A combined INS and DINS study of proton quantum dynamics of ice and water across the triple point and in the supercritical phase

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Abstract

We report new results of a combined analysis of previous Inelastic Neutron Scattering (INS) and Deep Inelastic Neutron Scattering (DINS) experiments on ice at \( T = 271 \) K and water at \( T = 285 \) K and \( T = 673 \) K. Proton quantum dynamics is discussed in terms of the total mean kinetic energy, \( E_k \), and its three principal direction components, \( E_{k,x} \), \( E_{k,y} \), \( E_{k,z} \), (with \( x = x, y, z \)), the lineshape momentum distribution, \( n(p) \), and its harmonic lineshape components, \( n_h(p) \). The results show that the single proton dynamics is ground-state dominated and that \( E_{k,x}, E_{k,y}, \) and \( E_{k,z} \) consist mainly of weighted averages of a mix of bending and librational, librational and stretching mean kinetic energy components, respectively. The stretching component \( E_{k,z} \) is redshifted respect to its harmonic component due to additional network mode contributions and softening caused by anharmonicity. The \( n(p) \) lineshapes derived at the investigated temperature reflect the anisotropy and quasi-harmonic nature of proton motion in ice and water.

1. Introduction

Detailed description of the structure and dynamics of the hydrogen-bond network in water is essential to reach a thorough understanding of the unique properties of this liquid, necessary both for the evolution of life and its continuance. The water properties are brought about by the hydrogen bonded environment, in a picture where each molecule is involved in about four hydrogen bonds with strengths considerably less than covalent bonds but considerably greater than the natural thermal energy. Hydrogen bonds are roughly tetrahedrally arranged with the possibility that, when strongly formed, the local clustering expands and density decreases. Evidence of the particular uniqueness of liquid water is in its many physical and chemical properties which occur for instance when low density structuring naturally occurs at low and supercooled temperatures.

The dynamics of the proton that participates in hydrogen bonding is a subject of great interest and the quantum effects associated with protons have a significant impact on the behavior of hydrogen bond networks. Quantum effects influence the vibrational dynamics probed by Inelastic Neutron Scattering, i.e. the protons participating in H-bonds, as well as the static properties of ice and water, with the quantum behavior originating from zero-point motion. It has been recently suggested that a detailed description of the strength of the hydrogen bond is a prerequisite to elucidate the influence of quantum nuclear effects on the hydrogen bonding [1]. The picture proposed is that this effect arises from a competition between anharmonic quantum fluctuations of intermolecular bond bending and intramolecular covalent bond stretching, where the latter fluctuations tend to strengthen H-bonds whereas the former to weaken H-bonds. Quantum effects, such as those associated with the breaking and distortion of hydrogen bonds are uniquely revealed by using Deep Inelastic Neutron Scattering (DINS), also called Neutron Compton Scattering (NCS) [3–5], measuring the proton momentum distributions, \( n(p) \), and mean kinetic energy, \( E_k \). In parallel novel simulation techniques have been also employed to calculate the \( n(p) \), using state of the art open path integral simulations [6,7] implemented with first principles molecular dynamics [8] within the Path Integral Car–Parrinello Molecular Dynamics (PICPMD) framework [9]. These theoretical calculations have been able to successfully reproduce the hydrogen momentum distribution in ice Ih [10]. However none of the existing electrostatic models, treating the intermolecular potential as unchanged by hydrogen bonding, are accurate enough to fully reproduce the experimentally determined \( n(p) \) and \( E_k \) of Ref. [11,12] as well as DINS results from metastable water as those shown in Ref. [13,14], and they are still awaiting a proper theoretical description. Over all in recent years several are the DINS and PICPMD investigations devoted to study both physical quantities in ice and water in a wide temperature range \( 269 < T < 673 \) K [3,7,10,13–22]. In the experimental studies one makes use of...
incident neutrons in the range 1–100 eV, and scattered wavevectors in the range of 20 Å⁻¹ < q < 250 Å⁻¹ to measure the n(p) line-shape of light and heavy ions [23,24]. The n(p), the diffraction pattern of the proton wave function, in nearly all cases is determined by the ground vibrational state of the protons. Hence it provides a unique probe of the effective potential the proton experiences in its local environment [3].

