Identification of normal modes responsible for ferroelectric properties in organic ferroelectric CBDC

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Abstract
Structure and dynamics of hydrogen bonded organic ferroelectric CBDC (1-cyclobutene-1,2-dicarboxylic acid, C₆H₈O₄) have been investigated using inelastic neutron scattering (INS) spectroscopy and first principles lattice dynamics. Vibrational modes of O–H–O bending, related with two different types of hydrogen bonds, inter and intra-molecular, are manifested as two sets of doublets in the range of 900–1400 cm⁻¹ in the INS spectrum. First principles density functional theory (DFT) is used to assign these doublets to out-of-the-plane and in-plane vibrations of these two types of O–H–O bending modes. Correlating structure and dynamics we find that although the local structures of the hydrogen bonded protons are similar, their medium range order may influence their vibrational frequencies. Vibrational modes of non-hydrogen bonded protons also are assigned separately in the spectrum. Comparing the calculated and the experimental INS spectra it is predicted that hydrogen bonded O–H bonds are more anharmonic than non-hydrogen bonded C–H bonds. From the calculated Born effective charge tensor it is predicted that inter-molecular hydrogen bonds contribute more to the ferroelectric polarisation of CBDC than intra-molecular ones. A large LO-TO splitting of the O–H stretching mode at 2471 cm⁻¹ is identified with the mode that has significant contribution to the ferroelectric polarisation. As this mode is sensitive to long range Coulomb interactions and is responsible for ferroelectric properties of the material, vibrational spectroscopy combined with DFT calculations is proposed as a characterisation tool to investigate ferroelectric properties in the CBDC molecular crystal.

1. Introduction

Room temperature organic ferroelectrics [1–4] are important functional materials for potential technological applications in flexible electronics. Flexible electronic devices are low cost, thin, soft, generally metal-free and have numerous state-of-the-art applications. Investigations of optical vibrational modes are extremely important for ferroelectric materials due to their contribution to the value of Born dynamical effective charge tensor which is an important parameter to estimate intrinsic electrical polarisation of materials [5, 6]. Furthermore, the effect of electric field on long range Coulomb interaction can be identified by inspecting the splitting of LO-TO vibrational modes. A large LO-TO splitting is a manifestation of strong coupling with the electric field and contributes more to the dynamical effective charge. Strong coupling with the electric field can also make the ferroelectric state of the material more sensitive to the electrostatic boundary condition and any disturbance of the vibrational mode can destroy ferroelectric properties. Thus microscopic knowledge of these modes are extremely important to predict the stability of ferroelectric properties of these materials.

In organic ferroelectric materials hydrogen bonds play an important role in determining chemical and electronic mechanisms of ferroelectricity. Reports of a number of hydrogen bonded molecular crystals showing very high electrical polarisability [1–4] motivate researchers to microscopic investigation of these molecular crystals. The local geometry of hydrogen bonds of these crystals determines the potential barrier height of the proton responsible for ferroelectric properties, and its dynamics determines the strength of the bulk...
polarisation. Hydrogen bonds in croconic acid, a room temperature organic ferroelectric which shows the strongest ferroelectricity in this class of materials, play a crucial role in the microscopic origin of its polarisability. Strong and flexible hydrogen bonds in croconic acid crystal support a Jahn-Teller type distortion leading to strong polarisation at room temperatures [7]. Inelastic neutron scattering (INS) along with first principles density functional theory (DFT) based lattice and molecular dynamics calculations help to underpin the dynamics of protons of its hydrogen bonds [8–10]. As a continuation of these investigations, in this article the focus is to investigate the vibrational modes related to hydrogen bonds in CBDC (1-cyclobutene-1,2-dicarboxylic acid, C₅H₆O₄), another hydrogen-bonded molecular crystal showing ferroelectric properties at room temperatures [2, 4].

