Anisotropy of the proton kinetic energy in ice Ih

Y. Finkelstein[a,*], R. Moreh[b], F. Bianchini[c], P. Vajeeston[c]

[a] Chemistry Division, Nuclear Research Center Negev (NRCN), Beer-Sheva 84190, Israel
[b] Physics Department, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel
[c] Center for Materials Sciences and Nanotechnology, Department of Chemistry, University of Oslo, N-0315 Oslo, Norway

A B S T R A C T

The partial vibrational density of states (pVDOS) of ice Ih, as simulated by first principle modeling based on density functional theory (DFT), is utilized for computing the Cartesian components of the proton and oxygen quantum kinetic energies, Ke(H) and Ke(O) respectively, along and perpendicular to the hydrogen bonds. The DFT method was found to yield better agreement with deep inelastic neutron scattering (DINS) measurements than the semi empirical (SE) calculations. The advantage of using the DFT method is to enable us to resolve the external and internal phonon bands of the Cartesian projections of the pVDOS, and hence those of the lattice and vibrational components of Ke(H). We show that a pVDOS analysis is a valuable tool in testing scattering results of complex systems and suggest its potential to explore competing quantum effects, e.g. on Ke(H) across phase transitions in water.

1. Introduction

A substantial body of experimental work exists on the proton kinetic energy, Ke(H), in ice and water. Only one scattering technique, namely deep inelastic neutron scattering (DINS), was utilized for measuring Ke(H) in H_2O phases. Out of those, DINS is regarded as the only standard method for *direct* Ke(H) determinations of the proton zero point kinetic energy (ZPKE), via a measure of the proton radial momentum distribution (RMD). Note that the kinetic energy of the H-atom in H_2O up to ~ 280 K is practically equal to its ZPKE [1]. Currently, measuring the ZPKE is provided only by the Vesuvio spectrometer at ISIS (Rutherford Appleton Laboratory, UK). Worth mentioning in that regard, is that Ke(H) may also be determined by inelastic neutron scattering (INS) [2]. Significantly different from DINS however, in INS one measures the fundamental frequencies of the condensed H_2O phase. These INS data are normally used as input for calculating Ke(H) in the semi empirical (SE) method in which the harmonic approximation (HA) is assumed [3].

Lately, an extensive experimental and theoretical emphasis is given in the literature for measuring and computing the Cartesian components of Ke(H) along and perpendicular to the hydrogen bond (HB) direction in H_2O [2,4,5,6,7,8,9]. In H_2O ice Ih, these components were measured directly by DINS [2,8] and calculated semi empirically by utilizing INS measurements [2]. By now such components were found to provide a direct estimate of competing quantum effects (CQEs) [5].

In the present work we report on the first DFT simulation of the Cartesian components of the H-VDOS in ice Ih from which the directional components of Ke(H) along and perpendicular to the hydrogen bond are resolved. It is encouraging that the currently deduced values are in good agreement with available measured DINS data on solid H_2O, a result which emphasizes the validity of the pVDOS approach as a powerful tool in exploring proton dynamics of HB containing systems. Our DFT findings are compared with recently reported path integral molecular dynamics (PIMD) simulations [10,11]. In general the present findings are in better agreement with the DINS measurements.

2. Theoretical remarks

In the following we emphasize the advantages of using a pVDOS analysis over the SE approach for treating the directional Ke(H) in ice.

2.1. pVDOS vs SE

The SE approach [1,2,3] is used to compute Ke(H) in condensed H_2O phases where it is assumed that the coupling of the H_2O modes of motion to the HBs network is fully accounted for by utilizing the *measured* frequencies of H_2O and its geometric parameters (R_{OH} and the HOH angle). For H_2O, five discrete frequencies exist arising from the two lattice modes (translation and libration of the entire H_2O molecule) and from its three internal vibrations (OHO bending and two OH

stretching modes). Theses frequencies are then reconstructed by solving the equations of motion of the oxygen atom and two protons of H_2O. This procedure yields the atomic amplitudes along any direction, thus providing the energy fractions shared by the constituent atom in each mode of motion along any direction. These fractions are used to deduce the Cartesian XYZ components of Ke(H) and Ke(O).