Inelastic Neutron Scattering (INS), currently used to determine the vibrational spectra of hydrogen bonded systems, is a technique which provides rather comprehensive, quantitative and more direct information on the vibrational spectrum through the measurement of the dynamical structure factor. The latter quantity is directly related to the density of vibrational states, weighted by the squared amplitudes of the atomic oscillations [25–27]. Hence using INS one can measure not only translational, librational and intra-molecular excitations energies but also spectral intensities. In this paper we will show that INS experiments at high incident energies and low momentum transfer can be also used to obtain additional and complementary information to DINS on the quantum nature of n(p) and (Ek).

Values of proton mean kinetic energy and momentum distributions can also be calculated using empirical models. In the latter case the frequencies of a set of decoupled quantum harmonic oscillators are derived from optical data and hydrogen projected vibrational neutron spectra, under the assumptions of decoupling between translational, rotational and vibrational degrees of freedom. This procedure has been already employed in solid and liquid H₂S [28] and in supercritical water [29]. In the harmonic calculations the average number of excited phonons, at the given temperature, determines the contribution of each harmonic oscillator to the (Ek).

This paper reports a study of the proton single particle dynamics in ice at T = 271 K and water at T = 285 K and T = 673 K performed by a combined and additional analysis of DINS and INS data from Refs [14,10,2]. Section 2 describes the experiments and data analysis, Section 3 presents and discusses results of the study and conclusions.

2. INS and DINS experiments and data analysis

Recent DINS and INS experiments on ice and liquid water have been performed on the VESUVIO spectrometer at the ISIS spallation neutron source (UK) [4] on an attosecond time scale (i.e. 10⁻¹⁵ s – 10⁻¹⁶ s) – at T = 271 K [10], T = 285 K [14] and T = 673 K [22] – and on the time-of-flight neutron Chopper spectrometer SEQUOIA at the Spallation Neutron Source (SNS) – at T = 271 K and T = 285 K [2] – using an incident neutron energy of the chopper of Eₙ = 600 meV, respectively. Full details of the experimental set up to both measurements can be found in Ref. [14,10,22,2].

The n(p) line-shapes for this set of DINS data have been fitted using the spherical average of an anisotropic Gaussian distribution [10]:

\[ n(p) = \frac{1}{\sqrt{8\pi^3}} \sigma_x \sigma_y \sigma_z \exp \left( -\frac{p_x^2}{2\sigma_x^2} - \frac{p_y^2}{2\sigma_y^2} - \frac{p_z^2}{2\sigma_z^2} \right) \]

with \( \langle A(p) \rangle \) being the solid angular average of A.

Using this equation for each temperature three variances \( \sigma_x^2 \) (with \( x = x, y, z \)) have been obtained fitting the n(p) line-shapes of DINS data from Ref. [14,10,22]. These variances can then be related to three components of the mean kinetic energy, \( (E_k)_x \), or to the three effective principal frequencies, \( \omega_x \), through the following expression [10]:

\[ h^2 \sigma_x^2 = (E_k)_x = \frac{h\omega_x}{4} \coth \left( \frac{h\omega_x}{2K_B T} \right) \]

Table 1 reports values of \( (E_k)_x \), total mean kinetic energy \( (E_k) \) and \( \omega_x \) for ice and water derived from Eq. (1) and Eq. (2). For T = 673 K we also report the total mean kinetic energy values obtained in Refs. [15,22], by expressing the n(p) in terms of the generalized Laguerre polynomials. At T = 673 K values of \( \omega_x \) from Ref. [17] are also listed. These effective frequencies agree, within the statistical accuracy, with those obtained in this work. We stress that the algorithm developed in the present analysis makes use of a finer angular mesh than that used in Ref. [17], which reduces the uncertainties due to the correlation matrix and thus the uncertainties of the individual \( \omega_x \).

