Coexistence of Order-Disorder and Displacive Features at the Phase Transitions in Hydrogen-Bonded Solids: Squaric Acid and its Analogs

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The systematic analysis of high-resolution NMR data, bond lengths, and isotropic ^{13}C chemical shifts of crystals of squaric acid (H_2SQ) and its deuterated compound (D_2SQ) yields convincing evidence that order-disorder and displacive features coexist at the antiferroelectric phase transition temperature. The experimental data are analyzed within a coupled pseudospin-lattice model which combines order-disorder and displacive dynamics and consistently describes the dynamics and the huge isotope effect observed. The results are considered to be of general importance for systems with collective proton ordering which is common to many organic compounds. [S0031-9007(98)08076-4]

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Hydrogen-bonded ferroelectric and antiferroelectric organic and inorganic compounds have the unique property that the hydrogen atoms in the O-H-O bonds occupy a double-well position above the structural phase transition temperature T_c with random occupation in either of the two sites. At T_c a collective proton ordering is observed together with the onset of a spontaneous polarization. The contribution to the polarization from the proton ordering is minor and arises mainly from the deformation of the host lattice. In all hydrogen-bonded ferroelectrics and antiferroelectrics a huge isotope effect on T_c and the Curie constant is observed upon deuteration. Because of this effect the conventional understanding of the order-disorder transition related to the protons is based on the pseudospin model [1], which assumes that the phase transition is essentially driven by the slowing down of the order-disorder dynamics of the hydrogen atoms in the O-H-O bonds. Recent high-resolution neutron diffraction data on the "prototype" hydrogen-bonded ferroelectric KH_2PO_4 (KDP) [2–4] and extended x-ray-absorption fine structure (EXAFS) measurements on related compounds [5] have provided increasing evidence that the former models have to be extended to account for structural changes in the hydrogen bond geometry [6–8] which requires a coupling of the order-disorder mode to the soft optic lattice mode [9]. A consistent approach to the coupled system has been given in [10]. The isotope effect has been shown there to arise from nonlinear polarizability effects of the host lattice and the details of the O-H-O bond geometry. In addition, the model explicitly predicts the coexistence of order-disorder and displacive dynamics on the same time scale above T_c. No data supporting this prediction have yet been reported for hydrogen-bonded systems, as both x-ray diffraction and EXAFS techniques are not sensitive to the position of the light atom. In this Letter we provide evidence that fully supports these predictions. The experimental data were obtained by NMR spectroscopy, which has the advantages of (a) being sensitive to essentially all atomic displacements, (b) its dynamical range covering both slow and fast motion regimes (10^3-10^{11} Hz), (c) its easy accessibility and simplicity in probing directly the dynamics and displacements of a given atomic site, and (d) the isotropic part of the chemical shift tensor, $\sigma_{\rm iso}$, being invariant to any rotational and translational change of a given molecular unit. We have utilized the ^{13}C NMR of squaric acid, $H_2C_4O_4$, and $D_2C_4O_4$. The temperature dependence of $\sigma_{\rm iso}$ and the O-H(D) and $O\cdots H(D)$ bond lengths have been measured in order to compare the results directly with the predictions from the coupled proton-lattice model [10].

Squaric acid (H_2SQ) was chosen because it has a very simple molecular structure. Planar sheets of the squarate (C_4O_4) groups are linked to each other in a two-dimensional network through $O\text{-}H\cdots O$ bonds with weak van der Waals forces [11,12]. The protons perform an order-disorder motion above the antiferroelectric phase transition temperature $T_c = 373$ K [11–14]; i.e., the distribution of long $O\cdots H$ and short O-H bonds is random. Below T_c the protons order antiferroelectrically and simultaneously the squarate units distort. Even though H_2SQ has been well investigated experimentally [13–18] and theoretically [19], the aspects of the coexistence of order-disorder and displacive effects in the vicinity of T_c have not been addressed previously.

