

Ultrafast Inversion of Ferroelectric Polarization in Photoexcited Croconic-Acid Crystal

We have investigated the mechanism of the ultrafast inversion of electric polarization in a photoexcited crystal of croconic acid. Based on density-functional calculations, first, we analyzed the ground-state potential surfaces with respect to proton displacements and found that approximately ten molecules can exhibit polarization inversions after absorbing one photon. Next, we analyzed the photoexcited states and found a notable initial relaxation path, of which the relaxation energy exceeds 2 eV. Furthermore, we identified two reaction paths associated with the domain dynamics and assigned them to the fast and slow decay components found in the experiments.

The croconic-acid crystal is known to be a ferroelectric material with electric polarization reaching $20 \mu\text{C}/\text{cm}^2$ [1], which is comparable to that of a typical ferromagnetic material, BaPbO_3 . Recently, a group from the University of Tokyo performed a pump-probe experiment for this material and found substantial suppression of electric polarization after light irradiation with excitation energy of around 3 eV [2]. In this experiment, the method of detection, namely, the probe, is second-harmonic generation (SHG) using light of 0.95 eV. Although SHG is a popular method for detecting the degree of broken inversion symmetry, its spatial resolution is limited to the scale of the light wavelength, for instance, $1 \mu\text{m}$, and consequently the detailed mechanism of this polarization suppression was not known.

Motivated by this finding and the necessity of theoretical clarification, we investigated the photoinduced effects in this crystal based on density-functional theory (DFT) [2]. We performed two types of calculation: a cluster calculation and a calculation using a periodic-boundary condition. After reproducing the actual magnitude of polarization using the latter method with an appropriate combination of density function and basis set, we switched to the former method while keeping the combination. In the former calculation, we also applied

time-dependent DFT to the cluster for the purpose of studying excited states in addition to the ground state.

Figure 1 shows the ground state potential curves. Since the crystal acid crystal has a layer structure and its polarization vector is parallel to the layer, we pick up one layer and cut out a part of it, as shown in the insets of **Fig. 1**. For the red curve, we moved the two protons near the central molecule to the right simultaneously. Note that, in this configuration, the protons, which provide a significant contribution to the polarization, are displaced in the left direction before the movements. This means a polarization directed to the left. The above movements of the protons therefore correspond to a “minimum domain” of polarization inversion. We emphasize that its creation energy of about 1 eV seen for the red curve is much less than the main absorption peak energy of 3.5 eV, indicating a rather easy formation of the minimum domain. Following this, we enlarged the domain in two ways. For the blue curve, the domain was extended horizontally, whereas the domain was enlarged horizontally and vertically. The modest energy increase for the blue curve indicates a prevalence of the corresponding type of domain, that is, the one-dimensional domain, in contrast to the two-dimensional domain.

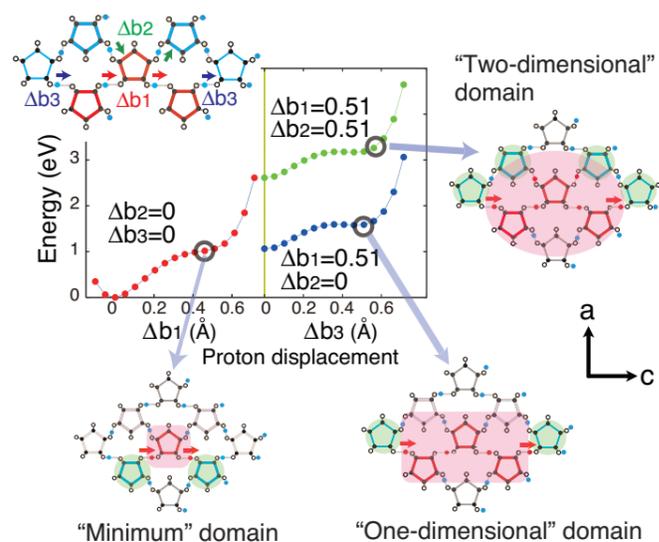


Figure 1: Ground state potential curves for the three typical domain states. This figure is reprinted from reference [2].

