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 H2O and D2O droplets at temperatures from 257 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 D2O is similar to H2O 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 H2O and D2O 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 H2O and D2O 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 D2O and H2O and a difference between them 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 D2O forms stronger hydrogen bonds than H2O 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 H2O and D2O, respectively), temperature of maximum density (277.13 and 284.34 K for H2O and D2O, respectively), and a singular temperature of an apparent power law for some thermodynamic properties, such as the isothermal compressibility (228 and 233 K for H2O and D2O, 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 H2O (647.10 K) is ∼3 K higher than that of D2O (643.85 K), indicating that D2O exhibits weaker H bonds than H2O 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.
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$_2$O is more structured than H$_2$O, which is consistent with the conclusion suggested by the observed thermodynamic properties. In 1986, the structure factor difference between H$_2$O and D$_2$O was extracted by γ-ray scattering measurements at room temperature [21]. Based on the fact that (1) NQEs in thermodynamics commonly show ∼ 5 K shift in temperature and (2) the measured difference in the structure factor of H$_2$O and D$_2$O [ΔS$_{H_2O,D_2O}(q, T)$] can be well explained by the temperature derivative of the structure factor [ΔS(q, T)/ΔT] of water multiplied by a temperature difference of ∼ 5 K at room temperature, Root et al. suggested that the NQEs on the structure can also correspond to ∼ 5 K shift, which simply means that the structure of D$_2$O corresponds to that of H$_2$O at ∼ 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 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$_2$O and D$_2$O is a constant 5 K over the whole temperature range.

The setup for wide-angle x-ray scattering measurements of supercooled H$_2$O and D$_2$O 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$_2$O [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$_2$O and D$_2$O. 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 S(q) of H$_2$O (top) and D$_2$O (bottom) are shown in Fig. 1(b). Both H$_2$O and D$_2$O 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$_2$O (red) and D$_2$O (blue) at the same temperature (∼ 249 K) are directly compared in Fig. 2(a). The main difference between them is the fact that D$_2$O 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 (∼ 4.5 Å). The larger splitting in D$_2$O indicates that the H bonding in D$_2$O is stronger than that in H$_2$O; therefore, D$_2$O is a more structurally ordered liquid than H$_2$O at the same supercooled temperature. This observation agrees well with the previous conclusions.

FIG. 1. (a) Schematic diagram of wide-angle x-ray scattering of supercooled H$_2$O and D$_2$O droplets under evaporative cooling condition. (b) Temperature-dependent scattering structure factor S(q) of H$_2$O (top) and D$_2$O (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.
supercooling, as suggested by previous x-ray scattering studies. The values from our data (from 246.8 to 265.5 K) and the structural measurements at room temperature [22] indicate the positions of the $S_1$ and $S_2$ peaks. (b) The difference scattering curve $\Delta S_{H,O-D,2O}(q, T)$ calculated by taking the difference between the $S(q)$ of $H_2O$ and $D_2O$ at the same temperature (249 K), 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 $\Delta S_{H,O-D,2O}(q, T)$ were calculated by taking the difference between $S(q)$ of $H_2O$ and $D_2O$ at the same temperature.

$\Delta S_{H,O-D,2O}(q, T)$ at 249 K is shown in Fig. 2(b) (black) and $\Delta S_{H,O-D,2O}(q, T)$ at 246.8, 251.4, and 265.5 K are shown in Fig. S3(a). The magnitude of $\Delta S_{H,O-D,2O}(q, T)$ [$\Delta S_{H,O-D,2O}(T)$] 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 $\Delta S_{H,O-D,2O}(T)$ 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, $\Delta S_{H,O-D,2O}(q, T)$ 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 $\Delta S_{H,O-D,2O}(q, T)$ 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:

$$\Delta S_{H,O-D,2O}(q, T_2) = \frac{S_{H,O}(q, T_2) - S_{H,O}(q, T_1)}{T_2 - T_1} \Delta T.$$  \hspace{1cm} (1)

$\Delta T$ 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 $\Delta S_{H,O-D,2O}(T)$ 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 $\Delta S_{H,O-D,2O}(q, T)$ 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

$$\Delta S_{H,O-D,2O}(q, T) = \left[\frac{\partial S_{H,O}(q, T)}{\partial T}\right]_\rho \Delta T,$$ \hspace{1cm} (2)

where $[\partial S_{H,O}(q, T)/\partial T]_\rho$ is the isobaric temperature derivative. ITD and $\Delta T$ 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), $\Delta T$, 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 $\Delta S_{H,O-D,2O}(q, T)$ was attributed to an enhancement of the magnitude of NQEs
as measured by $\Delta T$ (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, $\Delta T$, is $\sim 5$ K and independent of temperature even though $\Delta S_{H_2O:D_2O}(T)$ 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 $\Delta S_{H_2O:D_2O}(q,T)$. 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

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

(3)

and it was summed into a single value as

$$\text{ITD} = \frac{1}{N} \sum _{q=1.5}^{3.5} \left| \left[ \frac{\partial S_{H_2O}(q,T)}{\partial T} \right]_p \right| .$$  

(4)

Figure 3(a) shows the ITD of H$_2$O at three different temperatures: 243.3, 253.6, and 265.5 K. The magnitude of the ITD (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), ITD is greatly enhanced when the temperature is decreased, and the entire trend is very similar to the temperature-dependent behavior of $\Delta S_{H_2O:D_2O}(q,T)$ 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 $\Delta S_{H_2O:D_2O}(q,T)$ while the magnitude of NQEs on the structure of water stays constant ($\sim 5$ K). We also calculated the ITD and ITD of D$_2$O [Fig. S4 and blue triangles in Fig. 3(b)], and it exhibits the same temperature dependence as that observed in H$_2$O if the data points from D$_2$O are shifted by 5 K in the graph. This further supports the common 5 K shift model for H$_2$O versus D$_2$O in the structure of water. A functional form of $[A/(T-T_0) + B]$ was used to jointly fit the data from H$_2$O and D$_2$O 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, $\Delta q_{H_2O:D_2O}(r,T)$, are not possible. However, we can still investigate the tetrahedrality of H$_2$O and D$_2$O by converting the measured splitting ($\Delta q$) between the $S_1$ and $S_2$ peaks into the area ($A_2$) of the second peak 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$_2$O (squares) and D$_2$O (triangles) are shown in Fig. S6. As expected from previous studies [25,37], a large enhancement of the $A_2$ value occurs as H$_2$O and D$_2$O are cooled down to the deeply supercooled regime, indicating the accelerated growth of tetrahedral structures. It is also shown that D$_2$O has a more tetrahedral character than H$_2$O at the same temperature, which is consistent with previous observations [19–23]. The difference in $A_2$ between H$_2$O and D$_2$O 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$_2$O 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$_2$O 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.
and the phase transition between ice XI and ice Ih (4 K shift) at around 75 K [42] commonly correspond to \(\sim 5\) 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 \(\text{H}_2\text{O}\) and \(\text{D}_2\text{O}\) exhibit the same temperature dependence if the data points from \(\text{D}_2\text{O}\) 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 (\(\sim 2.4\) kJ/mol) is still much lower than the transition energy of the librational modes (\(\sim 8.2\) kJ/mol for \(\text{H}_2\text{O}\) and \(\sim 6.0\) kJ/mol for \(\text{D}_2\text{O}\)) and the O-H stretch vibration (\(\sim 40.7\) kJ/mol for \(\text{H}_2\text{O}\) and \(\sim 30.0\) kJ/mol for \(\text{D}_2\text{O}\)) 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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