PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 56, NUMBER 22 1 DECEMBER 1997-II

## RAPID COMMUNICATIONS

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# Picosecond ir hole-burning spectroscopy on HDO ice *Ih*

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(Received 13 June 1997)

Transient hole-burning experiments using picosecond ir pulses in the region of the OH stretching vibration of crystalline HDO (in $D_2O$) ice are reported; holes with a minimum width of 26 $cm^{-1}$ are measured, proving the OH band to be inhomogeneously broadened. The inhomogeneous distribution having a half width of approximately 25 $cm^{-1}$ can be related to structural disorder in ice. A vibrational lifetime of $0.5\ ps \leqslant T_1 \leqslant 2\ ps$ is found for the OH stretching mode. Additional features in the transient data are attributed to the dissipation of excess energy; particularly microscopic energy flow in the immediate surroundings of primarily excited OH groups can be monitored. [S0163-1829(97)50546-7]

## INTRODUCTION

Ice is undoubtedly one of the most investigated solids. Notwithstanding still a great number of studies on this substance being published every year proves the continuing interest in a more detailed understanding of structural and dynamical features of the solid phases of water. On the experimental side, neutron and x-ray scattering as well as ir and Raman spectroscopic methods are often successfully applied to learn more about particularly the characteristics of hydrogen bonding in ice. In the particular case of ir spectroscopy structural disorder is reflected, e.g., in the question, if the OH absorption band of ice is inhomogeneously broadened or not. Picosecond ir spectroscopic techniques, which in the last decade have widely been used for studies of vibrational and orientational relaxation[1–5] and transient hole burning[6–8] on various samples of condensed matter—but up to now only very scarcely on crystalline materials—have the ability to provide additional information about an inhomogeneous distribution of transition frequencies or, synonymously, hydrogen bond energies (and geometries). In this Rapid communications we report results from transient ir hole-burning experiments on crystalline samples of ice *Ih*.

## RESULTS AND DISCUSSION

All picosecond transient data shown below have been recorded with an infrared double-resonance spectroscopy (IRDRS) experiment applying two independently tunable infrared pulses (wavelength range approximately 2.5–4 $\mu$m), which can be delayed to each other. The setup is based on a 50-Hz pulsed Nd:YAG laser with energy stabilization[9] providing single pulses of 9–10 ps duration and total energy of ≈5 mJ with pulse-to-pulse stability of 5%. The mid-ir excitation and probing pulses (energy≈30 $\mu$J and $<1\ \mu$J, respectively) are generated in separate parametric conversion devices, where additionally pulse durations are shortened to 4 ps [determined by correlation measurements utilizing the nonlinear refractive index of $CS_2$ (Ref. 10)]; the spectral width of the pulses is typically 10 $cm^{-1}$ at a frequency of 3300 $cm^{-1}$. The experimental procedure has been described repeatedly in the past;[5,7,11] briefly, a significant energy fraction of the excitation pulses is resonantly absorbed by the sample molecules; the weak probe pulses measure the resulting transient changes in the absorption spectrum (and thus the fraction of currently excited oscillators) in the sample with time, frequency and polarization resolution. The signals $\Delta\alpha_{\parallel,\perp} := \ln(T/T_0)_{\parallel,\perp}$ are measured for probe polarization parallel and perpendicular to pump polarization simultaneously; $T$ and $T_0$ denote sample transmission with and without previous ir excitation; positive $\Delta\alpha$ values refer to bleaching. In the following only two arithmetic combinations of the signals are discussed, namely $\Delta\alpha_{\mathrm{rf}} := (\Delta\alpha_{\parallel} + 2\Delta\alpha_{\perp})/3$ and $\Delta\alpha_{\mathrm{ps}} := \Delta\alpha_{\parallel} - \Delta\alpha_{\perp}$. While $\Delta\alpha_{\mathrm{rf}}(\nu,t)$ is directly proportional to the excess population density $\Delta N(\nu,t)$ without any

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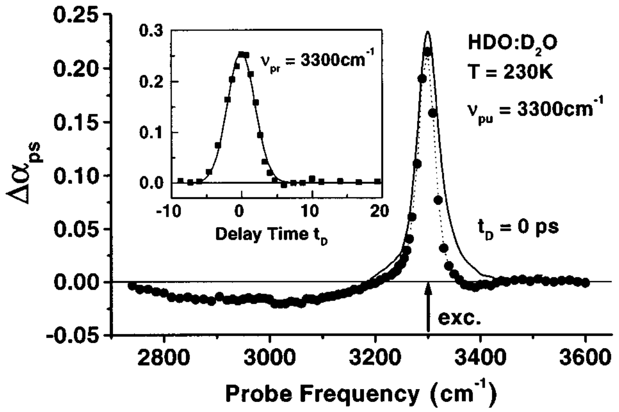

