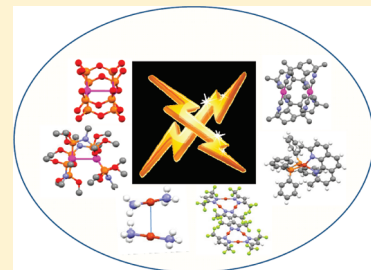


# Molecular Excited-State Structure by Time-Resolved Pump–Probe X-ray Diffraction. What Is New and What Are the Prospects for Further Progress?

Philip Coppens\*

Chemistry Department, University at Buffalo, Suny, Buffalo, New York 14260-3000

**ABSTRACT:** Time-resolved diffraction by laser pump–X-ray probe methods for the determination of the geometry of molecular excited states is discussed. A number of examples are presented and compared with theoretical results. The increasing brightness and time resolution of new light sources now becoming available will likely enable the tracking of dynamic processes in solids on femtosecond time scales.



The field of crystallography has been exceedingly successful in the past decades in elucidating solid-state structure with an accuracy of thousandths of an Å or less and at the mapping electron densities in crystals with a reproducibility similar to that of theoretical calculations. However, structural elucidation of short-lived species and rapid dynamic processes has lagged behind due to the considerable technical difficulties associated with measurements on time scales of microseconds or less.

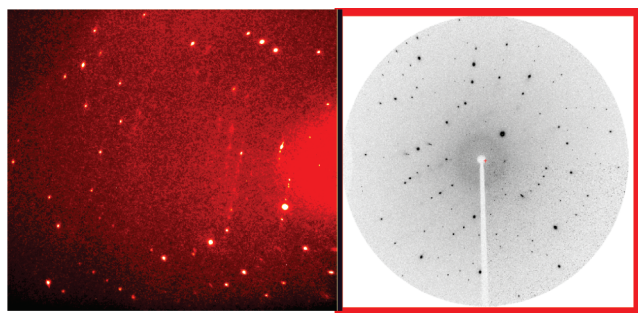
**Structural elucidation of short-lived species and rapid dynamic processes has lagged behind conventional structure determination due to the considerable technical difficulties associated with measurements on timescales of microseconds or less. With the advent of both high-brightness pulsed sources concentrating a large photon flux in a small area and powerful pulsed laser sources, such limitations are now disappearing.**

With the advent of both high-brightness pulsed sources concentrating a large photon flux in a small area and powerful pulsed lasers, such limitations are now disappearing. Third-generation synchrotron sources like the Advanced Photon Source at Argonne National Laboratory and the European Synchrotron Radiation Facility in Grenoble France are prime examples of the facilities being exploited in time-resolved (TR) studies. A further major advance now taking place is the development of X-ray free electron Lasers such as the Linear Coherent Light Source (LCLS) at SLAC (Stanford Linear Accelerator Center), which has started operation. The X-ray work has been stimulated by advances in related fields. They include the pioneering femtosecond TR electron diffraction studies of Zewail and co-workers on small-molecule reactions in the gas phase<sup>2–4</sup> and the many ultrafast UV, visible, and IR spectroscopic studies of the nature of light-induced transient species.<sup>5–9</sup> In addition to the latter, the detailed knowledge of the geometric structure of short-lived species remains a crucial component for our understanding of dynamic processes in a broad range of fields encompassing chemistry, materials science, and biology. In such studies, the solid state has the advantage that much more complex molecules can be studied than in the gas phase and that the periodic alignment of the molecules in the crystal enhances the transient signal. On the other hand, a molecule in a solid is not the same as an isolated molecule, which must be taken into account in interpretation of the results and comparison with isolated molecule theory.

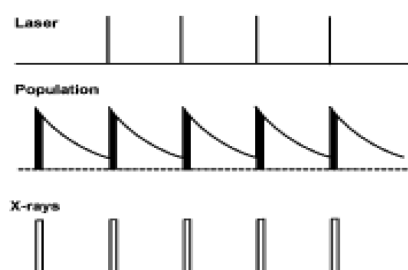
X-rays have the advantage that they interact less strongly with matter than electrons, which require very thin samples. On the other hand, the molarity of a molecular crystal is usually larger

**Received:** January 11, 2011

**Accepted:** February 1, 2011



**Figure 1.** (Left) Monochromatic diffraction pattern from a stroboscopic experiment at beamline 15-ID at APS, with 5000 pump–probe cycles and a total exposure of 1000 ns. (Right) Laue pattern with a total exposure of 70 ps collected at beamline 14-ID at APS.



