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ABSTRACT

Experiments investigating the properties of deeply supercooled liquid water are needed to develop a comprehensive understanding of water's anomalous properties. One approach involves transiently heating nanoscale water films into the supercooled region for several nanoseconds at a time and then interrogating the water films after they have quenched to cryogenic temperatures. To relate the results obtained with this approach to other experiments and simulations on supercooled water, it is important to understand how closely the quenched structure tracks the (metastable) equilibrium structure of water as a function of the transient heating temperature. A key step involves quantifying the extent to which water that is transiently heated to ambient temperatures [hyperquenched water (HQP)] subsequently relaxes toward the structure of low-density amorphous (LDA) ice as it cools. We analyzed the infrared reflection-absorption spectra of LDA, HQP, and crystalline ice films to determine their complex indices of refraction. With this information, we estimate that HQP retains ~50%–60% of a structural motif characteristic of water at high temperatures with the balance comprised of a low-temperature motif. This result, along with results from x-ray diffraction experiments on water and amorphous ices, allows one to quantify the fraction of the high-temperature motif at approximately zero pressure as a function of temperature from 150 to 350 K.

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I. INTRODUCTION

The anomalous properties of liquid water have been investigated for over 100 years.¹ Although no consensus exists, recent results from both experiments and molecular dynamics (MD) simulations provide increasing support for one of two closely related models—the liquid-liquid critical point hypothesis (LLCP) and the singularity-free scenario.^{1–7} In the LLCP hypothesis, water at low temperatures and high pressure can exist in one of two distinct phases, a high-density liquid (HDL) or a low-density liquid (LDL), that are separated by a first-order phase transition line that terminates in a critical point. While sharing many similarities with the LLCP hypothesis, phase separation does not occur in the singularity-free scenario. In both models, water at ambient pressures is predicted to be an inhomogeneous mixture of two preferred local structural motifs. In one motif, which we will call the low-temperature motif (LTM), a central water molecule has an approximately tetrahedral bonding arrangement with its neighbors leading to a lower local density and entropy. The second motif—the high-temperature motif (HTM)—is more disordered

with a fifth water molecule crowding into the interstitial region around the central water molecule, leading to higher density and entropy. (Note that several classification schemes and terminologies are used in the literature to describe similar concepts based on two structural motifs^{4,8,9}). The existence of two structurally distinct amorphous ices, low-density amorphous (LDA) ice and high-density amorphous (HDA) ice, that exhibit a first-order like phase transition provides support for the LLCP hypothesis.^{3,10,11} As the names suggest, LDA and HDA have different densities that arise due to differences in their hydrogen bonding network, and they are thought to be the low-temperature analogs of LDL and HDL, respectively.

Because LTM has lower enthalpy and entropy compared to HTM, the fraction of HTM is expected to decrease as the temperature decreases, with the most rapid changes occurring at temperatures between ~190 and 245 K at ambient pressures.^{1,3,4} For deeply supercooled water (e.g., $T < 235$ K), the timescale for crystallization becomes short compared to most experimental timescales and little data exist. To overcome the problem of rapid crystallization for deeply supercooled water, we have recently developed a technique in

which nanoscale water films can be transiently heated with a short laser pulse for a few nanoseconds per pulse.¹² The approach relies on rapid cooling of the thin water films to cryogenic temperatures to quench the structures so that they can subsequently be interrogated with non-time-resolved techniques such as infrared (IR) spectroscopy. Previously, we have used this approach to investigate the structural transformations in transiently heated H₂O and D₂O.^{13–16} One key observation from those studies was that, prior to the onset of appreciable crystallization, the IR spectra for a wide range of conditions displayed several isosbestic points and could always be reproduced as a linear combination of just two temperature-independent spectra for water prepared in two different states. One of those states—low-density amorphous (LDA) ice—was formed by isothermally annealing water at/near the glass transition temperature for low-density water, T_g , which is ~ 136 K.^{1,17,18} The second state, which we call hyperquenched water (HQW), was prepared by transiently heating water to ~ 300 K. Another key observation was that the steady state fraction of HQW, $f_{HQW}^{SS}(T_{max})$, decreased as the maximum temperature for transiently heated water, T_{max} , decreased.

The IR spectra for transiently heated water are similar to previous IR and Raman measurements on normal and mildly supercooled water that also had isosbestic points in the spectra,^{19–25} and these results were often analyzed in terms of two, temperature-independent components.^{19–22} Because the IR spectra of water are sensitive to its local structure,^{26,27} the observation that the spectra of water could always be represented as a linear combination of two spectra is consistent with the expectations of either the LLC hypothesis or the singularity-free scenario.¹ However, Geissler showed that temperature-dependent changes in the distribution of thermal fluctuations in water will produce apparent isosbestic points in spectra measured at different temperatures without the need to invoke distinct states in the water.²⁸ Because the IR spectra for the transiently heated water were all measured at the same temperature (typically 70 K), the observed changes in the spectra are not associated with the issues identified by Geissler. Instead, these experiments are analogous to molecular dynamics simulations that investigate the structure of water after it is instantaneously quenched to 0 K, producing what is called the inherent structure (IS) for the liquid.^{1,29} Simulations of the inherent structure for water vs temperature at 1 bar predict that the fraction of HTM, $f_{HTM}(T)$, continuously decreases with temperature until the low-temperature motif dominates for temperatures below ~ 200 K.^{30,31}

A model that accounts for the experimental observations discussed above is that the IR spectra for water that is instantaneously quenched from some temperature, T , to 70 K is a linear combination of two “basis” spectra: (i) the spectrum of water instantaneously quenched from near the boiling point to 70 K and (ii) the spectrum of water equilibrated at T_g and measured at 70 K. A technical point is that the quantity of interest, the imaginary component of the index, $k(\omega, T)$, can be calculated from the IR spectra (see Sec. II for details). If we call the first and second basis spectra $k_{HTM}(\omega)$ and $k_{LTM}(\omega)$, respectively, then we have

$$k(\omega, T) = f_{HTM}(T)k_{HTM}(\omega) + (1 - f_{HTM}(T)) \cdot k_{LTM}(\omega). \quad (1)$$

Ni and Skinner calculated the IR spectra for water at pressures ranging from 1 bar to 2.25 kbar and a variety of temperatures around the Widom Line.³² Because those calculations used molecular dynamics simulations, they were also able to calculate the oxygen–oxygen radial distribution corresponding to each IR spectrum. They found that the changes in IR spectra closely tracked the height of the second peak in that distribution, g_2 , which has been used to characterize the temperature-dependent changes in water’s structure.^{33–35} These calculations provide support for the assumption that IR spectra can be used to follow the structural changes in supercooled water.

