Temperature-Independent Nuclear Quantum Effects on the Structure of Water

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Nuclear quantum effects (NQEs) have a significant influence on the hydrogen bonds in water and aqueous solutions and have thus been the topic of extensive studies. However, the microscopic origin and the corresponding temperature dependence of NQEs have been elusive and still remain the subject of ongoing discussion. Previous x-ray scattering investigations indicate that NQEs on the structure of water exhibit significant temperature dependence [Phys. Rev. Lett. **94**, 047801 (2005)]. Here, by performing wide-angle x-ray scattering of H_2O and D_2O droplets at temperatures from 275 K down to 240 K, we determine the temperature dependence of NQEs on the structure of water down to the deeply supercooled regime. The data reveal that the magnitude of NQEs on the structure of water is temperature independent, as the structure factor of D_2O is similar to H_2O if the temperature is shifted by a constant 5 K, valid from ambient conditions to the deeply supercooled regime. Analysis of the accelerated growth of tetrahedral structures in supercooled H_2O and D_2O also shows similar behavior with a clear 5 K shift. The results indicate a constant compensation between NQEs delocalizing the proton in the librational motion away from the bond and in the OH stretch vibrational modes along the bond. This is consistent with the fact that only the vibrational ground state is populated at ambient and supercooled conditions.

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Understanding the quantum mechanical nature of molecular vibrations and how it affects the hydrogen bond (H bond) in water and aqueous solutions is essential since it can also affect the mechanism of many chemical and biological processes [1–4]. The difference in properties between H_2O and D_2O is often attributed to nuclear quantum effects (NQEs) since the amplitude of the vibrational wave functions depends on the mass of the involved nuclei and this amplitude has a particularly strong influence on the H-bonding nature. Accordingly, NQEs of water have been a topic of many studies [5–12], but its microscopic origin and the corresponding temperature dependence are not completely understood and still remain the subject of ongoing discussion.

Even though NQEs are important for both D_2O and H_2O and a difference between them thus is not reducible to the difference between a classical molecule and a quantum molecule, it provides a practical experimental way of studying NQEs. It is generally accepted that D_2O forms stronger hydrogen bonds than H_2O in the temperature range from the deeply supercooled regime to ambient conditions. This is based on the measured isotope effects in thermodynamic properties such as the melting point (273.15 and 276.97 K for H_2O and D_2O, respectively), temperature of maximum density (277.13 and 284.34 K for H_2O and D_2O, respectively), and a singular temperature of an apparent power law for some thermodynamic properties, such as the isothermal compressibility (228 and 233 K for H_2O and D_2O, respectively) [13,14]. These effects generally correspond to a shift of about 4–7 K in temperature depending on the property, but the trend can be inverted at very high temperatures. For example, the supercritical temperature of H_2O (647.10 K) is ~3 K higher than that of D_2O (643.85 K), indicating that D_2O exhibits weaker H bonds than H_2O in this temperature regime. The most recent and well-accepted interpretation of these observations is the so-called "competing model" [15,16]. Here, the NQEs result from an interplay between proton delocalization in the (1) librational motion and (2) in the O-H stretch vibrational motion along the H bond. The former will weaken H bonding through increased bending and distortions, whereas the latter strengthens the H bond. To validate the suggested model and completely understand the microscopic origin of NQEs in water, knowing the exact temperature dependence of NQEs is essential.

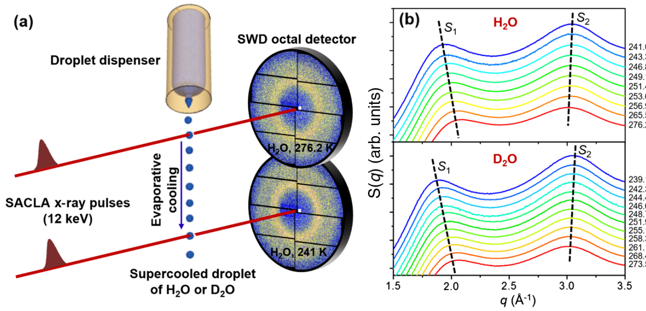

FIG. 1. (a) Schematic diagram of wide-angle x-ray scattering of supercooled H_2O and D_2O droplets under evaporative cooling condition. (b) Temperature-dependent scattering structure factor $S(q)$ of H_2O (top) and D_2O (bottom). Water temperature decreases from bottom to top, and the temperature of each $S(q)$ curve is indicated on the right-hand side. A constant offset has been introduced between the curves.