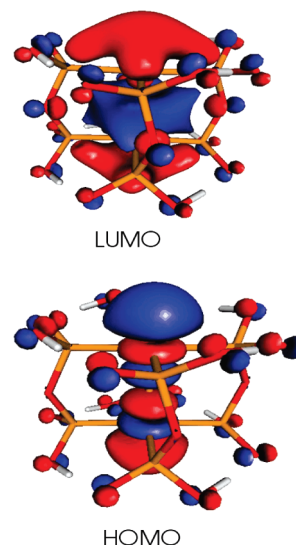
**Figure 2.** The stroboscopic pump–probe experiment. The pump–probe cycle is repeated as long as necessary to obtain adequate statistics before the read-out, which is followed by a dark cycle and a rotation of the sample, after which the process is repeated.

than 1, which limits the penetration of the laser pump beam and reduces the average conversion percentage in the crystal. Therefore, for sufficiently homogeneous light exposure of the crystal, samples of linear dimensions of 40  $\mu\text{m}$  or preferably less must be used.

In general, time-resolved studies represent a new dimension in chemical research. Structural studies are at the core of the field and are being interpreted in conjunction with spectroscopic and theoretical results. In this Perspective, we will concentrate on progress made in TR studies of excited molecular species in crystals and outline possibilities for future studies as ever brighter sources become available.

**Monochromatic versus Polychromatic Radiation.** Both monochromatic and polychromatic Laue methods have been employed for TR studies at synchrotron sources. In the polychromatic Laue technique, a much broader energy slice of the beam is used, leading to more efficient use of the synchrotron photons. This allows much shorter exposure times (Figure 1) and, therefore, higher temporal resolution down to the limit imposed by the narrowest of the synchrotron pulse width, which is  $\sim 70$  ps, and the laser pulse width, which is nanoseconds for Nd:YAG type lasers and femtoseconds for Ti:sapphire lasers. Single X-ray pulse exposures have indeed been used in the most recent work.<sup>10</sup>

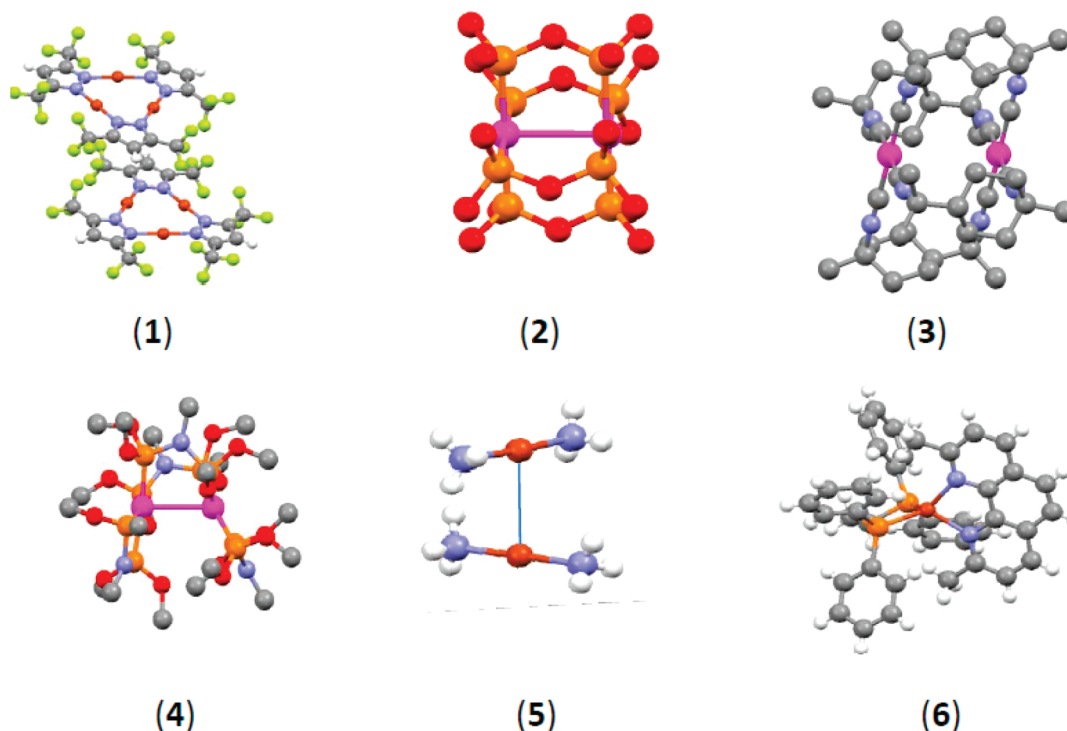
In monochromatic TR experiments, a stroboscopic technique (Figure 2) is used in which the signals of thousands of pump–probe cycles are accumulated on the detector surface before detector read-out. A drawback is that the repeated laser exposure causes a significant temperature increase in the sample even when cooled in a helium or nitrogen gas stream<sup>11</sup> and leads to more rapid sample deterioration. The Laue technique, on the



