Experimental Report

Proposal:	**7-04-111**	**Council:**	4/2012

Title: Origin of Above-room-temperature Ferroelectricity in Croconic Acid: The need for Inelastic Neutron Scattering

This proposal is a new proposal

Researh Area: Chemistry

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Samples: H2C5O5

Instrument	**Req. Days**	**All. Days**	**From**	**To**
IN1 LAG	4	3	29/10/2012	01/11/2012

Abstract:

In a groundbreaking study in 2010, Horiuchi et al have reported above-room-temperature ferroelectriciy in croconic acid, a strikingly simple-looking molecule. In spite of these recent and exciting developments, the microscopic origin of its ferroelectric behaviour remains a mystery. To fill this gap, we have performed X-ray and neutron diffraction experiments as a function of temperature on croconic acid single crystals. Our results show that thermal diffuse scattering as a function of temperature correlates almost perfectly with the increase in unit-cell polarisation. These results are highly suggestive of a hitherto unexplored type of dynamically induced ferroelectricity governing the emergence of a net (and strong) unit-cell electric dipole moment above room temperature. While insightful, these structural studies do not provide direct information on the specific physical origin of the motions responsible for diffuse scattering and ferroelectric behaviour. Inelastic neutron scattering is the method of choice to provide these key data, and the use of LAGRANGE is mandatory given present limitations to synthesize high-purity specimens.

Experimental Report *ILL Proposal 7-04-111 (IN1-LAGRANGE)*

Proposal Title: *Origin of Above-room-temperature Ferroelectricity in Croconic Acid: The Need for Inelastic Neutron Scattering*

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Motivation

Some polar substances are known to display so-called "ferroelectric" behaviour, a collective phenomenon leading to the emergence of a net bulk electric polarisation. In this situation, external fields can be exploited to control the direction and magnitude of the electric response in a multitude of practical scenarios including optoelectronic devices, temperature sensors, and switchable memories [1]. In analogy with magnetism, other possibilities in addition to ferroelectricity include the antipairing of nearest-neighbour electric dipoles (antiferroelectrics) or their complete randomisation (paraelectrics), the latter typically driven by temperature or doping.

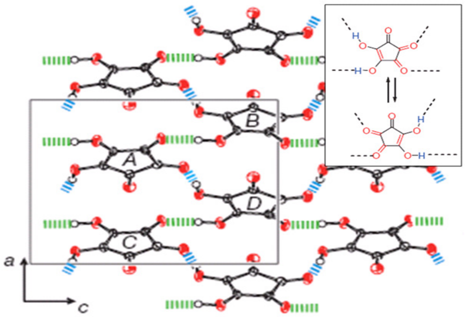

Figure 1. Crystal structure of CA. Green(blue) denotes in(out)-of-plane hydrogen bonds with respect to the *b-c* plane. The inset shows the π-bond alternation characteristic of this family of materials. Diagrams adapted from Ref [4].

The vast majority of ferroelectrics known to date are inorganic compounds. These include barium titanate ($BaTiO_3$), a ferroelectric material where the relative displacement of atomic ions in the crystalline lattice leads to an exceptionally high macroscopic polarisation; or potassium dihydrogen phosphate (or KDP), a widely investigated inorganic solid where dipolar ordering is triggered by proton motions associated with hydrogen bonding [2]. Contrary to naïve expectation, ferroelectricity in organic materials has proven quite elusive to date. The observation of organic ferroelectricity has so far been limited to polymers or multi-component molecular solids relying on charge or proton transfer across chemically distinct donor-acceptor pairs [3]. In a groundbreaking study, Horiuchi et al have reported ferroelectriciy above room temperature in croconic acid (CA), a strikingly simple-looking molecule [4]. Figure 1 shows its crystal structure at ambient conditions, as inferred from recent X-ray diffraction studies [5]. CA belongs to the polar space group $Pca2_1$ (lattice constants a=8.711Å, b=5.168 Å, c=10.956 Å) where the pentagonal rings are arranged in hydrogen-bonded layers and pleated sheets reminiscent of an accordion.

In spite of these recent and exciting developments, the microscopic origin of ferroelectric behaviour in CA remains a mystery. While it has been hypothesized that the location and motion of hydrogen atoms in the crystalline lattice might play an important role [4], no neutron studies prior to our present and ongoing efforts [6,7] have been reported to date in the literature. To fill this gap, we have performed detailed X-ray and neutron diffraction experiments as a function of temperature on high-quality single-crystal specimens. These data show a significant amount of temperature-dependent thermal-diffuse scattering correlating with an increase in unit-cell polarization. While insightful, these structural studies do not provide direct information on the specific dynamical origin of these motions. Inelastic neutron scattering (INS) is the method of choice to provide these key data.

