

# Temperature-Jump 2D NMR Spectroscopy in Crystalline Solids: A Technique for Correlating Molecular Reorientation across the Phase Boundaries of an Order–Disorder Lattice

R. Fu,<sup>†</sup> A. N. Klymachyov,<sup>‡</sup> G. Bodenhausen,<sup>§</sup> and N. S. Dalal<sup>\*,†,‡</sup>

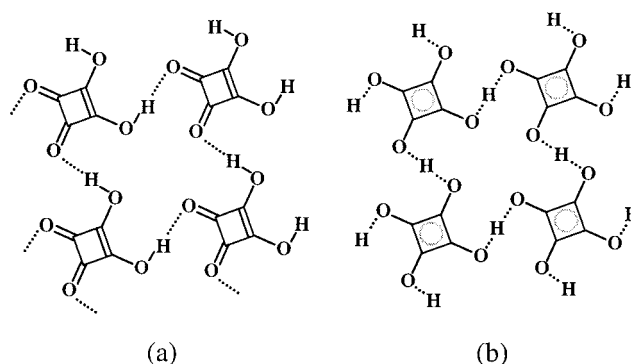
Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory,  
Department of Chemistry, Florida State University, 1800 East Paul Dirac Drive, Tallahassee, Florida 32310,  
and Département de Chimie, Ecole Normale Supérieure, 24 Rue Lhomond, 75231 Paris Cedex 05, France

Received: July 24, 1998

We describe a two-dimensional high-resolution solid-state NMR methodology for correlating the dynamics of molecular rearrangements around the critical points of equilibrium phase transitions in molecular solids. It combines the techniques of temperature-jump and two-dimensional (2D) NMR spectroscopy. The two spectral dimensions are the isotropic chemical shifts at different sample temperatures. The technique is illustrated by elucidating the dynamic rearrangement of the C<sub>4</sub>O<sub>4</sub> units of squaric acid (H<sub>2</sub>C<sub>4</sub>O<sub>4</sub>) in relationship to the mechanism of its antiferroelectric phase transition at  $T_N \sim 373$  K. These results clarify the apparent discrepancy between the conclusions derived earlier from NMR, X-ray, and Raman and neutron scattering studies. They were a direct consequence of the significant enhancement in the NMR spectral resolution through this technique, which thus might prove to be a significant new aid in understanding the mechanisms of phase transitions in molecular solids.

## Introduction

High-resolution solid-state NMR is becoming an important technique for probing the molecular mechanism of cooperative phenomena such as ferroelectric phase transitions.<sup>1</sup> There is, however, an everlasting quest for enhancement in the spectral resolution, since the transitions seem to involve rather minute changes in molecular structure and dynamics that could remain undetected in NMR measurements in solids. NMR studies of the antiferroelectric phase transition in squaric acid (H<sub>2</sub>C<sub>4</sub>O<sub>4</sub>),<sup>2,3</sup> the crystal structure of which is shown in Figure 1, at its transition temperature  $T_N$  ( $\sim 373$  K) provide an illustrative case. At  $T < T_N$ , high-resolution NMR measurements on single crystals of H<sub>2</sub>C<sub>4</sub>O<sub>4</sub> suggested<sup>2–5</sup> a regular trapezoidal shape for the C<sub>4</sub>O<sub>4</sub> fragment, while earlier X-ray and neutron diffraction studies<sup>6,7</sup> had established an irregular trapezoidal geometry for this moiety. This discrepancy was recently shown to be related to the lack of spectral resolution in earlier NMR measurements. Our recent NMR measurements with improved resolution, obtained by using single crystals in combination with magic angle spinning,<sup>8,9</sup> clearly supported the X-ray results: each of the four carbons of the C<sub>4</sub>O<sub>4</sub> unit exhibited a different isotropic chemical shift (cf. Figure 2b), compatible with an irregular trapezoidal carbon framework.<sup>6,7</sup> However, at temperatures close to  $T_N$ , the <sup>13</sup>C NMR line shapes exhibited additional, poorly resolved splitting. Moreover, in a temperature range of about 3 K around  $T_N$ , a new (central) peak emerged near the center of the spectrum (cf. Figure 2c), essentially at the position expected for motional narrowing of all the four peaks (cf. Figure 2d).<sup>4,5,8,9</sup> Interestingly, the shape of this peak appeared to be more complex than a simple Lorentzian expected for a fast



**Figure 1.** Crystal structure of squaric acid<sup>6,7</sup> in (a) low-temperature (antiferroelectric) and (b) high-temperature (paraelectric) phases. The unique axis *b* is perpendicular to the C<sub>4</sub>O<sub>4</sub> plane. The hydrogen bonds are indicated by dashed lines.