Because our LDA was prepared by isothermal annealing at T_g , and its structure does not change until it is heated above ~ 190 K,¹³ we expect that it consists almost entirely of LTM. Therefore, its spectrum, $k_{LDA}(\omega)$, corresponds to the second basis spectrum: $k_{LTM}(\omega) = k_{LDA}(\omega)$. In contrast, due to the finite cooling rates for transient heating experiments, we cannot directly measure $k_{HTM}(\omega)$. In particular, while the cooling rates were high ($\sim 5 \times 10^9$ K/s), they were still slow compared to the relaxation timescale for normal, and slightly supercooled, water.^{14,36,37} As a result, significant structural relaxation occurred as the water films cooled after heating to high temperatures such that HQW does not correspond to the structure of high-temperature water instantaneously quenched to 70 K. Instead, HQW should reflect the structure of water at a much lower temperature, perhaps ~ 235 K. However, the structure of HQW should still be a mixture of HTM and LTM. Therefore, from Eq. (1), we expect $k_{HQW}(\omega, T) = \alpha k_{HTM}(\omega) + (1 - \alpha) \cdot k_{LTM}(\omega)$, where α and $(1 - \alpha)$ are the fractions of HTM and LTM in HQW, respectively. If we can determine α , and thus HQW’s composition, then our previous results on the structural composition of supercooled water vs temperature can be more directly compared with the results of other experiments, theory, and simulations.

For experiments where water is transiently heated to high temperatures to produce HQW upon cooling to 70 K, Eq. (1) can be rearranged to give

$$k_{HTM}(\alpha; \omega) = \frac{k_{HQW}(\omega) - (1 - \alpha)k_{LDA}(\omega)}{\alpha}, \quad (2)$$

where we have replaced $k_{LTM}(\omega)$ with $k_{LDA}(\omega)$, as discussed above. The form of k_{HTM} derived from Eq. (2) depends on the (unknown) value of α , so we will refer to it as $k_{HTM}(\alpha; \omega)$. It is important to note that because water absorbs light, $k(\omega, T)$ must be greater than 0. As we show below, the constraint $k_{HTM}(\alpha; \omega) > 0$ limits the possible values of α and, as a result, the composition of HQW.

Here, we analyze the IR spectra of LDA, HQW, and crystalline ice (CI) to determine their complex indices of refraction. The IR spectra for the thin water films were obtained in reflection mode from a metal substrate at glancing incidence. Therefore, thin film optical effects were included in the analysis to obtain the optical constants for the water films. For CI, the values we determine for $\tilde{n}_{CI}(\omega) = n_{CI}(\omega) + ik_{CI}(\omega)$ are in good agreement with previous results.³⁸ For HQW and LDA, $k_{HQW}(\omega)$ and $k_{LDA}(\omega)$ have a similar shape in the OH-stretching band with the peak absorption for HQW red shifted by ~ 8 cm^{−1} with respect to LDA. Using Eq. (2), we estimate what the optical constants for water would be if it could be “instantaneously” quenched from high

temperatures to 70 K at ambient pressures. The calculated shape of $k_{HTM}(\alpha; \omega)$ in the OH-stretch and isolated OD-stretch bands for various values of α suggests that $\alpha \sim 0.5$ – 0.6 . In that case, the experimentally measured HQW would be a composition that is $\sim 50\%$ – 60% HTM. Recent experiments measured the IR spectra for HDA, LDA, and CI films in the isolated OD-stretch band,³⁹ and our results for $k_{LDA}(\omega)$ and $k_{CI}(\omega)$ closely match the corresponding spectra for LDA and CI. Furthermore, our most likely result for HTM— $k_{HTM}(\alpha = 0.5; \omega)$ —is quite similar to the IR spectra reported for HDA.³⁹

II. EXPERIMENTAL PROCEDURE

The experiments were conducted in an ultrahigh vacuum apparatus that has been described previously.¹² Nanoscale water films were deposited on either Pt(111) or graphene/Pt(111) surfaces held at 70 K (unless otherwise noted). Water films with a coverage of 50 monolayers were deposited at normal incidence with a molecular beam dosing system to produce a nonporous, amorphous solid water film (ASW).^{40–42} The as-deposited ASW films were subsequently thermally treated to produce films with one of three distinct hydrogen bonding structures—CI, LDA, or HQW. The CI films were prepared by pulsed heating at temperatures below the melting point (e.g., $T_{\max} = 221$ and 236 K for the results shown below) for a sufficient number of pulses to completely crystallize the films, as indicated by the IR spectra.⁴³ LDA films were produced by annealing ASW or HQW at or near the glass transition temperature for low-density water.^{1,17,18} Specifically, the films were annealed at 135 K for 130 s, but essentially identical results were obtained for a range of annealing times and/or temperatures centered around these values. HQW films were produced by transiently heating ASW or LDA films to ~ 300 K with a pulsed laser heating technique, which has been described previously.^{13,14} Because ASW is a kinetically arrested, nonequilibrium form of water, annealing it to 135 K or transiently heating it to 300 K resulted in irreversible structural transformations to produce LDA or HQW, respectively. In contrast, annealing HQW at 135 K or transiently heating LDA to 300 K resulted in reversible structural transitions to LDA or HQW, respectively.¹³ For the results presented here, the key point is that the cooling rates for the water films after they reach their maximum temperature, $T_{\max}$, are $\sim 5 \times 10^9$ K/s. As shown below, this cooling rate is large enough to avoid complete relaxation toward LDA. As a result, the pulsed heating experiments provide new insights into the structure of supercooled water at intermediate temperatures. Note that hyperquenched glassy water, which is made by depositing micrometer-sized liquid water droplets on a surface held at cryogenic temperatures, produces an amorphous solid whose structure is essentially identical to LDA.¹⁰ The slower cooling rate for hyperquenched glassy water ($< 10^7$ K/s) allows it to completely relax to LDA as it cools whereas the faster cooling rates for the current experiments prevent the complete structural relaxation of HQW to LDA.

The pulsed heating method has been described in detail elsewhere.¹² Briefly, the technique uses spatially tailored “flat-top” laser pulses from a Nd-YAG laser ($\lambda = 1064$ nm, pulse width ~ 10 ns, 1–5 Hz) to transiently heat the near surface region of the substrate and the adsorbed water film to a maximum temperature, $T_{\max}$. The

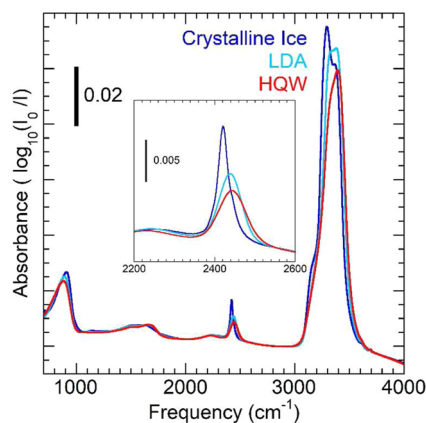


FIG. 1. IRAS spectra for 50 ML films of CI, LDA, and HQW (dark blue, cyan, and red lines, respectively). The inset shows an expanded view of the isolated OD-stretch region.

desorption of crystalline ice was used to determine $T_{\max}$ as a function of laser pulse energy. The water film was at/near $T_{\max}$ for ~ 3 ns, with maximum heating and cooling rates from 70 K to $T_{\max}$ of $\sim 10^{10}$ and $\sim 5 \times 10^9$ K/s, respectively.

