

Absence of an Isotope Effect in the Two Level Spectrum of Amorphous Ice

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We have measured the low temperature far infrared absorption in the high and low density amorphous phases of H₂O and D₂O in the region 2–30 cm⁻¹. For each isotope, resonant absorption by two level systems is observed for the high density amorphous phase but not for the low density amorphous one. In addition, within our experimental uncertainties no isotope effect is detected in the strength or extent of the two level spectrum in the high density phase. [S0031-9007(98)06008-6]

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Although the low lying excitation spectrum of two level systems (TLS) in glasses, first observed in the low temperature specific heat [1] and described as a tunneling entity of atoms or groups of atoms [2,3], has been studied for many years with a variety of experimental techniques and theoretical models [4] the source of these TLS remains outside the framework of lattice dynamics theory. The surprising report [5] that films of hydrogenated amorphous silicon do *not* show such TLS whereas films of amorphous silicon do only reinforces the puzzling nature of these near universal low energy excitations. Amorphous ice films which are topologically similar [6] to that of *a*-Si have also been studied. Some measurements of TLS related phenomena for vapor deposited amorphous ice were made using the spectral hole burning technique [7] and also internal friction [8]. Spectral hole burning experiments on hyperquenched glassy water [9] have revealed an independence of the dephasing time on deuteration indicating a bigger tunneling entity than one proton or deuteron in this phase. Surprisingly few measurements have been carried out on bulk amorphous ice produced by a pressure-induced amorphization process even though it has the added feature of two different amorphous phases, a low density amorphous (LDA) phase as well as a high density amorphous (HDA) one [10]. Both vapor deposited and hyperquenched amorphous films are known to be closely related to LDA [11] but as yet no TLS measurements have been performed on the HDA phase.

In this Letter we describe our investigation of the temperature dependent absorption of very far infrared radiation for the two forms of amorphous ice as well as its cubic and regular hexagonal crystalline phases for both H₂O and D₂O isotopes. The existence of the two different amorphous phases [12] enables one for the first time to look for correlations between structure of the phases and the properties of the spectrum of the TLS. Previously this quantitative spectroscopic technique has been used to identify TLS in glasses [13] and glassy crystals [14]. We find the surprising result that only the HDA phase shows a TLS spectrum and that within the experimental uncertainties of the measurements the TLS spectrum is independent of the H-D isotope effect.

The discovery of the irreversible production of an amorphous phase of ice by pressure at low temperature makes possible the measurement of bulk amorphous samples [15,16]. The HDA form is produced by the compression of regular ice at 77 K. Upon heating to ~120 K it transforms to the LDA form. At still higher temperatures ~145 K it transforms to the cubic crystalline phase I_c and then at 225 K to I_h the hexagonal crystalline phase [17]. So it is possible to make measurements on a variety of phases in a single sample.

The spectroscopic samples of the HDA ice were produced by compressing regular ice I_h at liquid nitrogen temperature to 1.5 ± 0.5 GPa. The regular ice was made from high performance liquid chromatography grade water from Fisher Scientific contained in indium open ended cups which had been placed in a standard 10 mm die set. The entire assembly was then immersed in liquid nitrogen. To prevent the ice from sticking to the anvils both were covered with a 6 μm Teflon film. The thickness of the resulting amorphous ice cylinders used in these experiments varied from 0.4 mm to 15 mm with a diameter between 7–8 mm. The samples were removed at atmospheric pressure and 77 K, mounted in the sample holder while still under liquid nitrogen, and the arrangement was then inserted into a precooled transmission light pipe-detector cryostat. Temperature dependent transmission spectra in the spectral region 2–30 cm⁻¹ were measured with a lamellar Fourier transform spectrometer together with a germanium bolometer which operates at 0.3 K. The details are described elsewhere [18].

At the conclusion of these measurements the LDA phase was prepared by first heating the samples to 135 K and cooling back to low temperatures, and the I_c phase by then heating to 175 K with subsequent cooling back to 4.2 K. The heat release associated with a phase transition was monitored using a differential thermocouple with one junction mounted on the sample holder while the other touched the sample. Typical traces of the differential signal versus temperature are shown in the inset in Fig. 1 where a heating rate ~2 K min⁻¹ was used. The HDA to LDA transition starts at about 95 K, has maximum rate at 118 K, and is finished by 126 K. The beginning of LDA to I_c transition