As far as the INS data are concerned, the corrected one-phonon incoherent dynamical structure factor, \( S_{\text{inc}}(h\omega,0) \) from Ref. [2] are reported in Fig. 1 for ice, at T = 271 K, and for water, at T = 285 K. These functions can be expressed in terms of the energy and wave-vector transfer, \( E = h\omega \) and \( q = k_I - k_f \), with \( k_I \) and \( k_f \) being the final and incident neutron wavevectors, to yield the \( S_{\text{inc}}(q, E) \) functions. By performing extrapolations of \( S_{\text{inc}}(q,E) \) functions at fixed E values for q → 0 one obtains, within the harmonic approximation, the hydrogen projected density of states \( g_{\text{exp}}(E) \) using the relation [25]:

\[ g_{\text{exp}}(E) = \lim_{q \to 0} \frac{S_{\text{inc}}(q,E)}{q^2} = \frac{2ME}{\pi |E|} e^{2W(q)/|E|} \]

with M being the proton mass, n(E) the Bose population factor. Full details of this procedure are described in previous papers [25,2]. From the OH stretching components of the hydrogen projected density of states, \( g_{\text{exp}}(E)_{\text{OH}} \), as calculated in Ref. [2], one can derive the proton mean kinetic energy for the OH stretching:

\[ (E_k)_{\text{OH}} = \frac{3}{4} \int_{355}^{480} g_{\text{exp}}(E)_{\text{OH}} \frac{dE}{d\Omega} = \frac{3h^2}{2M} \sigma_{\text{OH}}^2 \]

\( (E_k)_{\text{OH}} \) values for ice at T = 271 K and water at T = 285 K from Eq. (4) are reported in Table 2. For liquid water at T = 673 K the \( (E_k)_{\text{OH}} \) value has been derived using the \( g_{\text{exp}}(E)_{\text{OH}} \) line-shape from Fig. 4 of INS data of Ref [30]. The value, \( (E_k)_{\text{OH}} = 115 \pm 5 \), is also reported in Table 2.

From INS vibrational spectra an independent set of effective principal frequencies \( \omega_x \) can also be calculated as follows. Within

<table>
<thead>
<tr>
<th>T [K]</th>
<th>( (E_k)_x ) [meV]</th>
<th>( (E_k) ) [meV]</th>
<th>( \omega_x ) [meV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice</td>
<td>144 ± 10</td>
<td>152 ± 13</td>
<td>347 ± 11</td>
</tr>
<tr>
<td></td>
<td>285 ± 10</td>
<td>289 ± 21</td>
<td>381 ± 3</td>
</tr>
<tr>
<td></td>
<td>673 ± 10</td>
<td>867 ± 2.7</td>
<td>153.7 ± 2</td>
</tr>
<tr>
<td>Water</td>
<td>63 ± 9</td>
<td>183 ± 1.8</td>
<td>518 ± 4.0</td>
</tr>
<tr>
<td></td>
<td>207 ± 17</td>
<td>838 ± 2.5</td>
<td>153.9 ± 3.3</td>
</tr>
<tr>
<td></td>
<td>335 ± 10</td>
<td>925 ± 4.2</td>
<td>176.6 ± 4.4</td>
</tr>
<tr>
<td></td>
<td>193 ± 20</td>
<td>1780 ± 4.4</td>
<td>178.0 ± 11</td>
</tr>
</tbody>
</table>

Table 1: Ice, T = 271 K: \( \omega_x \) from Ref. [10]; the total kinetic energy \( (E_k) \) and three components of the mean kinetic energies, \( (E_k)_x \), calculated from Eq. (2). Water at T = 285 K: DINS data from Ref. [14] with \( (E_k)_x \) calculated fitting the n(p) line-shape according to Eq. (1); \( \omega_x \) calculated from Eq. (2) and total kinetic energy \( (E_k) \); Water, T = 673 K: DINS data from Ref. [22] with \( (E_k)_x \) calculated fitting the n(p) line-shape according to Eq. (1); \( \omega_x \), calculated from Eq. (2); \( (E_k)_x \), total kinetic energy \( (E_k) \); values of \( (E_k)_x \) from DINS data of Ref. [15] and Ref. [22] are also listed. Values of \( \omega_x \) from Ref. [17] are also listed.
the assumption of decoupled quantum translational, rotational and vibrational harmonic oscillators [15]. \(S_{\text{inv}}(\theta, \omega)\) data sets are fitted to derive three principal vibrational frequencies, i.e. \(\omega_{\text{lib}}, \omega_{\text{ben}}\), and \(\omega_{\text{str}}\). Let us apply this procedure for the INS data set of Ref. [2]. Multi-Gaussian fits of the \(S_{\text{inv}}(\theta, \omega)\) spectra for ice, at \(T = 271\) K, and water, at \(T = 285\) K are plotted in Fig. 1 as a green line. In the same figure the individual line shapes for the principal vibrational frequencies are also reported, for ice, as red dashed line, and for water, as blue dashed line. The distinct features of the Multi-Gaussian fit of water INS spectrum are highlighted in Fig. 2. In this figure one can appreciate a redshift of the stretching and bending bands, \(\omega_{\text{lib}} = 83\) meV, \(\omega_{\text{str}} = 417\) meV, \(\omega_{\text{ben}} = 203\) meV, for ice at \(T = 271\) K (left panel) and water at \(T = 285\) K (right panel) and corresponding component \(\langle E_k \rangle_{\text{lib}}\), derived from \(\omega_{\text{lib}}\) using Eq. (2), are reported in Table 2. For water at \(T = 673\) K the values of \(\omega_{\text{lib}}\) listed in the table are from Raman spectroscopic data of Ref. [30]. For the librational mode, a simple average of the three librational Raman frequencies has been considered.

