

Mainstream and alternative routes to photoinduced phase transitions

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The old adage, "seeing is believing", implies that our understanding of the working of nature is determined by our ability to capture a picture. A real time observation of temporally varying molecular structures during chemical reactions is a great challenge due to their ultrashort time scales. Ultrafast optical spectroscopies operating on the picosecond ($1\text{ps}=10^{-12}\text{s}$) and femtosecond ($1\text{fs}=10^{-15}\text{s}$) time scales have provided a wealth of information about the dynamics of chemical processes, such as bond breaking and bond formation, electron and proton transfer. Unfortunately the long wavelength of optical light precludes direct structural information at the atomic/molecular resolution. The early attempts in using monochromatic pulsed X-rays opened the doorway for visualizing photochemical dynamics in solution [1]. Technological innovations in synchrotron instrumentation [2,3,4,5], and the development of novel data analysis [6,7] have made it possible to track complex reactions by time-resolved X-ray diffraction to sub-100 ps temporal and sub-Angstrom spatial resolution. Several experiments at the cutting edge of the synchrotron and laser technologies have now provided essential insights into fields varying from the photoinduced phase transitions [8] to photochemistry [9,10] to protein crystallography [7]. The race for even better time resolution on high flux X-ray facilities has entered a new stage with the linear accelerator based X-ray Free-Electron Laser. Flux comparison with synchrotron sources show a 1000-fold increase of X-ray delivered per pulse in as short bursts as 100fs, or even shorter.

The general excitement born out of the ultrafast clock caused rush of new ideas, new materials, and new instruments. One feat in particular has been draining a lot

of effort, namely the control of materials with an ultrashort laser pulse. There is ample evidence now that materials can be directed between different macroscopic states by using appropriate electronic, or structural, excitations. The switching with a laser pulse of such materials can severely change their macroscopic properties (electric conductivity, magnetism, colour, etc.), whereby emerging cooperativity and coherence of different degrees of freedom underpin the resulting phase transitions of various sorts [11]. However, the pertinent time scales for photo-switching processes in materials have been rather difficult to scrutinise. The pioneering investigations dealt mainly with the electron/phonon dynamics immediately following the femtosecond excitation, or the kinetics of recovery to the thermally stable states. Time-resolved X-ray diffraction and ultrafast VIS-IR spectroscopy reveal that the degrees of freedom triggered by a femtosecond laser pulse in a spin-crossover (SCO) material follow a sequence by which they appear during the out-of-equilibrium dynamics [12,13], characterised by elongation of covalent bondlengths between central Fe atom and its ligand. The time course of thermodynamic parameters, such as volume and temperature, shows evolution at later scale (100 ns, 1 μs), and eventually the return of the entire system to the equilibrium state. Those steps dissected in time, provided a mechanistic picture of a material transformation driven under different regimes (coherent or stochastic), [14]. The role of coherent optical phonons has been under intense scrutiny, whereas that of acoustic phonons and cell deformations, albeit looked upon, has not benefited from the same surge of effort. A likely explanation for this deficiency in providing global picture of transitions, is that crystal deformations occur on the periphery of ultrafast timescale. They involve propagation of a strain waves, essentially determined by sound velocity. This coherent process has the long coherence time of acoustic phonons and long range of elastic interactions. The coupling between the strain wave and the order parameter field raises a challenging question whether such coupling can lead to material transformation. SCO crystals composed of bistable molecules where the cooperativity is mainly governed by the change of molecular "volume" between the two states provide an excellent test bed for addressing this question.

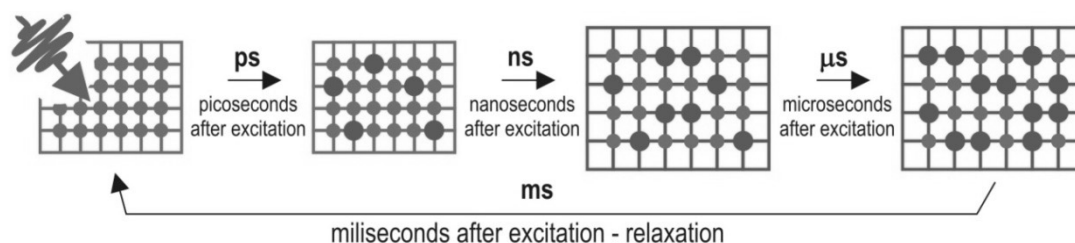


Figure 1. Schematic drawing of the spin-state switching dynamics: HS molecules (red circles) generated within 1 ps by laser pulse in the cold (blue) lattice with mainly LS molecules (blue circles), warm (red) lattice expansion on 10 ns generating more HS molecules, thermal stabilisation of HS population within μs . Recovery to thermal equilibrium of the crystal with the environment (cryostat) on ms time scale.

We have investigated such materials over several time decades, and on samples of very different size, from nano- to macro-crystals [15,16]. These studies bring the photo-switching of materials into new perspective, notwithstanding its common perception, uniquely related to electronic or optical phonon dynamics.

Photo-switching on the ultrafast timescale still remains a fundamental problem in physics because of extremely fast inter-system crossing, which defies conventional understanding. Experiments carried out with 100 femtosecond resolution provide compelling evidence for a breakdown of Born-Oppenheimer approximation or Fermi Golden Rule [17]. Recent experiments carried out on X-FEL, operated conjunctly with the timing tools [18], corroborate recent theory [19] that the intersystem crossing results from the dephasing of the photoexcited state into the photoinduced phonon states, thus hindering the quantum recurrence, and instead favoring efficient damping in the excited state (submitted).

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