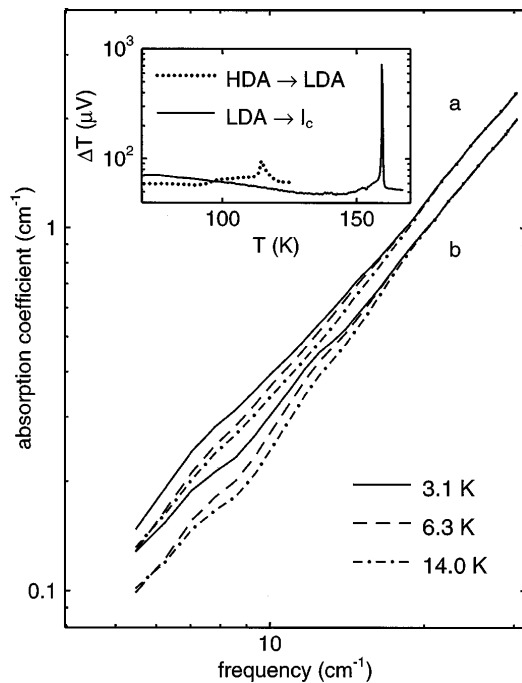


FIG. 1. Temperature dependence of the far infrared absorption coefficient of amorphous ice. (a) HDA H₂O; (b) HDA D₂O. Inset—Heat release during annealing of the ice sample. Dotted line: the HDA to LDA transition; solid line: the LDA to I_c transition for the same sample.

occurred at 153 K and was completed after a sharp maximum at 170 K. The polycrystalline ice I_h samples were produced by simply freezing the water at ambient pressure. The experimental procedures described above were also used for the preparation of the D₂O ice samples.

The amorphous structure of the samples was tested using x-ray diffraction. A thin (~1 mm) thick sample of HDA ice was prepared in the same way as the samples for the far infrared measurements. It was placed on a copper holder in a small Styrofoam Dewar so that the sample was located in the normal position of a powder diffractometer. The nitrogen vapor blocked the air from reaching the sample surface. Since the liquid nitrogen in the Dewar lasted for 7–8 min the x-ray scan duration in the region from 1 to 4 Å⁻¹ was set for 5 min. In order to produce LDA and I_c phases the sample was subsequently warmed *in situ* to 140 and 190 K, respectively, and cooled back to 77 K. Consecutive scans of all the phases were reproducible with no visible change appearing on the time scale of 1 h. The x-ray diffraction spectra of HDA ice did not reveal any additional reflections except those produced by the indium ring and the copper holder and the results corresponded well to the literature data both for vapor-deposited [19] and pressure-induced amorphous phases [20]. The LDA and I_c spectra also corresponded well to the literature data though small unidentified sharp reflections were observed at 1.58, 1.83, and 3.33 Å⁻¹ in the LDA phase. The intensity of these reflections totaled not more than 5% of the

wide LDA component so the fraction of the crystalline phases present in the LDA phase is estimated to be of the same order.

The absorption spectra for the HDA (a) H₂O and (b) D₂O ices are shown in Fig. 1. Both isotopes show a characteristic bleaching of the absorption coefficient with increasing temperature. Remarkably, the temperature dependent spectral region is nearly the same for both substances with the high frequency cutoff at ~20 cm⁻¹.

The low frequency absorption spectra at low temperatures for the HDA and the LDA phases of H₂O are shown in Fig. 2(a) while those for D₂O are shown in Fig. 2(d). A fairly large change in the absolute value of the absorption coefficient is produced by the HDA → LDA transition. Since the density of the H₂O changes from 1.17 to 0.94 g/cm³ [10] during the transition the amorphous material is extruded from the indium cup if the walls are too thick giving rise to additional scattering from the sample. This problem has been solved by making the walls of the cup thin enough so they expand with the ice.

