Isotope Quantum Effects on the Water Proton Mean Kinetic Energy

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A deep inelastic neutron scattering experiment, performed on D_2O in the stable and metastable liquid phases, provides evidence for isotope quantum effects in the proton or deuteron single particle dynamics along the hydrogen bond. The deuteron mean kinetic energy extracted from the experimental data in the metastable supercooled phase ($T = 276.15$ K) exceeds the zero point energy and scales as $\sqrt{2}$ with that of protons in supercooled light water, at $T = 269.15$ K. The present data support the suggestion that even small changes in the short range environment of a deuteron or proton have a strong influence on its quantum behavior.

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Nuclear quantum effects impact upon several aspects of the behavior of water, such as, for instance, its melting point[1] and microscopic structure [2]. In particular, the lower melting point of H_2O with respect to D_2O can be rationalized in terms of a less stable H-bond network, due to increased quantum tunneling and/or distortions from tetrahedrality, as discussed in Ref. [2]. Evidence for delocalization of the proton along the H-bond in low temperature light water has indeed been shown in two recent deep inelastic neutron scattering (DINS) experiments, [3,4] probing the momentum distribution of protons, $n(p)$, and their mean kinetic energy, $\langle E_k \rangle$. Quantum effects on these two quantities are sensible and show an intriguing temperature dependence, which has not yet been reproduced by computer simulations[5,6] or fully explained by theoretical models [7]. In particular, just below ambient temperature the proton mean kinetic energy increases towards a first maximum at 277 K, with a temperature dependence that is similar to that of the bulk water density. Upon further cooling into the metastable phase, $\langle E_k \rangle$ abruptly increases reaching a second large maximum between 269 and 271 K.

It has been suggested [4] that the excess of mean kinetic energy above and below the melting temperature may have different origins. In particular, the energy excess in the stable liquid phase manifests a clear correlation with the bulk water density, as already observed in He [8,9]. This correlation disappears below the melting point, where the second and larger maximum is found, while in this temperature range the bulk water density monotonically decreases. Moreover, only in the supercooled phase, the energy excess does couple with clear evidence for proton delocalization, as shown by the presence of a secondary maximum in the proton momentum distribution [10–12]. Interestingly it has been suggested that the presence of proton delocalization may be favored by a closer average distance between two water oxygens sharing a proton along the H-bond [3], which changes the potential landscape and proton wave function [13,14].

In this Letter we report a study of the isotope effect on the proton mean kinetic energy and momentum distribution. In the present study we compare the results of a DINS experiment on D_2O at two temperatures with results obtained on H_2O in the stable and metastable phase, respectively.

The experiment has been performed at the VESUVIO spectrometer [15], installed at the ISIS spallation neutron source (UK) [16]. This instrument gives access to energy transfers in the 1–50 eV region and momentum transfers between 30 and 200 Å^{-1}, enabling the neutron scattering events to be described within the impulse approximation, in which the target particle recoils as a free particle and the dynamic structure factor can be written as the radon transform of $n(\vec{p})$:

$$S(\vec{q}, \omega) = \int n(\vec{p}) \delta\left(\omega - \frac{\hbar q^2}{2M} - \vec{q} \cdot \frac{\vec{p}}{M}\right) d\vec{p} \qquad (1)$$

where $\hbar\omega$ and $\hbar\vec{q}$ are the transferred energy and momentum, respectively, and M the mass of the target particle. For isotropic samples, as those of interest here, the momentum distribution depends only on the modulus of $\vec{p}$ and can be expanded into a series of Laguerre polynomials, $L_n^{1/2}(\frac{p^2}{2\sigma^2})$:

$$n(p) = \frac{e^{-(p^2/2\sigma^2)}}{(\sqrt{2\pi}\sigma)^3} \left[1 + \sum_{n=2}^{\infty} a_n (-1)^n L_n^{1/2}\left(\frac{p^2}{2\sigma^2}\right)\right] \qquad (2)$$

where σ is proportional to the mean kinetic energy, $\langle E_k \rangle = \frac{3\hbar^2}{M}\sigma^2$. The non-Gaussian coefficients a_n are calculated, according to Refs. [10,17], by least squares fitting of the data expressed as $J(y) = \frac{\hbar q}{M} S(q, \omega)$, that is the so-called neutron-Compton profile, with $y = \frac{M}{\hbar q}\omega - \frac{\hbar q^2}{2M}$ being the West scaling variable. Further details about data analysis and treatment of small systematic effects due to final state distribution can be found in previous literature [10,15,17].