Although CBDC demonstrates fairly large ferroelectric polarisation, about 2.9 μC/cm² at room temperatures, very few reports on this material are available. The structure of CBDC and its ferroelectric properties have been reported using x-ray diffraction and polarization experiments, respectively [2, 4]. Microscopic investigations of its ferroelectric properties have been reported using first principles density functional theory (DFT) [11]. Main focus of this report has been put on the proton transfer mechanism across hydrogen bonds. In these DFT based calculations, the non-centrosymmetric structure of CBDC has been obtained as an unstable geometrical configuration associated with imaginary frequencies at low frequency vibrational modes. No detailed microscopic analysis has been done correlating the local structure and dynamics of hydrogen bonds with the ferroelectric properties so far. Experimental verifications of normal modes of vibrations, which are very important for the strength and stability of ferroelectric materials, are also missing. In the current article, experimental vibrational spectra of CBDC has been reported using INS spectroscopy in addition to assignments of important modes using first principles DFT calculations. Particular focus has been put on providing microscopic knowledge of the structure and dynamics of hydrogen bonds and their effects on ferroelectric polarisation in CBDC.

2. Experiments

Experiments are performed using commercially available powder from Sigma Aldrich with minimum 97% purity. About 2 g of the powdered sample is wrapped in aluminum foils and placed in an indium sealed aluminum sample container to measure the INS spectrum. INS experiments are done on TOSCA spectrometer at the ISIS Pulsed Neutron and Muon Source at temperature 10 K [13]. TOSCA is an time-of-flight, indirect geometry, high resolution INS spectrometer. With the analyser-detector modules in both forward and back scattering mode, TOSCA is one of the best high resolution crystal analyser INS spectrometer in the world [14] having energy resolution ΔE/E < 1% and energy transfer range up to 8000 cm⁻¹.

3. Calculations

Plane wave pseudo-potential electronic-structure calculations are performed as implemented in the CASTEP code [15] with optimized norm-conserving pseudopotentials [16] generated with the Perdew–Burke–Ernzerhof (PBE) [17] functional within the generalized-gradient approximation (GGA). The Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm are used for full-geometry optimizations with a force tolerance of 1.0 × 10⁻³ eV/Å. Dispersion corrections to the PBE functional (PBE+D) are included as proposed by Tkatchenko and Scheffler (TS) [18]. A plane-wave cutoff of 800 eV and a Brillouin-zone (BZ) sampling of 6 × 6 × 3 k-points (18 points when symmetry-reduced) are used to converge energy and atomic forces below 2.5 × 10⁻³ eV/Å and 1.0 × 10⁻³ eV/Å, respectively. Self-consistent single-point energy minimizations used a tolerance of 2.5 × 10⁻⁶ eV.

Lattice dynamics calculations are performed to find normal mode frequencies and eigenvectors of the resulting ground state structure by diagonalisation of dynamical matrices using density-functional perturbation theory (DFPT) and linear-response methods [19]. INS spectra are obtained from calculated eigenvectors and eigenenergies using the newly implemented abINS algorithm in Mantid [20, 21]. In the calculations of INS spectra, fundamentals, overtones and combination bands are included up to fourth order. Born effective charge tensors and LO-TO splitting of normal modes are calculated as implemented in the CASTEP code [15].

4. Results and discussion

CBDC is a hydrogen bonded molecular crystal with four molecular units in a unit cell as shown in figure 1. Earlier investigations using single crystal x-ray diffraction (XRD) report the crystal structure as monoclinic having space group 9 [4]. In each molecule, a four member C-ring forms almost an isosceles trapezoid where the
The ground state geometry of the crystal is obtained from cell-optimised first principle simulations. A comparison of the experimental structure with that obtained from DFT calculations is made in table 1. Calculated lattice parameters and angles obtained using PBE+D functional are consistent within 1.5% of values obtained from XRD measurements [1]. On the other hand, the difference between calculations and measurements is more than 10% in the structure obtained using only PBE functionals. This result shows that incorporation of dispersion corrections is essential to predict the structure accurately for the CBDC crystal. The difference between PBE and PBE+D calculations is consistent with the results obtained previously for croconic acid [10]. Calculations on CBDC using PBE functional published earlier does not report calculated lattice parameters, and so, a comparison with the results [11] is not possible. As presented in table 1, O—O distances and O—H—O angles across hydrogen bonds calculated using PBE+D functional are in good agreement within 2.0% and 0.2%, respectively of experimental results. Larger differences between calculations and experiments, however, are found in the hydroxyl and hydrogen bond lengths. This finding indicates the well known fact that XRD measurements underestimate hydroxyl bond lengths, and overestimate hydrogen bond lengths. Neutron diffraction experiments are, therefore, required to get the positions of hydrogen atoms within the lattice accurately.