The NMR measurements were performed at 360 MHz on natural abundance ^{13}C nuclei employing a ^{13}C-H double resonance [cross-polarization (CP)] technique and using a Chemmagnetics solid state NMR spectrometer equipped with magic angle spinning (MAS) [20]. The temperature control was accurate to 0.1 K over the 140–420 K range. The utilization of single crystals in CP-MAS experiments leads to an enhancement of spectral resolution by a factor of 5 in the ^{13}C peaks as compared to the use of powder in routine MAS studies [21].

This enabled us to measure the $\sigma_{\rm iso}$ for all four carbons of the C_4O_4 unit, which was crucial for the present study. The measured ^{13}C isotropic chemical shifts versus the C-H, C-D distances where obtained by using a simple polynomial fit between x-ray and neutron data for the undeuterated and deuterated compound and the four chemical shifts [22]. The analysis of the data is based on constructing a function $f(x)$ where x is the O-H, O-D distance which relates x to the chemical shift σ. An optimum function to the experimental data was obtained by $f(x) = a + bx + cx^2$ with coefficients $a = 158.3$ ppm, $b = 36.41 \text{ ppm A}^{-1}$, and $c = -8.392 \text{ ppm A}^{-2}$. The corresponding distances are listed in Table I.

The ^{13}C NMR single crystal data show, in contrast to powder samples, four well resolved peaks below T_c corresponding to the distortions of the C_4O_4 unit (for the original data see Ref. [22]). With increasing temperature they merge together, but being still well resolved and close to T_c ($T_c < 2$ K) a new peak appears at the average position of the four peaks. The new peak corresponds to the high temperature phase. The single crystal data could be fitted with four Lorentzians below T_c and one Lorentzian above T_c. The peak positions as a function of temperature are shown in Fig. 1, where the data for the low temperature phase correspond to performing the average over the four peak positions [22].

As is seen in Fig. 1 where the data are shown for H_2SQ (similar ones have been obtained for partially deuterated D_2SQ) a significant steplike (S-shape) increase in the average chemical shift occurs in the vicinity of T_c. This anomalous shift is not only related to the low temperature peak positions but is also present in the high temperature peak position. In the coexistence region which corresponds to a small regime in the S-shaped anomaly (see Fig. 1) the average of the four low temperature peaks and the high temperature peak coincides so there is no detectable break in the chemical shift as the crystal changes from the paraelectric to the antiferroelectric phase which would be expected from a 1st order order-disorder transition. A signature of the 1st order nature of the transition still remains as the intensity of the four low temperature peaks suddenly becomes zero before they actually merge on the high temperature peak. Even though it is well known that the protons spontaneously order at T_c corresponding to an order-disorder mechanism, the above data suggest that a displacive component is present causing the continuous shift in the NMR peak positions.

TABLE I. Bond distances for $H_2C_4O_4$ and $D_2C_4O_4$ as measured by NMR (distances are given in Å).

Bond	$H_2C_4O_4$	$D_2C_4O_4$
O(1)-H(1)	1.033 ± 0.002	1.013 ± 0.003
O(1)-H(2)	1.070 ± 0.002	1.055 ± 0.003
H(1)···O(3)	1.520 ± 0.004	1.555 ± 0.005
H(1)···O(4)	1.483 ± 0.004	1.513 ± 0.005
O(1)···O(3)	2.553 ± 0.006	2.568 ± 0.008
O(2)···O(4)	2.553 ± 0.006	2.568 ± 0.008

The data have been analyzed within the coupled proton-lattice model [10], which, without loss of generality, has been applied to KDP and its deuterated compound DKDP. As the structure of H_2SQ is less complex than that of KDP, the model is slightly simplified as compared to the one used in Ref. [10]. The Hamiltonian we use is thought to model the pseudo-two-dimensional structure of squaric acid where the C_4O_4 unit is represented by a single highly polarizable cluster coupled to the protons. The large polarizability of the squarate ion framework is modeled by the nonlinear shell model representation [23] which induces in perovskite-type ferroelectrics a displacive phase transition and causes the optic mode softening [24].