The sample, 99.994% D_2O from Sigma Aldrich, was contained in the same disk-shaped aluminum can (5 cm diameter, 1 mm thickness) with inner Teflon coating as used for previous experiments on H_2O [3,4]. Data have been collected at $T = (292.15 \pm 0.10)$ K and $T = (276.15 \pm 0.10)$ K, in order to compare with data for H_2O at 285.15 and 269.15 K from previous experiments [3,4], by applying a constant 7 K shift, as for the density maximum of the two liquids. This thermal offset has been adopted in order to account for the differences in the PVT data of the two water isotopes [18], as done in a previous neutron diffraction study [19]. Alternative choices for the thermal offset could in principle be adopted. In particular, x-ray diffraction experiments revealed a temperature dependent isotopic effect on the structure of water [20], resulting in a thermal offset inversely proportional to temperature. Conversely, analysis of the isotope effect on the dynamical properties of water, performed with a careful *ab initio* simulation, did not display a significant temperature dependence [21]. Given the above situation along with the relatively narrow range of temperature investigated in the present study, we preferred to adopt the *standard* thermal offset based on the temperature difference between the density maxima.

The $J(y)$ for the deuteron, measured at 292.15 K, is shown in Fig. 1, along with its fit and residual, as an example of the quality of data and fit. The data statistics in these kinds of experiments are determined by the acquisition time and incoherent scattering cross section of the sample: the latter for heavy water is lower than for light water by a factor ~50 [22]. Thus, in order to obtain the same statistics at each temperature, a D_2O experiment would require a beam time allocation as long as ~50 times the beam time allocated to the H_2O experiment. This fact has several implications. First, even though DINS data on D_2O are not available in the literature, the beam time allocation for an experiment at VESUVIO covering the entire temperature range investigated for H_2O is very hard or impossible to obtain, and consequently only two temperature states have been chosen for the present study. Second, in a reasonable acquisition time, the statistical fluctuations of the D_2O data, will be necessarily higher compared to previous data on light water [3,4]. Consequently, we will be able to evaluate the deuteron mean kinetic energy with great accuracy, while being less sensitive to details of the Compton profile, compared to the case of H_2O. The fitting parameters at the two temperatures are reported in Table I and the deuteron mean kinetic energy is compared with that of protons at the corresponding temperature states in Fig. 2.

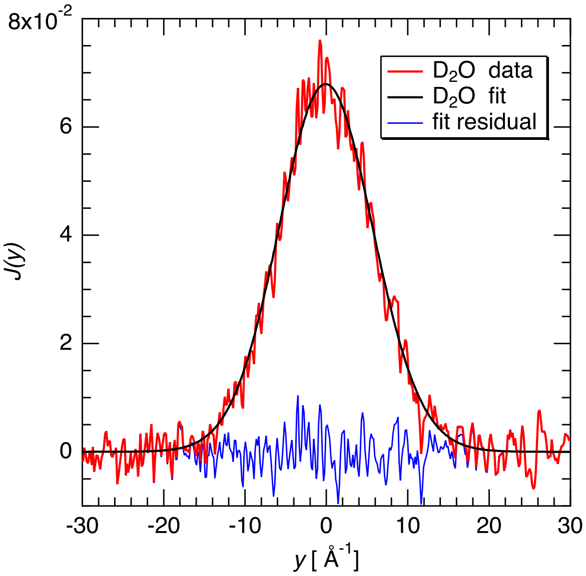

FIG. 1 (color online). The neutron-Compton profile measured at 292.15 K (red solid line), rebinned in the impulse approximation scaling variable y, compared with its series expansion fit (black solid line). The fit has been obtained by simultaneously fitting the data sets from the detectors showing the strongest D_2O signal (that is 22 detectors out of a total of 64 installed at VESUVIO), and including corrections for the instrumental resolution and final state distribution. The fit residual is reported in blue; the quality of the fit at 276.15 K is the same.

