

Two-time clock NMR observation of the ferroelectric transition in the organic compound cyclohexane-1,1'-diacetic acid

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The ferroelectric transition in the molecular organic ferroelectric material cyclohexane-1,1'-diacetic acid has been studied with a ^1H NMR two-time clock experiment. On the spin-lattice relaxation time scale (10^8 Hz) the molecular motions are observed as slow in both the paraelectric and the ferroelectric phase so that the instantaneous value of the crystal symmetry is observed in both phases and no symmetry breaking effectively takes place at T_c . On the kHz time scale of the NMR line shape and the dipolar relaxation time experiments, the phase transition is observed and confirms the model of a dynamically disordered structure in the paraphase. [S0163-1829(98)50714-X]

Among a huge total number of organic compounds only a few molecular organic crystals are known to be ferroelectric. This is in contrast to the inorganic materials where ferroelectricity has been reported in more than 200 pure compounds,¹ not including mixtures and liquid crystals. The recent overview of known ferroelectrics² contains merely the following molecular organics: thiourea, tanane, benzil, and phenanthrene. In addition, diacetylene [1,6-bis(2,4-dinitrophenoxy)-2,4-hexadiyne] and tetrathiafulvalene-*p*-chloranile show ferroelectricity at very low temperatures³ whereas ferroelectric properties of trichloroacetamide (TCAA) have been reported recently.⁴ In view of the extremely rich variety of organic compounds this surprisingly small number of molecular organic ferroelectrics has motivated a search for organic ferroelectric materials. Indeed, a systematic theoretical approach based on the consideration of crystal symmetries⁵ has predicted the possible existence of a ferroelectric phase in sixteen molecular organic compounds. Among these candidates the ferroelectric phase has recently been experimentally confirmed in cyclohexane-1,1'-diacetic acid (CDA) where the first-order ferroelectric phase transition^{6,7} occurs at $T_c = 398$ K.

CDA with the chemical formula $\text{C}_{10}\text{H}_{16}\text{O}_4$ crystallizes at room temperature in a monoclinic system with the polar space group⁸ Cc . The lattice parameters are $a = 1.3785$ nm, $b = 0.8151$ nm, $c = 1.0558$ nm, $\beta = 121^\circ$ and there are four molecules per unit cell. Each molecule satisfies a pseudosymmetry of a twofold axis. The largest displacements from the exact symmetry are exhibited by the three carbon atoms of the cyclohexane ring labeled as C(3), C(4), and C(5) (Fig. 1). Inside the unit cell the molecules are oriented in a way that the pseudosymmetry axis is parallel to the crystal b axis. In the crystalline state the molecules form infinite quasi one-dimensional rows along the $\mathbf{a} + \mathbf{c}$ direction where the neighboring molecules are hydrogen-bonded with two hydrogen bonds between carboxylic groups. The room temperature phase is ferroelectric and consists of two domain states corresponding to two orientations of the CDA molecules which are related to each other by the above-mentioned twofold axis.

The structure of the high-temperature nonpolar phase above 398 K has not been determined yet. There is in addition an open question about the microscopic model of the ferroelectric transition in CDA. One possibility is that the transition is of a displacive type where, on going into the high-temperature nonpolar phase, the atoms are shifted to positions in which the twofold symmetry is exactly obeyed by all the atoms of the molecule. The second possibility is that the high-temperature structure is a dynamically disordered superposition of both molecular orientations and thus of the two domain states related by the rotation by the angle π . In this case the time average of the two orientations is usually observed spectroscopically, yielding an increase of the time-average symmetry above the transition temperature T_c . The observation of the phase transition should actually depend on the frequency observation window of the spectroscopic technique used. Here we encounter an interesting situation of the phase transition which occurs in the "slow motion regime." Namely, structural phase transitions are normally observed in the "fast motion regime" where the time scale of the order parameter fluctuations is much shorter than the time scale of the observation technique. In such a case one observes time averaged physical quantities so that a symmetry-breaking order parameter can be defined; e.g., the frozen-out eigenvector of the soft mode, which is zero above T_c and nonzero below. The situation is completely different if the time scale of fluctuations is longer than the time scale of the experiment. In that case the instantaneous value of the eigenvector of the soft mode is observed, which is nonzero above and below T_c . The time-average order parameter can no longer be defined and the phase transition takes place in the slow motion regime where its observation depends on the frequency window of the spectroscopic technique. A class of inorganic solids which undergo structural phase transitions in the slow motion regime to a ferroelectric or antiferroelectric state has been discovered recently. This is the family of thiocyanates^{9,10} (KSCN, RbSCN, NH_4SCN , etc.). In RbSCN, for instance, ^{87}Rb NMR study of the antiferroelectric phase transition has shown¹¹ that at a certain temperature the sym-