$$H = H_T + H_L + H_{TL}\,. \tag{1}$$

H_T is given by the tunneling model [1] of N interacting protons

$$H_T = -\tfrac{1}{2}\sum_{ij} J_{ij} S_i^z S_j^z - \Omega S^x/\sqrt{N}\,, \tag{1a}$$

where the equilibrium positions of the proton are given by a two state pseudospin $S^z = \pm S^x$, J_{ij} is the proton-proton interaction, and Ω is the tunnel frequency. H_L is the lattice Hamiltonian related to the C_4O_4 cluster,

$$H = \tfrac{1}{2}\sum_{q} P_q P_{-q} + \tfrac{1}{2}\sum_{q,q'}\{\omega_q^2 Q_q Q_{-q} + g_2 Q_q Q_{-q}^{(v)} + \tfrac{1}{2} g_4 Q_q Q_{q'} Q_{-q}^{(v)} Q_{-q'}^{(v)}\}\,. \tag{1b}$$

P_q, Q_q refer to q-dependent momentum and displacement coordinate of the C_4O_4 core mass with shell displacement coordinate $Q_q^{(v)}$, ω_q^2 is the harmonic squared lattice mode frequency, and g_2, g_4 are on-site harmonic and 4th-order core-shell coupling constants. The coupling between lattice and protons is modeled by two back-to-back Morse potentials V^M between the protons and the shells of the two neighboring C_4O_4 groups where the shells act

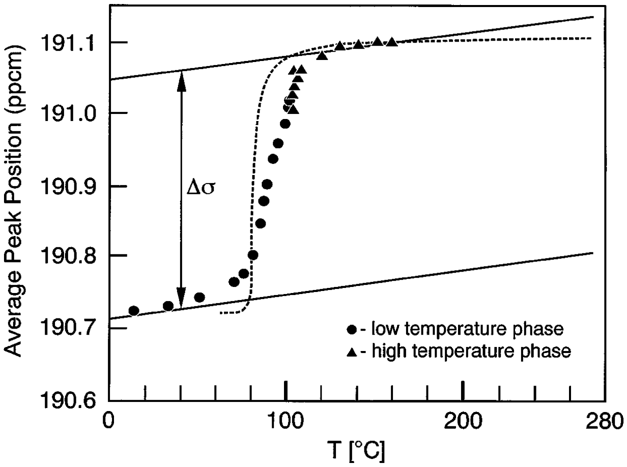

FIG. 1. Averaged NMR peak position of H_2SQ as a function of temperature. The dashed line corresponds to the calculated chemical shift.

alternatively as proton donors or acceptors [25],

$$H_{TL} = C\Sigma_q S^z Q_q^{(v)}\,, \tag{1c}$$

C provides here the harmonic coupling between the shells and the pseudospins and is, as has been shown in Ref. [10], linearly dependent on the proton-proton site separation δ which has been measured indirectly through the $O \cdots O$ bond distance of neighboring C_4O_4 groups (Table I). The interaction between pseudospins and shells leads to important renormalizations of the temperature dependent dynamics of the system as it provides the coupling of the displacive heavy ion unit to the order-disorder dynamics of the protons. Using a mean-field approximation the thermal expectation values of the phonon coordinates and the pseudospin operators have to be determined self-consistently. It is then easily verified that if $\langle S^z \rangle = 0$, $\langle Q \rangle = \langle Q^{(v)} \rangle = 0$ which holds in the paraelectric phase while $\langle S^x \rangle$ can be approximated by $\Omega/4k_BT$. The equations of motion are obtained by introducing collective Fourier transform variables for the pseudospin and phonon deviations operators. These equations provide explicitly the frequencies ω^2 of the coupled lattice-pseudospin system.

$$\omega_\pm^2 = (\omega_0^2 - C\chi_s) + \tfrac{1}{2}\Omega(\Omega - J_q\langle S^x \rangle - C^2\langle S^x \rangle/g_4T) \pm \{[(\omega_0^2 - CX_s) - \tfrac{1}{2}\Omega(\Omega - J_q\langle S^x \rangle - C^2\langle S^x \rangle/g_4T]^2 - 4\Omega C^2\chi_s\langle S^x \rangle/g_4T\}^{1/2}\,, \tag{2}$$

where $\chi_s = \delta S^x/\delta Q$ defines an effective pseudospin-pseudospin correlation function and $\langle(\delta Q)^2\rangle = \sum_q \hbar\omega_q \coth(\hbar\omega_q/2k_BT)$ which at $T = T_c$ simplifies like $\langle(\delta Q)^2\rangle = 2k_BT_c/\omega^2$. ω_0^2 is the $q = 0$ uncoupled soft lattice mode frequency. From Eq. (1) the coupled modes have been calculated as a function of temperature, and the results are shown in Fig. 2.