The structural changes of the water films were monitored by infrared reflection–absorption spectroscopy (IRAS). For the water source, a small amount of D_2O was added to H_2O such that the resulting mixture was $\sim 90\%$ H_2O and $\sim 9.5\%$ HOD. As described below, the isolated HOD provided useful information for estimating the fraction of HTM in the measured HQW spectra. The typical absorbance spectra were obtained with 500 scans of a Fourier-transform infrared (FTIR) spectrometer (Bruker, Vertex 70) at a resolution of 4 cm^{-1} . The absorbance, $A(\omega)$, is defined as $A(\omega) = \log_{10}[I_0(\omega)/I(\omega)]$, where $I(\omega)$ and $I_0(\omega)$ are the reflected signal with and without the adsorbed water layer, respectively. The vibrational spectra were analyzed across the OH-stretching and OD-stretching bands (~ 2000 – 4000 cm^{-1}). A linear combination of the HQW, LDA, and CI spectra was used to determine the fractional composition of the water sample as a function N_p for a given $T_{\max}$.^{13,14} The spectra for LDA and HQW shown in Fig. 1 are the average of 33 different experiments. Although the HQW and LDA spectra obtained in any individual experiment are very similar to the averages shown in Fig. 1, the individual experiments exhibit variations in the baseline that are related to small variations in the experimental conditions (such as the level of liquid nitrogen in the IR detector). The CI spectrum shown in Fig. 1 is the average of ten individual spectra (i.e., 5000 scans) for a film crystallized by $\sim 23\,000$ heat pulses at 221 K. A similar spectrum, discussed below, is obtained for a water film crystallized by heating to 236 K for 1500 pulses. Because the IR spectra of hexagonal and “cubic” ice (i.e., stacking disordered ice⁴⁴) are nearly identical,⁴⁵ we cannot determine which ice polymorph is formed in these experiments.

In previous experiments, the IR spectra for water have been measured in various geometries (e.g., transmission, reflection, and

attenuated total reflection), which produce differences in the spectra due to optical effects.^{21,22,39,46} To account for this, the raw IR spectra are typically analyzed to determine the complex index of refraction for the water as a function of temperature and frequency: $\tilde{n}(\omega, T) = n(\omega, T) + ik(\omega, T)$, where the imaginary component of the index, $k(\omega, T)$, which is responsible for the absorption of radiation, is the quantity of interest. Note that a closely related quantity, the absorption coefficient [$= 4\pi k(\omega)/\lambda$, where λ is the wavelength of the light] is sometimes reported. The restriction $k(\omega) > 0$, which we use in our analysis of the IR spectra, is most easily understood considering the absorption coefficient. In particular, the intensity of light as function of the distance, x , that it has propagated through a substance is given by the Beer–Lambert law, $I(x) = I_0 e^{-4\pi k(\omega)x/\lambda}$, where I_0 and $I(x)$ are the initial intensity and the intensity at x , respectively. From this, it is seen that $k(\omega) < 0$ would correspond to an (unphysical) exponential increase in the intensity as the light propagates.

For our experiments, the IR reflection from the thin water films was treated using a three-layer vacuum–adsorbate–substrate model.^{47,48} The inputs for the model included the complex index of refraction for the platinum substrate,^{49,50} $\tilde{n}_{Pt}(\omega) = n_{Pt}(\omega) + ik_{Pt}(\omega)$, and for the adsorbed water layer, $\tilde{n}_j(\omega) = n_j(\omega) + ik_j(\omega)$, where j refers to a particular water film (e.g., HQW, LDA, or CI). Trial functions for $k_j(\omega)$ were constructed using a series of Lorentzian functions with fixed widths and frequencies but variable intensities. For each trial, $n_j(\omega)$ was determined using the Kramers–Kronig relations. For the regression analysis, one Lorentzian from the series was chosen at random and its intensity was increased or decreased. If the change improved the overall fit for the spectra, it was accepted, otherwise it was rejected. The process was repeated until an acceptable fit was achieved. Note that because the nanoscale inhomogeneities associated with two structural motifs (HTM and LTM) are small compared to the wavelength of the IR light, the index of refraction is determined by the average response of both motifs. As a result, for the purposes of treating the thin film optical effects and determining $k(\omega)$, the water films can be treated as uniform films with interfaces only to the substrate and the vacuum.

Our previous experiments were conducted on both Pt(111) and graphene/Pt(111) surfaces as a test for the possible influence of the substrate.^{13,14} We found no appreciable differences in the results on either surface, and for the results reported below, the key observation is that the IR spectra for HQW and LDA are essentially identical on both surfaces. This result is unsurprising given that the IR absorption for graphene is approximately independent of frequency in the mid-IR region⁵¹ and its effects largely cancel when the absorbance is calculated. As a result, it was sufficient to only include the platinum in the modeling to extract the complex index of refraction for the water films.

Figure S1(a) shows an example of the fit obtained for IRAS spectrum for a CI film. The real and imaginary components of the index of refraction for this film are shown as blue lines in Fig. S1(b). For comparison, the optical constants for neat crystalline H₂O measured at 100 K³⁸ are also shown. Aside from the differences in the isolated OD-stretch band, which is absent from the data for neat H₂O, the overall agreement is quite good. We note that some differences should be expected because the size of the crystalline ice grains in the two experiments was different, and this should lead to some

differences in the derived optical constants.⁵² Due to limitations of our experiments for frequencies less than $\sim 1000\text{ cm}^{-1}$, we do not necessarily expect to reproduce the optical constants at low frequencies. The good agreement of optical constants for our CI film with previous results give us confidence that we can also determine the optical constants for LDA and HQW.

III. RESULTS AND DISCUSSION

Figure 1 shows IRAS spectra for 50 ML LDA, HQW, and CI films adsorbed on graphene/Pt(111). Note that the spectra for LDA and HQW adsorbed on Pt(111) are essentially identical to those shown in Fig. 1. The results show that the OH-stretch (i.e., $\sim 3000\text{--}3600\text{ cm}^{-1}$) and isolated OD-stretch ($\sim 2350\text{--}2500\text{ cm}^{-1}$) bands are distinct for LDA, HQW, and CI. While the low-frequency band ($< 1000\text{ cm}^{-1}$) is also different for each form of water, the low sensitivity of the spectrometer in this region, along with the frequency cutoff at $\sim 600\text{ cm}^{-1}$, makes quantification of the differences in this band difficult with our equipment. As a result, the analysis presented below will focus on the differences in OH-stretch and isolated OD-stretch bands.

