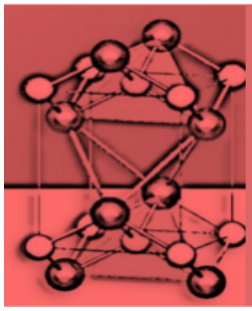

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Ab initio molecular dynamics and path integral Monte Carlo simulations of the ferroelectric phase transition in KDP

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The prototype of the H-bonded ferroelectrics KH_2PO_4 (KDP) was comprehensively studied in the past, although the explanation of its ferroelectric-paraelectric (FE-PE) phase transition and the associated huge isotope effect still remains elusive. We have carried out ab initio molecular dynamics (AIMD) and path integral Monte Carlo (PIMC) calculations to shed light in the nature of the FE phase transition. We included nonlocal dispersion corrections with the van der Waals functional vdW-DF, which are, together with nuclei quantum corrections, necessary to describe properly the H-bond geometry and the proton transfer energy barriers of the system. A first insight in the transition is achieved by AIMD simulations for classical nuclei with the lattice fixed to that for KDP and to the expanded one for the deuterated case (DKDP). The results for the DKDP lattice show a large increase in T_c, about $\sim 70K$, compared to the KDP case, in qualitative agreement with experiments. We also show that neighboring proton jumps, driving the disorder phase, are correlated at the transition, fulfilling the so called ice rules. In order to study nuclear quantum effects, we developed a 1D model with potential parameters adjusted to the ab initio results, which considers the bilinear proton-proton interaction in mean-field. PIMC simulations for this model show a huge isotope effect in the critical temperature originated in a strong feedback between tunneling and geometrical modifications of the H-bond, which is in very good agreement with experiments. By applying pressure we found a linear correlation between T_c and the proton/deuteron distance to the center of the O-H-O bond which agrees with neutron diffraction data. Our results show the relevance of the geometrical effects in the FE phase transition and the existence of a quantum paraelectric phase at a large critical pressure.