NQEs on the structure of water have been extensively studied both theoretically [17,18] and experimentally [19–23]. From the radial distribution functions (RDFs) extracted from scattering experiments, it is known that for a given temperature D_2O is more structured than H_2O, which is consistent with the conclusion suggested by the observed thermodynamic properties. In 1986, the structure factor difference between H_2O and D_2O was extracted by γ-ray scattering measurements at room temperature [21]. Based on the fact that (1) NQEs in thermodynamics commonly show $\sim$5 K shift in temperature and (2) the measured difference in the structure factor of H_2O and D_2O $[\Delta S_{\mathrm{H_2O\text{-}D_2O}}(q,T)]$ can be well explained by the temperature derivative of the structure factor $[\Delta S(q,T)/\Delta T]$ of water multiplied by a temperature difference of $\sim$5 K at room temperature, Root *et al.* suggested that the NQEs on the structure can also correspond to $\sim$5 K shift, which simply means that the structure of D_2O corresponds to that of H_2O at $\sim$5 K lower temperature. However, more systematic studies on the temperature dependence of NQEs on the structure of water ranging from 268 to 318 K were carried out by high-energy x-ray scattering measurements [19,20], and it was found that the magnitude of the structure factor difference increases by a factor of 3.5 as the temperature is decreased. Based on this result, it was claimed that the magnitude of NQEs is inversely proportional to the temperature. This observation would suggest that NQEs on the structure of water will be extremely enhanced in the deeply supercooled regime and could even lead to a shift as large as 30 K, contrary to the estimated temperature of the apparent power law fits in supercooled water, which show only a 5 K shift [13,14]. Therefore, to address this inconsistency, more experimental insights are needed.

Here, by performing wide-angle x-ray scattering of H_2O and D_2O droplets over the range from 275 to 240 K under evaporative cooling at an x-ray free-electron laser facility (SACLA) [24], we have investigated NQEs on the structure of water and the temperature dependence into the deeply supercooled regime and extended the previous x-ray scattering results over a broader temperature range. By analyzing the splitting of the two dominating $S(q)$ peaks, we can deduce the number of molecules in the second coordination shell centered at 4.5 Å, representing tetrahedrality [25], and observe an accelerated growth of tetrahedral structures with decreasing temperature. The offset in temperature between H_2O and D_2O is a constant 5 K over the whole temperature range.

The setup for wide-angle x-ray scattering measurements of supercooled H_2O and D_2O droplets under evaporative cooling is shown schematically in Fig. 1(a). The detailed experimental procedure and analysis are described in the Supplemental Material (SM) [26], and similar measurements have been conducted previously on H_2O [25,37]. Briefly, a continuous series of droplets with a uniform diameter of 20 μm were generated by a droplet dispenser under vacuum conditions. Since their temperature depends on the travel time in vacuum, various temperature points could be systematically measured by simply adjusting the distance between the dispenser and the measurement point. The temperature calibration [38,39] and error estimation of our temperature calibration method are described in detail in the SM [26] and in Ref. [25]. The estimated error is no more than 1 K down to 240 K for both H_2O and D_2O. The scattering patterns were generated by x-ray pulses with a photon energy of 12.1 keV provided by the BL3 beam line of the SACLA facility and were measured with an area detector. Background-subtracted and averaged water shots were angularly integrated into a 1D radial profile and converted into the scattering structure factor $S(q)$ by subtracting the contribution from the independent atomic scattering (see SM for details [26]).

The temperature-dependent scattering structure factor of H_2O (top) and D_2O (bottom) are shown in Fig. 1(b). Both H_2O and D_2O clearly show an increase of the splitting between the S_1 (located at around $q = 2$ Å^{-1}) and S_2 (located at around $q = 3$ Å^{-1}) peaks upon deep supercooling, which is a signature of the rapid growth of tetrahedral structures depending on the temperature [25].

