Perspective: On the relevance of slower-than-femtosecond time scales in chemical structural-dynamics studies

Philip Coppens
Chemistry Department, University at Buffalo, SUNY, Buffalo, New York 14260-3000, USA
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A number of examples illustrate structural-dynamics studies of picosecond and slower photo-induced processes. They include molecular rearrangements and excitations. The information that can be obtained from such studies is discussed. The results are complementary to the information obtained from femtosecond studies. The point is made that all pertinent time scales should be covered to obtain comprehensive insight in dynamic processes of chemical and biological importance.

I. INTRODUCTION

Time-resolved diffraction studies have a long history, but the definition of the concept time-resolution is broadly defined, and is used to describe a range of events from plate tectonics to electronic excitations and beyond. In Biology, Chemistry, and Material Science, the range is continuously expanding towards faster events and now includes ultrafast processes taking place in femtoseconds, driven by revolutionary technological developments. Spectacular new experimental information is becoming available on such timescales. New insight is gained in the initiating stages of dynamic processes like chemical reactions. However, novel dynamic information accessible in slower time domains is often complementary and frequently relevant in its own right. Some such information is summarized in Scheme 1. Whereas, the ultrafast femtosecond-timescale experiments give information on a timescale of instantaneous atomic motions, the slower ones typically provide information on the statistically averaged response of an assembly of molecules, related to the structural changes and kinetics of the system studied.

The study of photo-induced processes in crystals is generally referred to as photocrystallography. The well-defined structural environment of the photo-products in periodic crystals often has to be taken into account to reproduce the observations theoretically. The impact of the matrix surrounding the active species is by itself of more than fundamental interest as materials used in practical devices are typically solids.

We present a number of selected examples highlighting the application of structural dynamics studies of processes that proceed on slower timescales than femtoseconds, on which currently much attention is focused.

II. DIFFERENT TIME-DOMAINS

A. Processes taking hours

Chemical reactions in crystals tend proceed relatively slowly, but can be studied by diffraction methods at atomic resolution, in particular, if the reactions proceed in a topotactic way, which implies that the integrity of the crystal lattice is preserved in a single-crystal-to-single-crystal reaction. Time-dependent studies on the timescale of hours give information on the progress of a reaction within the periodic assembly of molecules and on the activation energies of the reaction if temperature dependent studies are included, rather than on the instantaneous mechanism of the reaction, which requires sub-picosecond studies. An example is the study of
the small olefin trans-tiglic acid (TA) (Scheme 2), which undergoes trans-cis photoisomerization around the C=C bond (Fig. 1). In a study of the Zn-(tiglic acid)$_2$ complex in a CECR matrix (Scheme 2, Fig. 3), the measurements were performed at four different temperatures in the 90–190 K range. The crystal contains two tiglic acid molecules in the asymmetric unit, both complexed to the same Zn atom, as shown in Figure 2. But the two molecules are located in cavities of very different sizes, indicated by the different color ellipses in Fig. 3. This implies
that TA molecule, encircled by the blue ellipse in Fig. 2, is more constrained than the second one within the red ellipse in the figure. Both the reaction rates and the composition of the photostationary states are strikingly different, as shown in detail in the reference (Zheng et al., 2008). Subsequent Arrhenius and Eyring kinetic plots lead to energies and enthalpies of both the forward and reverse crystal reactions amounting to several kJ mol\(^{-1}\). The results give quantitative evidence for the constraining effect of the crystal environments on the reaction, which is as expected more severe for the smaller cavity.

The photoinduced reactions of cinnamic acid and derivatives remain some of the most studied solid state [2 + 2] photodimerizations since the pioneering studies of Schmidt and

FIG. 2. 3D-supramolecular architecture viewed along the b-axis direction (Zn atom is displayed as a sphere). Large and small cavities marked by red and blue ellipses, respectively.