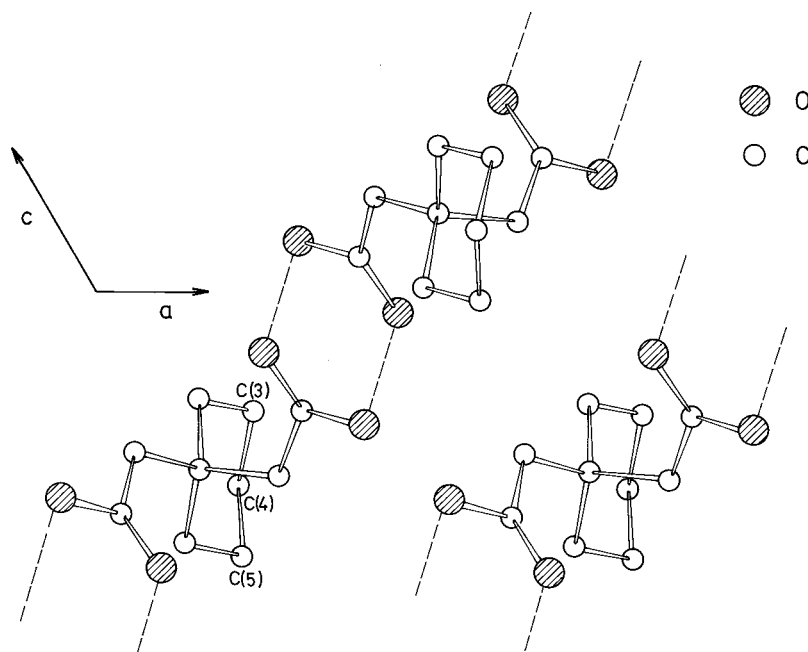


FIG. 1. A projection of the CDA crystal structure on the plane perpendicular to the b axis (hydrogen atoms not shown). Dashed lines represent the hydrogen bonds.

metry of the high-temperature tetragonal phase is dynamically broken on the nuclear Larmor frequency (10^{-8} s) time scale whereas the symmetry breaking terms are averaged out on the NMR line shape (10^{-3} s) time scale so that the high-temperature symmetry is still observed.

CDA seems to be another candidate for the phase transition which occurs in the slow motion regime. Dielectric measurements⁶ have reported recently an extremely low-frequency soft mode near and above the phase transition which slows down at T_c to 4 kHz only. This strongly suggests the hypothesis that the high-temperature phase is a dynamically disordered superposition of two molecular states where the molecules dynamically switch between the two orientations. The switching can be realized in two ways. The first is a reorientation of the molecule by the angle π about the pseudo-twofold axis. This involves an extensive movement of a rather heavy object and seems to be consistent with the observed low frequency of the soft mode.⁶ In the reorientation process the molecules can be considered as quasirigid and the switching is not accompanied by internal deformations. The second possibility is that the switching occurs via a dynamic intramolecular deformation. There the atoms would realize correlated displacements from their positions of one molecular orientation to the positions of the other. This concerns especially the three carbons C(3), C(4), C(5) whose displacements would be the largest (up to 0.18 nm)⁷ in that process. Such a dynamic intramolecular distortion would involve thermally activated transitions over a high potential barrier, considerably higher than in the case of a molecular reorientation as a rigid object. This makes the distortion switching less probable.