To extract more quantitative information from the IRAS spectra, optical simulations were used to determine the complex index of refraction for the LDA, HQW, and CI films. As described in Sec. II, the optical simulations used a three-layer (vacuum–adsorbate–substrate) model,^{47,48} where the index of refraction was regressed to yield the best fit to the experimental IRAS measurements. Figure 2(a) shows the experimental and simulated spectra for LDA and HQW. The corresponding optical constants for LDA and HQW are shown in Fig. 2(b). It is interesting to note that although the IR spectra obtained in reflection mode for LDA and HQW are distinct in the OH-stretch band, their optical constants—particularly for $k(\omega)$ —appear to have a similar structure, albeit with HQW shifted to somewhat higher frequencies. The optical constants determined here for LDA are similar to previous measurements in the OH-stretch region (see Fig. S2).⁵³

Equation (2) allows one to calculate possible forms of $k_{HTM}(\alpha; \omega)$ that would account for the experimentally observed IR spectrum for HQW assuming various values of α . Below, we argue that the most likely value for α that is consistent with other data and calculations is $\alpha \approx 0.5$ where the probability distribution smoothly transitions from likely to unlikely for values of α between 0.4 and 0.6 and values outside this range, respectively. Figure 3 shows $k_{HTM}(\alpha; \omega)$ corresponding to values of α ranging from 0.2 to 0.6. As seen in the figure, the nominal shape of the OH-stretch and isolated OD-stretch bands for HTM is quite sensitive to the value of α . For example, $k_{HTM}(\alpha = 0.2; \omega)$ has three distinct peaks in the OH-stretch band and, more importantly, it is negative in the isolated OD-stretch band (see inset in Fig. 3). Because $k_{HTM}(\alpha; \omega)$ must be greater than zero, this result indicates that α must be greater than 0.2. For somewhat larger values of α , the smaller peaks on the low-frequency side of the OH-stretch band would appear as shoulders in $k_{HTM}(\alpha; \omega)$. For $\alpha \geq 0.6$, the OH-stretch band, while broad, would be relatively featureless. A similar evolution is seen for the isolated OD-stretch band for different values of α : For $\alpha = 0.25$, the band would have two peaks at higher and lower frequencies than the corresponding peak for LDA. For $0.3 < \alpha < 0.5$, $k_{HTM}(\alpha; \omega)$ would have a single peak

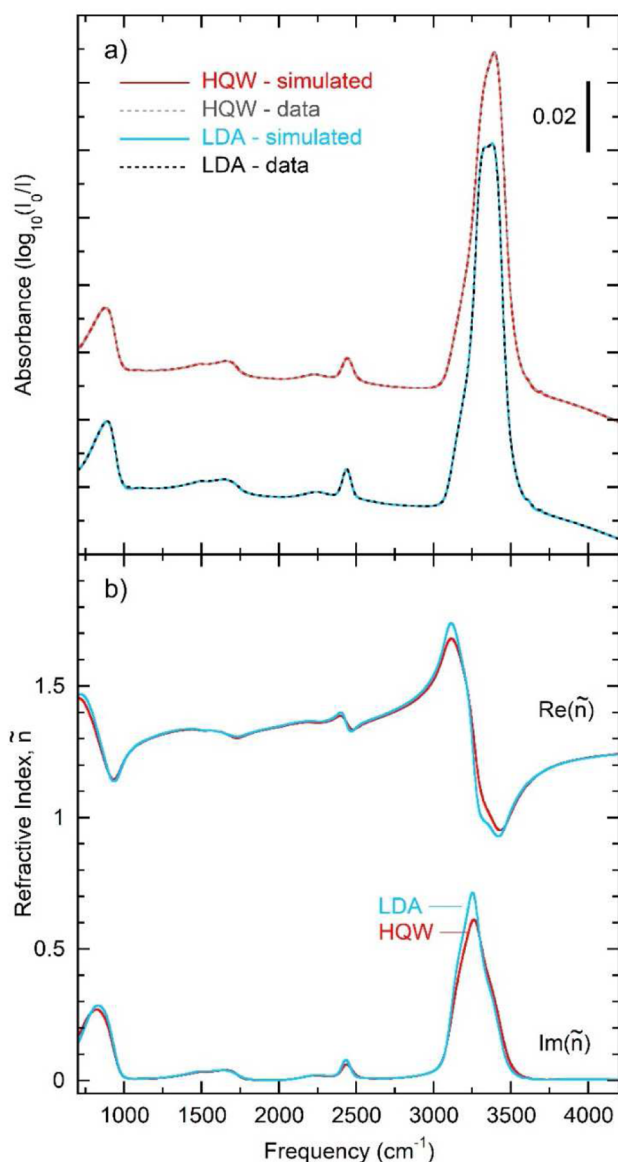


FIG. 2. (a) Measured (dotted lines) and simulated (solid lines) IRAS spectra for HQW and LDA. (b) The real (top) and imaginary (bottom) components of index of refraction for LDA (cyan) and HQW (red).

with a shoulder in the isolated OD-stretch band or a single peak for $\alpha > 0.5$.

For conditions where water's structure is dominated by one structural motif, experiments show that the isolated OD-stretch is consistent with an inhomogeneously broadened peak that does not have pronounced shoulders or secondary peaks. For example, for water near its boiling point at ambient pressures, where MD simulations and two-state models suggest that HTM dominates the structure,¹ the isolated OD-stretch band is approximately Gaussian.⁵⁴ Similarly, recent measurements of the isolated OD-stretch

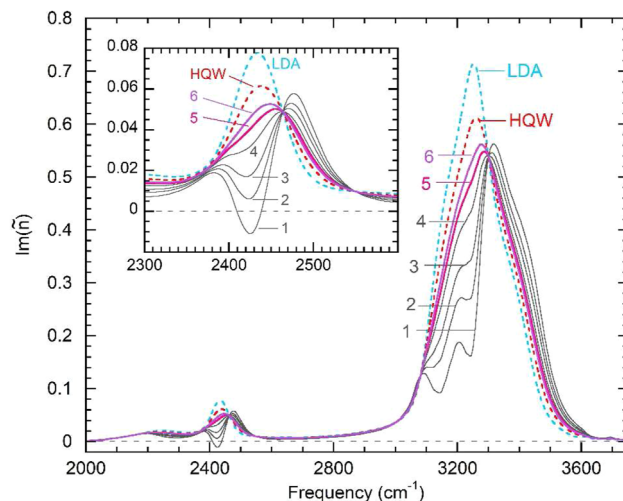


FIG. 3. Absorption vs frequency, $\text{Im}(\tilde{n}_j) = k_j(\omega)$, for $j = \text{LDA}$ (dashed blue line) and HQW (dashed red line). The spectra labeled 1–6 show possible forms for $k_{\text{HTM}}(\alpha; \omega)$ calculated using Eq. (2) with several different values of α : (1) $\alpha = 0.2$; (2) $\alpha = 0.25$; (3) $\alpha = 0.3$; (4) $\alpha = 0.4$; (5) $\alpha = 0.5$; (6) $\alpha = 0.6$. The inset shows an expanded view of the spectra in the isolated OD-stretch band. Based on the line shapes for $k_{\text{HTM}}(\alpha; \omega)$, values of $\alpha \leq 0.4$ are unlikely (see text).

