

First-Principles Calculations of the Ferroelectric Phase Transition in Pure Molecular Crystal Trichloroacetamide

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Trichloroacetamide (TCAA) forms a monoclinic molecular crystal within non-centrosymmetric space group $P2_1$ below 355 K that exhibits ferroelectricity. A single TCAA molecule has a dipole-moment, but the unit cell contains two crystallographically independent molecules, labelled A and B in figure 1, aligned anti-parallel to one another. The alignment is imperfect, however, so that a small polarization exists parallel to the b axis ($P_s = 0.2 \mu\text{C}/\text{cm}^2$). Experimentally, TCAA crystals have been found to transform to a paraelectric phase with space group symmetry $P2_1/c$ above 355 K [1], and this is attributed to rotation of the trichloromethyl (Cl_3) groups relative to one another [2]. Up to 150 K, with the crystal in its ferroelectric form, the Cl_3 groups are essentially “frozen” in position, but above 150 K the Cl_3 group of molecule B begins to rotate in an oscillatory manner, the magnitude of the rotation increasing until a temperature of around 350 K is reached. Above 355 K, the Cl_3 groups in both types of molecule rotate completely, cancelling each other’s dipole moment [2]. Here we report the first theoretical study of the ferroelectric phase transition behavior of this system based on first-principles total-energy minimization and first-principles molecular dynamics (FPMD) techniques. Calculations were performed using the projector augmented wave method of density functional theory. The molecule rotation behavior obtained from FPMD simulations at different temperatures is summarized in fig. 2. We show that the simulations reproduce the experimental features of the intramolecular order-disorder phase transition well.

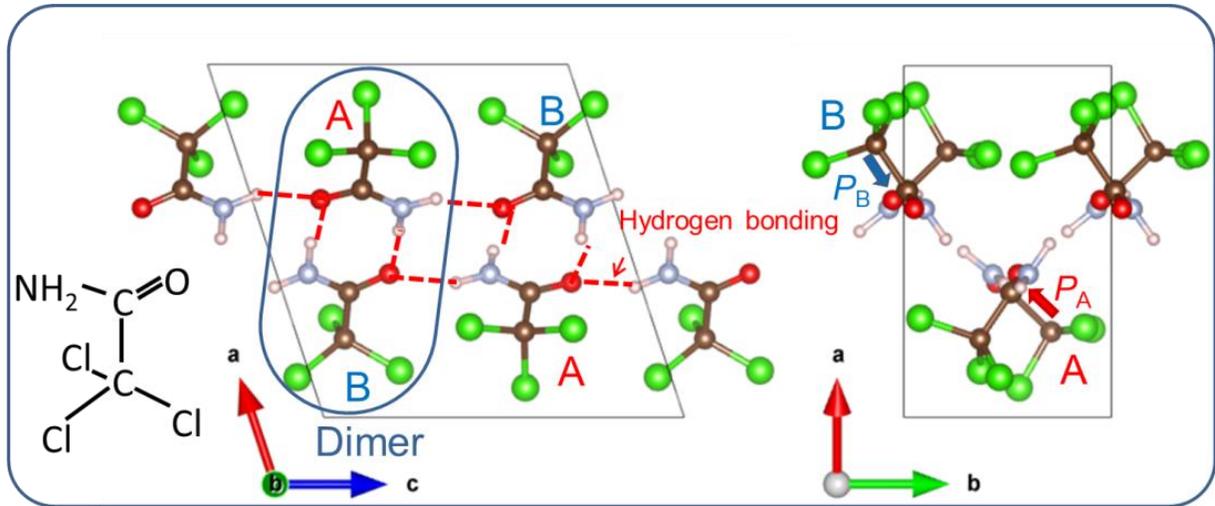


Fig. 1 Structure of a TCAA crystal. The unit cell contains two crystallographically independent TCAA molecules, labelled A and B. Each molecule has a dipole moment, P , and pairs of molecules (dimers) are aligned anti-parallel to one another.

References

- [1] Y. Kamishina: J. Phys. Soc. Jpn. **60** 2147 (1991).
[2] K. Saito, et al.: CrystEngComm **13** 2693 (2011).

