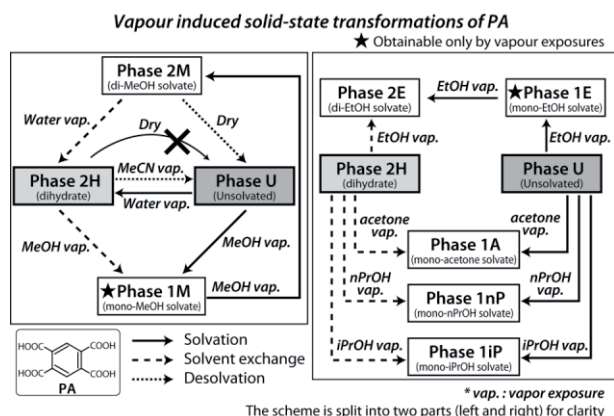


the difficulty to obtain the structural information of the resulted phase, which is mainly caused by the disintegration of the single crystalline form of the parent phase during the transformations. In such cases, the crystal structure determination from the powder X-ray diffraction data is clearly most powerful technique. Herein, we report several examples of the vapour induced crystalline transformations of organic materials investigated using *ab initio* powder diffraction analysis [1]- [3].

One of the examples is the vapour induced transformations of pyromellitic acid (PA : benzene-1,2,4,5-tetracarboxylic acid). As shown in the scheme (see below), PA exhibits a wide variety of the vapour induced transformations. Eight solvates and one unsolvated phase were found by vapour induced transformations. Single crystals of some solvates could be obtained by alternative crystallise pathway, however, some of the solvates (phase U, 1M, 1E and 1iP) could only be obtained by the vapour induced transformations. Thus, the crystal structures of these phases were determined from the powder X-ray diffraction data. The structural analyses revealed that phase 1M and 1E are the mono-methanol and mono-ethanol phases, respectively. Further vapour exposures on the mono-solvate phases gave di-solvate phases (2M and 2E) and these di-solvate phases were also obtained by recrystallisation from the solutions or from the slurry of PA in these solvents. Therefore, phase 1M and 1E are the metastable phases under the existence of the solvent vapour. These mono-solvate phases are obtainable only by the vapour exposure and it clearly shows that solvent vapour exposures are very useful technique to control pseudo-polymorphs.



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Keywords: *ab-initio* powder structure determination, solid-state transformation, pseudo-polymorphism

MS45.P02

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Time-resolved structure analysis of photo-induced molecular dynamics in TTF-CA

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Recent progress of the time-resolved X-ray diffraction technique

enables to elucidate photo-induced dynamics in some crystals [1,2]. But diffraction intensities' change was mainly discussed and three-dimensional geometrical change have not been clarified in detail. In this study, we reveal the photo-induced molecular dynamics in a crystal with subnanosecond time resolution by single crystal X-ray structure analysis.

Time-resolved X-ray diffraction experiment was performed at PF-AR NW14A in KEK [3]. The co-crystal of tetrathiafulvalene and *p*-chloranil (TTF-CA; Figure), which shows neutral to ionic phase transition by laser irradiation at 90 K, [4] was selected as a target sample. Diffraction data sets were collected at 150, 500, 800, 1000 ps after laser excitation.

In photo-induced phase transition of TTF-CA, intensity reconstruction of symmetrically forbidden Bragg spots should be observed [2]. But in this study, significant intensity of these spots were not observed in all data sets. This indicated that phase transition was not fully progressed and recovered to the initial phase within the time-resolution of X-ray (pulse width = 150 ps) due to a weak excitation condition to minimize the damage by laser irradiation for prolonged data collection time. However, gradual movement of Cl and O in CA was observed by crystal structure and precise electron density analyses. These movements are assigned as thermal relaxation from the photo-induced ionic phase. Moreover, shortening of C=O in CA, which corresponds to enhancement of the neutral character of CA, was observed. These molecular dynamics indicates thermal relaxation from photo-induced ionic phase to initial phase go through the novel phase which has more strong neutral character than the initial phase. That novel phase was not generated by heating, so to speak, 'hidden' in the thermal process [1,5].

In sum, we succeeded to clarify the photo-induced dynamics of TTF-CA by time-resolved crystal structure analysis. In our excitation condition, the photo-induced 'hidden' phase was generated in subnanosecond time scale. This result will lead the progress of study about non-equilibrium dynamics in condensed matters.

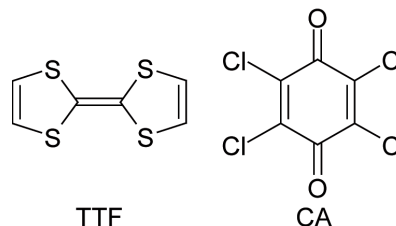


Figure. TTF and CA

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Keywords: time-resolved crystallography, photocystallography, non-equilibrium dynamics

MS45.P03

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Reorientation of hydrogen bonds in clathrates of Dianin's compound and hydroquinone

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Hydrogen bonded rings are a common structural feature of many host lattices. A reorientational process has been reported in the six-membered ring of O-H...O hydrogen bonds in the clathrate of Dianin's compound (DC) with ethanol [1]. Hydroxyl groups were found to exhibit concerted rotational jumps involving approximate rotations around C-O bonds, thus changing the direction of hydrogen bonding in the ring. Although an analogous six-membered hydrogen bonded ring is present in host structure of hydroquinone, a similar reorientational process has not been reported in any of its clathrates.