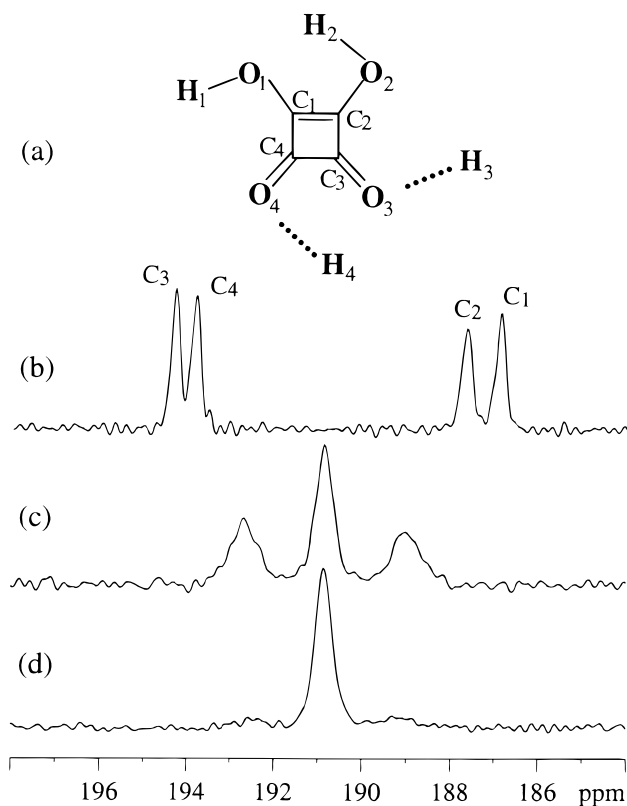
exchange process.<sup>8,9</sup> It has thus not been possible to ascertain the origin of these unusual NMR line shapes. It was also apparent that a further enhancement in spectral dispersion would be helpful, thus providing the main impetus for the present study.

In the present work, we used a two-dimensional (2D) NMR technique<sup>10,11</sup> that combines a temperature-jump with 2D exchange NMR spectroscopy.<sup>12</sup> The two domains utilized are the isotropic chemical shifts  $\delta_{iso}$  at different sample temperatures ( $T$ ) as measured by a standard cross-polarization technique<sup>13</sup> combined with magic angle spinning (CPMAS). One of the temperatures is selected to be in the low-temperature (antiferroelectric) phase while the other one is in the vicinity of the phase transition temperature,  $T_N$ . In the case of squaric acid, our results show that the technique significantly enhances the spectral dispersion in the vicinity of structural phase transition and has thus led to an enhanced understanding of the transition mechanism.

<sup>†</sup> National High Magnetic Field Laboratory, FSU.

<sup>‡</sup> Department of Chemistry, FSU.

<sup>§</sup> Ecole Normale Supérieure.



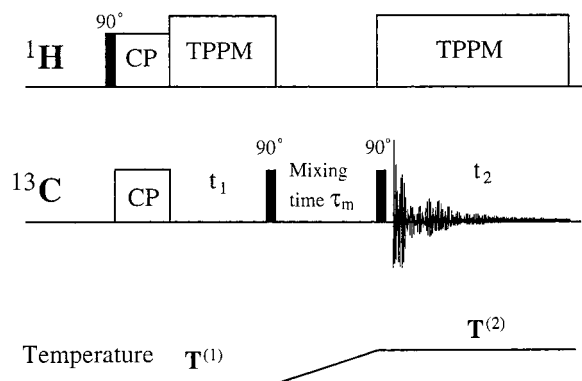
**Figure 2.** Squaric acid and its  $^{13}\text{C}$  CPMAS NMR spectra at different temperatures. (a) Molecular structure of squaric acid. (b) Spectrum obtained at 303 K (antiferroelectric phase) where all four peaks are well-resolved. The peak assignment suggested by Klymachyov and Dalal<sup>9</sup> is as follows:  $\sigma(\text{C}_1) = 187.0$  ppm,  $\sigma(\text{C}_2) = 187.7$  ppm,  $\sigma(\text{C}_3) = 194.3$  ppm, and  $\sigma(\text{C}_4) = 193.9$  ppm. (c) Spectrum recorded at 372 K where an additional central peak appears in the vicinity of phase transition. (d) Spectrum taken at 374 K in the paraelectric phase.

