample is measured for parallel ($\|$) and perpendicular ($\perp$) polarization with respect to the linear polarization of the pump and compared with the probe transmission $T_0(\nu)$ with blocked excitation beam. The resulting relative transmission changes $\ln(T/T_0)_{\|,\perp}$ for variable probe frequency ν and delay time t_D represent the relevant quantities, from which an isotropic signal, $\ln(T/T_0)_{\mathrm{is}} = [\ln(T/T_0)_{\|} + 2\ln(T/T_0)_{\perp}]/3$, the anisotropic signal, $\ln(T/T_0)_{\mathrm{anis}} = \ln(T/T_0)_{\|} - \ln(T/T_0)_{\perp}$, and the induced dichroism $\ln(T/T_0)_{\mathrm{anis}}/3\ln(T/T_0)_{\mathrm{is}}$ are determined [12]. For negligible energy transfer processes, the time evolution of the induced dichroism is governed by the reorientation time constant τ_{or} (second order reorientational correlation time), while the isotropic signal delivers information on the vibrational population dynamics. A HDO concentration of 0.8 M is adjusted in heavy water.

An example for transient spectral hole burning in the high-frequency part of the OH band is demonstrated in Fig. 1. The anisotropic signal contribution is plotted versus probe frequency for $\nu_{Pu} = 3490\ \mathrm{cm}^{-1}$ and $T = 343$ K. At early delay times of -2 ps (a) a narrow bleaching with width of 45 ± 5 cm^{-1} is indicated at the frequency position of the pump pulse, representing the spectral hole. The spectral feature is due to a depletion of the vibrational ground state and a corresponding population of the first excited state via excitation of a selected ensemble of molecules. Increasing t_D to 1 ps the Lorentzian-shaped transient hole [dotted line, Fig. 1(b)] has grown in amplitude and a broader shoulder appears.

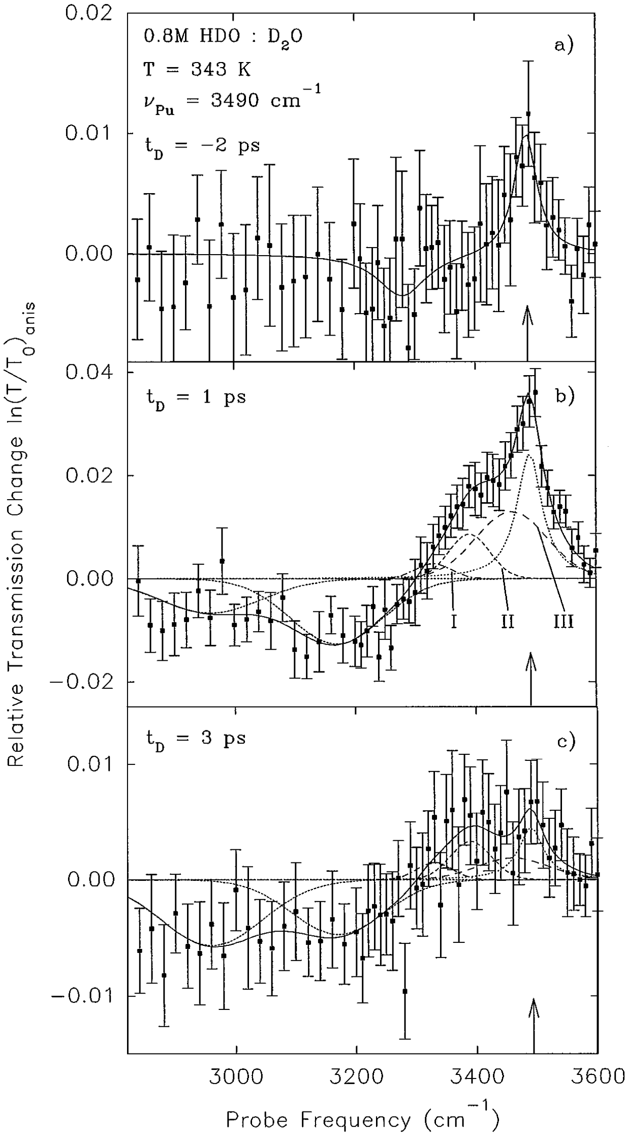

FIG. 1. Transient spectrum of 0.8 M HDO in D_2O (anisotropic signal) in the OH-stretching region at 343 K for different delay times: −2 ps (a), 1 ps (b), and 3 ps (c); excitation at 3490 cm^{-1} (arrow). A spectral hole with width of 45 ± 5 cm^{-1} is observed; note different ordinate scales. Experimental: points; calculated: curves.