band for LDA, HDA, and CI are also consistent with an inhomogeneously broadened peak³⁹ (see Fig. 4). Based on these results, we expect that the spectrum derived for HTM in the isolated OD-stretch band should also be an inhomogeneously broadened peak. For the potential HTM spectra shown in Fig. 3, only $\alpha \geq 0.5$ gives a single peak in the isolated OD-stretch band. Figures S3(a) and S3(b) the isolated stretch bands calculated for CI, LDA, and HDA⁵⁵ to the current measurements for CI and LDA along with those derived for HTM assuming $\alpha = 0.5$ or 0.6 . The calculated band for HDA shows an inhomogeneously broadened peak without significant structure, and the general trends in peak width and peak positions for CI, LDA, and HDA/HTM are consistent for the calculations and experiments with $\alpha \sim 0.5$ – 0.6 .^{22,55–59} The shape of the OH-stretch band, which is broad and relatively smooth for HTM with $\alpha > 0.4$ (see Fig. 3), provides further support for values in this range. For example, the IR spectra of normal and mildly supercooled water are broad and relatively smooth in the OH-stretch region.^{22,56–59} The measured spectrum for LDA is also broad with indistinct shoulders at ~ 3160 and 3370 cm⁻¹. For $\alpha < 0.4$, the simulated spectra in Fig. 3 indicate that HTM would be more structured than LDA, which seems unphysical and inconsistent with Fig. S3(c), which compares the spectra for CI, LDA, and HDA calculated by Skinner and co-workers⁵⁵ to the current results for CI, LDA, and HTM with $\alpha = 0.5$. For HDA, the calculated spectrum is broad without prominent shoulders in the OH-stretching region and is consistent with the line shape for HTM if $\alpha \sim 0.5$ – 0.6 but not if $\alpha < 0.4$. While these considerations are not hard constraints, they do suggest that the measured HQW water spectrum has substantial contributions from the high-temperature structural motifs that would dominate if the experiments could be done at significantly faster cooling rates.

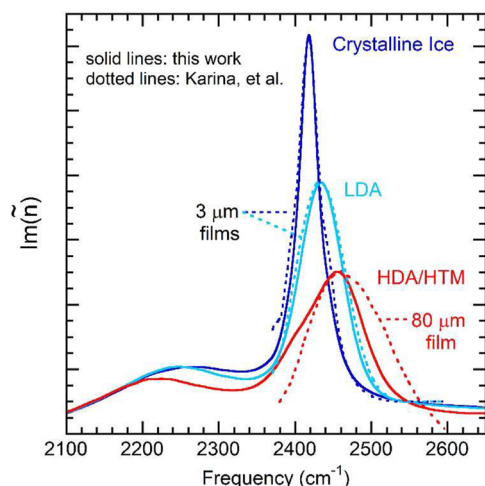


FIG. 4. The imaginary component of the index of refraction for crystalline ice (dark blue lines), LDA (cyan lines), HDA (dotted red line), and HTM for $\alpha = 0.5$ (solid red line) in the isolated OD-stretch region. The results for the current experiments are shown with solid lines, while recent experimental results from the study of Karina *et al.*³⁹ are shown as dotted lines (see text for details).

As mentioned above, recent measurements of the IR spectra of bulk LDA, relaxed HDA (“eHDA”), and crystalline ice support the hypothesis that HQW obtained from the transiently heated water films has a substantial contribution from HTM (i.e., $\alpha \geq 0.5$).^{39,46} Those measurements, which were also performed in vacuum, also used H₂O mixed with a small amount of D₂O so that the resulting spectra had an isolated OD-stretch band. Figure 4 compares $k_{CI}(\omega)$ (dark blue line) and $k_{LDA}(\omega)$ (cyan line) derived from our IRAS spectra (solid lines) to the corresponding absorbance spectra measured in transmission for a 3 μm thick film (dashed lines, taken from Fig. S4 in Ref. 39). The 3 μm thick LDA and CI films were prepared by vapor depositing ASW on a cold substrate and subsequently annealing it 130 and 160 K, respectively. The transmission spectra were taken at 80 K, while our spectra were taken at 70 K. The intensities of the transmission spectra (which were reported in arbitrary units) have been scaled to match our results. Aside from this scale factor, the two sets of results are essentially identical, suggesting the (local) structure is the same for the crystalline ice and LDA films in both experiments. In a separate set of experiments, an $\sim 80 \mu\text{m}$ thick film of HDA was produced at high pressures and subsequently transferred to a cryostat in vacuum to measure the IR spectra in transmission.³⁹ In the isolated OD-stretch band, the HDA has a single, relatively broad peak that is shifted to higher frequency compared to either CI or LDA (Fig. 4, red dashed line). The solid red line in Fig. 4 shows $k_{HTM}(\alpha = 0.5; \omega)$, which is the smallest value for α that does not have a peak or prominent shoulder on the low-frequency side of the band. Compared to HDA, the isolated OD-band for $k_{HTM}(\alpha = 0.5; \omega)$ is somewhat narrower and slightly red shifted. However, the qualitative agreement between the two experiments is good [as described in the supplementary material for Ref. 39, the shape of the HDA peak for the thick films, particularly on the high frequency side, is probably affected by the background

subtraction method that was used to analyze that data (see Fig. S4)]. Raman spectra of the isolated OH (OD) for HDA and LDA⁶⁰ also show that the peak for HDA is blue shifted and broadened with respect to LDA, indicating a more inhomogeneous local environment with, on average, weaker binding. Note, however, that the magnitude of the Raman peak shifts for both HDA and LDA, compared to crystalline ice, is considerably larger than those observed with IR.

To gain more insight into the possible composition of HQW, it is useful to compare the optical constants for LDA, HQW, and HTM to those for liquid water and crystalline ice at various temperatures, which have been investigated over many years.^{22,45,53,56–59,61–65} Because our spectra are measured at 70 K, the likely temperature dependence of $k(\omega)$ for water and ice also need to be considered. The optical constants for crystalline ice have been measured from cryogenic temperatures up to nearly the melting point.^{38,45,61,62,64,65} In the OH-stretch band for ice, the maximum intensity of the band, k_{bm} , increases, and the frequency at the maximum, ω_{bm} , redshifts as the temperature decreases.^{63,65,66} Figure 5 shows ω_{bm} for crystalline ice vs temperature for our experiments (solid blue circles) and several previous reports (blue symbols). For $T > 130$ K, ω_{bm} increases approximately linearly, while for lower temperatures the rate of change gradually decreases. Our results for crystalline ice (solid blue circles) show the same trends. For LDA and HQW (Fig. 5, cyan and orange triangles, respectively), the band maxima are at higher frequencies, but the trends with temperature are similar to those for CI. The difference in ω_{bm} for LDA and CI, $\Delta\omega_{bm}(\text{LDA-CI})$, is 27 cm^{-1} . LDA was measured up to the point where crystallization begins to interfere at 140 K. For HQW, structural relaxation toward LDA, which occurs with a broad distribution of relaxation times,¹⁴ makes accurate measurements of the IR spectra difficult for $T > 100$ K.

For liquid water with $T \geq 269$ K, ω_{bm} also increases approximately linearly, but it does so with a larger slope than for CI (Fig. 5, red symbols). There are only a few measurements for supercooled water,^{25,58,59,67} but they show similar trends with temperature compared to normal water (Fig. 5, purple symbols). For both crystalline ice and liquid water, the general trends for ω_{bm} vs temperature are similar for different experiments, but there are differences in the actual values reported for ω_{bm} . The scatter in data for water (normal and supercooled) is somewhat larger than it is for crystalline ice.