The experimental INS spectrum of CBDC is presented in figure 2. As there is no selection rule in the INS spectrum, this spectrum is expected to give the true account of the normal mode vibrations in the material [22, 23]. However, in INS spectrum, vibrational densities of states (VDOS) of the crystal are weighted by neutron scattering cross sections of individual elements responsible for the vibrations. Due to the fact that neutron scattering cross section of hydrogen is order of magnitude higher than that of other elements present in CBDC, such as C and O, the INS spectrum is dominated by the contribution of hydrogen atoms and is suitable for understanding the property of hydrogen bonds.
Figure 2, the full calculated vibrational densities of states (VDOS) and atom projected VDOS are presented along with the experimental INS spectrum. Lattice dynamics calculations are performed on the optimised structure obtained using PBE + D functional and all subsequent calculations are done using the functional. Calculations predict that there are 192 normal modes in the CBDC crystal. Among them 100 modes are both IR and Raman active. Contrary to a previous report [11], there is no negative frequency in the calculated phonon modes indicating that the hydrogen bonded non-centrosymmetric ground state structure obtained by PBE + D functional is stable. As expected, vibrational peaks at the low energy transfer region up to 1000 cm$^{-1}$ are...

Table 1. Lattice parameters of CBDC obtained from XRD experiments and DFT calculations. The structure of the crystal is monoclinic and crystallographic angles $\alpha$ and $\gamma$ both are 90°. The differences in parameters are given in parentheses in %.

| Calculations | Experiment [4] | PBE | PBE + D |
|--------------|---------------|-----|---------|
| Lattice and bond parameters | | | |
| $a$ (Å) | 5.481 | 5.920 (8.00) | 5.516 (0.64) |
| $b$ (Å) | 13.423 | 13.766 (2.55) | 13.400 (0.17) |
| $c$ (Å) | 8.522 | 9.594 (12.38) | 8.575 (0.62) |
| $\beta$ (°) | 100.0 | 88.271 (11.72) | 98.427 (1.57) |
| $O$–$H(T)$ (Å) | 0.779 | 1.032 | 1.033 |
| $O$–$H(C)$ (Å) | 0.848 | 1.033 | 1.036 |
| $H(T)$–$O$ (Å) | 1.838 | 1.560 | 1.528 |
| $H(C)$–$O$ (Å) | 1.757 | 1.532 | 1.524 |
| $O$–$O[T]$ (Å) | 2.603 | 2.562 | 2.560 |
| $O$–$O[C]$ (Å) | 2.610 | 2.537 | 2.555 |
| $O$–$H(T)$–$O$ (°) | 175.255 | 175.256 | 175.544 |
| $O$–$H(C)$–$O$ (°) | 171.550 | 171.545 | 171.953 |

Figure 2. Experimental INS spectra is plotted along with calculated VDOS. VDOS($X$ = H, C, O) represents atom projected VDOS. VDOS(Total) is the total VDOS of the unit cell. See text for more details.
dominated by oxygen, those around 1000–2000 cm$^{-1}$ are dominated by carbon and hydrogen, and those above 2000 cm$^{-1}$ are mostly dominated by hydrogen.

INS peaks observed around 3000 cm$^{-1}$ are due to C–H(B) stretching frequencies. Two peaks around 3060 cm$^{-1}$ and 3000 cm$^{-1}$ are due to asymmetric and symmetric stretching of polar C–H(B) bonds at the base of the trapizoidal C-ring mentioned above. The hydroxyl ion (O–H) stretching band around 2500 cm$^{-1}$ is almost invisible in the INS spectrum. Apart from low VDOS of this mode, around this wavenumber region the INS spectra is dominated by recoil effects and not entirely on the VDOS of the molecular crystal. The vibrational frequency of free O–H stretch mode is 3600 cm$^{-1}$. The strong red-shift of the frequency combined with low VDOS indicates very strong hydrogen bonding in the crystal. This strong hydrogen bonding is consistent with the almost linear structure of the O–H—O bond presented in table 1.