A careful analysis of data with varying pump frequency and delay time shows that the shoulder consists of three further bleaching components I–III of approximately Gaussian shape, as indicated by calculated curves in the figure. In addition, a redshifted induced absorption occurs around 3200 cm^{-1}, obviously due to excess population of the $v = 1$ state of the OH-stretching vibration that gives rise to excited state absorption with corresponding anharmonic frequency shift. At $t_D = 3$ ps [Fig. 1(c)] the pump-induced anisotropy of the sample has notably decreased indicating short relaxation times $\leq$2 ps.

The temperature dependence of the transient spectra is illustrated by Fig. 2 for excitation close to the band maximum (note vertical arrows). The anisotropic signal is plotted for $t_D = 0$ ps. At a temperature of 273 K [Fig. 2(a), undercooled liquid] no evidence for a transient hole at the excitation frequency is obtained but a Gaussian component with a width of 80 cm^{-1} (dashed line, II) and two further contributions in the red and the blue part of the spectrum (dash-dotted curve, I, and long-dashed line, III, respectively). Increasing the temperature to 298 K [Fig. 2(b)] results in the appearance of a transient spectral hole (dotted curve) while the contributions I–III are still present, however, with considerable amplitude changes. Component III has grown in amplitude with a frequency down-shift of approximately 50 cm^{-1} and an increasing width up to 140 cm^{-1} that is supported by additional measurements in the range 275–290 K (data not shown). Heating the sample up to 343 K [Fig. 2(c)] the bleaching part of the anisotropic spectrum is mainly formed by the broad component III and the transient hole (long-dashed and dotted curves, respectively).

The measured transient spectra taken for various delay times (–2 to 6 ps), excitation frequencies within the width of the OH band and temperatures (273–343 K) is well described by model calculations based on the following physical picture: The bleaching part of the transient spectrum consists of three major contributions that are assigned to HDO molecules in preferred, yet rapidly fluctuating local structures [5]. Components I and II are positioned, respectively, around 3340 and 3410 cm^{-1} with widths of approximately 60–80 cm^{-1}. Species III shows up at 3500 cm^{-1} at 273 K; raising the temperature to 300 K, a frequency down-shift to 3450 cm^{-1} occurs and spectral broadening from 80 to 140 cm^{-1}, with little further changes at higher temperature. The relative amplitudes of the spectral constituents depend on temperature and excitation frequency. Details of these results will be published elsewhere [13]. Component I is believed to represent an icelike structure as suggested from infrared spectroscopy [14]. The large spectral widths may be taken as evidence for local fluctuations, e.g., for the icelike structure in the liquid phase thus differing from the linear H bonds of crystalline ice with spectral width of approximately 40 cm^{-1} [14]. The argument is somewhat different for the 140 cm^{-1} wide component III that dominates the OH absorption above room temperature, where we are able to observe transient holes, indicating relatively slow fluctuations on the time scale of the measurement. We also notice that species III appears close to a frequency position ($\simeq$3435 cm^{-1}) [15] that is proposed to be related to molecules with a bifurcated hydrogen bond [16]. The particularly large bandwidth of component III should be contrasted to the stronger H bonds of structures I and II that appear to be quasihomogeneously broadened under our experimental conditions.

The distinct reshaping of the transient spectrum, i.e., time evolution of the amplitudes of the components