Ni and Skinner have simulated the IR spectra for supercooled water above and below the LLC for the E3B3 water model.³² Those simulations suggest that the IR spectra for HDL should be blue shifted relative to LDL and the maximum intensity should also be lower. Both of those observations are consistent with the changes predicted here for LDA and HTM. Figure 5 shows the calculated ω_{bm} at 2.25 kbar for three temperatures above (red triangles) and below (open cyan triangles) the LDL–HDL coexistence line.³² Upon crossing the coexistence line, ω_{bm} decreases by $\sim 18 \text{ cm}^{-1}$ in those simulations. For transiently heated water, the predicted difference between ω_{bm} for HTM and LDA, $\Delta\omega_{bm}(\text{HTM-LDA})$, depends on the fraction of HTM in the HQW spectra with larger values of α leading to smaller values for $\Delta\omega_{bm}(\text{HTM-LDA})$. For the most likely compositions of HQW, corresponding to $\alpha = 0.5\text{--}0.6$, $\Delta\omega_{bm}(\text{HTM-LDA}) \sim 35\text{--}24 \text{ cm}^{-1}$. The magnitude of these predicted shifts in the band maximum between LDA and HTM are qualitatively consistent

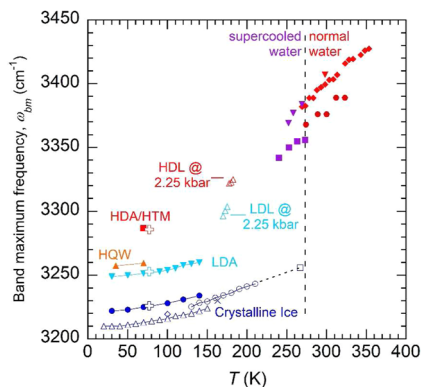


FIG. 5. Frequency at the OH-stretch band's maximum intensity, ω_{bm} , with temperature for several water polymorphs. For crystalline ice, the measured temperature dependence for the current results (solid blue circles) is similar to previous results (blue triangles,⁶⁵ circles,⁶³ square,⁶¹ diamond,³⁸ and $\times$ ⁶²). For LDA (solid cyan triangles) and HQW (solid orange triangles), the band maxima are blue shifted relative to those for CI. The solid red square shows ω_{bm} for HTM assuming $\alpha = 0.5$. The rate of change for ω_{bm} for LDA (cyan triangles) is considerably lower than that for normal water (red diamonds,²² circles,⁵⁶ and triangle⁵⁷) and supercooled water (purple triangles⁵⁸ and squares⁵⁹). Using the E3B3 water model, Ni and Skinner calculated the IR spectra for water at 2.25 kbar for temperatures just above and below the HDL-LDL coexistence line (HDL, open red triangles; LDL open cyan triangles).³² Skinner and co-workers also calculated the spectra for CI, LDA, and HDA at atmospheric pressure and low temperatures (blue, cyan, and red crosses, respectively).⁵⁵ The calculated band maxima positions have all been shifted down by 8 cm^{-1} to highlight the general agreement with the current results for CI, LDA, and HTM (with $\alpha = 0.5$).

with the shifts that might be expected for LDA and HDA in the OH-stretch band. As discussed above, the observed shifts in the isolated OD-stretch band are also consistent (see Fig. 4). Tainter *et al.* calculated the IR spectra for HDA, LDA, and CI at 1 bar and 77 K [see Fig. S3(c)].⁵⁵ In those calculations, $\Delta\omega_{bm}(\text{LDA-CI}) = 27 \text{ cm}^{-1}$ and $\Delta\omega_{bm}(\text{HDA-LDA}) = 33 \text{ cm}^{-1}$. These differences very closely match our measured value for $\Delta\omega_{bm}(\text{LDA-CI})$ and calculated values for $\Delta\omega_{bm}(\text{HTM-LDA})$ assuming $\alpha \sim 0.5$ – 0.6 . The crosses in Fig. 5 show ω_{bm} from those calculations, where they have all been shifted down by 8 cm^{-1} to illustrate the overall agreement with the experiments. While the good agreement between the experiments and simulation is perhaps fortuitous, it does suggest that the most likely value for α is ~ 0.5 – 0.6 , which agrees with our analysis of the line shape of the calculated OH-stretch and isolated OD-stretch for HTM (see Figs. 3 and S3).

We previously measured $f_{HQW}^{SS}(T_{\max})$ for transiently heated water films for $180 \text{ K} \leq T_{\max} \leq 260 \text{ K}$.¹³ By construction, $f_{HQW}^{SS} = 1$ at high temperatures where the structural relaxation rate was large relative to the experimental cooling rate. However, based on the data and analysis discussed above, it is likely that the structure for HQW is approximately a 50–50 mixture of high- and low-temperature structural motifs. Therefore, we can now estimate the fraction of HTM at steady state, $f_{HTM}^{SS}(T_{\max})$, and compare it to previous experiments at higher temperatures. Figure 6 shows $f_{HTM}^{SS}(T_{\max})$ assuming $\alpha \sim 0.5$ (blue circles), and the dotted blue

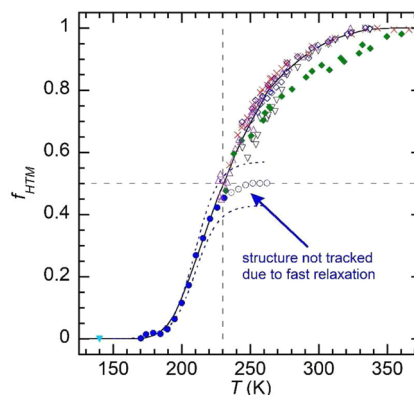


FIG. 6. Fraction of HTM vs temperature derived from transiently heated water films (solid and open blue circles) and x-ray structural data. The blue dotted lines show the likely range of values for the data on the transiently heated water films. The green diamonds show Shi and Tanaka's analysis of x-ray scattering data.⁸ The blue diamonds and purple triangles are determined from measurements of g_2 .^{33,35,68} The red $\times$'s are derived from n_{int} .^{35,68–70} and the black triangles are derived from S_2 .^{35,68} The solid black line shows a smooth curve to guide the eye. The vertical line indicates the approximate temperature, 230 K, where $f_{HTM} \sim 0.5$. For temperatures above $\sim 230 \text{ K}$, the structural relaxation rate in water is too fast for the experiments with the transiently heated water films (open blue circles) and the results deviate from the trend observed in the x-ray scattering experiments.

lines show our estimate of likely range of values (corresponding to $0.4 < \alpha < 0.6$). For water transiently heated to $T > 230 \text{ K}$, water's structural relaxation rates are sufficiently fast compared to the experimental cooling rates that the experiments can no longer track the structural changes (Fig. 6, open blue circles). As a result, $f_{HTM}^{SS}(T_{\max})$ remains at ~ 0.5 for higher temperatures. Figure S5 illustrates the behavior that might be expected for $f_{HTM}^{SS}(T_{\max})$ if the experiments could be conducted with larger cooling rates.