The ferroelectric phase transition in CDA has been studied by a "two-time clock" experiment, where the same transition is observed simultaneously on two experimental time scales. Such a possibility is provided by the use of different NMR spectroscopic techniques. For instance, the NMR spin-

lattice relaxation time T_1 measurements are sensitive to internal molecular motions with frequencies close to the nuclear Larmor frequency which is on the scale 10^7 – 10^8 Hz. In contrast, NMR line shape measurements and the dipolar relaxation time T_{1D} are sensitive to motions on the kHz frequency scale, thus a factor 10^4 slower.

We analyze first the phase transition when observed on the T_1 frequency scale. The proton spin-lattice relaxation time measurements were performed on a CDA monocrystal in the temperature interval between 293 and 430 K at two Larmor frequencies $\nu_0(^1H) = 270$ and 32 MHz. The crystal melts at 453 K and care has been taken not to go too close to that temperature to avoid crystal decomposition. The temperature dependence of T_1 is displayed in Fig. 2. T_1 is the longest at room temperature and decreases monotonically to-

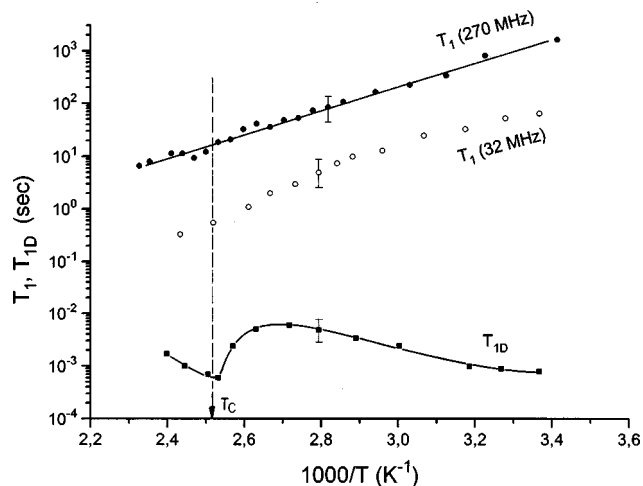


FIG. 2. Temperature dependence of the proton spin-lattice relaxation time T_1 and the dipolar relaxation time T_{1D} in CDA. Solid lines are guides for the eye.

wards higher temperatures. No anomaly is observed at the phase transition at 398 K. There is also a marked frequency dependence of T_1 when compared on the 270 and 32 MHz scales.

The spin-lattice relaxation time of protons induced by the random molecular reorientations is given by¹²

$$\frac{1}{T_1} = \sum_{i < j} \frac{3}{10} \frac{\gamma^4 \hbar^2}{r_{ij}^6} \left(\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right). \quad (1)$$

Here ω_0 is the nuclear Larmor frequency, r_{ij} the interproton distance, γ the gyromagnetic ratio, and τ_c the autocorrelation time for molecular reorientations. In the fast motion limit ($\omega_0 \tau_c \ll 1$) T_1 becomes independent of the Larmor frequency. Assuming Arrhenius thermally activated form of the autocorrelation time with the activation energy E_a ; $\tau_c = \tau_\infty \exp(E_a/k_B T)$; T_1 increases towards higher temperatures in that limit. In the slow motion limit ($\omega_0 \tau_c \gg 1$), on the other hand, T_1 depends on frequency as $T_1 \propto \omega_0^2$ and decreases towards higher temperatures. In CDA the frequency dependence and the decrease of T_1 towards higher temperatures have been observed in the whole investigated temperature range. This demonstrates that the internal molecular motions are slow on the frequency scale of the spin-lattice relaxation technique in both the paraelectric and the ferroelectric phase. The activation energy $E_a = 435 \pm 10$ meV was determined from the T_1 slope. The high E_a value demonstrates that rather heavy objects are involved in the dynamics of CDA and is consistent with the picture that the molecules undergo classical thermally activated reorientations about their pseudo-twofold axes. The reorientational frequencies are slow on the observation time scale of the T_1 experiment both below and above T_c so that the reorienting molecules are observed at their instantaneous orientations rather than at a time average and no symmetry breaking is observed on crossing T_c .

