New Spectroscopy of Water Using Tunable Picosecond Pulses in the Infrared

H. Graener, G. Seifert, and A. Laubereau
Physikalisches Institut, Universität Bayreuth, D-8580 Bayreuth, Federal Republic of Germany

(Received 19 October 1990)

Spectral hole burning is observed for the OH stretching mode of HDO dissolved in D_2O at 298 K after intense infrared excitation. Three spectral components are inferred from the transient band shapes and related to an icelike molecular environment and other hydrogen-bonding configurations. A population lifetime of $T_1 = 8 \pm 2$ ps and an anharmonic frequency shift of 270 ± 20 cm^{-1} are measured.

PACS numbers: 61.25.Em, 33.20.Ea, 42.65.Ft, 78.47.+p

It is commonly believed that the properties of the OH stretching vibration are strongly related to the structure of the hydrogen bridge bond. Vibrational spectroscopy was, therefore, widely used in the past to investigate hydrogen-bonded systems.[1] For some liquids, e.g., alcohols, ir-absorption studies allow the determination of a few different hydrogen-bonded species and of the corresponding association parameters.[2] Matrix isolation techniques show that a larger number of transition frequencies can be discerned.[3] The relation of these observations to liquids is not well understood. For water, the situation is particularly complicated, since each molecule can form up to four hydrogen bonds. Several attempts have been reported to deduce structural information on this system from infrared, Raman, or attenuated-total-reflectance spectroscopy.[4] These results gave some evidence for a discrete substructure of the OH absorption that was attributed to different hydrogen-bonded environments. A final answer to such questions is still lacking; obviously more powerful spectroscopic techniques are required, e.g., time-resolved infrared spectroscopy[5] as demonstrated very recently for a H-bonded polymer.[6]

In this Letter spectral hole burning on the picosecond time scale is reported for the first time for the vibrational spectrum of HDO dissolved in D_2O. Direct evidence is obtained for a discrete substructure of the OH stretching band at 3400 cm^{-1}. Three spectral components are deduced from the transient band shapes supporting a multicomponent model of water.[7]

Details of the experimental system were described recently.[5] In short, a first intense ir pulse (energy ~50 μJ, duration 11 ± 2 ps, bandwidth 18 ± 2 cm^{-1} around 3400 cm^{-1}) is tuned to the desired excitation frequency and resonantly pumps the OH stretching mode. A second, independently tunable, weak pulse probes the sample transmission $T(\nu, t_D)$ as a function of delay time t_D or probe frequency ν; $t_D = 0$ marks the maximum of the pump pulse. Most of the measurements are performed with parallel polarization of the excitation and interrogation pulses. The common small-signal transmission $T_0(\nu)$ is measured blocking the pump beam.

The samples (length 100 μm) were 0.5–1 mol/l HDO in D_2O prepared by mixing corresponding amounts of demineralized, bidistilled H_2O in highly purified D_2O (99.996% isotopic purity). After proton exchange, the residual H_2O content of the samples was less than 0.01 mol/l. Figure 1(a) shows the absorption band of a HDO sample (1 mol/l, experimental points) obtained by a commercial infrared spectrometer after correction for the D_2O background. The broad OH absorption is centered at 3420 cm^{-1} with a bandwidth (FWHM) of 260 cm^{-1}.

Examples for the transient spectra taken early during the excitation process are presented in Fig. 2 ($t_D = -3$ ps, experimental points). The relative transmission change $\ln(T/T_0)$ generated by the pump pulse is plotted