The temperature- and pressure-dependent structure of water has been extensively investigated with MD simulations.^{1,5} In addition, two-state mixture models,^{9,71,72} which provide a simplified thermodynamic model for water, can be fit to a wide range of experimental data with a modest number of parameters. One of the key predictions of the simulations and the two-state models is that the fraction of the high-temperature structural motif, $f_{HTM}(T)$, will smoothly decrease with temperature as the water adopts a more ordered, tetrahedrally bonded configuration for pressures at or below 1 bar.^{4,72} X-ray^{33,35,68,69} and neutron diffraction^{73–76} studies of normal and supercooled water provide support for these models. Several features in the diffraction data have been correlated with structural changes in water including the number of interstitial molecules, n_{int} , the heights of the second and fifth peaks in the oxygen–oxygen pair distribution function, g_2 and g_5 , and the height of the second sharp diffraction peak, S_2 .³⁵ For example, the presence or absence of a fifth molecule close to a central water molecule is considered to be a good indicator for distinguishing between the two structural motifs, and several of the order parameters commonly used in MD simulations are based on this idea in one way or another.^{31,71,77,78} The number of “interstitial” molecules, which

are between the first and second coordination shells for water, has also been determined for both water and LDA.^{35,68,69} The results show that the number of interstitials, $n_{\text{int}}(T)$, decreases steadily with temperature and it is much lower for LDA.

Figure 6 shows several estimates of $f_{\text{HTM}}(T)$ derived from x-ray diffraction data. For example, Shi and Tanaka recently proposed an analysis of the “first sharp diffraction peak” in terms of an “ordinary” and “anomalous” component, where the anomalous component corresponds to LTM (Fig. 6, green diamonds).⁸ For some of the parameters, $X(T)$, that are related to water’s structure, one can estimate the fraction of HTM as

$$f_{\text{HTM}}(X; T) = (X(T) - X(\text{LDA})) / (X(T \sim 350 \text{ K}) - X(\text{LDA})) \quad (3a)$$

for a parameter that increases with increasing temperature or

$$f_{\text{HTM}}(X; T) = (X(T \sim 350) - X(T)) / (X(\text{LDA}) - X(T \sim 350)) \quad (3b)$$

for a parameter that decreases with increasing temperature. In Eqs. (3a) and (3b), $X(\text{LDA})$ and $X(T \sim 350 \text{ K})$ are the values of the parameter for LDA and at $\sim 350 \text{ K}$, respectively. Here, we take $T \sim 350 \text{ K}$ as an approximate temperature above which the two-state character of water has essentially disappeared. Using n_{int} (Fig. 6, red triangles), $f_{\text{HTM}}(n_{\text{int}}; T)$ is predicted to decrease at an increasing rate down to the lowest temperatures measured for liquid water (234.8 K). Essentially identical behavior is found using g_2 (Fig. 6, blue diamonds and purple triangles) and S_2 (Fig. 6, black triangles). The key observation is that $f_{\text{HTM}}^{\text{SS}}(T_{\text{max}})$ derived from the pulsed heating experiments for $\alpha \sim 0.50$ and $T_{\text{max}} < \sim 230 \text{ K}$ (Fig. 6, solid blue circles) is consistent with these estimates of $f_{\text{HTM}}(T)$ based on x-ray data for $T > 228 \text{ K}$ and provides valuable information at low temperatures that were previously inaccessible. In Fig. 6, $f_{\text{HTM}}(T) = 0.5$ is at $\sim 230 \text{ K}$ (vertical dashed line), which is consistent with previous results.^{8,79,80} As described previously (e.g., Fig. S12 in Ref. 13), the pulsed heating experiments do not capture the behavior at temperatures above $\sim 230 \text{ K}$ where the structural relaxation rate is too large for it to be followed in those experiments.

The results in Fig. 6 suggest that the same structural changes in water that are probed directly by x-ray diffraction measurements are also observed in the IR spectra. This observation is supported by the results of Ni and Skinner (discussed above) who calculated both g_2 and the IR spectra for water at a variety of temperatures and pressures.³² Their results showed that changes in the IR spectra closely tracked the changes in g_2 . While the results shown in Fig. 6 are plausible, estimates of $f_{\text{HTM}}(T)$ using a similar approach with other experimental data show considerably more variation. Furthermore, functions other than Eq. (3) for relating the experimental measurements to the structure might also be appropriate. Therefore, more data are needed before firm conclusions can be drawn.

A recent study used molecular dynamics simulations with TIP4P/ICE to investigate the structural evolution of water subjected to rapid heating and cooling cycles that mimic our experimental procedure.³¹ Those simulations and the analysis presented here draw several similar conclusions. For example, the simulations predict that at lower temperatures where the relaxation rate in water

is slow compared to the cooling rate, the structure measured after pulsed heating to the steady state is essentially the same as the inherent structure. Conversely, for pulsed heating to higher temperatures where the relaxation rate is fast, the steady state structure measured at cryogenic temperatures after rapid cooling is a mixture of the high- and low-temperature structural motifs. In the simulations, the pulsed heating structure tracks the inherent structure once the characteristic number of pulses, N_{rel} , needed to relax to the steady state structure is greater than ~ 2 , which also appears to match the experimental results. In particular, for HQW at $T_{\text{max}} \sim 225 \text{ K}$, $N_{\text{rel}} \sim 2$,¹⁴ which corresponds to the temperature in Fig. 6 where $f_{\text{HTM}}^{\text{SS}}(T_{\text{max}}) \sim 0.45$ (depending on the precise value of α). For $T_{\text{max}} < 225 \text{ K}$, the pulsed heating data appear to be a smooth continuation of trends observed at higher temperatures for liquid water, whereas for $T_{\text{max}} > 225 \text{ K}$, the pulsed heating data begin to deviate from the liquid water data.

The primary difference between the pulsed heating simulations³¹ and the experiments is the extent of relaxation toward LDA as the water cools from high temperatures. In the simulations, $f_{\text{HTM}}^{\text{SS}}(T_{\text{max}}) \sim 0.30$ for $T_{\text{max}} \geq 270 \text{ K}$, whereas in the experiments $f_{\text{HTM}}^{\text{SS}}(T_{\text{max}}) \sim 0.5\text{--}0.6$ for $T_{\text{max}} > 240 \text{ K}$, which indicates that the simulations significantly overestimate the relaxation compared to the experiments. This difference can probably be traced to the fact that structural relaxation occurs much faster in the simulations than the experiments. This point is highlighted by noting that transiently heating to temperatures from ~ 180 to $\sim 240 \text{ K}$ produces changes in the structure and kinetics with the experimental cooling rate of $\sim 5 \times 10^9 \text{ K/s}$.^{13,14} In contrast, the pulse heating simulations using this same cooling rate produce water that is essentially 100% LDA, independent of the pulsed heating temperature.³¹ To observe temperature-dependent changes in the structure similar to those seen in the experiments, the simulations needed to use cooling rates that were 50–100 times larger than the experimental rate. Specifically, the system cooled from T_{max} to 100 K in 400 ps in the simulations, which corresponds to cooling rates ranging from $2.75 \times 10^{11} \text{ K/s}$ at $T_{\text{max}} = 210 \text{ K}$ to $5 \times 10^{11} \text{ K/s}$ at $T_{\text{max}} = 300 \text{ K}$. It is unclear why the structural relaxation is so much faster in the simulations compared to experiments, or if the discrepancy is worse for deeply supercooled water, as suggested recently.⁸¹ However, the fast relaxation of water toward LDA in MD simulations is not unique to the pulsed heating simulations or the TIP4P/ICE water model. LDA has been produced in simulations with cooling rates ranging from 1×10^7 to $3 \times 10^{10} \text{ K/s}$ depending on the model,^{82–84} including a rate of 10^{10} K/s for TIP4P/ICE.⁸⁵ Starting with equilibrated water at 240 K , the authors of the study of Handle *et al.* investigated the influence of cooling rates on the formation of LDA at 0.1 MPa for TIP4P/2005.⁸⁴ They found that cooling rates from 10^7 to 10^{11} K/s produced LDA with only minor differences observed in its structure and its subsequent transformation to HDA upon compression.