To investigate the NQEs on the structure of water upon deep supercooling, the scattering structure factor $S(q)$ of H_2O (red) and D_2O (blue) at the same temperature ($\sim$249 K) are directly compared in Fig. 2(a). The main difference between them is the fact that D_2O has larger splitting (Δq) between the S_1 and S_2 peaks. As shown in the SM [26] and in previous work [25,37], this splitting can be used as a direct measure of the structural ordering of water since there is a clear monotonic correlation between the splitting and the area (A_2) of the second peak in the O-O RDF [see Fig. S5(b)]. The second peak in the O-O RDF corresponds to the second-nearest-neighbor distance in tetrahedral coordination ($\sim$4.5 Å). The larger splitting in D_2O indicates that the H bonding in D_2O is stronger than that in H_2O; therefore, D_2O is a more structurally ordered liquid than H_2O at the same supercooled temperature. This observation agrees well with the previous conclusions

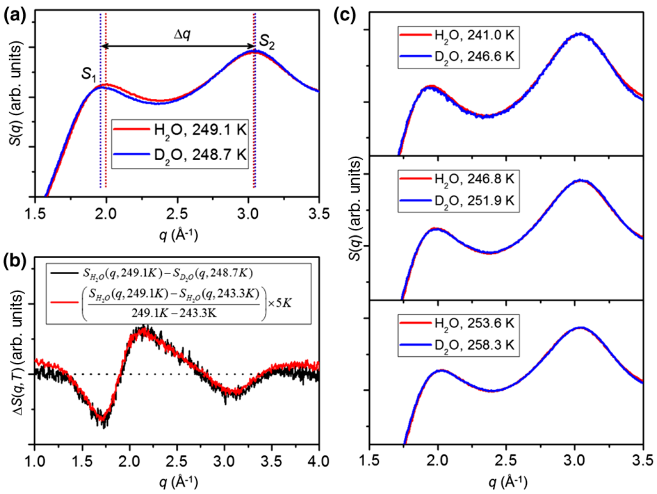

FIG. 2. (a) Scattering structure factor $S(q)$ of H_2O (red) and D_2O (blue) at the same temperature (~249 K). The vertical dotted lines indicate the positions of the S_1 and S_2 peaks. (b) The difference scattering curve $\Delta S_{H_2O\text{-}D_2O}(q,T)$, calculated by taking the difference between the $S(q)$ of H_2O and D_2O at the same temperature (~249 K, black), is compared with the temperature derivative $\Delta S/\Delta T$, calculated by taking the difference between the $S(q)$ of H_2O at two different temperatures (249.1 and 243.3 K, red). (c) Direct comparison of the scattering structure factor $S(q)$ between H_2O (red) and D_2O (blue) at three different temperature points. The ~5 K warmer temperatures for D_2O are selected to test the 5 K shift model (241.0 versus 246.6 K, 246.8 versus 251.9 K, and 253.6 versus 258.3 K are shown in the top, middle, and bottom panels, respectively).

given by structural measurements at room temperature [22] and inferred from observations regarding many thermodynamic properties.

For a more quantitative analysis of the temperature dependence of NQEs on the structure of water, we followed the same analysis scheme used in the previous x-ray scattering studies [19,20]. First, difference scattering curves $\Delta S_{H_2O\text{-}D_2O}(q,T)$ were calculated by taking the difference between $S(q)$ of H_2O and D_2O at the same temperature.

$\Delta S_{H_2O\text{-}D_2O}(q,T)$ at 249 K is shown in Fig. 2(b) (black) and $\Delta S_{H_2O\text{-}D_2O}(q,T)$ at 246.8, 251.4, and 265.5 K are shown in Fig. S3(a). The magnitude of $\Delta S_{H_2O\text{-}D_2O}(q,T)$ [$\overline{\Delta S}_{H_2O\text{-}D_2O}(T)$] was calculated by using Eqs. (S3) [26], and the values from our data (from 246.8 to 265.5 K) and the values from Fig. 4 of Ref. [20] (from 268 to 318 K) are shown in Figs. S3(b) and S3(c), respectively. The functional form $[A/(T-T_0)+B]$ was used to simultaneously fit the data shown in Figs. S3(b) and S3(c), and it gives very good agreement. This indicates that $\overline{\Delta S}_{H_2O\text{-}D_2O}(T)$ is inversely proportional to the temperature also upon deep supercooling, as suggested by previous x-ray scattering studies [19,20].