It is interesting to compare this result with the observation of the same phase transition on a four orders of magnitude slower time scale of the proton NMR spectrum experiment which has the frequency observation window in the kHz range. The shape of the proton spectrum is primarily determined by the secular part of the magnetic dipole interaction between protons. This is a traceless interaction, depending on the angle θ between the external magnetic field and the position vector joining the two proton nuclei as $1 - 3 \cos^2 \theta$. Fast isotropic motion averages this interaction to zero, producing a complete narrowing of the rigid lattice spectrum. The motion anisotropic in space produces, on the other hand, only partial narrowing, reflecting the fact that not all of the molecular orientations on the sphere are equally probable. The study of the motionally narrowed spectrum thus provides a way to distinguish between the isotropic and hindered motions.

The line shape $I(\omega)$ is given by the Fourier transform of the free induction decay function $G(t)$

$$I(\omega) = \int G(t) \exp[i(\omega_0 - \omega)t] dt. \quad (2)$$

In the case of random stochastic fluctuations of the nuclear resonance frequency, $G(t)$ can be expressed as¹³

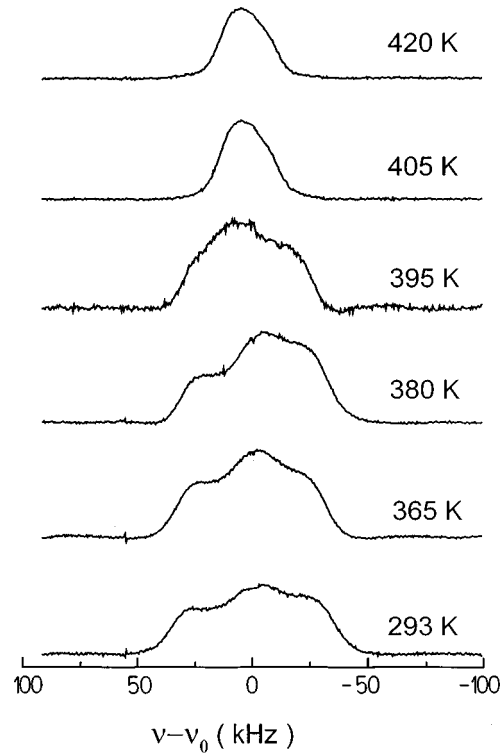


FIG. 3. Proton NMR spectra at $\nu_0(^1H) = 270$ MHz of a CDA monocrystal above and below the ferroelectric transition ($T_c = 398$ K).

$$G(t) = \exp\left(-\frac{1}{2} \omega_p'^2 t^2\right) \exp\left(-\omega_p'^2 \int_0^t (t-\tau) g_\omega(\tau) d\tau\right). \quad (3)$$

Here the second moment of the absorption line is assumed to be a sum of two contributions; $\omega_p'^2 = \omega_p'^2 + \omega_p''^2$. The first term $\omega_p'^2$ is destroyed by the motion characterized by the reduced autocorrelation function $g_\omega(t) = \exp(-t/\tau_c)$ whereas the second term $\omega_p''^2$ is not affected by the motion and determines the width of the motionally averaged spectrum. For the isotropic motion one has $\omega_p''^2 = 0$ and an infinitely narrow spectrum results in the fast motion limit whereas for the anisotropic motion the spectrum exhibits a residual width determined by $\omega_p''^2 \neq 0$.

Proton NMR spectra of a CDA single crystal have been measured between room temperature and 440 K (Fig. 3). The full width at half height (FWHH) of the absorption spectrum (Fig. 4) exhibits a motional transition in the vicinity of T_c . This transition is typical for molecular dynamics which slows down from the fast to the slow motion limit on the experimental time scale when the temperature is decreased. In the paraphase the motions are fast on the observation scale so that a motionally averaged spectrum is observed, whereas far below T_c the crystal structure is observed as frozen static and the rigid lattice spectrum results. The FWHH value $\Delta\nu_{1/2} = 16$ kHz at the highest measured temperature in the paraphase is quite large demonstrating that the molecular motion responsible for the line narrowing is highly anisotropic in space. This supports the hypothesis that the reorientations of the CDA molecules are performed about their pseudo-twofold axes which have a well-defined orientation