FIG. 1. Experimental data ($\Delta\alpha_{ps}$) of HDO:$D_2O$ ice at 230 K, excitation frequency $\nu_{pu}=3300\,\mathrm{cm}^{-1}$. (i) Main graph: transient spectrum, delay time $t_D=0$ ps, experimental points (solid circles) connected by dotted line for better visibility; conventional, background-corrected ir absorption band (solid curve), scaled for simple comparability. (ii) Inset: time dependence at probe frequency $\nu_{pr}=3300\,\mathrm{cm}^{-1}$, experimental points (solid squares), Gaussian least-squares fit (solid curve).

influence from molecular orientation, $\Delta\alpha_{ps}(\nu,t)$ represents a product of $\Delta N(\nu,t)$ and the $P_2$ term in a Legendre polynomial expansion of the orientational distribution of excited oscillators.[11,12] Accordingly $\Delta\alpha_{ps}$ is only sensitive to anisotropic absorption changes; i.e., molecules keeping the orientational information of the (linearly polarized) pump process, while $\Delta\alpha_{rf}$ also comprises isotropic contributions to observed transmission alterations. The latter may occur as secondary—quasithermal—effects: when the originally located vibrational energy is dissipated into the bulk, structural modifications in the sample may arise, but due to the participation of all molecules in the excitation volume corresponding transmission changes have no orientational preference (for a more detailed discussion, see Ref. 7).

All data presented in this work refer to samples of HDO in $D_2O$, HDO concentration $\approx 0.5$ mol/l at a temperature of 230 K. The solutions were made mixing proper amounts of bidistilled $H_2O$ and highly purified $D_2O$ in the liquid phase (at room temperature). After the proton/deuteron exchange—being well known to take place very rapidly—most hydrogen atoms are located in HDO molecules, and the residual content of $H_2O$ (approximately $10^{-3}$ mol/l) is negligible compared to HDO concentration. Isotopic dilution is suggested by two reasons: first, data from the OH stretching region can be interpreted much more straightforward, because only a single, well isolated vibrational OH absorption has to be regarded; second, due to the very small penetration depth of ir radiation in isotopically pure water ($<1\,\mu$m in the maximum of OH or OD band) the absorbed pump energy would cause local melting even in an ice sample at very low temperature.

The actual samples were prepared cooling down a thin layer ($d=100\,\mu$m) of the appropriate HDO/$D_2O$ mixture between 2 $CaF_2$ windows directly in the cryostat cell of the IRDRS experiment. Using a rather low cooling rate in the surroundings of freezing point sufficiently large regions of crystalline ice with excellent transparency in the visible, i.e., negligible scattering of pump intensity, could be obtained. The latter is a necessary condition to get reliable data in transmission geometry; for future experiments the usage of internal reflection geometry in IRDRS (which was demonstrated very recently[13]) will allow us to investigate also ice samples of lower optical quality (e.g., polycrystalline ones). Additionally conventional ir spectra of the ice samples have been taken with a Perkin-Elmer FTIR-1760 X spectrometer revealing that crystalline ice *Ih* is created by the above-described procedure.

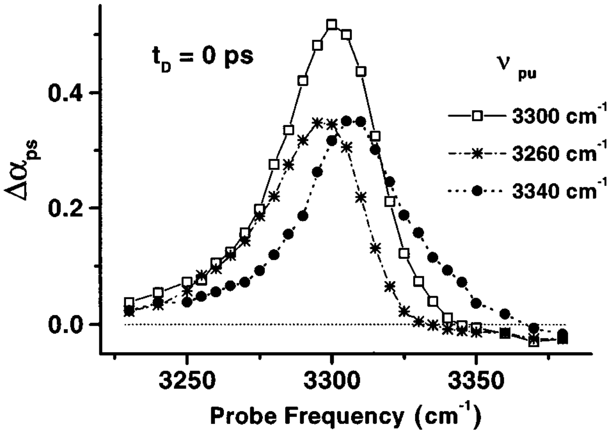

FIG. 2. Transient spectra ($\Delta\alpha_{ps}$) of HDO:$D_2O$ ice at 230 K for three different pump frequencies at delay time $t_D=0$ ps; $\nu_{pu}=3260\,\mathrm{cm}^{-1}$ (stars), $\nu_{pu}=3300\,\mathrm{cm}^{-1}$ (open squares), and $\nu_{pu}=3340\,\mathrm{cm}^{-1}$ (solid circles); experimental points connected by lines for better visibility.