As explained in the introduction, it is known that NQEs of water in $S(q)$ are analogous to a temperature effect. For example, $\Delta S_{H_2O\text{-}D_2O}(q,T)$ between H_2O and D_2O at room temperature can be explained by the temperature derivative of water $[\Delta S(q)/\Delta T]$ times ~5 K [21,23]. To check that this relationship is still valid upon deep supercooling, we compared $\Delta S_{H_2O\text{-}D_2O}(q,T)$ at ~249 K with the temperature derivative calculated by taking the difference between $S(q)$ of H_2O at two different temperatures ($T_2 = 249.1$ K and $T_1 = 243.3$ K) as follows:

$$\Delta S_{H_2O\text{-}D_2O}(q,T_2) = \frac{S_{H_2O}(q,T_2) - S_{H_2O}(q,T_1)}{T_2 - T_1}\Delta T. \qquad (1)$$

ΔT directly corresponds to the magnitude of NQEs in terms of the temperature shift, and was determined to be 5 K. As shown in Fig. 2(b), the two curves are nearly identical, indicating that NQEs on the structure of water at 249 K can be well explained by a 5 K shift in temperature.

Since NQEs on the structure of water at room temperature and at 249 K commonly correspond to a 5 K shift in temperature, we could assume that the constant 5 K shift explains the temperature-dependent NQEs ranging from the deeply supercooled regime to ambient conditions in general. To verify this common 5 K shift model, we directly compared the scattering structure factor $S(q)$ of H_2O (red) and D_2O (blue) at three different temperatures, as shown in Fig. 2(c). In that comparison, ~5 K warmer temperature points for D_2O were selected. As a result, 241.0 versus 246.6 K, 246.8 versus 251.9 K, and 253.6 versus 258.3 K for H_2O versus D_2O are shown in the top, middle, and bottom panels of Fig. 2(c), respectively. All three cases show very good agreement, indicating that the common 5 K shift model is valid regardless of temperature in the supercooled regime, and there is thus no $1/T$ dependence in the NQEs on the structure of water. This is contrary to the conclusion suggested by previous x-ray scattering studies [19,20], even though $\overline{\Delta S}_{H_2O\text{-}D_2O}(T)$ calculated both from our data and their data has clear $1/T$ dependence. This observation raises the following question: if the magnitude of NQEs is constant over a wide temperature range, what is then the origin of the major temperature-dependent enhancement of $\Delta S_{H_2O\text{-}D_2O}(q,T)$ shown in Fig. S3?

The idea that for water the NQEs on $S(q)$ can be described as a temperature effect can be written as

$$\Delta S_{H_2O\text{-}D_2O}(q,T) = \left[\frac{\partial S_{H_2O}(q,T)}{\partial T}\right]_P \Delta T, \qquad (2)$$

where $[\partial S_{H_2O}(q,T)/\partial T]_P$ is the isobaric temperature derivative (ITD) and ΔT is the amount of temperature shift needed to explain NQEs on $S(q)$ as a temperature effect. Here, we used isobaric temperature derivative since our measurement was done under constant pressure [25]. While the second term on the right-hand side of Eq. (2), ΔT, directly represents the magnitude of NQEs on the structure of water, the first term, ITD, is purely a property of water. When the previous x-ray scattering studies were performed, it was generally thought that the ITD is invariant in terms of temperature [40,41], and therefore, the enhancement of $\Delta S_{H_2O\text{-}D_2O}(q,T)$ was attributed to an enhancement of the magnitude of NQEs as measured by ΔT (3.6 K shift at 318 K and 7.1 K shift at 279 K) [19]. However, as clearly shown in Fig. 2 and in the studies at room temperature, the magnitude of NQEs, ΔT, is $\sim$5 K and independent of temperature even though $\overline{\Delta S}_{\mathrm{H_2O\text{-}D_2O}}(T)$ is greatly enhanced. This naturally leaves us only one possible explanation: ITD should have $1/T$ dependence and must be the cause of the enhancement in $\Delta S_{\mathrm{H_2O\text{-}D_2O}}(q,T)$. This is actually not a surprising conclusion because the ITD signal comes from the increased splitting between the S_1 and S_2 peaks, as shown in Fig. 1(b), and we have already shown in previous studies that the splitting, which reflects the degree of tetrahedrality in the liquid, is accelerated when the temperature is decreased [25,37].