### Materials and Methodology

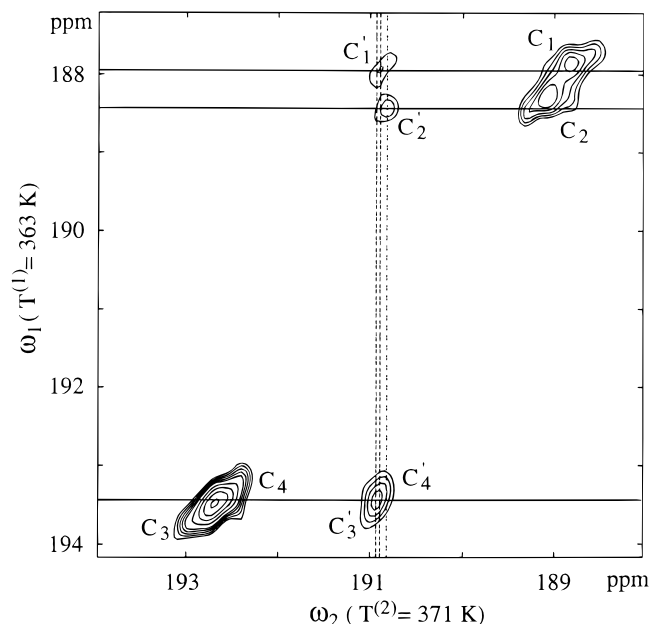
Squaric acid was purchased from Aldrich, and the single crystal was grown by slow evaporation of an aqueous solution. Squaric acid was selected for several reasons. First, the molecular basis of its antiferroelectric behavior is not well understood, despite over two decades of theoretical and experimental studies.<sup>2–5,8,9</sup> Further investigation is worthwhile because squaric acid is considered to be a good model for understanding the many unusual structural and dynamic aspects of hydrogen-bonded systems. Second, as pointed out earlier, this compound has been well investigated by solid-state NMR techniques,<sup>2–5</sup> but the spectral line shapes (cf. Figure 2b), particularly in the vicinity of its phase transition, are known to be complex and not well understood.

The NMR experiments were carried out on a Bruker DMX-300 spectrometer ( $B_0 = 7$  T) with Larmor frequencies of 75 MHz for  $^{13}\text{C}$  and 300 MHz for protons. A small ( $\sim 3 \times 3 \times 3$  mm<sup>3</sup>) single crystal of squaric acid, spinning at 6 kHz about the magic angle, was used to enhance the spectral resolution.<sup>8,9</sup> The sample temperature was controlled by a variable temperature unit BVT-2000 to within 0.1 K. Temperature jumping was accomplished with the same unit.

The pulse sequence used is shown in Figure 3. In the *preparation period*, the sample temperature is stabilized at  $T^{(1)}$ , which corresponds to the low-temperature phase. After enhancement by cross-polarization, the  $^{13}\text{C}$  magnetization evolves during the *evolution period*  $t_1$ . A  $90^\circ$  pulse is applied to restore the  $^{13}\text{C}$  magnetization along the  $z$  axis before the *mixing period*



**Figure 3.** Pulse sequence for temperature-jump 2D NMR experiment. See the text for details.



**Figure 4.** A typical  $^{13}\text{C}$  CPMAS temperature-jump 2D spectrum of squaric acid, where the temperature in the  $t_1$  domain was stabilized at  $T^{(1)} = 363$  K while the temperature in the  $t_2$  domain was about 371 K. The mixing time was 35 s to allow temperature jump. The spectrum was recorded with  $64 \times 256$  data points on a Bruker DMX 300 spectrometer. For each  $t_1$  increment, 32 scans were accumulated. The recycle time was 10 min to allow for stabilizing the  $T^{(1)}$ .

$\tau_m$ , during which the temperature is jumped from  $T^{(1)}$  to  $T^{(2)}$ . The NMR signal at  $T^{(2)}$ , which corresponds to the high-temperature phase, is recorded in the *detection period*  $t_2$  after a second  $90^\circ$  pulse. Proton decoupling<sup>14</sup> is applied during the evolution period  $t_1$  and the detection period  $t_2$ . It is worthwhile to note that the temperature-jump rate during the mixing time  $\tau_m$  is critical, depending upon the spin–lattice relaxation time ( $T_1$ ) of the spins under investigation. With the use of pulsed microwaves,<sup>15–17</sup> one can increase the temperature-jump rate and thus be able to observe rapid phase changes between isotropic and anisotropic phases in liquid crystals. In the case of squaric acid, the  $^{13}\text{C}$  relaxation time is about 80 min;<sup>18</sup> thus, no special heating device was needed for the temperature-jump studies.

