H-bonded Ferroelectrics from First-Principles and Derived Modeling

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Hydrogen bonded ferroelectrics of the KH_2PO_4(KDP)-type family, have attracted much attention in the last decades due to the controversy in the origin of its phase transition and the observed huge isotope effect by deuteration. Experiments like neutron diffraction [1] or Compton scattering [2] as well as diverse models [3] have contributed to shed light in the dispute between tunneling and geometrical effects as the root of the dramatic effect. However the phenomenon has been elusive and the knowledge gained in the last decades is still incomplete. We have tackled this problem in recent years with first-principles calculations in order to unveil some of the microscopic clues responsible of such striking behaviors. In this talk, I will briefly discuss the most important results obtained from first-principles and derived model calculations in two prototypes of these systems: ferroelectric KDP and antiferroelectric $NH_4H_2PO_4$ (ADP). [4-7] I will show that in KDP, tunneling is only possible by means of clusters containing both light and heavy atoms and that the huge isotope effect is a consequence of a self-consistent amplification between tunneling and the geometrical effect in the H-bonds in accordance with experiments [4,5]. The origin of ferroelectricity in KDP is attributed to the proton off-centering, while the stabilization of the antiferroelectric phase in ADP is originated in an optimization of the N-H-O bonds [6]. Finally, I will briefly comment on a first-principles based shell-model which was derived for KDP [7]. This model reproduces phonons, structural and energetic features and will enable us to study the quantum dynamics near the phase transition in large-scale simulations.

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