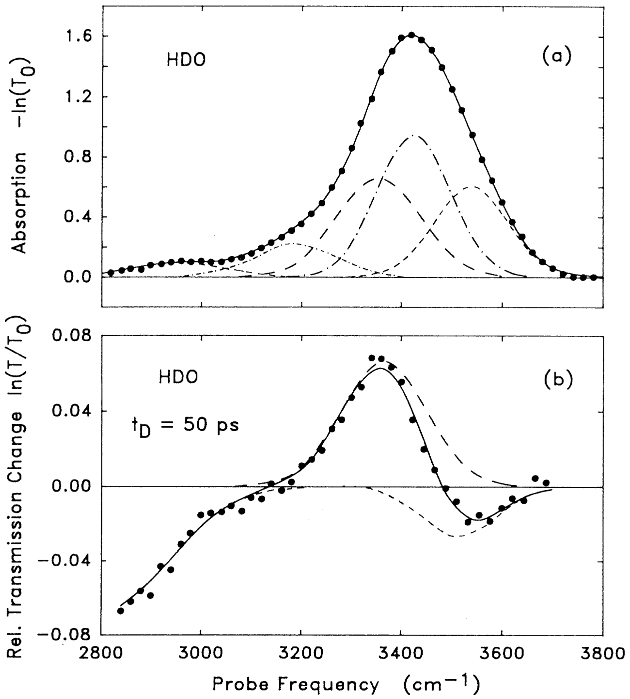

FIG. 1. (a) Conventional ir-absorption spectrum of the OH stretching mode of $HDO:D_2O$ (1 mol/l) after correction of the D_2O background; (b) transient infrared probe spectrum of the same sample, 50 ps after excitation at 3400 cm^{-1}. Experimental points and calculated curves (see text).

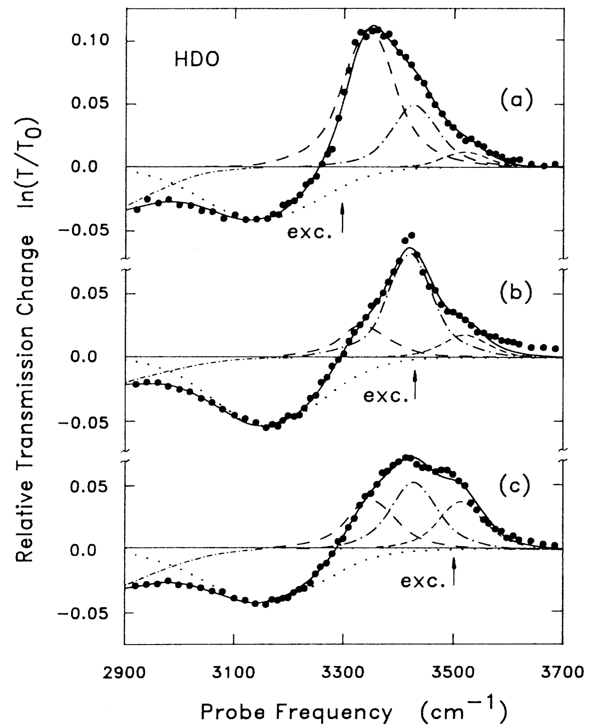

FIG. 2. Transient infrared probe spectra of HDO:D$_2$O (0.5 mol/l) early during the excitation process ($t_D = -3$ ps, to minimize thermal effects) for excitation at (a) 3300 cm^{-1}, (b) 3430 cm^{-1}, and (c) 3500 cm^{-1}. The varying band shapes directly indicate inhomogeneous broadening; experimental points and calculated curves.

versus probe frequency. The different excitation frequencies of 3300, 3430, and 3500 cm^{-1} for Figs. 2(a), 2(b), and 2(c), respectively, are indicated by vertical arrows. Data were also taken for other pump frequencies. Common to all these measurements is the observation of a transmission increase [$\ln(T/T_0) > 0$, bleaching] for $\nu \geq 3300$ cm^{-1}, while a transmission decrease (induced absorption) occurs for probe frequencies below 3250 cm^{-1}. The differences of the transient band shapes for varying excitation frequencies directly indicate inhomogeneous broadening.[6] Of particular interest are the shoulders and positions of the band maxima of Fig. 2: The latter may differ considerably from the pump frequencies. These findings reveal that the spectral inhomogeneity does not consist of a smooth, singly peaked frequency distribution.

Figure 1(b) shows the measured transmission changes of HDO in D$_2$O, 50 ps after excitation at 3400 cm^{-1}. Between 3200 and 3450 cm^{-1} a broad bleaching is observed. In the wings, induced absorption occurs that clearly differs from Fig. 2. Similar spectra, but with different amplitudes, are obtained at $t_D \gtrsim 50$ ps for other excitation frequencies and smaller HDO concentrations. Comparison of Figs. 1(b) and 2 shows that drastic spectral changes occur within ≃50 ps after excitation. The curves in Figs. 1 and 2 are calculated and will be discussed below.