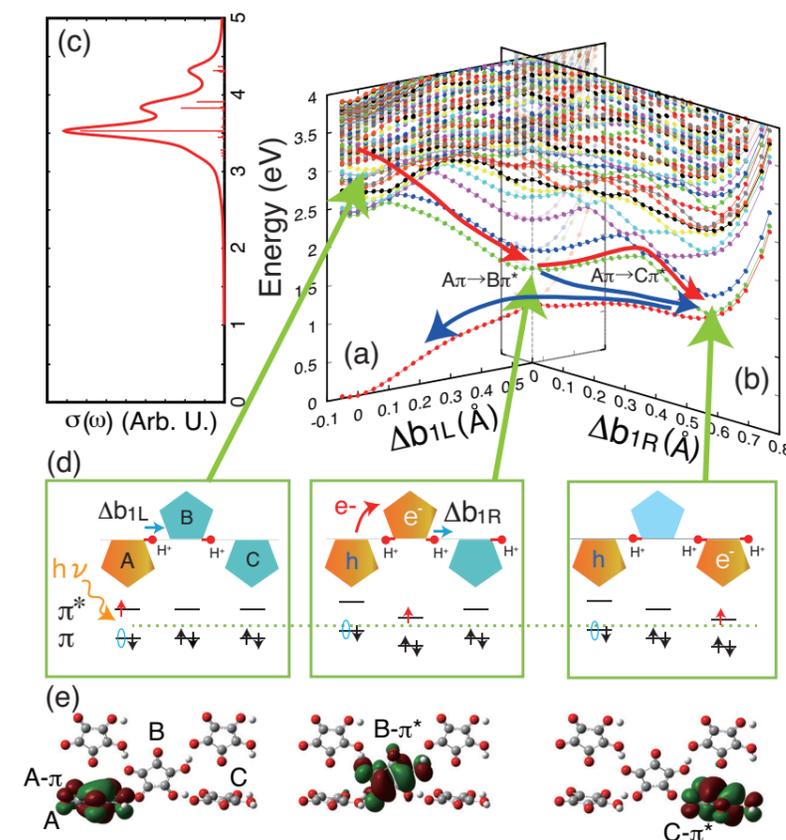


Figure 2: (a) and (b) Potential curves in the ground and excited states, (c) calculated optical conductivity spectrum at the origin (the initial state), (d) schematic electronic states on the paths, and (e) related molecular orbitals. This figure is reprinted from reference [2].

Figure 2 shows the detailed structure of excited states relevant to such one-dimensional domain. To save computer time, we here move the proton one by one as shown in the schematics of **Fig. 2d**. The resultant potential curves as functions of the first and second movements are plotted in **Fig. 2a** and **2b**, respectively, with the optical conductivity spectrum at the initial state in **Fig. 2c**. From these potential curves, we recognize the following two points. One is the large energy relaxation seen for the lowest excited state shown by the red arrow in **Fig. 2a**. The relaxation energy exceeds 2 eV, which indicates a very large proton- π -electron coupling. The other point is the shapes of the curves in the latter part of the paths appearing in **Fig. 2b**. Namely, the curve in the first excited state has a substantial potential barrier, whereas that in the ground state has no barrier. These properties indicate that the path on the first excited state (red arrow in **Fig. 2b**) is expected to lead to metastable states with a relatively long time and is assigned to slow decay components observed in the experiment. Regarding the dynamics in the ground state, on the other hand, we expect the paths shown

by the blue arrows in **Figs. 2a** and **b**. Namely, the domain growth occurs along the rightward arrow in **Fig. 2b** via non-adiabatic transition and leads to a domain state around $(\Delta b_{1L}, \Delta b_{1R}) = (0.55, 0.55)$ and other domain states with more extended sizes. After they reach a maximum size, the domain states are expected to shrink rather quickly and return to the initial state, as shown by the leftward arrow in **Figs. 2a** and **b**, since the associated curve is almost flat there. We assign such dynamics to the fast decay component observed in the experiment. We expect that such microscopic understanding of the mechanism of polarization inversion will lead to further exploration of polarization control in this and analogous materials.

REFERENCES

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