The SE approach was found to work flawlessly as it successfully predicted DINS Ke(H, D, O) values in various phases of $H(D)_2$ and $H(D)_2O$ [12,13]. In fact, it was established as a powerful tool for predicting atomic KE values, already around 40 years ago, of $^{15}N/^{13}C$, contained in a variety of molecular systems; the results were in excellent agreement with nuclear resonance photon scattering/fluorescence (NRPS/NRF) experiments [14,15,16,17,18,19].

It is also very interesting to note that despite the fact that the SE method relies on the HA, it was found to be applicable to cases involving strong anharmonic potentials [20]. Examples include [20]: ferroelectric crystals of the KDP family (MH_2PO_4; M = K, Rb, Cs), and the super protonic conductor $Rb_3H(SO_4)_2$ in which HB symmetrization is very nearly realized. In such systems, it is necessary to account for the pVDOS, i.e. the part of the VDOS shared by the protons (H-VDOS), as simulated by DFT or molecular dynamics (MD) [20]. Note that the pVDOS approach is more accurate than the SE method as it accounts for both the continuous phonon distribution of the system and for the fraction shared by the proton in all vibrational states (phonons). Moreover, the energy fractions distribution is self-contained in the pVDOS and it is unnecessary to calculate it in advance as in the SE approach.

A breakdown of the SE approach in predicting Ke(H) values was first demonstrated in DINS studies of *nanoconfined* H_2O where anomalous Ke(H) deviations of ± 30 to 50% (from the standard value of Ke(H) ~ 152 meV measured in e.g. ice) were reported. These were found in cases such as protein hydration shell water [21] and in water nanoconfined in silica gels [22,23], in carbon nanotubes [24] and in Beryl [25]. Note that while path integral molecular dynamics (PIMD) and path integral monte Carlo (PIMC) calculations revealed exact description of DINS observables in liquid and solid phases of light and heavy water [4,26,27,28,29,30], they were not applied to the systems for which Ke(H) anomalies were revealed by DINS. And yet, very recently a first success was reported by utilizing first principle based DFT simulations of the *partial* H-VDOS in the H_2O@Berryl system [31]. By treating the whole system, of the hosting Beryl lattice and the confined H_2O, as a single quantum system, the deduced Ke(H) at 5 K was found to conform precisely to the DINS measured anomalous value, Ke(H) = 104 meV [25]. The key insight here is that under nano-confinement, the coupling of the water modes of motion to host lattice modes yield proton states distinctly different from those of ordinary water phases [32]. This success was in fact the first accurate theoretical reconstruction of an anomalous DINS Ke(H) value in nanoconfined water. Worth mentioning in that regard, is that the approach of pVDOS analysis was already utilized for studying atomic kinetic energies for testing observables of DINS and electron Compton scattering (ECS) in other, non H_2O, molecular systems. Examples are LiF [33,34], Li_2CO_3 and SiO_2 [35].

2.2. SE calculation

In the following we stick to the notation of Ref. 2 by selecting the direction of OH1 covalent bond to be the same as the Z Cartesian direction and along the HB direction in ice Ih. The relative directions of the abc crystallographic axes and the Cartesian XYZ ones are defined in Fig. 1.