**Figure 3.** The HOMO and LUMO orbitals of the binuclear Pt complex (2) discussed in the text, illustrating the antibonding to bonding transition. From ref 1.

other hand, has been notoriously inaccurate due to its dependence on the spectral distribution of the probe beam and the enlargement of spot size and change in shape inherent in the broader wavelength spread. These disadvantages have now been alleviated in TR studies by basing the analysis on the ratios of the light-on and light-off reflections,<sup>12</sup> which are wavelength-independent if unit cell changes are small, and on spot integration techniques which do not depend on profile fitting.<sup>13</sup> As a result, in a recent Laue study, a higher accuracy was reached than was attained in monochromatic studies,<sup>10</sup> but additional development of interpretation methods is nevertheless called for. The monochromatic technique has not yet been used at beamlines outfitted with flux-enhancing multilayer optics. The higher flux would greatly reduce the number of pump–probe cycles required in the stroboscopic technique and make monochromatic methods competitive again and perhaps even preferred.

**Time-Resolved Diffraction in Chemistry.** As the field of time-resolved diffraction is still in its infancy, available results are scattered over a number of areas of interest, and large systematic studies are still lacking. A number of binuclear metalloorganic complexes with the metal atom in a  $d^7$ ,  $d^8$ , or  $d^{10}$  configuration have been studied, as detailed below. They show a somewhat counterintuitive contraction of the molecule upon excitation, which is easily understood in terms of a promotion of an electron from an antibonding to a nonbonding or weakly bonding orbital (Figure 3).<sup>1,14–16</sup> A second example of electron promotion within the atomic orbital manifold is spin-crossover systems, which can be switched from a low-spin to a high-spin state with corresponding changes in magnetic and optical properties by light irradiation, temperature changes, and other external perturbations.<sup>17</sup> A further effect of considerable practical importance is electron transfer. Intramolecular electron transfer includes MLCT (metal-to-ligand charge transfer), studied for the Cu(I) dimethylphenanthroline-1,2-bis(diphenylphosphino)ethane photosensitizer complex.<sup>18,19</sup> Intermolecular effects studied by TR methods include photoinduced charge transfer in the segregated stack molecular crystal TTF-chloranil (TTF = tetrathiofulvalene)<sup>20</sup> and bimolecular excimer formation in

Scheme 1. Complexes Discussed in the Text<sup>a</sup>

<sup>a</sup> Pt and Rh: pink; Cu: orange—red; P: orange; oxygen: red; nitrogen: blue; carbon: grey; hydrogen (where included): green—yellow.

{[3 5-(CF<sub>3</sub>)<sub>2</sub>pyrazolate]Cu}<sub>3</sub><sup>21,22</sup> (1), in which adjacent molecules in homogeneous stacks form weakly connected dimers.