We now recall that nine is total number of degrees of freedom of one water molecule and that the classical translational contribution is \(\frac{1}{2}K_B T\), with a fraction \(\frac{1}{2}\) being associated to the hydrogen atom. Labelling \(\omega_{\text{lib}}\) the rotational contribution and \(\omega_{\text{str}}\) the average contribution due to the symmetric and anti-symmetric stretching modes, the directional contributions to the total kinetic energy can be written as follows [28]:

\[
\langle E_k \rangle_i = 2S_i\hbar\omega_{\text{lib}} + \frac{1}{2}K_B T
\]

\[
\langle E_k \rangle_s = 2S_s\hbar\omega_{\text{str}} + \frac{1}{2}K_B T
\]

\[
\langle E_k \rangle \text{tot} = \sum_i S_i \langle E_k \rangle_i + \sum_s S_s \langle E_k \rangle_s
\]

with \(S_i\) being the fractions of kinetic energy as defined by an harmonic model for the free molecule [29]. The calculated values for \(\langle E_k \rangle_i\) according to Eq. (6) and the total mean kinetic energy \(\langle E_k \rangle_{\text{tot}}\) are reported in Table 3, together with the corresponding values for the DINS data from Table 1 and the \(\langle E_k \rangle_{\text{OH}}\) from Table 2. In the last column of Table 3 we calculate the ratio between the OH stretching mean kinetic energy, from INS analysis, and the total mean kinetic energy.

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**Fig. 1.** The \(S_{\text{inv}}(\theta, \omega)\) dynamical structure factors from INS experiments of Ref. [2] are plotted as black dots for ice at \(T = 271\) K (left panel) and water at \(T = 285\) K (right panel) together with the Multi-Gaussian fits (green lines). The individual line shapes corresponding to elastic, libration, bending and stretching modes for ice and water are also plotted as red dashed line in the left panel and as blue dashed line in the right panel, respectively. Values for \(\omega_{\text{lib}}, \omega_{\text{str}}\) and \(\omega_{\text{ben}}\) for ice and water resulting from the Multi-Gaussian fits of both spectra are also reported. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Fig. 2.** Multi-Gaussian fits of the \(S_{\text{inv}}(\theta, \omega)\) spectra from INS experiment of Ref. [2] for ice at \(T = 271\) K (red line) and water at \(T = 285\) K (blue line), for a scattering angle \(\theta = 20\). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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**Table 2**

Values of \(\omega_{\text{str}}\) from Eq. 5 and INS data of Ref. [2], obtained using Eq. 7: the stretching kinetic energy component \(\langle E_k \rangle_{\text{str}}\) is obtained from Eq. (4). Values for \(\omega_{\text{str}}\) from Raman data of Ref. [30] for water at \(T = 673\) K and the stretching kinetic energy component \(\langle E_k \rangle_{\text{OH}}\) is obtained from Ref. [30] (see text).