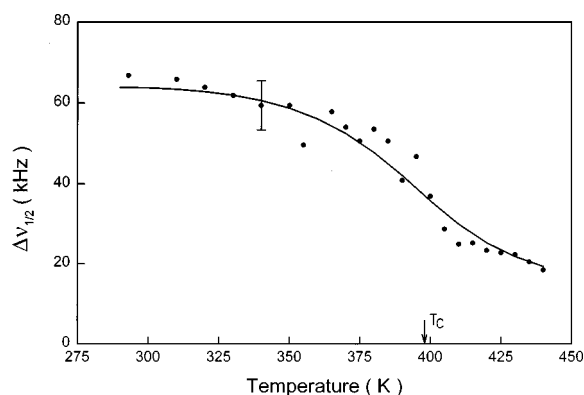


FIG. 4. Full width at half height of the proton NMR spectrum as a function of temperature in CDA. Solid line is the fit with Eqs. (2) and (3).

in the unit cell. Unfortunately the FWHH could not be measured at still higher temperatures to reach the saturation value of the completely motionally narrowed spectrum because of crystal melting. In the ferroelectric phase the spectrum broadens continuously and reaches the low-temperature saturated FWHH value of 65 kHz around room temperature. Below that temperature the motions are observed as static on the experimental time scale. The slowing-down dynamics of the ferroelectric phase transition in CDA is thus clearly observed on the kHz scale. The temperature dependence of the FWHH has been reproduced by Eqs. (2) and (3) (solid line in Fig. 4) with the fit parameters $\omega'_p = 2\pi \times 50$ kHz, $\omega''_p = 2\pi \times 6$ kHz, $\tau_\infty = 8 \times 10^{-12}$ s, and $E_a = 435 \pm 10$ meV. Here it is important to note that this value of the activation energy—determined from the linewidth transition—is the same as that determined from the T_1 measurement, demonstrating that the same motion is observed in both experiments but on different experimental time scales.

Another independent observation of the phase transition in CDA on the kHz frequency scale is made by measuring the NMR dipolar relaxation time T_{1D} of protons. The dipolar relaxation time is conveniently measured by the Jeener-Broekaert pulse sequence¹⁴ which transfers the high-field Zeeman spin order into the dipolar order by the application

of a pair of phase-shifted rf pulses. In this way the dipolar energy reservoir is efficiently cooled resulting in a very low spin temperature. The evolution of the dipolar spin temperature towards the equilibrium then proceeds with the time constant T_{1D} . The change of the spin temperature is induced by the transitions between the energy levels of proton magnetic dipole moments in the dipolar fields of their neighbors. The transition frequencies fall into the kHz frequency range. The temperature dependence of proton T_{1D} measured on the CDA monocystal is displayed in the lower part of Fig. 2. T_{1D} exhibits a clearly observed anomaly at the phase transition. The minimum in T_{1D} at T_c reflects the presence of dynamic fluctuations in the paraphase which slow down into the kHz frequency range on going towards the phase transition. The ferroelectric transition is thus clearly observed on the time scale of the NMR dipolar relaxation time experiment.

To summarize, the ferroelectric transition in CDA has been observed on two experimental time scales. In the NMR spin-lattice relaxation experiment the molecular dynamics is observed as slow on the time scale 10^8 Hz both above and below T_c so that the instantaneous crystal symmetry is observed in both phases and no symmetry breaking effectively takes place at T_c . When the phase transition is observed on the kHz time scale of the NMR line shape and dipolar relaxation time experiments, the phase transition is clearly observed. This is demonstrated by the motional transition in the proton NMR linewidth which changes from the fast to the slow motion limit in the vicinity of T_c where also the dipolar relaxation time T_{1D} exhibits a minimum. The ferroelectric phase transition in CDA thus belongs to the interesting class of phase transitions which take place in the slow motion limit where the observation of the phase transition actually depends on the experimental time scale. Among ferroelectrics such a situation has been found so far only in the inorganic thiocyanates family. CDA is, to the best of our knowledge, the first molecular organic ferroelectric crystal belonging to this class.

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