To verify this conclusion, we calculated the ITD at various temperatures by using the temperature-dependent $S(q)$ curves of water shown in Fig. 1(b). The ITD at the temperature point T_i was calculated through

$$\left[\frac{\partial S_{\mathrm{H_2O}}(q,T)}{\partial T}\right]_P = \frac{1}{2}\left(\frac{S(q,T_{i+1})-S(q,T_i)}{T_{i+1}-T_i}+\frac{S(q,T_i)-S(q,T_{i-1})}{T_i-T_{i-1}}\right), \quad (3)$$

and it was summed into a single value as

$$\overline{\mathrm{ITD}} = \left(\sum_{q=1.5}^{3.5}\left|\left[\frac{\partial S_{\mathrm{H_2O}}(q,T)}{\partial T}\right]_P\right|\right)/N. \quad (4)$$

Figure 3(a) shows the ITD of H_2O at three different temperatures: 243.3, 253.6, and 265.5 K. The magnitude of the ITD ($\overline{\mathrm{ITD}}$) was calculated by using Eq. (4) and plotted as a function of temperature in Fig. 3(b) (red squares). As seen in both Figs. 3(a) and 3(b), $\overline{\mathrm{ITD}}$ is greatly enhanced when the temperature is decreased, and the entire trend is very similar to the temperature-dependent behavior of $\Delta S_{\mathrm{H_2O\text{-}D_2O}}(q,T)$ shown in Fig. S3. This observation indicates that the temperature-dependent enhancement of the ITD, which is a property of water, is actually responsible for the temperature-dependent enhancement of $\Delta S_{\mathrm{H_2O\text{-}D_2O}}(q,T)$ while the magnitude of NQEs on the structure of water stays constant ($\sim$5 K). We also calculated the ITD and $\overline{\mathrm{ITD}}$ of D_2O [Fig. S4 and blue triangles in Fig. 3(b)], and it exhibits the same temperature dependence as that observed in H_2O if the data points from D_2O are shifted by 5 K in the graph. This further supports the common 5 K shift model for H_2O versus D_2O in the structure of water. A functional form of $[A/(T-T_0)+B]$ was used to jointly fit the data from H_2O and D_2O and gives good agreement.

A more intuitive picture of the H-bonding network can be achieved by connecting the measured q-space data to the real-space RDF. Since the q range of our experiment is limited, a direct Fourier transform and subsequent analysis of the difference RDF, $\Delta g_{\mathrm{H_2O\text{-}D_2O}}(r,T)$, are not possible. However, we can still investigate the tetrahedrality of H_2O and D_2O by converting the measured splitting (Δq) between the S_1 and S_2 peaks into the area (A_2) of the second peak

