

Anisotropy of the proton kinetic energy in CsH_2PO_4 and KH_2PO_4

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ABSTRACT

The strong *anisotropy* of the proton mean kinetic energy, $\text{Ke}(\text{H})$, in a single crystal of KH_2PO_4 (KDP), measured by deep inelastic neutron scattering (DINS), is compared with that calculated for its Cs analogue, CsH_2PO_4 (CDP) in the ferroelectric (FE) and paraelectric (PE) phases. Empirical lattice dynamics (LD) calculations were used to simulate the *partial* vibrational density of states shared by the protons (H-VDOS), from which $\text{Ke}(\text{H})$ values were deduced. Good agreement was found between the measured and calculated $\text{Ke}(\text{H})$ values of the two samples despite the different hydrogen bond dynamics. However, the *directional* components of $\text{Ke}(\text{H})$ in the two samples were quite different. In both cases, the $\text{Ke}(\text{H})$ tensor is nearly an ellipsoid of rotation: in KDP the shape is oblate around the major axis while being prolate in CDP. By resolving the *directional* $\text{Ke}(\text{H})$ values of the two non-equivalent protons of CDP, a possible signature of competing quantum effects is indicated.

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1. Introduction

Recently, significant progress was achieved in understanding the nature and dynamics of the hydrogen bond (HB) in various systems. This was done by density functional theory (DFT) calculations of the proton mean kinetic energy, $\text{Ke}(\text{H})$ [1,2] using the H-VDOS. This approach, provided accurate predictions of DINS $\text{Ke}(\text{H})$ values in *anharmonic* proton potential systems, e.g. in KH_2PO_4 and in the super protonic conductor $\text{Rb}_3\text{H}(\text{SO}_4)_2$ [1]. More recently, the same VDOS approach was successfully applied to water nanoconfined in beryl ($\text{H}_2\text{O}@\text{Beryl}$) [2], resulting in $\text{Ke}(\text{H}) = 105$ meV in accurate agreement with DINS measurement [3]. Note that this new approach treats the $\text{H}_2\text{O}@\text{Beryl}$ as a *single quantum harmonic system*.

The H-VDOS may be alternatively calculated by empirical lattice dynamics (LD) methods, as applied for KDP analogues, namely CsH_2PO_4 (CDP) [4] and TiH_2PO_4 (TDP) [5] and their deuterated forms, DCDP [6] and DTDP [7]. The results were later used to study $\text{Ke}(\text{H})$ in these compounds [1]. Lately, DINS studies are mainly focused on deducing the projections of the proton momentum distribution, $n(p)$, along various directions relative to the HB in various benchmark systems [8,9,10,11,12]. It should be stressed in that regard that the directional components of the proton kinetic energy discussed here, are derivatives of the directional $n(p)$, thus reflecting the anisotropy of the local potential sensed by the proton. Regarding KDP unfortunately, DINS results which revealed a strong $n(p)$ anisotropy along *orthogonal* crystallographic directions, exist only for KDP [13] but not for its analogue forms. Here, this anisotropy

is compared with LD simulations of CDP [4,5], used for deducing the $\text{Ke}(\text{H})$ values along the Cartesian directions. We treat individually each of the protons of the *non-equivalent* HBs occurring in CDP across the ferro-/para-electric phase transition ($T_c \sim 154$ K) [14]. Similar to the DINS results of KDP, the calculated $\text{Ke}(\text{H})$ for CDP also reveals strong anisotropy, but to a lesser extent. The difference well conforms to that occurring between the orientations of HBs in these two family members.

2. Theoretical remarks

The kinetic energy of atoms in a molecular solid is contributed by three types of motion: *external* (lattice) translational-vibrations and librations (hindered rotations) of the whole molecule, and *internal* molecular vibrations (normal modes). In a crystal, the complexity and variety of modes (phonons) projected on each constituent proton is completely structured in the *partial* H-VDOS of the proton, $g_H(\nu)$. Thus, the proton mean kinetic energy, $\text{Ke}(\text{H})$, in the crystal may be expressed as [15]:

$$K_e(H) = \frac{3}{2} \int_{\nu_0}^{\nu_f} g_H(\nu) \alpha(\nu) d\nu / \int_{\nu_0}^{\nu_f} g_H(\nu) d\nu \quad (1)$$

with $\alpha(\nu, T) = \hbar\nu / [e^{\hbar\nu/kT} - 1] + \frac{1}{2}$, the kinetic energy of a quantum *harmonic* oscillator with ν_0 and ν_f the frequency boundaries of $g_H(\nu)$, k the Boltzmann constant and T , the thermodynamic temperature. The factor $1/2$ is related to the zero point energy. The partial VDOS of each proton in CDP and along its crystallographic axes was deduced by LD calculations, with a model based on the potential function that accounts