<table>
<thead>
<tr>
<th>(T) [K]</th>
<th>(\omega_{\text{str}}) [meV]</th>
<th>(\omega_{\text{lib}}) [meV]</th>
<th>(\omega_{\text{ben}}) [meV]</th>
<th>(\langle E_k \rangle_{\text{str}}) [meV]</th>
<th>(\langle E_k \rangle_{\text{OH}}) [meV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice</td>
<td>271</td>
<td>83 ± 2</td>
<td>143 ± 5</td>
<td>417 ± 5</td>
<td>104 ± 1.2</td>
</tr>
<tr>
<td>Water</td>
<td>285</td>
<td>72 ± 3</td>
<td>139 ± 6</td>
<td>429 ± 6</td>
<td>107 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>59</td>
<td>130</td>
<td>445</td>
<td>113</td>
</tr>
</tbody>
</table>

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\[
\omega_{\text{str}} = \omega_{\text{lib}}
\]

\[
\omega_{\text{str}} = \frac{1}{2}(\omega_{\text{lib}} + \omega_{\text{ben}})
\]

\[
\omega_{\text{str}} = \omega_{\text{str}}
\]

These expressions are exact in the limit of infinite mass for the oxygen atom, and in the limit of \(\hbar \omega_{\text{lib}} \gg 2K_BT\), where \(\omega_{\text{lib}}, \text{ ben}\) and \(\text{str}\).

For ice at \(T = 271\) K and water at \(T = 285\) K values of \(\omega_{\text{str}}\) and \(\langle E_k \rangle_{\text{str}}\), derived from \(\omega_{\text{str}}\) using Eq. (2), are reported in Table 2. For water at \(T = 673\) K the values of \(\omega_{\text{str}}\) listed in the table are from Raman spectroscopic data of Ref. [30]. For the librational mode, a simple average of the three librational Raman frequencies has been considered.

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\[
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\]

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\omega_{\text{str}} = \frac{1}{2}(\omega_{\text{lib}} + \omega_{\text{ben}})
\]

\[
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\]

These expressions are exact in the limit of infinite mass for the oxygen atom, and in the limit of \(\hbar \omega_{\text{lib}} \gg 2K_BT\), where \(\omega_{\text{lib}}, \text{ ben}\) and \(\text{str}\).

For ice at \(T = 271\) K and water at \(T = 285\) K values of \(\omega_{\text{str}}\) and \(\langle E_k \rangle_{\text{str}}\), derived from \(\omega_{\text{str}}\) using Eq. (2), are reported in Table 2. For water at \(T = 673\) K the values of \(\omega_{\text{str}}\) listed in the table are from Raman spectroscopic data of Ref. [30]. For the librational mode, a simple average of the three librational Raman frequencies has been considered.

We now recall that nine is total number of degrees of freedom of one water molecule and that the classical translational contribution is \(\frac{1}{2}K_B T\), with a fraction \(\frac{1}{2}\) being associated to the hydrogen atom. Labelling \(\omega_{\text{lib}}\) the rotational contribution and \(\omega_{\text{str}}\) the average contribution due to the symmetric and anti-symmetric stretching modes, the directional contributions to the total kinetic energy can be written as follows [28]:

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\langle E_k \rangle_i = 2S_i\hbar\omega_{\text{lib}} + \frac{1}{2}K_B T
\]

\[
\langle E_k \rangle_s = 2S_s\hbar\omega_{\text{str}} + \frac{1}{2}K_B T
\]

\[
\langle E_k \rangle \text{tot} = \sum_i S_i \langle E_k \rangle_i + \sum_s S_s \langle E_k \rangle_s
\]

with \(S_i\) being the fractions of kinetic energy as defined by an harmonic model for the free molecule [29]. The calculated values for \(\langle E_k \rangle_i\) according to Eq. (6) and the total mean kinetic energy \(\langle E_k \rangle_{\text{tot}}\) are reported in Table 3, together with the corresponding values for the DINS data from Table 1 and the \(\langle E_k \rangle_{\text{OH}}\) from Table 2. In the last column of Table 3 we calculate the ratio between the OH stretching mean kinetic energy, from INS analysis, and the total mean kinetic
energy, from DINS analysis, $\frac{h_{EK}}{h_{DINS}}$, for ice and water at the investigated temperatures. From this Table at all temperatures we can appreciate a quite good agreement between $h_{EK}^{z}$ values obtained from Eq. (6) and $h_{EK}^{OH}$ values of derived independently from the OH stretching components of the hydrogen projected density of states through Eq.(4).