In Fig. 1 a transient spectrum of a HDO:$D_2O$ sample with the above given parameters is shown. The excitation frequency was tuned to the peak of the OH stretching absorption at $\nu_{pu}=3300\,\mathrm{cm}^{-1}$, delay time was adjusted to $t_D=0$ ps, i.e., maximum temporal overlap of pump and probe pulses. The solid circles (connected by a dotted line for better visibility) represent the anisotropic transmission change $\Delta\alpha_{ps}$, the solid line gives a conventional absorption spectrum (corrected for OD background, referring also to a temperature of 230 K) for comparison. The main features seen in the spectrum are a relatively narrow region of strong transmission increase around the excitation frequency being clearly narrower [full width at half maximum (FWHM) 36 $\mathrm{cm}^{-1}$] than the OH absorption band (FWHM 47 $\mathrm{cm}^{-1}$), and a very broad range of induced absorption between 2700 and 3200 $\mathrm{cm}^{-1}$. Additionally a rather weak band of absorption increase is found at the high-frequency side of the OH band around 3390 $\mathrm{cm}^{-1}$. In the inset of Fig. 1 the corresponding time development at the position of maximum bleaching (probe frequency $\nu_{pr}=3300\,\mathrm{cm}^{-1}$) is given; as is easily seen regarding the Gaussian fit curve (dotted line) the experimental points (solid squares) agree well with a correlation of pump and probe pulses; particularly no indication for a slower decay is found. Identical time dependence of $\Delta\alpha_{ps}$—within experimental accuracy—was measured also at any other probe frequency showing detectable transmission changes. As coherent artifacts can be excluded, e.g., from the data of Fig. 2 (see below), it is reasonable to describe the anisotropic signal $\Delta\alpha_{ps}$ simply in terms of nonequilibrium population of vibrational states. Accordingly the bleaching is assigned to reduced population difference between ground and excited state of the OH stretch, the absorption increase to

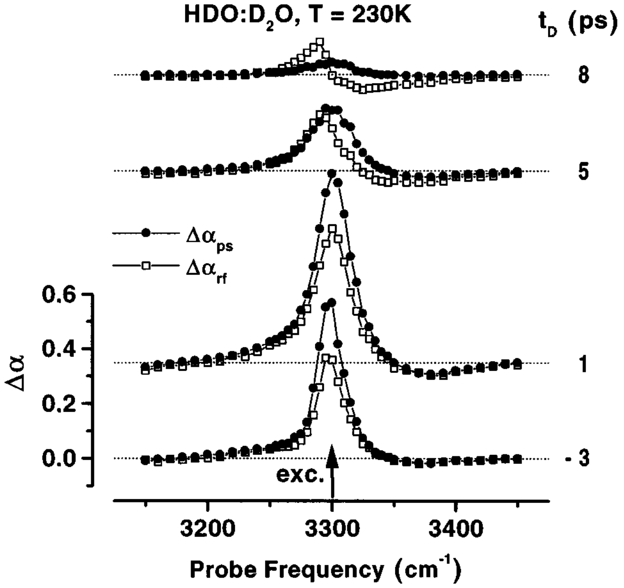

FIG. 3. Time dependence of transient spectra of $\Delta\alpha_{ps}$ (solid circles) and $\Delta\alpha_{rf}$ (open squares) for excitation at 3300 cm$^{-1}$; increasing delay time from bottom to top ($t_D = -3$, +1, 5, and 8 ps).

excited state absorption (from first to higher vibrational energy levels) with large anharmonic redshift (about 300 cm$^{-1}$) and broadening (FWHM $\approx 250$ cm$^{-1}$). The vibrational lifetime of the OH stretch of HDO/D$_2$O ice cannot be determined directly from the current (time resolved) data, but an upper limit of $\approx 2$ ps—representing the time resolution of the experimental system—can be given. A lower limit can be obtained from the minimum linewidth of bleaching; this question and the characteristics of the observed induced absorptions will be discussed below.