LAGRANGE Experiments

The primary aim of this four-day experiment carried out on IN1-LAGRANGE in October 2012 was to obtain INS spectra of CA up to energy transfers of ca 4000 cm^{-1}. To this end, a pristine CA single-crystal specimen was ground to a fine powder in a dry glove box and kept under oxygen-free conditions at all times. An incident-energy range of 216-3500 cm^{-1} was accessed via the use of Cu(220) and Cu(331) monochromator reflections on the incident beam (accessible energy-transfer range E=180-3500 cm^{-1}). Additional measurements at lower energy transfers were performed using Si(111) and Si(311) monochromator reflections. In addition to the requisite ancillary measurements, INS spectra of CA were collected at T=5, 50, 100, 150, and 200K using both Cu and Si reflections, and at 250 and 300K using Cu(331).

Figure 2 shows a representative INS spectrum measured at T=5K over the entire spectral range accessible on the instrument (both Cu and Si reflections). These INS measurements at base temperature have served to assess a series of first-principles models, as described in more detail in Ref. [6]. Overall, we find that the inclusion of non-local *van der Waals* interactions within the generalized-gradient approximation proves essential in order to provide a self-consistent picture of the observed optical response of CA in the visible region of the electromagnetic spectrum, as well as its crystal and vibrational structure. On the basis of these first-principles calculations and simulated INS spectra, the prominent doublet observed ca 1000 cm^{-1} can be assigned to out-of-plane motions associated with two distinct types of hydrogen bonds in the material, corresponding to the ‘hinge’ and ‘terrace’ positions in a pleated, accordion-like structure (cf. Fig. 1). A more detailed analysis of our computational model in terms of calculated Born-effective-charge tensors yields anomalously high dynamic charges centred on the ‘hinge’ protons, a finding which serves to identify the primary motif underpinning ferroelectric behaviour in the material [7].

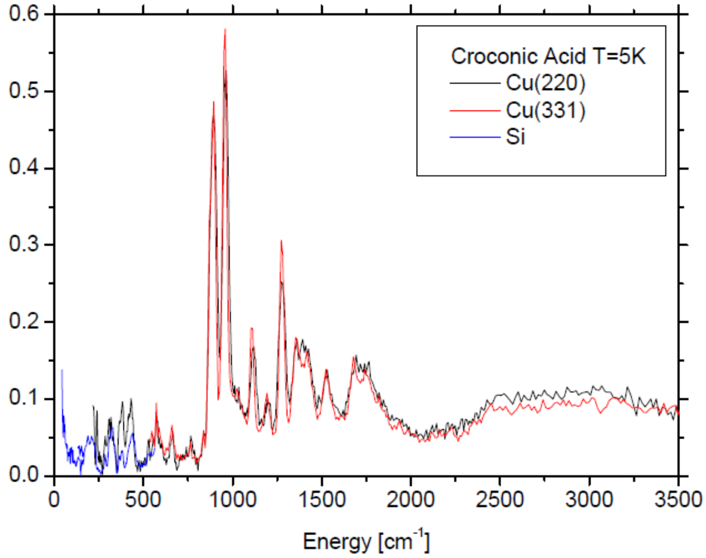

Figure 2. INS spectra of CA at T=5K using both Cu and Si monocromator reflections.

INS spectra measured up to T=300K are also interesting in their own right since (and much to our surprise) they display well-defined spectral features around the aforementioned doublet over the entire temperature range. As such, these data demonstrate to us that it is possible to follow their temperature dependence all the way up to room temperature, including quantitative estimates of mode softening and spectral broadening. In conjunction with temperature-dependent structural studies, these INS data are currently being analysed within the framework of the quasi-harmonic approximation. At energy transfers below 300 cm^{-1}, we also observe the onset of additional INS intensity peaking at around 150 cm^{-1} above T=100K. Work is underway to understand the link between these INS features and parallel quasielastic neutron scattering studies.

In closing, we note that the results of this experiment have so far resulted in two publications in 2013 [6,7], and a third one is currently in preparation.

References

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[5] D Braga et al, *Cryst Eng Comm* **6** 1 (2001).
[6] F Fernandez-Alonso et al, *J Phys Soc Japan* **82** SA001 (2013).
[7] S Mukhopadhyay et al, *Chem Phys* (in press, 2013).