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Isotope effect on the collective proton transfer in hydrogen and deuterium fluoride crystals

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The orthorhombic structure of hydrogen fluoride (HF) consisting of planar hydrogen-bonded zigzag chains of HF molecules [1-2] offers the possibility of collective multiple proton hopping, as in liquid water [3] and ordinary ice (hexagonal ice Ih) [4]. The collective proton transfer could occur through the formation and concomitant cleavage of covalent bonds involving neighboring molecules. The small mass of the proton means that it is inherently quantum mechanical in nature, and nuclear quantum effects (NQE) such as zero-point motion, quantum delocalization, and quantum tunneling are relevant. Among the hydrogen halides, HF is the one having the strongest hydrogen bond because the largest electronegativity of fluorine and hence provides a rich playground for the study of the impact of NQE on proton position disorder.

We report a simulation study at $T = 100$ K of the HF and DF crystals by using the quantum thermal bath path-integral molecular dynamics (QTB-PIMD) simulation technique [5] that efficiently takes into account the NQE. The interactions were modeled from first principles within the framework of density functional theory (DFT).

An important isotope effect on the proton position disorder has been observed. The deuterons within a zigzag chain simultaneously flip between covalent and hydrogen bonds. Correlatively, the distances between their two first fluoride neighbors vary and reach a minimum value at the saddle point. The height of the associated static barrier normalized for one deuteron is 29.2 meV between two close wells corresponding to a deuteron hopping length of 0.36 Å. The simulated probability density for DF indicates that the deuterons flip between two stable positions due to the barrier crossing through the tunnel effect. In the case of HF, the protons are located at mid-distance between their two first fluoride neighbors. This evidences the symmetrization of the H-bonds, and indicates that the proton zero-point energy is above the barrier top. The overall decrease of the F–H–F length in both crystals corresponds to a large decrease of the H-bond length and a slight increase of the length of the covalent bond. In agreement with experimental data, the deuteration results in an Ubbelohde effect [6] which corresponds to an increase of the hydrogen bond length and an elongation of the F–F distance.

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