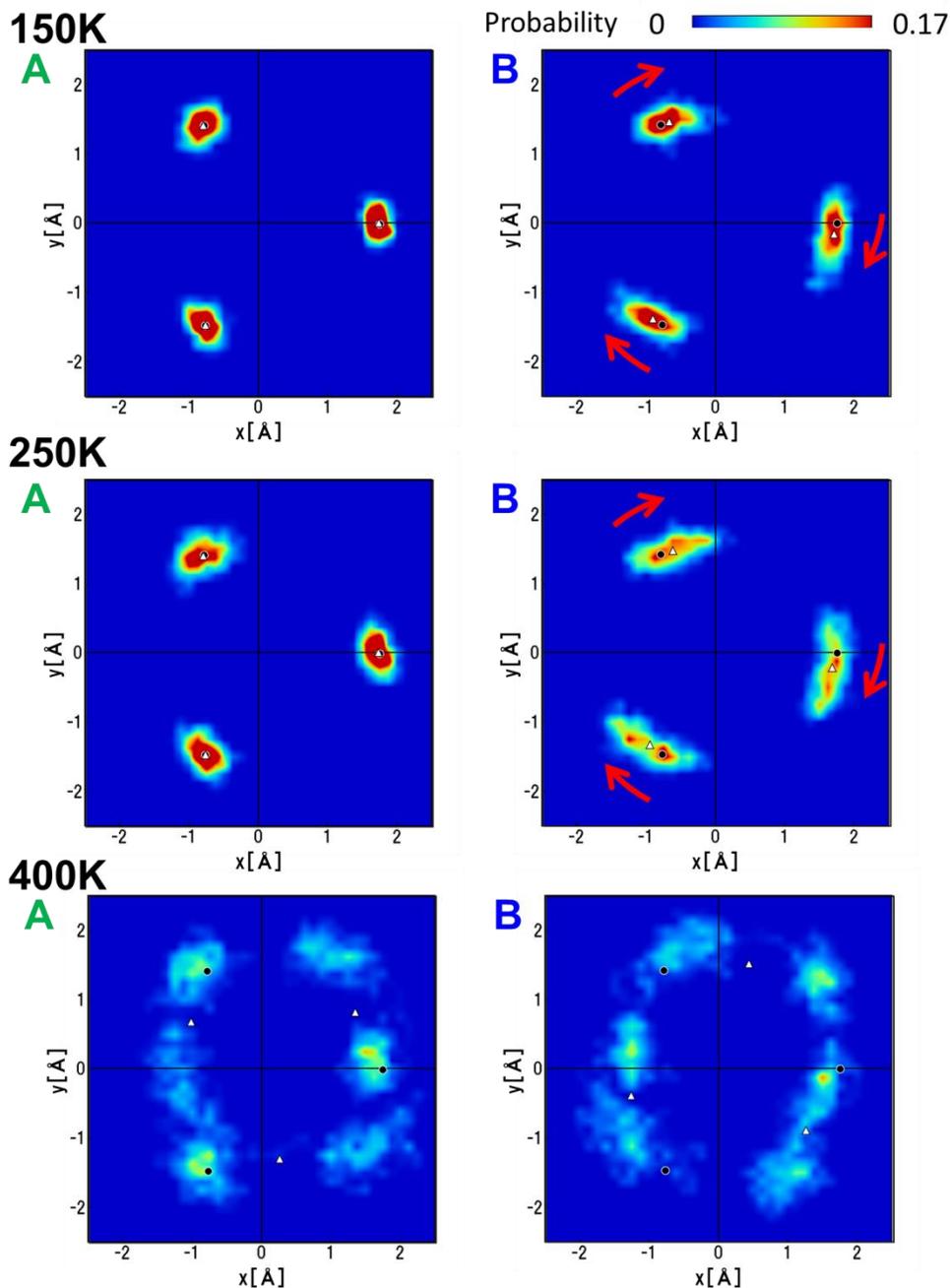


Fig. 2 Probability plots of positions of atoms in the trichloromethyl (Cl_3) group about the C-C axis in TCAA molecule types A and B at 150 K, 250 K and 400 K according to first-principles molecular dynamics simulations. The Cl positions at 0 K are indicated by black circles and the mean positions at each temperature are indicated by white triangles. At 150 K, only Cl atoms in molecule B have begun to rotate. The rotation angle increases with temperature.