We have performed molecular dynamics simulations of the ethanol clathrates of DC and the methanol clathrate of hydroquinone. The simulations reproduce the observed reorientational process in the clathrate of DC but not in the clathrate of hydroquinone. We attribute this difference in behaviour to the larger ring size in the clathrate of DC as well as its greater flexibility.

We have also investigated the role of the guest molecules in the reorientational process. In the case of DC, ethanol appears to serve as a mediator, lowering the activation energy of reorientation through hydrogen bonding to oxygen atoms in the ring. The flexibility of the six-membered ring in DC enables hydroxyl groups of the ring to participate in hydrogen bonds with the guest.

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Keywords: host-guest systems, dynamics, simulations

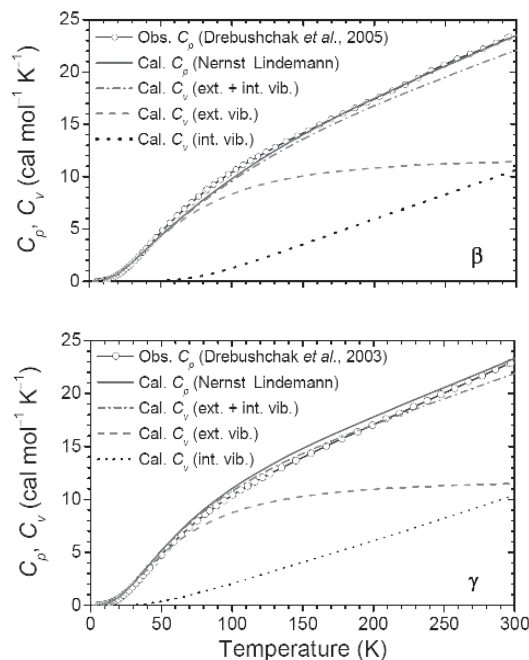
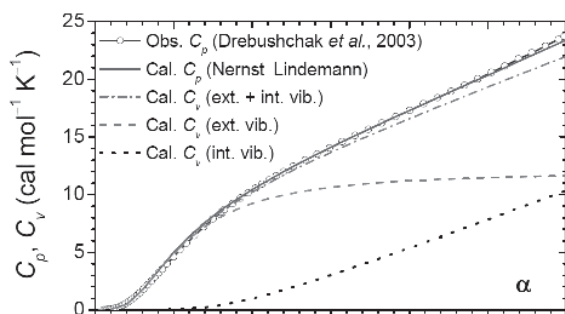
MS45.P04

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Dynamic and thermodynamic properties of glycine polymorphs from diffraction data

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Synchrotron data to 0.5 Å resolution of the α -, β - and γ -polymorphs of glycine were collected between 10 and 298 K at KEK, SPring-8 and the ESRF. Data were processed with RAPID AUTO, DENZO/SCALEPACK or SAINT+ and structures were refined with SHELXL-97, yielding $R_{\text{int}} \approx R_1 \leq 5\%$. Simultaneous analyses of the multi-temperature atomic displacement parameters were performed to obtain librational and translational frequencies [1]. The external vibration frequencies from a normal mode analysis and the internal vibration frequencies from a two-layer ONIOM(B3LYP/6-311+G(2d,p):PM3) method and a glycine cluster model were used together with the Einstein, Debye, and Nernst-Lindemann molecular models to determine heat capacities C_V , C_p that are in agreement with C_p from calorimetry [2-3].



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Keywords: dynamics, thermodynamics, polymorphs

MS45.P05

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Observation of the photo-excited state of $[\text{Co}^{\text{III}}(\text{en})_3]^{3+}$ by picosecond time-resolved XAFS

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Studying photochemical reaction in liquid with subnanosecond time-resolution gives information for understanding fundamental chemistry, biology and also for developing new materials and devices. [1]-[4] Monitoring the dynamic phenomenon requires a sensitive tool to investigate the electronic state and the structure with atomic resolution. However, studies of the excited state of tris(ethylenediamine)cobalt(III) ($[\text{Co}^{\text{III}}(\text{en})_3]^{3+}$) have been performed only using optical spectroscopic methods, [5] from which it is difficult to estimate the molecular structure with atomic resolution. Here, we have performed time-resolved X-ray absorption fine structure (TR-XAFS) on the $[\text{Co}^{\text{III}}(\text{en})_3]^{3+}$ dissolved in aqueous.

All measurements were performed in fluorescence method at the cobalt *K*-edge on the undulator beamline NW14A at the Photon Factory Advanced Ring. [6] X-ray pulses at 794 kHz were monochromatized by a Si(111) monochromator and used for the probe. A third harmonic of Ti:Sapphire laser operating at a frequency of 945 Hz was used for the pump source. The pump and probe measurements were performed