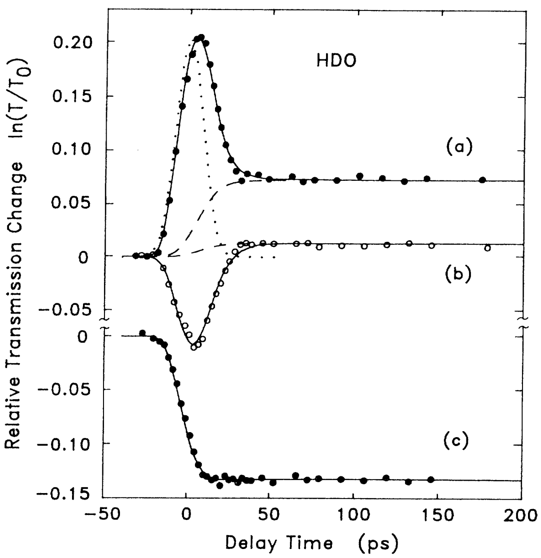

FIG. 3. Relative transmission change of HDO:D$_2$O (0.5 mol/l) vs delay time for excitation at 3390 cm^{-1} and three frequency positions of the probe pulse: (a) 3390 cm^{-1}, (b) 3140 cm^{-1}, and (c) 2750 cm^{-1}. Experimental points and calculated curves yielding $T_1 = 8 \pm 2$ ps; cross-correlation function of pump and probe pulses (dotted line).

Quantitative data on the time evolution of the ir spectrum are presented in Fig. 3 for constant pump frequency, $\nu_p = 3390$ cm^{-1} (experimental points). The calculated instrumental response function is illustrated by the dotted curve. Figure 3(a) shows measurements with probe frequency $\nu = 3390$ cm^{-1} ($=\nu_p$). A rapid transmission increase is followed by a somewhat slower decay, from which a time constant of $T_1 = 8 \pm 2$ ps is deduced. For longer times up to several nanoseconds (not shown in Fig. 3) the transmission remains constant at an elevated level. For a probe frequency of 3140 cm^{-1} [see Fig. 3(b)] the transmission change is negative at early times and again relaxes with 8 ± 2 ps to a positive value. In Fig. 3(c) the probe frequency is tuned to 2750 cm^{-1}, where only the OD absorption of the solute and solvent molecules is present. The measured absorption increase for small t_D is notably slower than that of Fig. 3(b); i.e., a finite rise time is involved.

The basic excitation process is the population of the OH stretching vibration. Correspondingly, a short-lived bleaching of the fundamental transition around the pump frequency and a redshifted excited-state absorption (vibrational anharmonicity) are expected; the latter represents a direct measure of the population of the first excited level, $v = 1$.[5] Subsequent relaxation of vibrational energy involves (also) thermalization processes. This picture completely agrees with our observations [compare Figs. 3(a) and 3(b)]. Population changes up to 10% are inferred from the data. The time constant T_1 is correspondingly interpreted as the effective population lifetime of the OH mode. The same time constant is obtained by additional measurements in the range $\nu = 3040\text{–}3150\ \text{cm}^{-1}$ of excited-state absorption, and also for so-called rotation-free polarization conditions. This interpretation is supported by results on a crystalline HDO:D_2O sample (0.5 mol/l) at −55 °C, where $T_1 = 7 \pm 2$ ps and a less complex band shape are found. The anharmonic shift of the $v=1 \rightarrow v=2$ transition is estimated from our transient spectra (Fig. 2) to be $\Delta\nu \simeq 270\ \text{cm}^{-1}$.

For longer delay times, when the vibrational energy has thermalized, a temperature increase of the sample is expected with corresponding rearrangement of hydrogen bonds. Using literature data for the temperature dependence of the OH and OD bands,[8] a temperature rise of 5 ± 2 K is deduced from Fig. 1(b) in agreement with estimates from the deposited energy. Model calculations suggest a fast thermalization rate of the H bonds close to $1/T_1$, i.e., no measurable delay between the observed population decay [points and fitted solid curves in Figs. 3(a) and 3(b)] and the computed temperature effect (dashed lines). The absorption increase at $2750\ \text{cm}^{-1}$ is the corresponding thermal rearrangement of OD groups [solid curve in Fig. 3(c)]. A similar effect is found for the OH groups around $3450\ \text{cm}^{-1}$ [Fig. 1(b)].