### Results and Discussion

Figure 4 shows a typical 2D spectrum obtained by jumping the sample temperature between  $T^{(1)}$  and  $T^{(2)}$ . The spectrum shows the correlation of the  $^{13}\text{C}$  signals at these two temperatures.  $T^{(1)}$  is 363 K, corresponding to the antiferroelectric phase,

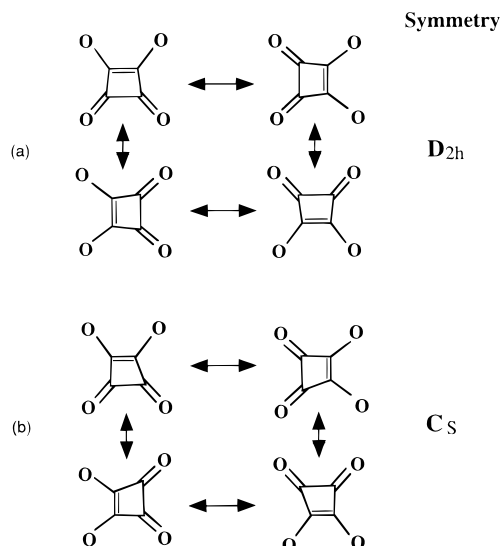
while  $T^{(2)} = 371$  K where both phases coexist (cf. Figure 2c). The middle peaks around 191 ppm in the  $\omega_2$  domain, labeled  $C_1'$ ,  $C_2'$ ,  $C_3'$ , and  $C_4'$ , originate from  $C_1$ ,  $C_2$ ,  $C_3$ , and  $C_4$ , respectively, as indicated by the solid horizontal lines. The projection of these peaks on the  $\omega_2$  domain corresponds to the central peak in Figure 2c. The positions of the middle peaks are highlighted by the dashed vertical lines in Figure 4. The chemical shift difference between  $C_1'$  and  $C_2'$  is only 0.1 ppm, while that between  $C_3'$  and  $C_4'$  is even smaller, but the resolution was good enough to render them distinguishable. This result implies a multiple structure of the central peak in Figure 2c, in contrast to the many earlier NMR studies wherein this peak was considered to be a single, exchange-narrowed Lorentzian signal.<sup>2-5,8,9,18,19</sup> It can thus be noted that even for the CPMAS experiment, 2D spectroscopy with temperature jump leads to a substantial enhancement in the spectral dispersion.

An important point to be noted from Figure 4 is that the horizontal lines, which are drawn to indicate the centers of the  $C_1'$  and  $C_2'$  peaks, do not pass through the positions (maximum intensities) of the  $C_1$  and  $C_2$  peaks. Although less clear, this appears also to be the case for  $C_3'$  and  $C_4'$  in relationship to  $C_3$  and  $C_4$ . These results imply that  $C_1'$  and  $C_2'$  emerge from parts, rather than from the whole, of the  $C_1$  and  $C_2$  peaks. From this observation we can conclude that the  $C_1$  and  $C_2$  peaks must result from a superposition of at least two types of clusters, only a fraction of which is dynamic and contributes to  $C_1'$  and  $C_2'$ . Similarly,  $C_3'$  and  $C_4'$  can be considered to originate from only a part of  $C_3$  and  $C_4$ . These data suggest that as the temperature approaches  $T_N$ , the low-temperature long-range ordered antiferroelectric domains start to fragment and lead to small disordered local regions. Above  $T_N$ , the middle peaks remain the only feature in the spectrum (cf. Figure 2d), implying that now all the ordered microdomains (represented by  $C_1$ ,  $C_2$ ,  $C_3$ , and  $C_4$ ) have changed into a nonordered, paraelectric structure.

These results help explain a long-standing controversy in the literature on the molecular model of squaric acid in its high-temperature, paraelectric phase. As mentioned in the Introduction, the earlier high-resolution NMR measurements utilizing static single crystals had indicated<sup>2-5</sup> that, in its high-temperature phase, the structure of squaric acid was a time-averaged form of a *regular* trapezoid as depicted in Figure 5a. This structure has a  $D_{2h}$  symmetry. On the other hand, NQR<sup>19</sup> and neutron as well as Raman scattering<sup>20</sup> measurements demonstrated that, at several degrees above the  $T_N$ , the site symmetry was  $C_s$ . These data thus indicated that the molecular structure in the high-temperature phase was a time average between *irregular* trapezoidal shapes, as depicted in Figure 5b. As discussed above, the higher resolution possible with the 2D NMR spectroscopy in the present study enables us to detect the fine structure in the time-averaged NMR spectra in the high-temperature phase, thereby demonstrating that the molecular structure in this phase is indeed the time average of the structures shown in Figure 5b, and not Figure 5a. Our results thus support the NQR<sup>19</sup> and scattering data,<sup>20</sup> thereby resolving the above-mentioned controversy between the results obtained from various techniques. Studies are under progress in utilizing these data to arrive at a detailed model of the proton dynamics around the phase transition.