FIG. 3. Data point is based on refined occupation parameters. Converted fraction of \(\beta\)-cinnamic acid as a function of irradiation time. The curved line is a fit with \(n = 1.43\) and \(k = 6.5 \times 10^{-7} \text{ s}^{-1}\). Reprinted with permission from Benedict, J. B. and Coppens, P., J. Phys. Chem. 113, 3116–3120 (2009). Copyright 2009 American Chemical Society.
co-workers in the sixties established the topochemical principles governing such reactions (Cohen et al., 1964; Schmidt, 1964; 1971). The kinetics of the dimerization reaction in a series of compounds has been analyzed by the JMAK kinetics of Johnson, Mehl, Avrami, and Kolmogorov (Kolmogorov, 1937; Avrami, 1939; and Johnson and Mehl, 1939). Crystals of \( \alpha \)-cinnamic acid were studied by two-photon excitation (Benedict and Coppens, 2009), which increases the likelihood of single-crystal-to-single-crystal transformations (Naumov et al., 2002; Harada et al., 2008). The fraction converted vs. time curve is S-shaped (Fig. 3). A fit of the curve against the equation \( y = e^{-kt^n} \), where \( y \) is the conversion percentage and \( n \) is related to the dimensionality of the seed growth of the nucleus, with a value of \( n = 1 \) corresponding to an equal-growth probability in all directions. For the \( \alpha \)-cinnamic acid polymorph \( n \) was found to be 1.43 (8) (Fig. 3), suggesting a hybrid mechanism combining homogeneous nucleation with one-dimensional growth of the nuclei. The results agree within the experimental uncertainties with an earlier solid state NMR study which led to an \( n \) value of 1.66 (Bertmer et al., 2006). In a subsequent study of the molecule 1,4-dimethylpyridone surrounded in the lattice by a cavity formed by inactive hosts at 230 K and 280 K, a similar hybrid model of the dimerization was found with \( n = 1.6 \) (1) and 1.5 (1) at the two temperatures, respectively. An activation energy of 32.5 kJ/mol was calculated from the kinetic plot. A very different Avrami exponent of 0.55 was found for the \([4+4]\) photodimerization of 9-anthracene carboxylic acid (Taylor et al., 1998). It would imply a negative dimensionality, a result interpreted as a negative autocatalytic step, or auto inhibition, during the photoreaction (Moré et al., 2010). Further studies on additional systems are needed before a comprehensive theory on the progress of this type of reactions in crystals can be formulated.

### B. Timescales of milliseconds

Many photo-induced processes in the solid state involve the intramolecular rearrangement of groups of atoms or transfer of atoms to different parts of a molecule. Linkage isomerizations were already reviewed in 1968 (Burmeister, 1968). The kinetics of the rearrangements is typically temperature-dependent, with many of the isomers being unstable at room temperature. However, at reduced temperatures intermediates and final products can be identified. Species discovered on light-exposure of sodium nitroprusside \( \text{Na}_2[\text{Fe(CN)}_5(\text{NO})]\cdot 2\text{H}_2\text{O} \) were originally described as electronically excited states with unusually long lifetimes at 100 K (Hauser et al., 1977b; 1977a). However, crystallographic studies in the mid-nineties showed that they are in fact metastable linkage isomers in which the nitrogen-bound NO group is either inverted or sideways bound, as illustrated in Fig. 4 (Carducci et al., 1997). Many chemically related complexes undergo similar isomerizations (Coppens et al., 2002; Bitterwolf, 2006) and extensive photocystallographic work is continuing. The rearrangements of many of such compounds are accompanied by color, refractive index, and magnetic changes and have potential for use in optical switching and memory devices (Gütlich et al., 2001; Fally et al., 2004; and Schaniel et al., 2007).

**FIG. 4.** The nitroprusside ion (left) and its photo-induced linkage isomers.
Reduction of the temperature slows down the decay processes and allows identification of possible intermediates and, by measurement of the decay at different temperatures, determination of the kinetics and identification of possible intermediates. This approach has been pursued by Hatcher, Raithby, and co-workers. They report photo-activated reorientation of one of the nitro groups in \([\text{Ni}(\text{Et}_4\text{dien})(\eta^2-\text{O},\text{ON})(\eta^1-\text{NO}_2)]\) \((\text{Et}_4\text{dien} = \text{N},\text{N},\text{N}',\text{N}'\text{tetraethyl} \text{d}i\text{ethylenetriamine})\). The group rearranges from N-bound \(\eta^1-\text{NO}_2\) to O-bound \(\eta^1-\text{ONO}\) (nitrito) \((\text{Figure 5})\), on exposure to 500 nm light \((\text{Hatcher et al.}, 2014; \text{Hatcher et al.}, 2011)\). Variable temperature studies in the 150–165 K range show the activation energy of decay to be 48.6 kJ/mol. A second “pseudo steady-state” experiment with continuous light exposure give evidence for a transient intermediate species existing in the 145–165 K region in which the \(\eta^1-\text{ONO}\) nitrito group is differently oriented. The laser pump/X-ray pulse technique with variable pump-probe delay times, discussed in Sec. II C, is well suited for the identification of intermediates, as illustrated by the detailed studies on the photo-induced cycle of photo-active-yellow protein (PYP) \((\text{Tripathi et al.}, 2012; \text{Ihee et al.}, 2005; \text{and Anderson et al.}, 2004)\).

C. Timescales of microseconds and nanoseconds: The pump-probe technique

Triplet and singlet photo-induced excited states of molecular species, with typical lifetimes of microseconds and nanoseconds, respectively, tend to be highly reactive and precursors of photochemical reactions. Such lifetimes are well matched to the time-resolution of synchrotron sources with their \(\sim50–100\) ps time limit imposed by the pulse lengths of the sources. Timeslicing methods can produce shorter pulses \((\text{Schoenlein, 2000})\), but imply a considerable loss in intensity, which is prohibitive for many experiments.

Which structural and electronic features of the excited states are responsible for the high reactivity of the photo-excited states? Once their structure has been determined, theoretical calculations can provide insight in the second part of this question.