For an explanation of the spectra of Figs. 1 and 2, we propose a discrete set of subcomponents of the OH band. The interaction of a pump pulse at fixed frequency ν_p with these components (subscript i) can be described by effective cross sections σ_i and population density changes $\Delta N_i(\nu_p)$. Since a simple two-level description does not account for the observations, and in analogy to solvent effects on electronic transitions,[9] we distinguish the parameters for absorption ($0 \rightarrow 1$, index a) and stimulated emission ($1 \rightarrow 0$, index e). This approach implies that the solvent-solute interaction (i.e., hydrogen bonds) may be notably affected by vibrational excitation. The following transmission change at frequency ν results:

$$\ln\left(\frac{T}{T_0}\right) \simeq \sum_i \left\{ \sigma_i L\left(\frac{\nu-\nu_i}{\Gamma_i^a}\right)\Delta N_i^a + \sigma_i L\left(\frac{\nu-\nu_i}{\Gamma_i^e}\right)\Delta N_i^e \right\}. \tag{1}$$

Here $L((\nu-\nu_i)/\Gamma_i)$ denotes the normalized line-shape function (assumed to be Gaussian or Lorentzian) with center frequency ν_i and linewidth Γ_i (FWHM). Approximately equal-integrated strength ($\sigma_i^a \simeq \sigma_i^e = \sigma_i$) and frequency positions ($\nu_i^a \simeq \nu_i^e = \nu_i$) are considered for absorption and stimulated emission, while the peak cross sections implicitly vary according to the differences of the linewidths Γ_i^a, Γ_i^e. An equation similar to (1) holds for thermally induced transmission changes but with negligible excited-state population, $\Delta N_i^e \simeq 0$. The small-signal (steady-state) absorption is given by

$$-\ln T_0 \simeq \sigma_i L((\nu-\nu_i)/\Gamma_i^a)N_i\,, \tag{2}$$

with number density N_i of the HDO molecules contributing to transition i. The solid lines in Figs. 1 and 2 are calculated from Eqs. (1) and (2) using also rate equations for the transient population changes with time constant T_1. The results for the parameters ν_i are presented in Table I. It is important to note that for the transient bleaching spectra (Fig. 2) a distinct substructure with three prominent peaks I–III is found. Two further components are required to account for the excited-state absorption (ESA) (dotted curve, a possible substructure is not considered) and for the transient changes in the wing of the OD absorption (short-dash–dotted line).

The independent numerical decomposition of the steady-state OH band [Fig. 1(a)] into three components nicely reproduces the frequencies ν_{I} to ν_{III} determined from the transient spectra and delivers values for the bandwidths Γ_{I}^a–Γ_{III}^a (Table I). In the low-frequency wing of the absorption band two additional, weaker components are found that are believed to originate from overtone and combination band absorption. The thermally induced transmission changes [Fig. 1(b)] are dominated by the components I and III and the wing of the OD absorption.

The linewidths Γ_{I}^e to Γ_{III}^e in Table I originate from the transient spectra using also the Γ_i^a numbers deduced from Fig. 1(a). The smaller widths in the excited vibrational level should be noted as compared with the ground state, $\Gamma_i^a/\Gamma_i^e = 2.3 \pm 0.2$ ($i = \text{I–III}$). Gaussian line shapes are assumed that lead to a better fit than for Lorentzians. A possible inhomogeneous substructure of spectral species I–III cannot be excluded by the available data. Comparing the bleaching spectra for different pump frequencies [similar to Figs. 2(a) and 2(c)] with the steady-state absorption we find a larger transmission increase on the low-frequency side of the band ($\nu_p < 3400\ \text{cm}^{-1}$) than for $\nu_p > 3400\ \text{cm}^{-1}$. In other words, the cross sections differ in the wings of the OH band, $\sigma_{\text{I}} > \sigma_{\text{II}} > \sigma_{\text{III}}$.

It is interesting to discuss the physical origin of the

TABLE I. Spectral components of the OH band of HDO (in D_2O, 298 K).