For the uncoupled system two transition temperatures are obtained where one transition is purely 1st order order-disorder related to the protons, while the other is purely 2nd order displacive related to the heavy ions. For small coupling the displacive lattice mode frequency hardens slightly and becomes discontinuous at T_c, while the tunnel mode already adopts a small displacive component appearing by a rounding in the temperature dependence of this mode close to T_c. Also the transition temperature is raised as compared to the uncoupled case. For strong enough coupling C both transition temperatures coincide and a substantial displacive component appears in the tunnel mode frequency, while the soft lattice mode hardens more and has a small discontinuity at T_c; i.e., the transition is 1st order in both subsystems. It is also important to note that T_c of the proton system is strongly enhanced as compared to the uncoupled or weakly coupled system. In the vicinity of T_c the frequencies of both systems are nearly degenerate, and it is no longer possible to make a clear distinction between the lattice mode and the tunnel mode; i.e., displacive and order-disorder features coexist as is also observed experimentally. As the double-well potential of the proton system is not rigid above T_c but temperature dependent due to the coupling to the soft lattice mode, the isotropic part of the chemical shift tensor $\sigma_{\rm iso}$ can be expressed as the sum of a temperature independent part σ_0 and a temperature dependent quantity $\sigma(T) = \sigma_T\langle(\delta Q^{(v)})^2\rangle$, with $\langle(\delta Q^{(v)})^2\rangle = \sum_q(\hbar/\omega \coth \hbar\omega)/2k_BT$. Inserting for ω the lattice related frequency as obtained from Eq. (2) and shown in Fig. 2 the chemical shift $\sigma_{\rm iso} = \sigma_0 + \sigma(T)$ is calculated and shown as a function of temperature in Fig. 1 (dashed line) together with the experimental data. Even though the calculated transition is less broad the agreement between experiment and theory is rather good. As the discontinuity in the lattice related mode is small at T_c where T_c corresponds to $\omega = 0$, the calculated chemical shift does not show a discontinuity at T_c within the numerical accuracy. It is also important to point out that the S shape in $\sigma(T)$ is a direct consequence of using the renormalized frequencies as defined by Eq. (2) in the calculation.

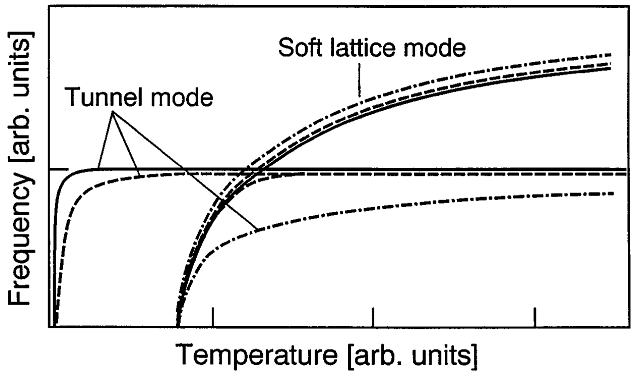

FIG. 2. Tunnel and lattice mode frequencies as a function of temperature with parameters $J/\Omega = 18.2$, $g_2/g_4 = -0.8$ Å^2, $\Omega/\omega_q = 0.46$). Solid lines: uncoupled system ($C = 0$); dashed line: weakly coupled system ($C = 1 \times 10^4$ K/Å); dash-dotted line: strongly coupled system ($C = 5.7 \times 10^4$ K/Å).

Assuming that the proton-proton site separation δ is linear in x in $H_{2-x}D_xC_4O_4$ the coupling C between pseudospins and squarate is linear in x as well [10]. As the soft mode and T_c are substantially renormalized through C, $\sigma_{\rm iso}$ is also renormalized through $\sigma(T)$.

