STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 73 (2017)

Supporting information for article:

In-house time-resolved photocrystallography on the millisecond timescale using a gated X-ray hybrid pixel area detector

Nicolas Casaretto, Dominik Schaniel, Paul Alle, Emmanuel Wenger, Pascal Parois, Bertrand Fournier, El-Eulmi Bendeif, Cyril Palin and Sébastien Pillet

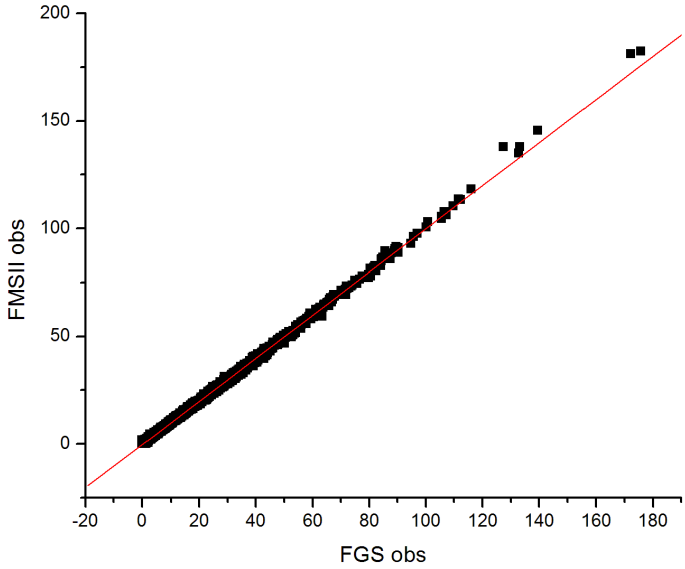

Figure S1 Measured structure factor moduli $|F_{MSII}(\vec{H})|$ as a function of $|F_{GS}(\vec{H})|$. Red line : linear fit to the experimental data with refined slope of 1.0017(8).

S1. Dependence of the diffracted intensity as a function of time delay

The scattering factor for a crystal containing a fraction p of molecules in the metastable state, and $1-p$ molecules in the ground state with a random spatial distribution can be written :

$$F(\vec{H}) = p \times F_{MSII}(\vec{H}) + (1-p) \times F_{GS}(\vec{H})$$

So that the scattered intensity is simply:

$$I(\vec{H}) = \left(p \times F_{MSII}(\vec{H}) + (1-p) \times F_{GS}(\vec{H})\right) \times \left(p \times F^*_{MSII}(\vec{H}) + (1-p) \times F^*_{GS}(\vec{H})\right)$$

In a time resolved experiment, the metastable state population is time dependent so that the intensity becomes:

$$I(\vec{H},t) = \left[p(t) \times F_{MSII}(\vec{H}) + (1-p(t)) \times F_{GS}(\vec{H})\right] \times \left[p(t) \times F^*_{MSII}(\vec{H}) + (1-p(t)) \times F^*_{GS}(\vec{H})\right]$$

For an exponential relaxation with lifetime τ of the metastable state and initial population p_0 :

$$p(t) = p_0 exp^{\frac{-t}{\tau}}.$$

For a centrosymmetric crystal like SNP, $F_{MSII}(\vec{H})$ and $F_{GS}(\vec{H})$ are real quantities.

$$I(\vec{H},t) = \left(p_0 exp^{\frac{-t}{\tau}} \times F_{MSII} + \left(1 - p_0 exp^{\frac{-t}{\tau}}\right) \times F_{GS}\right)^2$$

$$I(\vec{H},t) = {p_0}^2 exp^{\frac{-2t}{\tau}} \times {F^2}_{MSII} + \left(1 - p_0 exp^{\frac{-t}{\tau}}\right)^2 \times {F^2}_{GS} + 2p_0 exp^{\frac{-t}{\tau}} \times \left(1 - p_0 exp^{\frac{-t}{\tau}}\right) \times F_{MSII} F_{GS}$$

$$I(\vec{H},t) = F^2{}_{GS} + 2F_{GS}(F_{MSII} - F_{GS}) \times p_0 exp^{\frac{-t}{\tau}} + (F_{MSII} - F_{GS})^2 \times p_0{}^2 exp^{\frac{-2t}{\tau}}$$

The structural difference between GS and MSII is limited so that the difference between $F_{MSII}(\vec{H})$ and $F_{GS}(\vec{H})$ is also quite small. In the previous equation the second term on the right hand side is dominant with respect to the last term for small initial population p_0, so that in a first approximation, the time resolved Bragg intensity follows a single exponential dependence with time constant τ.

The following figure illustrates the simulated normalized intensity of the (240) reflection as a function of time with different values of the initial population p_0. As can be seen, all the curves follow in a first approximation a single exponential decay with time constant τ very close to 14 ms.

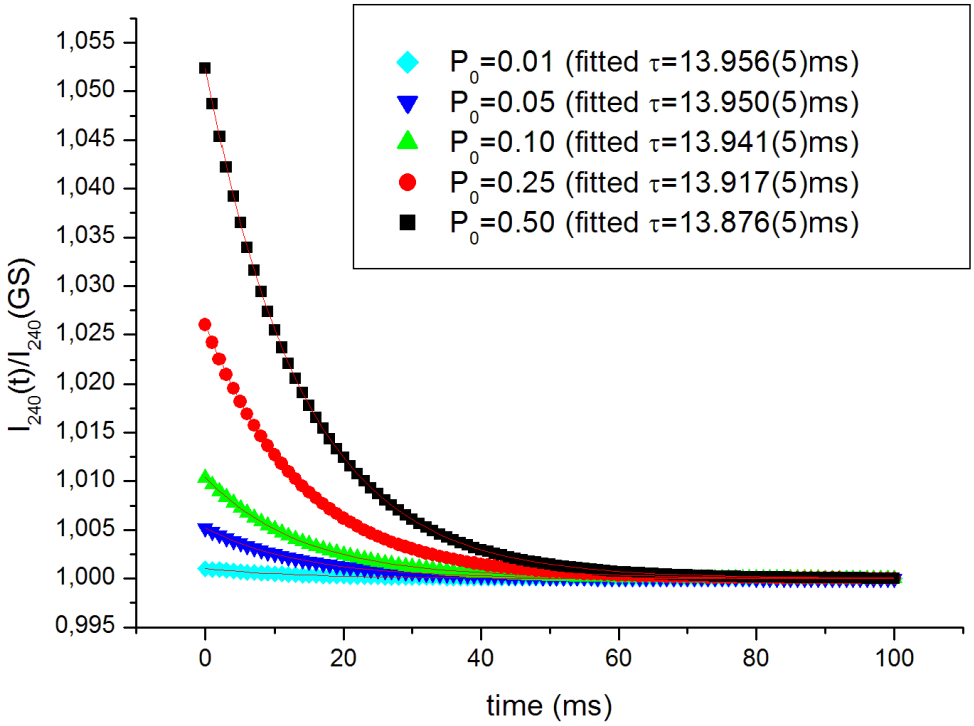

Figure S2 Simulated normalized intensity of the (240) reflection as a function of time with different values of the initial population p_0. All the curves have been adequately fitted to a single exponential decay.