

Hydrogen bonded solids: Cooperative proton ordering, isotope effect and coexistence of order-disorder and displacive dynamics

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Hydrogen bonded systems play an extremely important role in solid state physics, chemistry and biology. Many of their interesting properties are due to the proton dynamics which frequently show cooperative ordering as function of temperature, pressure, isotopic substitution, or chemical changes in composition. One of the most outstanding properties of all these systems is observed upon isotopic exchange of hydrogen, which significantly influences the proton dynamics and the corresponding onset of cooperative ordering. Even though considerable experimental as well as theoretical effort has been invested in understanding this effect, an unique agreement has not yet been possible to achieve, especially in biological systems, mostly due to the complexity of the corresponding structures. In order to obtain a microscopic understanding of the unusual properties, the dynamics of the hydrogen bonds can be studied more easily in inorganic crystalline solids, where translational invariance and less complex compositions are found than in organic and biological systems.

A prototypical hydrogen-bonded crystalline solid is the KH_2PO_4 (KDP)-family, which is well-known to undergo a ferroelectric, antiferroelectric, or dipolar glass transition with decreasing temperature or increasing pressure. In these compounds, deuteration has the effect to nearly double the corresponding transition temperature T_c at which proton ordering and the simultaneous appearance of a spontaneous polarization are observed. Due to this coincidence, the conventional understanding of the phase transition mechanism has long been believed to be solely due to the protons, in particular since they occupy a local ‘double-well position’ with random distribution in either of the wells above T_c and cooperative ordering below T_c . Even though this pseudo-spin approach seems to offer a natural explanation for the phase transition mechanism, it suffers from two shortcomings: The isotope effect on, T_c , can only be obtained upon unphysical changes in the model parameters, and the spontaneous polarization is

nearly exclusively carried by the heavy ion sublattice which is considered to be unimportant in this approach. In addition, new ultra-high resolution X-ray and NMR experiments revealed that the O...H...O bond geometry significantly contributes to the large isotope effect, and an unexpected displacive component is present in the vicinity of T_c which is not consistent with order-disorder proton dynamics. In order to understand and interpret these new experiments, a coupled proton-lattice interaction model has been proposed where the pseudo-spin representation and the nonlinear host lattice dynamics have been combined, with special emphasis on the exact O...H...O bond geometry. The most important aspects of this new approach are that the coupling between both sublattices is linearly dependent on the H–H (D–D) split position and the heavy ion displacive dynamics are combined with the proton order-disorder dynamics.

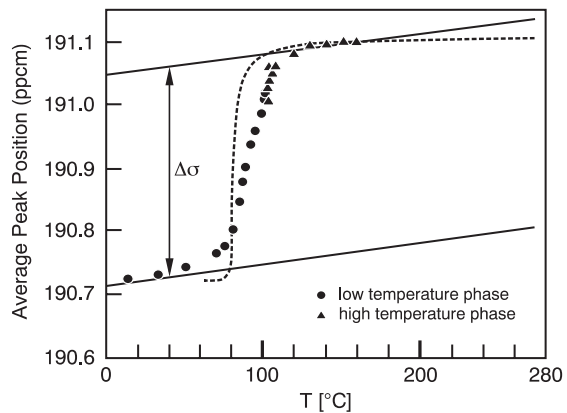


Figure 4: Averaged NMR peak position of squaric acid as a function of temperature. The dashed line corresponds to the calculated chemical shift.

As a consequence the isotope effect arises through polarizability induced changes in the bond geometry and the coexistence of order-disorder and displacive features is naturally explained by the proper combination of the different dynamics of the constituting subsystems. In a numerical investigation of this model, high resolution magic angle spinning ^{13}C NMR data of squaric acid have been simulated. These data show an anomalous S-shape dependence of

the O...H...O bond length in the vicinity of T_c , which has been taken as evidence for the coexistence of order-disorder and displacive dynamics on the same time scale (Fig. 4).

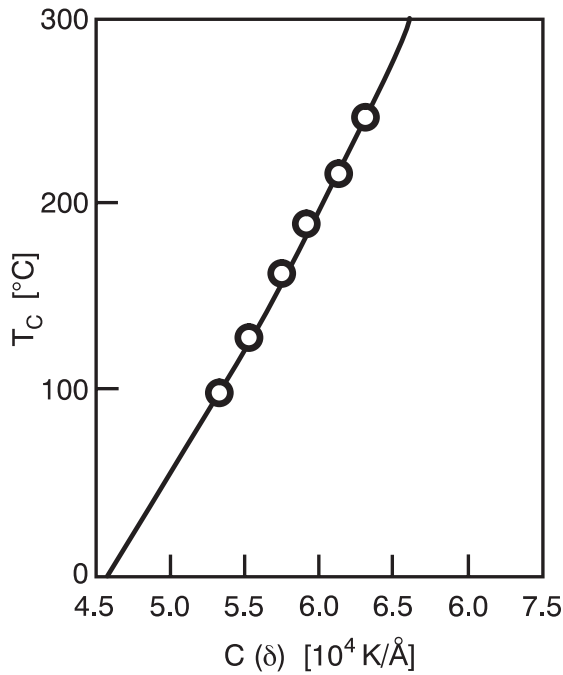


Figure 5: T_c as a function of coupling constant C : Comparison between experimental data (open circles) and theoretical results (solid line).

Due to the coupling between the tunneling protons and the nonlinearly polarizable heavy ion host lattice, the calculated chemical shift (dashed line in Fig. 4) reproduces remarkably well the experimental data. A similarly good agreement between experiment and theory has also been obtained for the isotope effect on T_c (Fig. 5), for both KDP and squaric acid. In Fig. 5, T_c is shown as a function of the bond length δ -dependent coupling $C(\delta)$ for the example of squaric acid.

The new approach to model hydrogen bonded systems carries various important implications for more structures complicated than those used as model compounds. Especially in biological systems, the exact geometry of the hydrogen bonds with respect to the host matrix is expected to be crucial for the physical properties. The coexistence of displacive and order-disorder behavior should show up in dominant polarization induced contributions to the cooperative proton dynamics and substantial changes in the critical behavior at phase changes are expected.