The notably smaller bandwidth of bleaching compared to the conventional absorption band strongly suggests that a transient vibrational hole is observed, or, in other words, the OH band in ice is inhomogeneously broadened, the width of the inhomogeneous distribution being of the same order as the homogeneous linewidth. This interpretation is proven by the data of Fig. 2, which illustrate the effect of tuning the excitation frequency off resonance (any other experimental settings are kept unchanged with respect to the situation in Fig. 1). As is easily seen for three quite different excitation frequencies, i.e., $\nu_{pu}$=3260 cm$^{-1}$ (data points represented by stars), $\nu_{pu}$=3300 cm$^{-1}$ (open squares), $\nu_{pu}$=3340 cm$^{-1}$ (solid circles), the peak of the transient hole shifts according to the pump frequency, but only for an amount of less than 10 cm$^{-1}$ in either direction despite the rather large shift of the excitation. While this general trend is a typical behavior for transient hole burning, the rather small shift of the hole in accordance with pump detuning is a special consequence of or, vice versa, a strong hint for the presence of a quite narrow inhomogeneous distribution.[14] In addition, this finding allows us to exclude coherent artifacts, which could only arise directly at the excitation frequency. The relatively large amplitudes of the given data with off resonant pumping compared to central excitation suggest a significant degree of saturation in the experiments.

The main features of time development in the bleaching region and additional information about the dissipation of relaxed vibrational energy can be recognized looking at the transient spectra of both $\Delta\alpha_{ps}$ (solid circles) and $\Delta\alpha_{rf}$ (open squares) given in Fig. 3 for four different delay times $t_D = -3$, 1, 5, and 8 ps (increasing from bottom to top); the excitation frequency is $\nu_{pu}$=3300 cm$^{-1}$ in each case. At the two early delay positions both signals exhibit very similar profiles; namely, an intense and rather narrow hole at the pump frequency with a slight asymmetry, which is best seen at $t_D = 1$ ps as bleaching at the low-frequency wing, but induced absorption at the high-frequency side of the band. For later delay positions significant differences arise: $\Delta\alpha_{ps}$ does not change its principal shape, only its amplitude decreases (for delay times $\leqslant 10$ ps it has returned to zero within experimental accuracy) and the hole is slightly broadened with increasing delay time. The ''rotation free'' signal $\Delta\alpha_{rf}$ however evolves to a very different contour (bleaching below 3300 cm$^{-1}$, induced absorption above), which finally remains constant for the whole delay range of the experiment, i.e., up to $t_D = 3$ ns. This long time spectrum in accordance with previous work on hydrogen bonded systems[5,7,14] is attributed to local temperature rise (of the order of 10 K) in the excitation volume (after thermalization of the vibrational energy) shifting the hydrogen bond distribution on average to lower energies, and thus the OH absorption band to higher frequencies. As all HDO molecules in the probed volume are involved, this is an isotropic effect seen only in $\Delta\alpha_{rf}$.

For the early delay times, the amplitude ratio of $\Delta\alpha_{ps}$ and $\Delta\alpha_{rf}$ reveals a molecular reorientation time $\tau_{rot} \gg T_1$ confirming the expectation that in a crystalline sample no fast orientational motion should be present. The minimum FWHM of $\Delta\nu = 26$ cm$^{-1}$ found at $t_D = -3$ ps can be used to get a lower limit for both energy relaxation ($T_1$) and dephasing ($T_2$): calculating an effective relaxation time $\tau = (\pi c \Delta\nu)^{-1}$ comprising both processes yields $\tau \approx 400$ fs, even if the finite width of pump and probe pulses is not accounted for. So 400 fs is clearly a lower limit for vibrational lifetime and dephasing of the OH stretching mode in crystalline HDO ice. Regarding the width of the conventional ir absorption band, a half width of the inhomogeneous distribution of approximately 25 cm$^{-1}$ can be estimated. Due to hole asymmetry and probable saturation effects no additional information about, e.g., spectral diffusion can be drawn from the observed increase of hole width.