Steady state ν_i (cm^{-1})	 Γ_i^a (cm^{-1})	Transient ν_i (cm^{-1})	 Γ_i^e (cm^{-1})	Assignment
2960 ± 10	200 ± 10	⋯	⋯	$2\nu_2$ overtone
3190 ± 5	195 ± 5	⋯	⋯	Combination
⋯	⋯	3150 ± 15	250 ± 10	ESA
3355 ± 5	200 ± 5	3345 ± 10	87 ± 5	I (icelike)
3425 ± 5	175 ± 5	3422 ± 7	76 ± 5	II
3540 ± 10	170 ± 5	3520 ± 20	74 ± 7	III

three spectral species. Component I at $\simeq 3350\ \mathrm{cm}^{-1}$ lies in the range of the OH band of HDO in crystalline D_2O, 3280–3370 cm^{-1}.[10] It is suggested that this species corresponds to an icelike configuration, i.e., with four hydrogen bonds of HDO (maximum redshift). Partial formation of H bridges will lead to higher OH frequencies (components II and III). The varying cross sections σ_i give some support to this physical picture. Evidence for three components was also obtained from overtone ir spectra.[11,12] Following these authors, species III is attributed to "free" or weakly bonded OH groups while II represents moderately strong bonds. The spectroscopic results are consistent with molecular-dynamics calculations that identified three classes of sites in the water network with respect to preferred bond angles.[13]

We finally comment on the simultaneous excitation of the three species in our measurements [Figs. 2(a)–2(c)]. Because of the small HDO concentration, energy transfer between molecules at different sites cannot be relevant. It is suggested that spectral overlap of the different species accounts (at least in part) for the simultaneous excitation with amplitudes that are also effected by the different cross sections. Rapid fluctuations of the hydrogen bonds with corresponding frequency changes may also play a role (time scale $\leq$ a few ps); no measurable differences are indicated by the present data for the time evolutions of components I–III.

In summary, it is pointed out that we have performed picosecond double-resonance spectroscopy of the OH stretching vibration of HDO in D_2O. Transient spectral hole burning directly shows that the OH absorption is inhomogeneously broadened. Strong evidence is obtained for three prominent spectral components related to different hydrogen-bonded environments, including an icelike structure in the liquid at room temperature. A lifetime of the spectral species of a few picoseconds and changes of the solvent-solute interaction with vibrational excitation are suggested by the data.

---

[1] See, for example, D. Hadzi and S. Bratos, in *The Hydrogen Bond,* edited by P. Schuster, G. Zundel, and C. Sandorfy (North-Holland, Amsterdam, 1976), Vol. II, p. 565ff.

[2] U. Liddel and E. D. Becker, Spectrochim. Acta **10**, 70 (1957).

[3] See, for example, H. E. Hallam, in *The Hydrogen Bond* (Ref. 1), Vol. III, p. 1065ff.

[4] D. E. Hare and C. M. Sorensen, J. Chem. Phys. **93**, 25 (1990); for a review, see G. E. Walrafen, in *Water, A Comprehensive Treatise,* edited by F. Franks (Plenum, New York, 1972), p. 151ff.

[5] H. Graener, R. Dohlus, and A. Laubereau, Chem. Phys. Lett. **140**, 306 (1987).

[6] H. Graener, T. Q. Ye, and A. Laubereau, Phys. Rev. B **41**, 2597 (1990); H. Graener, T. Lösch, and A. Laubereau, J. Chem. Phys. **93**, 5365 (1990).

[7] H. S. Frank, in *Water, A Comprehensive Treatise* (Ref. 4), p. 515ff.

[8] H. R. Wyss and M. Falk, Can. J. Chem. **48**, 607 (1970).

[9] W. Liptay, in *Excited States,* edited by E. C. Lim (Academic, New York, 1974), Vol. I.

[10] D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford Univ. Press, London, 1969).

[11] W. A. P. Luck and W. Ditter, Z. Naturforsch. **24b**, 482 (1969).

[12] C. A. Angell and V. Rodgers, J. Chem. Phys. **80**, 6245 (1984).

[13] F. H. Stillinger and A. Rahman, J. Chem. Phys. **55**, 3336 (1971).