## Conclusions

This study describes a temperature-jump 2D technique that enhances the spectral dispersion in high-resolution NMR spectra in the vicinity of a solid–solid-phase transition. Earlier studies



**Figure 5.** Possible structures of the high-temperature forms of squaric acid: (a) regular trapezoid and (b) irregular trapezoid. The H's are omitted for the sake of clarity. The present study supports the geometrical form represented in (b).

of the temperature-jump NMR technique include those by Naito, Akasaka, and their co-workers,<sup>10,11,15-17</sup> Haw and co-workers,<sup>21</sup> and Gullion and Conradi.<sup>22</sup> Naito et al. investigated the correlation of signals in the nematic to isotropic phase of liquid crystals. Haw and co-workers used a laser pulse to investigate the correlation of signals from the solid and melted phases of camphor. Gullion and Conradi investigated the twisting of molecular sites in a phase transition of *p*-terphenyl, though not by a standard 2D technique. To our knowledge, the present study is the first application of the temperature-jump 2D NMR technique to a solid–solid-phase transition. It is demonstrated that the technique enables one to correlate molecular reorientation across a solid–solid-phase boundary. In the case of squaric acid, it has enabled us to explain long-standing discrepancies between NMR, Raman scattering and neutron scattering, and X-ray diffraction techniques. This methodology may thus lead to an enhanced understanding of the molecular mechanism of the order–disorder behavior of molecular solids.

**Acknowledgment.** This research was supported in part by the National Science Foundation.

## References and Notes

- (1) Blinc, R.; Zeks, B. *Ferroelectrics* **1987**, *72*, 193.
- (2) Mehring, M.; Suwelack, D. *Phys. Rev. Lett.* **1979**, *42*, 317.
- (3) Mehring, M.; Becker, J. D. *Phys. Rev. Lett.* **1981**, *47*, 366.
- (4) Suwelack, D.; Mehring, M. *Solid State Commun.* **1980**, *33*, 207.
- (5) Becker, J. D.; Suwelack, D.; Mehring, M. *Solid State Commun.* **1978**, *25*, 1145.
- (6) Semmingsen, D. *Tetrahedron Lett.* **1973**, *11*, 807.
- (7) Wang, Y.; Stucky, G. D.; Williams, J. M. *J. Chem. Soc., Perkin Trans. 2* **1974**, 35.
- (8) Klymachyov, A. N.; Dalal, N. S. *Solid State Nucl. Magn. Reson.* **1996**, *7*, 127.
- (9) Klymachyov, A. N.; Dalal, N. S. *Z. Phys.* **1997**, *B104*, 651.
- (10) Naito, A.; Imanri, M.; Akasaka, K. *J. Magn. Reson.* **1990**, *87*, 429.
- (11) Akasaka, K.; Naito, A.; Imanari, M. *J. Am. Chem. Soc.* **1991**, *113*, 4688.
- (12) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Clarendon Press: Oxford, 1987.
- (13) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.
- (14) Bennett, A. E.; Rienstra, C. M.; Auger, M.; Lakshmi, K. V.; Griffin, R. G. *J. Chem. Phys.* **1995**, *103*, 6951.

- (15) Naito, A.; Imanari, M.; Akasaka, K. *J. Magn. Reson.* **1991**, 92, 85.
- (16) Naito, A.; Imanari, M.; Akasaka, K. *J. Chem. Phys.* **1996**, 105, 4505.
- (17) Akasaka, K.; Kimura, M.; Naito, A.; Kawahara, H.; Imanari, M. *J. Phys. Chem.* **1995**, 99, 9523.
- (18) Fischer, G.; Peterson, J.; Michel, M. *Z. Z. Phys.* **1987**, B67, 387.
- (19) Seliger, J.; Zager, V.; Blinc, R. *J. Magn. Reson.* **1984**, 58, 359.
- (20) Samuelsen, E. J.; Buchenau, U.; Dieter, M.; Ehrhardt, K.; Fjar, E.; Grimm, H. *Phys. Scr.* **1982**, 25, 685.
- (21) Ferguson, D. B.; Krawietz, T. R.; Haw, J. F. *Chem. Phys. Lett.* **1994**, 229, 71.
- (22) Gullion, T.; Conradi, M. S. *Phys. Rev. B* **1984**, 30, 1133.