Ab initio vibrational properties and isotope effect in H-bonded ferroelectric materials

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Motivated by the miniaturization of devices to nano levels, the interest in reducing power consumption and improving energy efficiency has continuously grown over the last years. Within this scenario, ferroelectric materials offer a wide range of useful properties, such as nonzero switchable electric polarization in the absence of an external field, piezoelectricity and pyroelectricity. This makes them promising candidates for applications such as capacitors, memories or energy harvesting devices.[1, 2]

In this work, we report the *ab initio* structural, vibrational and isotope effect properties of potassium dihydrogen phosphate (KDP or KH_2PO_4), a prototype member of the hydrogen-bonded ferroelectric compounds. A striking manifestation of its phenomenology is the huge isotope effect in its ferroelectric-paraelectric transition temperature T_c, which changes from 122K to 229K upon deuteration.

Using KDP as a case model, we have developed a novel method for selecting the exchange-correlation functional in Density Functional Theory calculations. This method incorporates quantum nuclear effects *a posteriori* in the description of the system, allowing to take them into account in the selection process. For KDP, the nonlocal van der Waals functional vdW-DF was selected as it provided the best agreement with H-bond geometries experimental data. With this choice of functional, we computed the phonon modes at the Γ point of the Brillouin zone, the phonon dispersion curves and the phononic contribution to specific heat. We were also able to calculate the electric polarization and to identify the microscopic mechanism that originates it. [3] The devised method might be useful in the study of other H-bonded materials where the isotope effect proves to be of crucial importance. [4]

References

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Figures

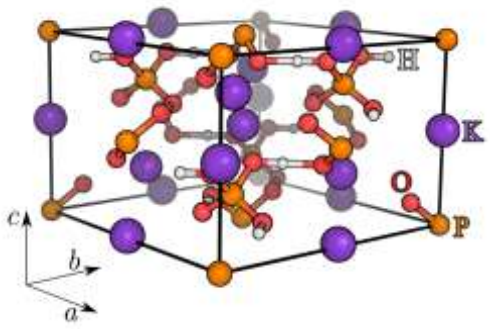

Figure 1. Schematic view of the internal structure of