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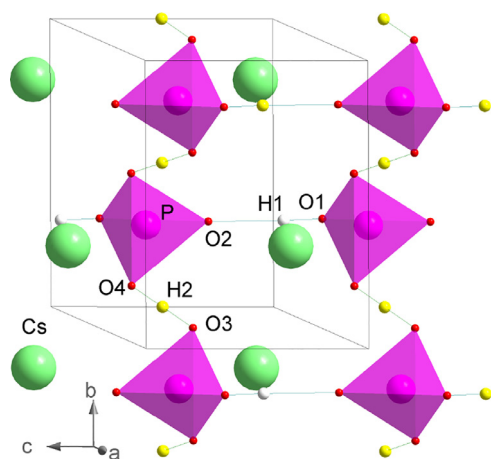


Fig. 1. Crystallographic axes (a , b , c) representation of PE CDP at room temperature ($P2_1/m$ phase) [22]: Cs-green, PO₄ groups (O-red and P-shaded pink) are presented in polyhedral representation. Transparent box indicates the unit cell. Non-equivalent protons are marked H1 (white) and H2 (yellow). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

for the long-range Coulomb, short-range Born–Mayer type, covalent and van der Waals interactions. Explicit details may be found elsewhere [4,5,6,7].

3. Results

3.1. Partial VDOS

Partial VDOS were calculated for each atom of CsH₂PO₄ in both ferro (FE) and para (PE) electric phases in the Cartesian frame ($x \perp (b,c)$, $y||b$, $z||c$, where a , b and c are the monoclinic crystallographic axes, with $\beta = 17.73^\circ$ and 18.24° , the angle between the a crystallographic axis and the x Cartesian axis in the PE [16] and FE [17] phases respectively). For the protons, simulations were carried out by distinguishing between the two *non-equivalent* HBs occurring in CDP. For analyzing the Ke(H) anisotropy, we first examine the various orientations of HBs in the crystal. As an illustrative example we briefly review the structure of PE CDP (at 300 K) occurring in a monoclinic symmetry ($P2_1/m$ phase) [18]. Note that below T_c , the monoclinic symmetry is kept, however lowered to the acentric $P2_1$ space group, where the crystal becomes ferroelectric [18]. The discussion given here of the calculated directional VDOS and the KE values in CDP applies also to its FE phase. Both FE and PE CDP structures have been studied by n- [14,16,19,20,21] and x-ray [14] diffraction. Fig. 1 depicts the crystal structure of PE CDP at RT.

The unit cell, containing two CsH₂PO₄ formula units, comprises two non-equivalent HBs, differing in O–H...O length (R_{OO}): (1) short, O₃–H2...O₄ (2.472 ± 0.007) Å [16], linking the PO₄ tetrahedrons in a zig-zag fashion into chains running along the b -axis [18,23,24], and (2) long, O₁–H1...O₂ (2.537 ± 0.007) Å [16], which is always ordered, approximately directed along the c -axis, crosslinking the chains to form the [100] layers [25]. The shorter HB, being disordered in the PE phase, is responsible for the FE transition below T_c . The unequal bond-lengths triatomic O₁–H1...O₂ bond ($r_{O_1-H_1} = 0.955 \pm 0.007$ Å, $r_{O_2-H_1} = 1.530 \pm 0.007$ Å) is bent at a $(173.2 \pm 0.5)^\circ$ angle [24], with all three atoms laying on the (a,c) mirror plane [23]. In that sense, the O₁ and O₂ sites form a conventional O₁–H1...O₂ HB configuration. From n-diffraction it was determined that $r_{O_4-H_2} = (1.00 \pm 0.02)$ Å, $r_{O_3-H_2} = (1.46 \pm 0.02)$ Å, with a $(174 \pm 4)^\circ$ bending angle [24]. In summary of the PE CDP structure, with emphasis on the HBs orientations, it is clear that the nearly linear O₁–H1...O₂ bond is directed nearly parallel to the c -axis, and that the nearly linear O₃–H2...O₄ bonds are arranged spirally-like around the b (y) axis and are oriented out of the (a,c) plane, alternately pointing towards and counter the b -axis direc-