From the $h_{EK}^{z}$, DINS, INS and Raman values of Table 1 and Table 2 one can retrieve the variances $\sigma_{r}^{2}$, via Eq. (2), and further can derive the proton momentum distribution, $n(p)$ and the harmonic components of proton momentum distribution $nh(p)$. The radial component of both momentum distribution line shapes, i.e. $4\pi p^{2}n(p)$ and $4\pi p^{2}nh(p)$, are plotted for ice at $T = 271 \text{ K}$ in the left panel of Fig. 3 in black and red color. For interpretation of color in Fig. 3, the reader is referred to the web version of this article.

### 3. Results and conclusions

A first comment is relative to the values of the total mean kinetic energy of ice and water, $\langle E_{k} \rangle$, reported in the penultimate column of Table 3, which have been derived from the analysis of independent INS and DINS data sets through Eqs. (2) and (6). These
values result in a satisfactory agreement for all the investigated temperatures, within the statistical accuracy.

The stretching components of the mean kinetic energy derived from INS data for ice at $T = 271$ K and water at $T = 285$ K through Eq. (6), $\langle E_k \rangle_p$, are in excellent agreement with $\langle E_k \rangle_{OH}$ at the same temperatures derived in Ref. [2] from the OH stretching components of the hydrogen projected density of states, $g_{\text{exp}}(E)_{\text{OH}}$, through Eq. (3). This confirms the reliability of the harmonic description of Eq. (6) used to calculate the individual components $\langle E_k \rangle_p$ in the present study and to describe the mean kinetic energy components in a previous study of H$_2$S [28]. In Table 3 we observe that the stretching components $\langle E_k \rangle_p$ are redshifted in respect to their relative harmonic components at all investigated temperatures. This finding, already emerged in a recent DINS study of ice at $T = 271$ K [10], is interpreted as due to additional network mode contributions and softening caused by anharmonicity. Further in Table 3 the $\langle E_k \rangle_p$ DINS components show a clear blue shift, larger in water than in ice, with respect to the corresponding $\langle E_k \rangle_p$ INS components. Following this finding supports a picture with weaker hydrogen bond network in liquid phase than in ice.

The $n(p)$ lineshape, as derived from DINS, and its harmonic component, $n_h(p)$, derived from the INS analysis, are shown in Fig. 3 for ice at $T = 271$ K and water at $T = 285$ K and $T = 673$ K with their experimental error. For each temperature, the harmonic components have been plotted as a red line for ice (left panel) and as a blue line for water (central and right panels). The difference between the two line shapes $[n(p) - n_h(p)]$ are plotted. The two lineshapes differ significantly for $p < 5 \, \text{Å}^{-1}$, minor differences are found in the range $6 \, \text{Å}^{-1}$ to $10 \, \text{Å}^{-1}$ and beyond $10 \, \text{Å}^{-1}$. These differences are better emphasized in the radial representation of the $n(p)$ lineshape, $4\pi p^2[n(p) - n_h(p)]$, plotted in Fig. 4. One comment regards the anisotropy of the $n(p)$ function, as fingerprinted in the different values of the three variances $\sigma^2_p$, i.e. of the three $\langle E_k \rangle_p$ in Table 3 derived from Eq. (2). In Fig. 2 this feature is clearly highlighted by both the decrease of the stretching frequency value and the increase of librational frequency value and by the shape of the two ellipsoids, red for ice and blue for water, schematically plotted at the top right corner of the figure. In conclusion $n(p)$ lineshapes derived at the investigated temperature reflect the anisotropy and quasi-harmonic nature of proton motion in ice and water.

The last column of Table 3 shows the ratio $\frac{\langle E_k \rangle_{\text{DINS}}}{\langle E_k \rangle_{\text{INS}}}$ where the $\langle E_k \rangle_{\text{DINS}}$ is that obtained in the present study, i.e. by the sum of the three $\langle E_k \rangle_p$ components fitted to the $n(p)$ line shapes through Eq. (1). The latter procedure highlights the contributions from intramolecular modes, in particular of the OH stretching, to the hydrogen motion in a way more directly related to a decoupled harmonic model than using $\langle E_k \rangle_p$ values obtained by Gauss–Hermite fits as in Ref. [15,22].

This study although confirms the effectiveness of the DINS techniques to provide quantitative values of $n(p)$ and $\langle E_k \rangle_p$ further shows how a combined use of DINS and INS can provide additional and unique information on the harmonic components of these physical quantities.

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**References**