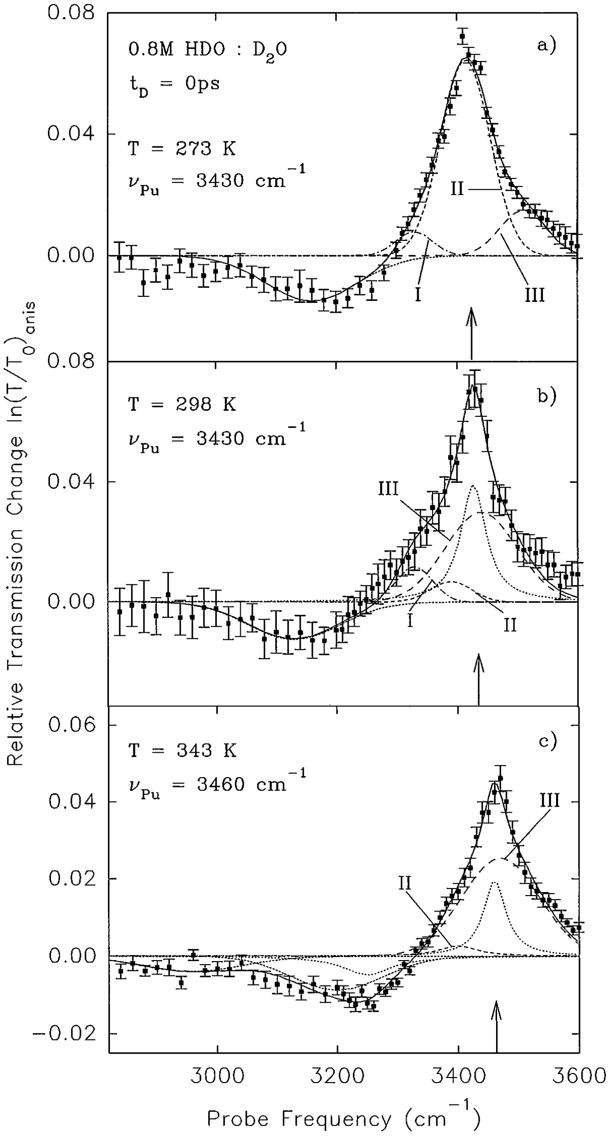

FIG. 2. Same as Fig. 1 but constant delay time, $t_D = 0$ ps, and three different temperatures: 273, 298, and 343 K; excitation at 3430 cm^{-1} [(a),(b)] and 3460 cm^{-1} (c), respectively. Hole burning is seen only in (b) and (c) (dotted curves). Experimental: points; calculated: lines.

I–III reveals fast spectral relaxation. The phenomenon is assigned to rearrangement of the hydrogen-bond environment with corresponding frequency shifts of the excited OH groups, i.e., conversion of a vibrating molecule from one species to another. Some results on the spectral reshaping are presented in Fig. 3 (isotropic signal) for excitation at 3410 cm^{-1}. The relative amplitudes of components I (hollow and filled squares) and II (hollow and filled circles) as obtained from the decomposition of the transient spectra are plotted versus delay time for two temperature values, 273 and 298 K (dashed and full lines, respectively). It is interesting to see the time evolution of component II that is excited close to resonance and rises rapidly according to the duration of the pump pulse, with a slightly delayed maximum at $t_D = 1.5$ ps. Component I, on the other hand, is almost not directly excited by the pump pulse and displays a slower amplitude growth presenting evidence for cross relaxation, i.e., conversion of molecules in environments I to II. The corresponding amplitudes of component III are located between the one of I and II at $T = 273$ K, while III is directly excited at room temperature (data not shown).

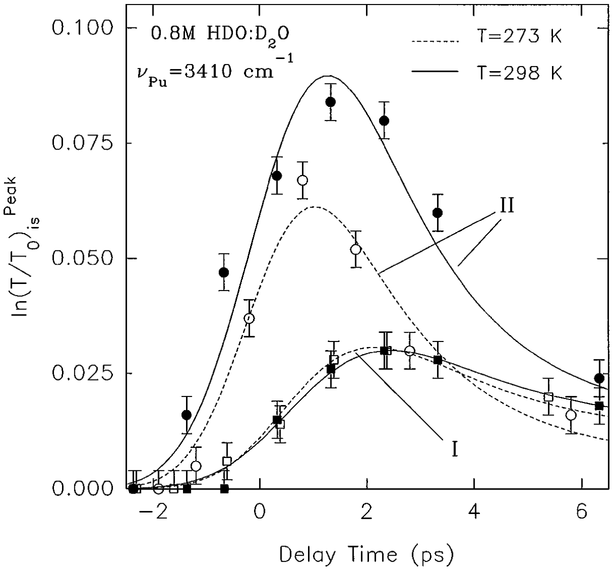

FIG. 3. Spectral relaxation of the OH band; the amplitudes of components I (icelike, squares) and II (circles) deduced from the isotropic part of the transient spectra are plotted versus delay time for two temperatures, 273 K (hollow symbols, dashed calculated lines) and 298 K (filled symbols, solid calculated lines); excitation at 3410 cm^{-1}.