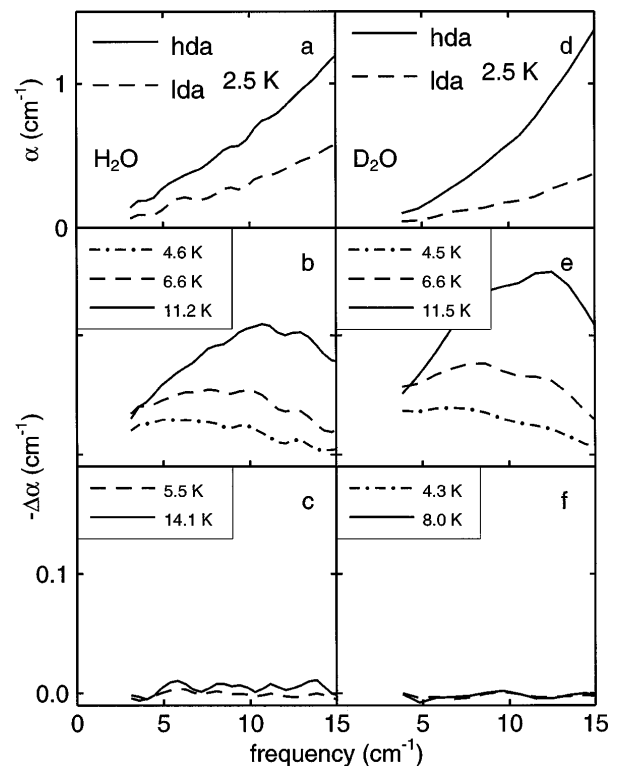


FIG. 2. Absorption coefficient and its temperature dependence for the two amorphous phases of the two isotopes. (a) Low temperature absorption coefficients for HDA (solid line) and LDA (dashed line) phases of the same H₂O sample. (b) Temperature dependence of the HDA absorption coefficient. (c) Temperature dependence of LDA absorption coefficient. (d) Low temperature absorption coefficients for HDA (solid line) and LDA (dashed line) phases of a D₂O sample. (e) Temperature dependence of the HDA D₂O absorption coefficient. (f) Temperature dependence of LDA D₂O absorption coefficient.

The LDA \rightarrow I_c transition does not change the far infrared absorption coefficient value but in the case of thick walled samples some additional scattering was observed because of the continued extrusion of the ice. The absorption coefficient for the regular I_h is the same as the literature data [21] within experimental error. The crystalline I_c form of the ice produced by annealing is polycrystalline and inhomogeneous resulting in higher scattering and absorption compared to the I_h sample made by simple freezing of water though these two forms are indistinguishable in terms of their spectral properties.

Figures 2(b) and 2(c) illustrate the effect of the HDA \rightarrow LDA transition on the temperature dependent part of the absorption coefficient of H_2O ice while Figs. 2(e) and 2(f) show the same results for D_2O ice. For both isotopes the temperature-induced bleaching effect (decrease in absorption with increase of temperature) is at least an order of magnitude weaker for LDA when compared to HDA. It is also absent for both the I_c and I_h phases.

If the temperature dependence of the resonant absorption by TLS is responsible for the bleaching effect shown in Figs. 1 and 2 then the effect is described by the expression [13]

$$\alpha_{\text{res}}(\omega) = \frac{4\pi^2 N(\omega) \mu^2 \omega}{3c\sqrt{\epsilon_0}} \tanh\left(\frac{\hbar\omega}{2kT}\right), \quad (1)$$

where $N(\omega)$ is the density of TLS states, ϵ_0 is the dielectric constant, c is the speed of light, k is Boltzmann constant, and $\mu^2 = \mu_b^2[(\epsilon_0 + 2)/3]^2$ is the modulus squared of the effective electric dipole matrix element of the transition between the two states assuming a standard local field correction. The quantity $N(\omega)\mu_b^2$ in Eq. (1) will be referred to as the weighted spectral density (WSD) of TLS states. When the temperature dependent change of the absorption coefficient is plotted against the change in the population factor the data should fall on a straight line for the purely resonant absorption described by Eq. (1).

Figure 3 shows that at least up to 15 K (the highest temperature point shown) the TLS spectrum describes the experimental results. From the slopes of the lines in Fig. 3 which identify a nonlinear least squares (NLS) fit to the experimental points the weighted density of states of TLS $N(\omega)\mu_b^2$ can be determined given the value of the dielectric permittivity ϵ_0 . For the HDA ice $\epsilon_0 = 5.1 \pm 0.5$, which is obtained from the channel spectrum for a thin sample. This is somewhat larger than the value of regular crystalline ice $\epsilon_0 = 3.17$ in the microwave region [22]. The channel spectrum could not be observed for LDA ice because of sample deformation. The same value of ϵ_0 was assumed as for I_c and I_h based on their similar vibrational spectra as determined by inelastic neutron scattering [23].

Figure 4 summarizes our measured weighted density of states (WSD) for TLS for HDA, LDA, I_c , and I_h phases for H_2O and D_2O ices. Only the HDA phase shows this contribution and within experimental error its magnitude