The first atomic-resolution studies reported involved binuclear metalorganic complexes with the metal atom having \(d^7\), \(d^8\), or \(d^{10}\) configurations. A contraction of the molecule on excitation, resulting from a promotion of an electron from an anti-bonding to a weakly bonding orbital, was observed when the first results on the 50 \(\mu\)s lifetime 16 K excited state structure of \([\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]^{4-}\) became available \((\text{Novozhilova et al.}, 2003; \text{Kim et al.}, 2002)\). Contractions

FIG. 5. Diagram of \([\text{Ni}(\text{Et}_4\text{dien})(\eta^2-\text{O},\text{ON})(\eta^1-\text{NO}_2)]\), showing O-bound \(\eta^1-\text{ONO}\) (nitrito) and the \((\eta^2-\text{O},\text{ON})\) nitro group after irradiation with 500 nm light in which the N-bound NO2 group has been reoriented to O-bound.
of binuclear complexes on excitation have since been observed in several systems (Coppens et al., 2004; Zheng et al., 2005; and Makal et al., 2011). Structural modifications have been determined for spin-crossover systems, which can be switched between low- and high-spin states by light irradiation, temperature variation, and other external perturbations, with parallel changes occurring in magnetic and optical properties (Cailleau et al., 2010).

Many crystals contain more than one molecule in the asymmetric unit. Such chemically equivalent, but crystallographically independent molecules can show different distortions on excitation and differences in wavelength and lifetime of their luminescence (Makal et al., 2012; Coppens et al., 2013). Comparison of results of isolated-molecule calculations with calculations in which the lattice is taken into account confirms such differences. Large differences are often observed, as in the recent study of a Ag-Cu coinage metal complex, in which theoretical contraction of \(-0.534\) and \(-0.932\,\text{Å}\), were reduced to \(-0.345\) and \(0.438\,\text{Å}\), respectively, when the environment was taken into account in the calculation, in much better agreement with the experimental results (Jarzembska et al., 2014). The photodifference maps and the structural changes on excitation are illustrated in Fig. 6.

Other studies involve intramolecular electron transfer (MLCT, metal-to-ligand charge transfer), in a number of highly luminescent Cu(I) dimethyl-phenanthroline photosensitizer complexes (Vorontsov et al., 2009; Makal et al., 2012). Such complexes are typical for use as light-emitting diodes (Armaroli et al., 2006; Yersin et al., 2011). Bi-molecular excimer formation has been observed in crystals of \([[3\,\text{5–(CF}_3)\text{2pyrazolate}]\text{Cu}_3]\) through photoinduced dimerization of a pair of molecules with a molecular stack (Vorontsov et al., 2005).

FIG. 6. (a) Photodifference map of Ag2Cu2L4. Solid and transparent surfaces at 0.55 and 0.35 eÅ\(^{-3}\), respectively. (b) The observed change from Z- to rhomb-shape of the central cluster due to shortening of the Ag-Cu and Ag-Ag distances on excitation by 0.4–0.5 Å. (c) Photodeformation map based on the refined model; blue: positive, red: negative. Reprinted with permission from Jarzembska et al., Inorg. Chem. 53, 10594–10601 (2014). Copyright 2014 American Chemical Society.
A 100 ps time resolved study at the Advanced Ring at the Photon Factory at KEK on the photo-induced the neutral (N) to ionic (I) phase transition in tetrathiafulvalene (TTF)-chloranil was reported by Collet and co-workers (Guerin et al., 2004; Collet et al., 2003). The transition was first discovered as a thermal process occurring at \( T_c = 81 \) K (Torrance et al., 1981). It involves dimer formation along heterogeneous stacks with ferroelectric ordering in the I stacks, consisting of positive donor (D) TTF molecules and negative acceptor (A) chloranil species. The transition involves a space group change in which a center of symmetry disappears in the low-temperature-stable I phase which can be photochemically converted to N at 70 K, while the reverse process can be triggered above \( T_c \). Time-resolved analysis of changes in the diffuse scattering pattern at the 50 ps resolution available at the Advanced Ring, allowed identification of I precursor strings of at least eight (D\(+\) A\(-\)) pairs being generated in the N columns prior to completion of the phase transition (Guerin et al., 2010).

Overall, the microsecond-nanosecond domain allows investigation of a large number of excitations with the concomitant change in properties. The field is largely unexplored.

III. CONCLUDING REMARKS

We conclude that many significant scientific issues remain to be addressed on the slower-than-femtosecond timescales. Structural information can be obtained at atomic resolution and is often complementary to what can be achieved at femtosecond time scales, at which the important initial stages of chemical processes can be revealed. The pronounced shape-changes of photactive yellow protein on exposure to blue light, for example, are triggered by a trans-cis isomerization of the \( p \)-coumaric acid chromophore, the initial stages of which have not yet been explored, but the subsequent dynamic isomerization processes are to be studied at slower time scales (Schmidt et al., 2013; Tenboer et al., 2014), as was done for the related isomerization of tiglic acid described above. Many commercial applications involve the millisecond to nanosecond time domains. They include luminescence, optical switching, biological processes, and catalysis. Structural dynamics studies remain essential for their elucidation.

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