Further, down to the energy transfer around 1300–1600 cm$^{-1}$, the bands are dominated by C=O stretching modes together with O–H—O and H–C–H bending modes. Calculated C–C–C bending modes related with four member C-ring are also present in this energy transfer region. The H–C–H bending, twisting and wagging symmetric modes are mixed with in-plane O–H—O bending modes around 1400–1550 cm$^{-1}$. The band related to C=O stretching modes, which are often considered as very good probes for understanding hydrogen bonds in peptides and proteins, are located near 1250–1300 cm$^{-1}$. In comparison to the observed modes in free carboxylate species [24], the redshift of about 150 cm$^{-1}$ of the C=O stretching modes is also the result of strong hydrogen bonds associated with carboxyl groups.

Calculations predict that in-plane and out-of-plane bending modes of O–H—O are around 1250–1350 cm$^{-1}$ and 1000–1100 cm$^{-1}$, respectively. The wagging and twisting asymmetric modes of H–C–H are also in the 1120–1240 cm$^{-1}$ spectral region. More complicated H–C–C–H dihedral twisting and bending modes are below 900 cm$^{-1}$. Further down to the energy transfer range, the contributions come mainly from oxygen, but contributions from C and H are also not negligible. Mainly collective modes associated with long range order of the crystal are also dominated in this region.

The calculated INS spectrum is presented in figure 3 along with the measured one. Partial INS of H(B), H(T) and H(C) are plotted in figure 4. The calculated spectrum labeled as 'Fundamentals' is calculated only from normal modes and can be compared with the VDOS presented in figure 2. Calculated spectra using fundamental modes as well as overtones and combination modes are presented in the panel labeled as 'Full'. From figure 3, it is clear that the doublet at 900 cm$^{-1}$, which is similar to that observed in the INS spectrum of croconic acid, [7–10] is blue shifted by about 150 cm$^{-1}$ in the calculated spectra. These dominant vibrations, as observed in INS at 880 and 900 cm$^{-1}$, are predicted as the out-of-plane bending modes of protons for O–H(T)—O and O–H—O.
(C)—O, respectively (See figure 4). The magnitudes of blueshifts in these modes are similar to those found in croconic acid [9, 10]. Contributions from symmetric and asymmetric O–H(C)—O and O–H(T)—O in-plane bending modes are predicted around 1276 cm⁻¹ and 1340 cm⁻¹, respectively. In the experimental spectrum, these modes are found at 1175 cm⁻¹ and 1190 cm⁻¹, respectively. Although the short range structure of H(C) and H(T), such as O–H bond lengths are within 1% (See table 1) of each other, separations of their bending modes may be due to the medium range order, such as O–H—O angles and torsion angles. The difference in O–H(T)—O and O–H(C)—O angles are about 3% (see table 1) and the torsion angles (not shown in table 1) of O–H(T)—O are order of magnitude smaller than that of O–H(C)—O.

Calculations predict that the broad bump observed in INS just above 1200 cm⁻¹ is part of the triplet which in the calculated spectrum is blue shifted to 1300 cm⁻¹. Modes associated with the triplet are in-pane bending of O–H—O as mentioned above, twisted motion of H(B)–C—H(B) at the base of C-ring, and librational motion of H(B), respectively. Overtones and combination bands also appear in this region of the INS spectra. The C–H(B) stretching mode found around 3000 cm⁻¹ agrees very well with calculations without any blue shift. It is speculated that the blue shifts obtained in the calculated spectrum may be due to the anharmonicity in vibrational potentials, which is not considered in current calculations. Different amounts of blue-shifts associated with the modes are due to various amounts of anharmonicity of the modes related with their local environment and nature of bonding. Comparing with experiments it can be said that vibrational potentials of hydrogen bonded O–H bonds are more anharmonic than non-hydrogen bonded C–H bonds. More calculations will be reported on the anharmonicities elsewhere.