We notice that upon cooling, deuterons exhibit an excess of kinetic energy, compared to their zero point energy (ZPE) [23,24]. Although at the highest temperature investigated $\langle E_k \rangle$ is compatible with ZPE within 1 standard deviation, at 276.15 K the kinetic energy excess is well outside the statistical uncertainty. Thus an excess of mean kinetic energy is present also in supercooled D_2O, although it is less pronounced than in H_2O [3], as expected for a heavier mass. Unfortunately, the need for long data acquisition time has prevented collection of more data at different temperatures; thus, we cannot argue whether $\langle E_k \rangle$ of deuterons shows the same intriguing temperature behavior as for protons, although at both investigated temperatures the ratio of the kinetic energy scales by $\sqrt{2}$ within a confidence level of 95%, being equal to (1.51 ± 0.14) and (1.59 ± 0.11) at $T = 292.15$ K and $T = 276.15$ K, respectively.

Deviations of the mean kinetic energy from the ZPE value must have signatures in the shape of the momentum distribution. Since these are usually visible in the tails of the $n(p)$, it is usual to plot the radial proton or deuteron

TABLE I. Fitting parameters of the $J(y)$ function. All a_n coefficient, but a_2 are negligible.

T (K)	σ(Å^{-1})	$\langle E_k \rangle$ (meV)	a_2
292.15	5.83 ± 0.15	106.0 ± 5.3	0.034 ± 0.061
276.15	6.32 ± 0.11	125.0 ± 4.4	0.175 ± 0.043

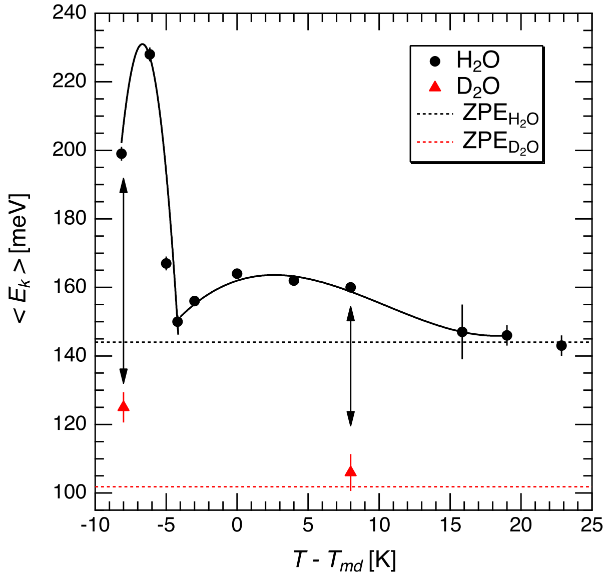

FIG. 2 (color online). The mean kinetic energy of protons (black circles), from Refs. [3,4], and that of deuterons (red triangles) from the present experiment, as a function of temperature distance from the point of maximum density, T-$T_{\rm md}$. The arrows join the pairs of data at the corresponding temperatures. The black and red dashed lines indicate the zero point energy level of H_2O [23] and D_2O [24], respectively. The black solid lines through the H_2O data are guides for the eye.

momentum distribution, $4\pi p^2 n(p)$, (see Fig. 3). In the case of protons [3], this function has a main peak at about 7 Å^{-1} and is slightly asymmetric with a tail extending towards high momentum transfer values, in the stable liquid phase. It develops, instead, a shoulder centered at about 17 Å^{-1} in the metastable supercooled phase: this shoulder is considered as evidence for quantum tunneling, or coherent delocalization of the protons over two sites of a double well potential [25–27], which has been suggested to be favored by a closer average distance between two oxygen sites along the H-bond [3]. In the case of deuterons no shoulder is visible at both investigated temperatures, although the tail of the lowest temperature radial momentum distribution is higher than that in the stable liquid phase. This may be due to the statistics of the present data, or rationalized in terms of the structural differences among light and heavy water. For instance at ambient conditions, the covalent OH bond length is 0.9724 Å and the H-bond length is 1.74 Å, giving an average OO distance of 2.71 Å, while for heavy water the covalent bond length is 0.9687 Å and the D-bond length is 1.81 Å, giving in total a longer average OO distance [2]. This may be the reason for smaller quantum effects in D_2O compared to H_2O. We notice also that the radial momentum distribution of deuterons has the maximum at higher p values, compared to that of protons (see Fig. 3), in agreement with the shorter OD bond [2].