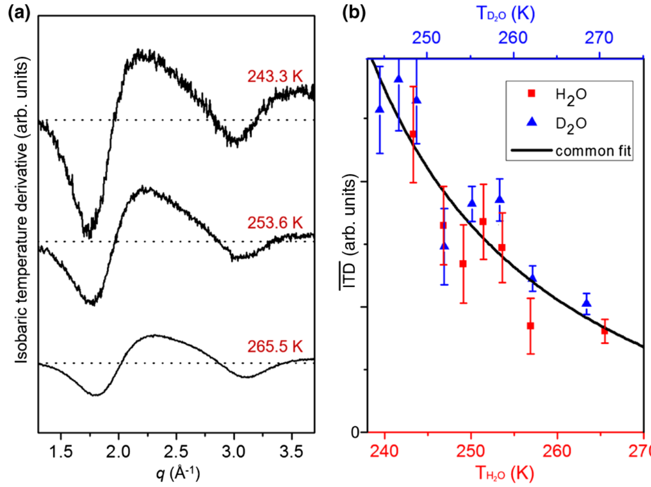

FIG. 3. (a) Isobaric temperature derivative $[\partial S_{H_2O}(q,T)/\partial T]_P$ of H_2O at three different temperatures (243.3, 253.6, and 265.5 K). (b) To obtain a q-independent measure of the variation in the magnitude of the ITD of H_2O (red squares) and D_2O (blue triangles) with temperature, the ITD for different q values are summed into single values and plotted as a function of temperature. The data points from D_2O are shifted by 5 K in the graph, and the temperature for D_2O is indicated at the top axis. The temperature-dependent magnitude of the ITD of H_2O and D_2O is indicated by the common fit (black solid line) that has a functional form of $[A/(T-T_0)+B]$.

in the O-O RDF [25,37]. This measures the degree of tetrahedral coordination since this peak ($\sim$4.5 Å) is related to the second-nearest-neighbor distance in tetrahedral coordination, as shown in Fig. S5 (see SM for details) [26]. The temperature-dependent A_2 values of H_2O (squares) and D_2O (triangles) are shown in Fig. S6. As expected from previous studies [25,37], a large enhancement of the A_2 value occurs as H_2O and D_2O are cooled down to the deeply supercooled regime, indicating the accelerated growth of tetrahedral structures. It is also shown that D_2O has a more tetrahedral character than H_2O at the same temperature, which is consistent with previous observations [19–23]. The difference in A_2 between H_2O and D_2O looks diverging, but it is simply due to the accelerated behavior of the A_2 value (property of water) [25,37]. The least-squares fit to the H_2O data with a functional form of $[A/(T-T_0)+B]$ (red solid line) and its 5 K shifted curve (blue solid line) are shown together in Fig. S6. The 5 K shifted curve explains the D_2O data very well without any other adjustment, and this further supports the common 5 K shift model for NQEs on the structure of water.

Our experimental results regarding the common 5 K shift model account for the results of previous studies on the NQEs on thermodynamic properties even though the exact value of the temperature shift varies between 4 and 7 K depending on the properties. For example, the melting temperature (3.82 K shift) and the temperature of density maximum (7.21 K shift) around ambient condition, singular temperature (5 K shift) in the deeply supercooled regime

[13,14], and the phase transition between ice XI and ice Ih (4 K shift) at around 75 K [42] commonly correspond to ~5 K shift. Temperature-dependent NQEs on thermodynamics, such as molar density and isothermal compressibility, are shown in Figs. S7(a) and S7(b), respectively [26]. It is shown that H_2O and D_2O exhibit the same temperature dependence if the data points from D_2O are shifted in the graph by 6 K, which is consistent with our observations.

For simple liquids we can potentially expect the NQE to be connected to the thermal de Broglie wavelength and thereby increase with decreasing temperature [26]. The observation here that NQE is independent of temperature is related to the fact that in liquid water the anomalous collective fluctuations [43] into tetrahedral structures dominate over simple thermally induced random fluctuations when it comes to the structural change. The NQE is reflected in differences in the ability of the water molecules to form strong hydrogen bonds in the tetrahedral structures, and this property is temperature independent. Since many other water properties, such as molar density and compressibility, are also related to anomalous fluctuations, the NQEs on these also become independent of temperature.

The constant shift indicates that the competition between librational and OH stretch vibrations is constant over the current temperature range. This means that both vibrations are populated only in the ground state. This is consistent with an energy analysis since the kT value at room temperature (~2.4 kJ/mol) is still much lower than the transition energy of the librational modes (~8.2 kJ/mol for H_2O and ~6.0 kJ/mol for D_2O) and the O-H stretch vibration (~40.7 kJ/mol for H_2O and ~30.0 kJ/mol for D_2O) of water. We expect, at higher temperature, when kT comes closer to the energy to excite the libration mode, the balance between the two competing effects will be changed and, therefore, the temperature dependence will become different.

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