Born effective charge tensor, which is often an indicator of strength of electric polarisations, is anisotropic in this crystal. To get the idea of the magnitude and direction of the polarisation, the effective charge tensors for individual atoms are diagonalised. Results show that H(C) has the anomalous Born effective charge of 2.44 |e| towards Z-axis, while charge towards all other primary axes are negligibly small. This result is consistent with the experimental observation that the polarisation of CBDC crystal is perpendicular to crystallographic b direction with 2.9 µC/cm² and 0.9 µC/cm², in crystallographic c and a directions, respectively [4]. The effective charge on H(T) for all three cartesian directions are negligibly small. This result predicts that the intermolecular hydrogen bonded H(C) is responsible for the ferroelectricity in CBDC This result is consistent with the finding reported earlier [11].

To understand more about the particular mode or modes responsible for the contribution to the dynamical effective charge, the LO-TO splitting of normal modes are analysed. It has been found that maximum contribution comes from the symmetric O–H stretching mode at 2471 cm⁻¹. Both H(C) and H(T) contribute in that mode. The next dominant contributing mode is in-plane O–H(C)—O bending mode at 1276 cm⁻¹. The contribution to dynamic charge from out-of-plane O–H—O bending modes are comparatively small. Both in-plane and out-of-plane O–H(C)—O bending modes are observed in INS spectrum as doublets as shown in

![Figure 4](image-url)

Figure 4. Contributions of different hydrogens in calculated INS spectrum is presented in panels (top) H(T); (middle) H(C); (bottom) H(B). See text for more details.
The highest contributing O–H stretching modes are not visible in INS. As mentioned previously, these modes showing large LO-TO splitting are sensitive to long range Coulomb interactions. The current observation thus can lead to an important inference that due to the sensitivity of the OH-stretching mode on long range Coulomb interaction any defect or domain structure which disturbs the long range interaction may affect the mode strongly in the current experimental sample. Ferroelectricity of the material may have been affected due to the distortion of the mode as well. The other modes, such as in-plane and out-of-plane O–H—O bending modes, are less sensitive to the long range interactions and so are found in INS. Due to the importance of identification of the normal mode for ferroelectric polarisation, vibrational spectroscopy can be used as a characterisation tool for ferroelectric properties of CBDC crystals. This technique can be extended to other ferroelectric materials by combining INS spectroscopy with state of the art DFT based calculations. More experiments will be undertaken in future to support this interpretation.

5. Conclusions

In this article the structure and dynamics of hydrogen bonds in organic ferroelectric CBDC have been investigated using INS experiments and first principles lattice dynamics simulations. It has been found that dispersion corrected PBE functional is essential to predict the correct structure of this molecular crystal. Vibrations of two hydrogen bonded protons have been identified as doublets for out-of-plane and in-plane O–H—O bending modes in the range 880–1200 cm$^{-1}$. The non-hydrogen bonded proton modes also have been assigned to the INS peak observed around 1250 cm$^{-1}$ and 3000 cm$^{-1}$ as the H–C–H twisting and C–H stretching modes, respectively. Although local structure of two hydrogen bonded protons are similar, the differences in the medium range order leads to the splitting of these modes. Comparing calculated INS with experimentally observed and analysing using partial atom projected INS, it is found that hydrogen bonded O–H vibrational potentials are more anharmonic than non-hydrogen bonded C–H bonds. Analysis using Born dynamical charge tensor predicts that the protons in the intermolecular hydrogen bond are responsible for the intrinsic ferroelectricity of that material. Further investigation reveals large LO-TO splitting of O–H stretching modes indicating that hydrogen bonded protons are most sensitive to electric fields and contributes more to the ferroelectric properties of the materials. Due to the sensitivity of these O–H stretching modes on long range Coulomb interactions, any distortion in that interaction may affect the ferroelectric properties of that material. Vibrational spectroscopy combining with DFT calculations has been proposed as a characterisation tool for predicting ferroelectric properties of CBDC crystals.

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