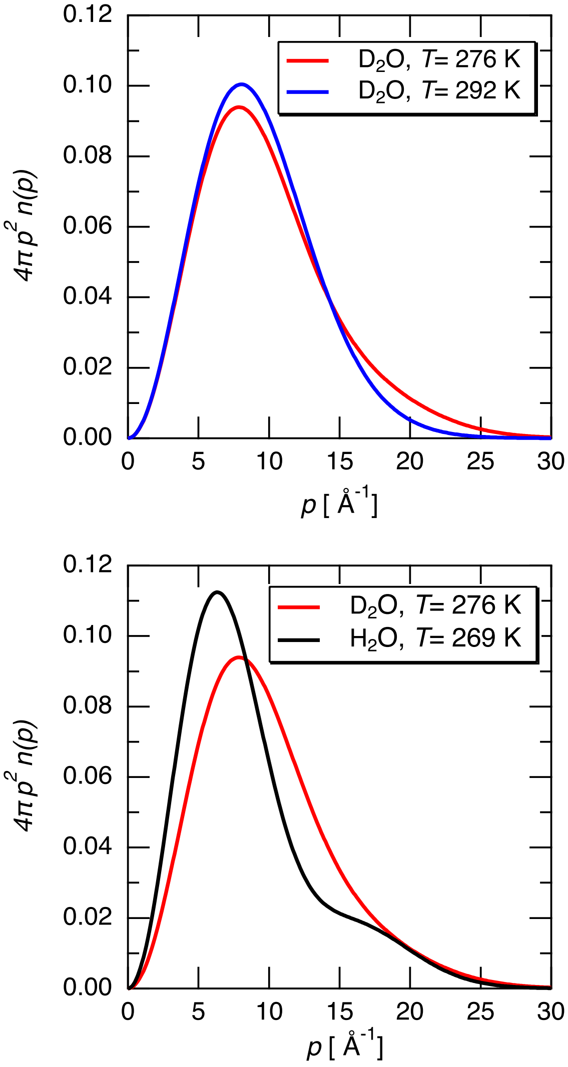

FIG. 3 (color online). Top panel: The radial momentum distribution of deuterons at $T = 292.15$ K (blue) and $T = 276.15$ K (red). Bottom panel: The radial momentum distribution of deuterons at $T = 276.15$ K (red) compared with that of protons at $T = 269.15$ K (black), according to the shift of 7 K of the temperature of maximum density.

In summary, by performing a DINS experiment on D_2O in the stable and supercooled liquid phases, we report evidence for quantum effects on the deuteron dynamics. The deuteron mean kinetic energy exceeds the ZPE in the supercooled phase by about 25 meV. As expected the energy excess is lower than in the case of supercooled light water, nevertheless we notice that at both temperatures investigated the ratio of the proton to deuteron mean kinetic energy is close to $\sqrt{2}$, thus confirming its vibrational character. The mean kinetic energy measured by DINS spectroscopy is indeed due to the motion of protons or deuterons along an intermolecular H-(D-)bond and is sensitive to the local environment experienced by protons or deuterons. Changes of this environment modify the energy landscape seen by these atoms and promote their coherent delocalization about two neighboring oxygens. Apparently the shortening of the oxygen-oxygen distance brought by supercooling in light water produces a huge increase of the proton mean kinetic energy and the development of a secondary maximum in the radial momentum distribution. Present data on heavy water show the expected isotopic effect on the mean kinetic energy and confirm the relevance of the average oxygen-oxygen distance in promoting quantum coherent motion of protons or deuterons. Even if a limited number of data set is presented, we believe that these results can be a timely stimulus for *ab initio* computer simulations and theoretical studies.

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