From Eq. (2) T_c is given by the condition that $\omega_\pm^2 = 0$. At $T = T_c$, $g_2 + g_4\langle(\delta Q^{(v)})^2\rangle = 0$; i.e., $T_c \cong -g_2/g_4$, and $\langle S^x \rangle = \Omega/4T_c$. T_c is determined numerically from Eq. (2) and shown as a function of $C(\delta)$ ($\delta := H \cdots H$, $D \cdots D$ site separation) in Fig. 3 where the numerical results are compared to the experimental data from Refs. [13,14]. Even though C is linear in δ and x, T_c is nonlinearly dependent on C as is obvious from Eq. (2). In the investigated regime of T_c and C shown in Fig. 3 a close to linear dependence of T_c on C is obtained where C is calculated within the scheme used in Ref. [10]. It is

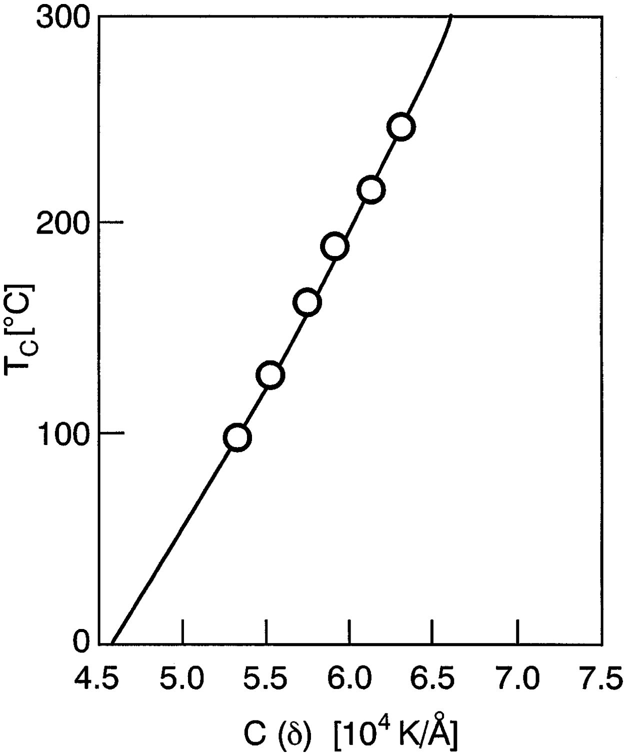

FIG. 3. T_c as a function of coupling constant C: Comparison between experimental data (open circles from Refs. [13] and [14]) and theoretical results (full line).

important to emphasize that the experimentally observed linearity [14] represents an exception as compared to other H-D mixed systems where deviations from linear behavior have been observed [26] and can be well described by our analysis.

An approximate analytical solution for T_c yields that the transition temperature is independent of the tunnel mode frequency Ω which is in accordance with the conclusions drawn in Ref. [13]. Experimentally, it is found that Ω changes substantially with deuteration. This observation is not contradictory to our results as the tunnel mode is renormalized through the coupling C like $\Omega_r = \frac{1}{2}\Omega(\Omega - J_q\langle S^x\rangle - C^2\langle S^x\rangle/g_4T)$. As C increases with H $\cdots$ H, D $\cdots$ D site separation, Ω_r decreases in agreement with experiment but remains unimportant for the absolute value of T_c [13].

In conclusion, we have presented experimental data on the O $\cdots$ H, O $\cdots$ D bond length in H_2SQ, D_2SQ which show that at the phase transition, order-disorder and displacive components coexist which obey the same time scale. The data have been analyzed within a lattice dynamical model which couples the order-disorder dynamics of the pseudospins to the displacive dynamics of the nonlinear lattice and consequently combines the two aspects of the phase transition. It has been shown that a 1st order phase transition results where—even though cooperative proton ordering persists at T_c—the tunnel mode adopts displacive character and the soft mode becomes discontinuous at T_c. The data and their analysis are not only important with respect to ferroelectric and antiferroelectric systems, but carry significant implications for other organic and inorganic compounds where collective tunneling is present and the hydrogen bond symmetry is crucial.

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