To deduce quantitative information from signal transients like those of Fig. 3, we have performed model calculations for three HDO species with spectral positions and widths as determined from the transient spectra. A redistribution time τ_s describing the buildup of a quasiequilibrium between the three components is determined. The single time constant τ_s for the cross relaxation among the three species is assumed for simplicity and interpreted as a structural relaxation time of the solvent. The model also includes population decay to the vibrational ground state of the OH mode. Comparison of the rate equation model with the experimental data of Fig. 3 suggests $\tau_s = 1.5 \pm 0.5$ ps at $T = 273$ K, while a slightly shorter value of 1.0 ± 0.4 ps is inferred for $T = 298$ K (calculated lines in Fig. 3). Additional data (not shown) yield a value of $\tau_s = 0.8 \pm 0.4$ ps at $T = 343$ K.

Structural relaxation is accompanied by the loss of the pump-induced anisotropy: the signal amplitudes have already strongly decreased at $t_D = 3$ ps [Fig. 1(c)]. We have studied the induced dichroism of HDO in the accessible temperature range for excitation frequencies located at the centers of the prominent structural components I–III. The fastest orientational motion is found for species III with time constant $\tau_{\mathrm{or}} = 3 \pm 1.5$ ps in the range 273–343 K. Slower dynamics are seen for the icelike structure I and also component II: τ_{or} decreases monotonically from 15 ± 5 ps at 273 K for I and II to, respectively, 5 ± 1 ps and 7 ± 1 ps for species I and II at 343 K. The higher rotational mobility of component III supports its assignment as a weakly bonded water conformation. Component III may be compared with results of transient IR spectroscopy on water monomers in different solutions, where $\tau_{\mathrm{or}} \simeq 2$ ps was reported in the case of weak hydrogen bonds [17]. The larger reorientation times compared to τ_s suggest that the rearrangement of the water structure is only partially due to angular changes but considerably supported by translational motion, i.e., variation of $O \cdots O$ distances of H bonds.

It is interesting to compare the results on τ_s with the lifetime of 1 ± 0.4 ps of the spectral holes assigned to component III. The latter time presents independent information on spectral changes initiated by structural relaxation. The value is fully consistent with the data of Fig. 3 and gives support to our water model with three major constituents. Our result favorably compares with the lifetime of a hydrogen bond as predicted by computer simulation [18,19]. The theoretical data support the interpretation of the measured spectral relaxation time in terms of a reorganization of H bonds. It is also interesting to compare our data with the frequency shift correlation function of the vibrational modes of water obtained from MD calculations. Recently a bimodal decay of this function was predicted for HDO in D_2O at 300 K and density 1.1 g/cm^3 with two exponential time constants of 50 and 800 fs for all three modes [20]. The occurrence of two vastly different time scales is consistent with the physical picture discussed here. The existence of the slower component is a necessary prerequisite for the observation of spectral holes and the spectral relaxation time τ_s reported here. This time constant and the measured hole lifetime agree well with the larger value of 800 fs disregarding the higher density value ($p \approx 2$ kbar) of the computation. The shorter time, on the other hand, indicates the mean duration of rapid frequency fluctuations, the amplitude and lifetime of which determine the spectral bandwidths. The value of $\tau_c = 50$ fs suggests homogeneous broadening for the measured halfwidths (FWHM Γ) of species I and II and of the spectral holes of component III, i.e., $\tau_c \Gamma c < 0.5$.

In conclusion, we have demonstrated for the first time transient hole burning and spectral cross relaxation in the OH-stretching band of HDO in D_2O. The structural relaxation is shown to proceed with a time constant of $\tau_s \approx 1$ ps in the investigated temperature range. Hole burning is observed for the dominant, broad component at 3450 cm^{-1}, related to molecules with weak hydrogen bonding. A reorientation time of approximately 3 ps is found for this component while two other structures exhibit a slower reorientational motion depending on temperature. Our data also suggest that an icelike structure (I) exists in water up to 70 °C, the abundancy decreasing with temperature.

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