The structural relaxation observed in the pulsed heating simulations³¹ provides additional evidence that the experimental HQW retains a significant amount of the high-temperature structural motif. Experimentally, the relaxation of HQW toward the steady state structure at a lower T_{max} could be described by a stretched exponential function.¹⁴ The stretching exponent, β , is a measure of how much the relaxation deviates from simple exponential relax-

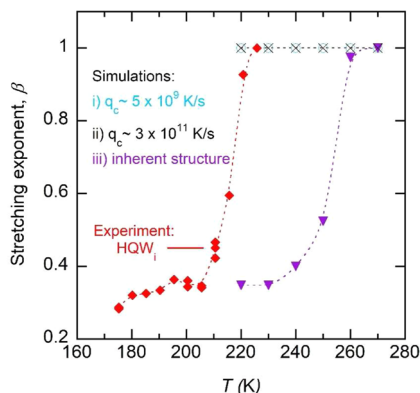


FIG. 7. Stretching exponent, β , for structural relaxation in transiently heated HQW water films¹⁴ and molecular dynamics simulations with TIP4P/ice.³¹ For simulations where the initial water structures are $\sim 100\%$ LDA (cyan circles, $q_c \sim 5 \times 10^9$ K/s) or primarily LDA (black x's, $q_c \sim 3 \times 10^{11}$ K/s), simple exponential relaxation, $\beta = 1$, toward the new equilibrium configuration was predicted for all isothermal annealing temperatures. For isothermal simulations starting with the inherent structure (IS) of water at 350 K (purple triangles) and for pulsed heating experiments starting with HQW (red diamonds), stretched exponential relaxation was observed at low temperatures with a relatively abrupt transition to simple exponential relaxation at higher temperatures.

ation ($\beta = 1$), with smaller values corresponding to increasingly non-exponential relaxation. Experimentally, β was found to drop rapidly from ~ 1 for $T_{\max} > 225$ K to $\beta \sim 0.35$ for $T_{\max} < 210$ K (Fig. 7, red diamonds).¹⁴ In the study of de Almeida Ribeiro *et al.*, the relaxation of water that was held isothermally at various temperatures, T_{iso} , when starting with three different initial configurations was investigated.³¹ Those configurations were (i) water cooled from 300 to 100 K at $q_c \sim 5 \times 10^9$ K/s (Fig. 7, cyan circles), (ii) water cooled from T_{iso} to 100 K at $q_c \sim 3 \times 10^{11}$ K/s (Fig. 7, black x's), and (iii) water quenched instantaneously from 350 to 0 K (Fig. 7, purple triangles). For the first case, where the structure was essentially 100% LDA or the second case where it was primarily LDA, the relaxation was described by a simple exponential for all temperatures ($\beta = 1$). However, when starting with the inherent structure (IS) of water at 350 K [case (iii)], the stretching exponent, β , decreased significantly at lower temperatures. Thus, the simulations suggest that relaxation from a high-temperature structure to a lower temperature structure is complex (i.e., $\beta < 1$) for sufficiently low temperatures. In this context, the complex kinetics observed for HQW in the experiments suggest it has an appreciable amount of HTM and retains this upon cooling to 70 K where the IR spectra are acquired. Experiments investigating the dielectric relaxation in HDA and LDA ices also show that the dynamic heterogeneity in HDA is larger than in LDA.^{86–88}

The analysis presented here focuses on the structure of transiently heated water films after they reach “steady state” at $T_{\max}$, which in practice means that the IR spectra are no longer changing when more heat pulses are applied. The experiments do not allow us to directly assess the relationship between the steady state structure and water’s equilibrium structure at $T = T_{\max}$ (or the corresponding inherent structure). However, MD simulations suggest

that cooling water from above the melting point at a rate that is fast enough to prevent complete relaxation to LDA, such as what we observe for HQW, leads to nonequilibrium structures,⁸² and (ii) during repeat heating and cooling cycles, equilibrium structures are not accessed when only a few pulses are needed to reach steady state.³¹ Based on this, it is plausible that the structure of HQW does not correspond to any equilibrium temperature. On the other hand, for $T_{\max} \lesssim 225$ K, the characteristic number of pulses for the films to reach steady state is quickly increasing.¹⁴ As seen in Fig. 6 (blue circles), for temperatures below 225 K $f_{\text{HTM}}^{\text{SS}}(T_{\max})$ follows the apparent trend line for the x-ray data, while it deviates from the trend above this temperature.

IV. CONCLUSIONS

Previous experiments investigating the properties of transiently heated supercooled water showed that for a wide range of conditions, its structure was a linear combination of just two structures—LDA and HQW. Due to experimental limitations, the HQW was expected to be a mixture of both high- and low-temperature structural motifs. However, the amount of each local structural motif in HQW was unknown. Here, we analyzed the IR spectra of HQW and LDA to provide an estimate for the composition of HQW with respect to LDA and HTM. The IRAS spectra for nanoscale CI, LDA, and HQW films were used to determine the frequency-dependent complex index of refraction for these water polymorphs. The optical constants determined for CI and LDA agree well with previously reported results. The characteristics of the potential spectra for HTM, constructed from the spectra of LDA and HQW, suggested that HQW is most likely 50% or more HTM. The current results, along with existing x-ray data for normal and supercooled water, provide a consistent picture for the composition of liquid water at low pressures (≤ 1 bar) from 70 to 350 K.

SUPPLEMENTARY MATERIAL

The supplementary material contains the following: Figure S1 IRAS, showing the experimental and simulated spectrum and optical constants for crystalline ice; Figure S2, comparing the optical constants ($2nk$) for LDA with previous experiments; Figure S3, comparing $\text{Im}(\tilde{n})$ for CI, LDA, and HTM to calculated IR spectra for CI, LDA, and HDA; Figure S4, comparing $\text{Im}(\tilde{n})$ for CI, LDA, and HTM in the isolated OD-stretch region for 50 ML and 80 μm films; and Figure S5, presenting a schematic showing the expected effect of different cooling rates on the measurement of $f_{\text{HTM}}(T)$.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Loni Kringle: Conceptualization (supporting); Investigation (lead); Methodology (equal); Writing – review & editing (equal). **Bruce D. Kay:** Conceptualization (supporting); Methodology (equal); Writing – review & editing (equal). **Greg A. Kimmel:** Conceptualization (lead); Methodology (equal); Writing – original draft (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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