Accounting for the directions defined in Fig. 1, the following relations apply to the H1 atom [2,36]:

$$Ke_x(H1) = S_t\alpha(\upsilon_t) + (S_{Ry} + S_{Rz})\alpha(\upsilon_R) \tag{1}$$

$$Ke_y(H1) = S_t\alpha(\upsilon_t) + S_{Rx}\alpha(\upsilon_R) + S_2\alpha(\upsilon_2) \tag{2}$$
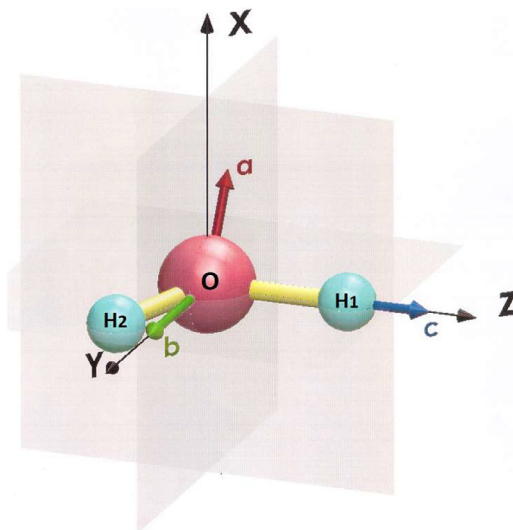

Fig. 1. Definition of the XYZ Cartesian directions in H_2O: the OH1 covalent bond is along z, and the (Y, Z) plane coincides with the H_2O molecular plane. The relation of the Cartesian axes frame to the abc crystallographic one of hexagonal ice (see Fig. 2), is also shown: c||Z, (b, c)||(Y, Z), b⊥c, a⊥c, ∠ab = 120° (∠aX = 30°, ∠Yb ~ 17°).

$$Ke_z(H1) = S_t\alpha(\upsilon_t) + S_1\alpha(\upsilon_1) + S_3\alpha(\upsilon_3) \tag{3}$$

S_t, $S_{Rx,y,z}$, $S_{1,2,3}$ are the KE fractions shared by H1 in the translational, rotational (around the Cartesian axes passing through the molecular center of mass) and the three internal frequencies of H_2O respectively. $\alpha(\upsilon_j) = \frac{h\upsilon_j}{2}\left(\frac{1}{e^{\frac{h\upsilon_j}{kT}} - 1} + \frac{1}{2}\right)$, is the KE of the corresponding Planck oscillator, with υ_j (j = t, r, bnd, ss, as) the *measured* characteristic frequency of translation, libration and three internal (bending and symmetric and asymmetric stretch) modes of motion of H_2O. It should be noted that in this simplified model, one accounts in each mode for the same characteristic frequency (measured for the studied water phase) regardless of the direction, thus coupling effects of the water molecule to surrounding lattice modes are ignored.

2.3. pVDOS calculation

A detailed discussion of the KE calculation by the pVDOS method may be found elsewhere [20]. Here we just mention that by accounting for the lth Cartesian component (l = X, Y, Z) of the H-VDOS, $g_{H_l}(\nu)$, the directional component of Ke(H), $Ke_l(H)$, may be deduced directly by:

$$Ke_l(H) = \frac{\frac{3}{2}\int_{\nu_0}^{\nu_f} g_{H_l}(\nu)\alpha(\nu, T)d\nu}{\int_{\nu_0}^{\nu_f} g_{H_l}(\nu)d\nu} \tag{4}$$

with ν_0 and ν_f the frequency limits of $g_{H_l}(\nu)$.

2.4. DFT simulation of $g_{H_l}(\upsilon)$

Total energies have been calculated using the projected-augmented plane-wave (PAW) implementation of the Vienna *ab initio* simulation package (VASP) [37,38]. All these calculations were made with the Perdew, Burke, and Ernzerhof (PBE) [39] exchange correlation functional. Ground-state geometries were determined by minimizing stresses and Hellman–Feynman forces using the conjugate-gradient algorithm with a force convergence threshold of 10^{-3} eV Å^{-1}. Brillouin zone integration was performed with a Gaussian broadening of 0.1 eV. From various sets of calculations it was found that 512 **k** points in the Brillouin zone and a 600 eV plane-wave cut-off are sufficient to ensure optimum accuracy in the computed results. The **k**-points were generated using the Monkhorst–Pack method with a grid size of 8 × 8 × 8.