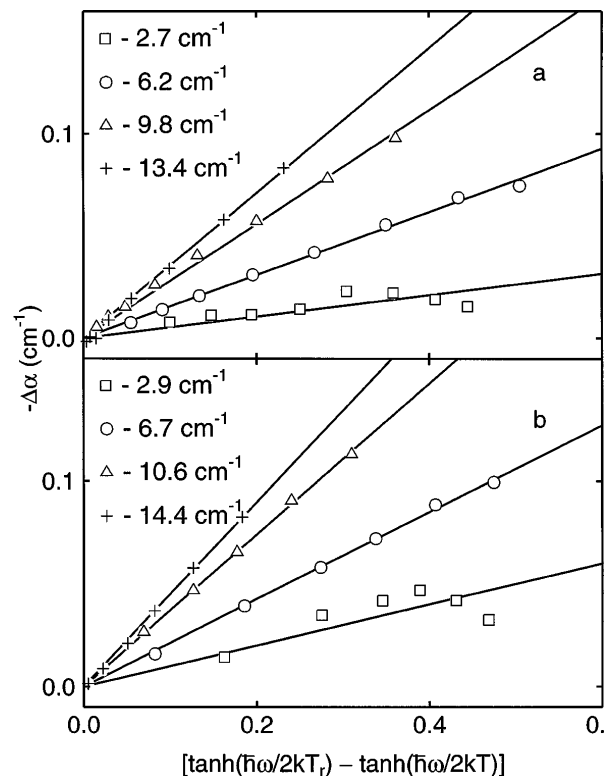


FIG. 3. Temperature dependence of the absorption coefficient versus the population difference parameter for both isotopes illustrating two level behavior. (a) For HDA H_2O and (b) for HDA D_2O . The reference temperature $T_R = 2.5$ K. The straight lines represent the NLS fit to the experimental points.

and spectral range is the same for both isotopes. To compare with other glasses its magnitude is about half the value of that found for bulk soda-lime-silica glass [24]. Some differences in the magnitude of WSD observed for H_2O and D_2O ices can originate from slightly different pressures applied in the amorphization process and the fact that the pressure where the sample appears homogeneous in Raman scattering is 1.5 GPa for H_2O (Ref. [25]) but is still undetermined for D_2O .

Quite unexpectedly the LDA H_2O and D_2O ices do not reveal a comparable temperature dependent resonant absorption from TLS and, in addition, the transition from LDA \rightarrow I_c gives rise to essentially unchanged far infrared spectral properties for both sample isotopes. This finding puts bulk LDA ice in line with another exotic amorphous thin film system $Si_{0.99}H_{0.01}$ which does not possess TLS [5]. In principle there is a possibility that the electric dipole moment is vanishingly small for the former while the elastic dipole moment is vanishingly small for the latter but this seems highly unlikely in the case of H_2O since it is a disordered solid consisting of dipolar molecules.

In summary, we have measured the low temperature far infrared absorption spectra for HDA, LDA, I_c , and I_h phases of bulk ice and heavy bulk ice. It is shown that

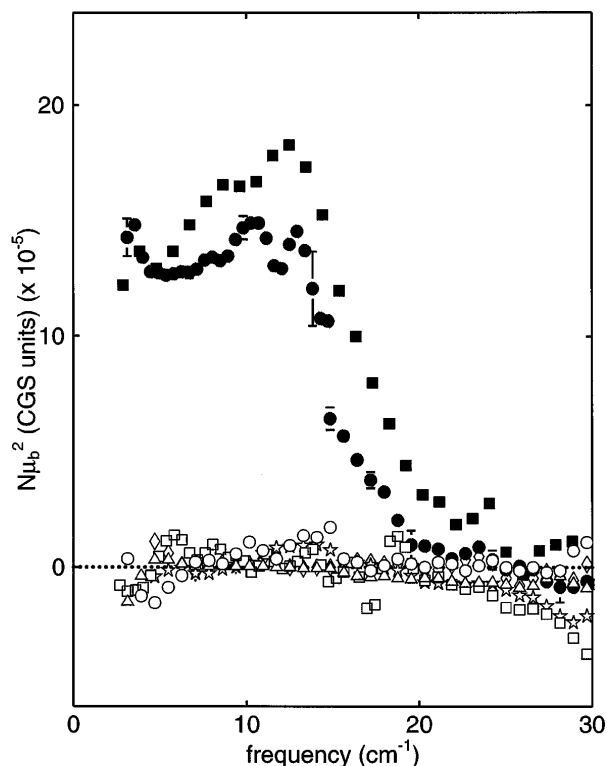


FIG. 4. Weighted density of states for the TLS spectrum versus frequency. Filled circles—HDA H₂O; filled squares—HDA D₂O; open squares—LDA H₂O; stars—LDA D₂O; open triangles—I_c H₂O; diamonds—I_c D₂O; open circles—regular I_h H₂O.

the LDA phase does not display TLS despite its known amorphous properties. This represents the second observation of the absence of TLS in an amorphous material and the first for a bulk solid. In addition no TLS absorption was found for the crystalline phases of ice which contain a disordered hydrogen sublattice in agreement with internal friction experiments [8]. Only for the HDA phase has far infrared absorption by TLS been detected. Deuteration does not change the high frequency cutoff of the TLS spectrum indicating that at least whole molecules and not just hydrogen or deuterium participate in the tunneling entity. Note that this result is not inconsistent with the tunneling of special localized acoustic modes [26]. Finally, it should be emphasized that our discovery that the TLS spectrum of this simple bulk amorphous system can be turned off through temperature cycling to another amorphous phase should provide new and defining experimental

opportunities for identifying the source of these low energy excitations.

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