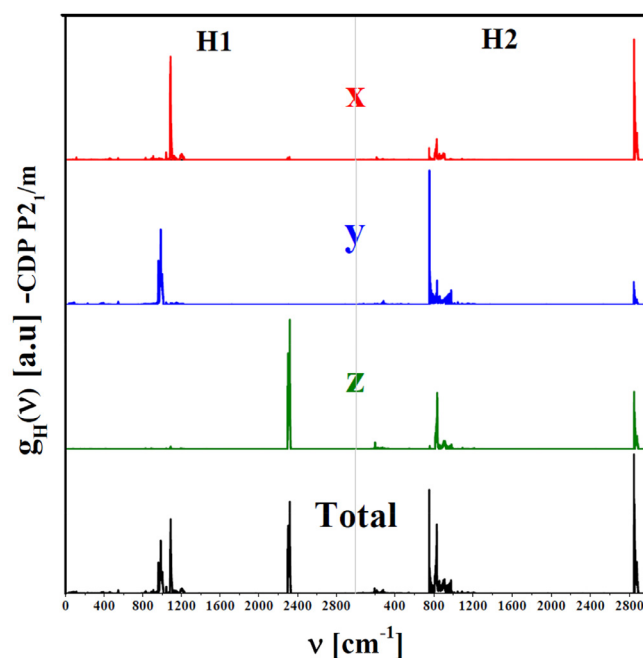


Fig. 2. Calculated H-VDOS profiles of the non-equivalent, H1 and H2, protons in PE CDP at RT. Bottom: *average* H-VDOS, Top: *directional* H-VDOS along the three Cartesian axes. For clarity, the directional H-VDOS are all equally scaled. The total H-VDOS corresponds to the algebraic average over the directional ones.

tion. Altogether a large Ke(H1) anisotropy and a much smaller one for Ke(H2) are expected. Here, we discuss the calculated *directional* components of the partial H-VDOS in CDP, and show how they conform to the above expectations. The ‘average’ Ke(H) discussed hereby, corresponds to that obtained using a non-oriented sample and is deduced from the H_k -VDOS ($k = x, y, z$) components.

Fig. 2 depicts the simulated *directional* H-VDOS profiles of the non-equivalent H1 and H2 protons in PE CDP at RT, and their averages.

According to IR [26,27,28], Raman [26,27,29] and inelastic n-scattering (INS) [30,31] studies, the calculated H-VDOS [4,5] of Fig. 2 are understood, and their frequencies assigned as follows: first, phonon states above ~ 2250 cm^{−1} correspond to O–H stretching modes. Note in that regard, that all KDP type crystals contain strong HBs, whose OH stretch frequencies are lower than that of condensed H₂O occurring at 3153 and 3385 cm^{−1} [32]. That the shortest possible r_{OO} is ~ 2.4 Å (realized under HB symmetrization, e.g. in ice VII and Rb₃H(SO₄)₂) [33], and $r_{OO} \sim 2.8$ Å in H₂O [32,34], emphasize the fact that the $r_{O_1O_2} = 2.51$ Å and $r_{O_3O_4} = 2.46$ Å occurring in CDP indeed represent markedly short, and thus high strength HBs. Second, the 750–1300 cm^{−1} band belongs to the stretch vibrations ($\nu_1 = 940$ cm^{−1}, $\nu_3 = 1100$ cm^{−1}) of PO₄ groups [35], into which in-plane (δ_{OH}) and out-of-plane (γ_{OH}) O–H bending/deformation frequencies, also fall. Finally, the region below ~ 580 cm^{−1} corresponds to vibrations of HBs coupled to lattice translations and librations of PO₄ groups (0–350 cm^{−1}), and to internal bending vibrations, $\nu_2 = 420$ cm^{−1}, $\nu_4 = 560$ cm^{−1} [35]. As evident however in Fig. 2, the shares of the protons in these modes are very small, with nearly null phonon intensities along all three directions for either the long (H1) or short (H2) HBs. The significance of the above to Ke(H) is straightforward, as the intensities of the H1- and H2-VDOS, $g_{H1}(v)$ and $g_{H2}(v)$, are proportional to the fractions shared by the H1 and H2 protons in the average kinetic energy of CDP in each of the vibrational states (phonons).

A strong anisotropy of the H1-VDOS is evident in Fig. 2 when comparing the strong 2310 cm^{−1} peak along the z -direction (H1 z) with the very weak ones along the y (H1 y) and x (H1 x) directions. Such anisotropy may be understood by noting that the O₁–H1...O₂ bond

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