Turning to a microscopic view of energy dissipation a rather plausible explanation for the hole asymmetry seen in $\Delta\alpha_{ps}$ is suggested by the above findings: in a first step after deexcitation of an OH stretching vibration the relaxed energy will still be located in the immediate surroundings of the originally excited molecule, thereby modifying hydrogen bonding only in the small volume directly around this molecule; most likely the bonds will on average be weakened like in the case of temperature rising, even if the notion ''temperature'' is not appropriate for the molecular scale. The next neighbors of an HDO molecule however are with high probability only D$_2$O molecules, because at the given concentration of 0.5 mol/1 HDO on average only roughly 1 HDO molecule is found within 100 D$_2$O molecules or, synonymously, the average distance between next neighbors is larger by nearly a factor of 5 for HDO compared to D$_2$O (as is easily seen taking simply the cubic roots of concentrations). So effects in the transient spectra (in the OH spectral region) corresponding to this situation immediately after relaxation of an individual quantum of vibrational energy can only be due to the primarily excited HDO molecule. Corresponding transmission changes are likely to be similar to the bulk thermal effect with regard to its principal spectral shape (bleaching at the low-frequency side of the band, induced absorption at the high frequency side), but as an HDO molecule in the ice lattice can hardly change its orientation, the orientational information of the excitation process will be conserved, i.e., the changes must be anisotropic and can thus be seen also in $\Delta\alpha_{\mathrm{ps}}$. With ongoing dissipation the relaxed energy will be distributed over a larger volume gradually affecting more HDO molecules with varying orientation and of course smaller amount of energy per individual OH group, so that finally the orientational information is lost and the spectral changes approach the isotropic thermal (bulk) effect. It is interesting to estimate local energy densities at different stages of the discussed thermalization process: in an individual early situation, where only one HDO molecule and its four next neighbors in the tetrahedral geometry are affected by the energy of one relaxed vibrational quantum, the local energy density is equivalent to a temperature rise by about 200 K (calculated simply from molecular density and specific heat); macroscopically, however, the situation of the long time spectrum, i.e., homogeneous distribution of the whole pump energy in the excitation volume, corresponds to a temperature increase of only $\approx 10\,\mathrm{K}$ (assuming previous single excitation of each HDO molecule).

Sticking to this interpretation the hole asymmetry can be explained simply by overlap of the prominent effect, the actual nonequilibrium vibrational population, with the anisotropic effects of energy dissipation; as to the short vibrational lifetime—compared to the applied pulse duration—no delay between these two contributions should be measurable. This suggestion is proved by the fact that time resolved data of $\Delta\alpha_{\mathrm{ps}}$ at any probe frequency show identical, particularly correlationlike time dependence, which at the same time allows us the conclusion that the typical time for the described thermalization of relaxed vibrational energy on the molecular scale can also only be of the order of 1 ps or shorter.

Finally some remarks on the broad excited state absorption. Empirically the extraordinarily large width and anharmonic shift are in fair agreement with rather old findings from conventional ir overtone spectra on HDO ice.[15] A possible explanation for this huge width can be found regarding the potential for a proton between two oxygen atoms in the ice lattice, which is usually described as asymmetric double-well potential with a barrier height being of the order of the energy of the $v=2$ state of the OH stretching vibration.[15,16] In this model the possibility of proton transfer to the second, less deep minimum (either directly or via tunneling, depending on the concrete barrier height) causes very fast phase fluctuations being responsible for a significant part of the large width of the observed $v=1$ to $v=2$ transition. But also fast energy relaxation may play an important role, because higher vibrational states in strongly anharmonic potentials are known to often have significantly shorter lifetimes than the first excited state.

To find out more details about ultrafast dynamics and structural disorder in ice we are already preparing further experiments applying better temporal resolution, extended frequency range and/or refined techniques of sample preparation (including use of internal reflection). Also the investigation of other structural modifications (amorphous ice) may provide additional information about, e.g., the question, how fast structural changes can take place.

## SUMMARY

In conclusion it is pointed out that transient hole-burning experiments were performed on crystalline HDO ice revealing that the OH vibrational absorption band is inhomogeneously broadened due to proton disorder, but only with a quite narrow inhomogeneous distribution. Regarding the observed homogeneous linewidth ($\leqslant 25\,\mathrm{cm}^{-1}$) and the temporal resolution of the experiment, a vibrational lifetime of the OH stretching mode in HDO ice at 230 K of $0.5\,\mathrm{ps} \leqslant T_1 \leqslant 2\,\mathrm{ps}$ is found; the lower limit is also valid for the dephasing time $T_2$. The observed slight asymmetry of the vibrational holes is interpreted as overlap between the hole itself and the effect from relaxed energy in the immediate surroundings of originally excited molecules. In other words, microscopic ‘‘heat’’transfer on a molecular scale with a time constant below 1 ps has been observed.

## ACKNOWLEDGMENT

The authors gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft.

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