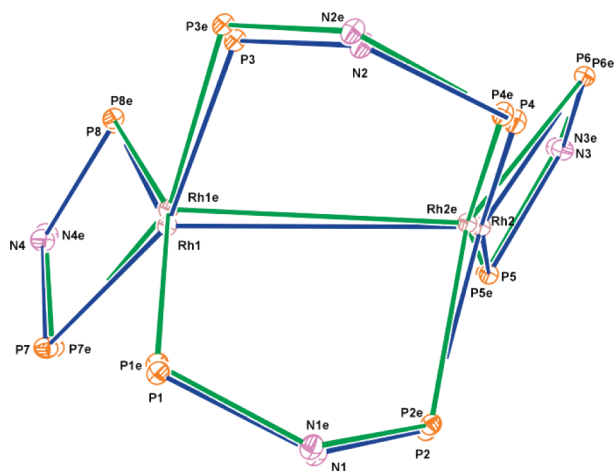
All of these studies concern excited states with lifetimes of milliseconds, microseconds, or less. The short lifetime allows repetition of the pump—probe cycle and subsequent data collection at a series of angular settings of the sample. Fast unidirectional processes such as chemical reactions in crystals pose a greater challenge as the pump—probe cycles cannot be repeated rapidly enough to follow processes taking place on a very rapid time scale, as further discussed below.

The binuclear complexes studied include the [Pt<sub>2</sub>(pop)<sub>4</sub>]<sup>4-</sup> ion (pop = pyrophosphate, (H<sub>2</sub>P<sub>2</sub>O<sub>5</sub>)<sup>2-</sup>) (2) in its (TEA)<sub>3</sub>H-(Pt<sub>2</sub>(pop)<sub>4</sub>), (TEA = tetraethyl ammonium)<sup>14</sup> and TBA (TBA = tetrabutyl ammonium)<sup>24</sup> salts, the [Rh<sub>2</sub>(1,8-diisocyano-*p*-menthane)<sub>4</sub>]<sup>2+</sup> ion in its PF<sub>6</sub> salt (3),<sup>15</sup> Rh<sub>2</sub>( $\mu$ -PNP)<sub>2</sub>(PNP)<sub>2</sub>BPh<sub>4</sub>, where PNP = CH<sub>3</sub>N(P(OCH<sub>3</sub>)<sub>2</sub>)<sub>2</sub> and BPh<sub>4</sub> = tetraphenylborate (4),<sup>10</sup> and [Cu(NH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[THPE]<sup>-</sup> · 3.25H<sub>2</sub>O (5)<sup>22</sup> incorporated in a supramolecular framework of THPE anions (H<sub>2</sub>THPE<sup>-</sup> = the monoanion of tris(hydroxyphenyl)ethane) (see Scheme 1).<sup>1</sup> For (2), contractions of 0.28(9)<sup>14</sup> and 0.24(3) Å<sup>24</sup> were observed in two different X-ray diffraction experiments, in agreement with an earlier value of ~0.21 Å derived from spectroscopic measurements.<sup>25</sup> The results were confirmed by two more recent solution scattering experiments. An EXAFS study of an ethanol solution<sup>26</sup> gave a 0.31(5) Å contraction for the Pt—Pt bond length and, for the first time, a likely significant elongation of 0.010(6) Å for the Pt—P bonds, in agreement with the theoretical calculations (for details on the refinement procedure of the X-ray diffraction data, see ref 23), whereas an X-ray scattering experiment on an aqueous solution led to a Pt—Pt contraction of 0.25(6) Å.<sup>27</sup> Thus, all experiments on (2) done so far agree within the respective experimental accuracies. Subtle

differences which could be expected from the different media employed in the experiments may be masked by the rather large experimental errors and warrant further investigation.

The first X-ray diffraction result on (2) was used to differentiate between alternative theoretical calculations which gave quite different geometries depending on the DFT functional used and the relativistic treatment. However, subsequent studies on (3) and (4) showed that the geometric change in the crystal is frequently different from that calculated for the isolated molecule, so that calibration of theory based on isolated molecules may have to be re-examined. The largest contraction was observed for the binuclear Rh(II) compound (3), which was studied with monochromatic X-rays at 17 K. The experimental change is from the very large Rh—Rh distance in the PF<sub>6</sub> salt of 4.496(1) to 3.64(5) Å. However, DFT calculations predict an even larger contraction from 4.553 to 3.05 Å. A similar discrepancy between experiment and isolated molecule theory is observed in the Rh(I)—Rh(I) complex (4), for which neither the ground-state nor the excited-state geometries are well-predicted by a variety of DFT calculations.<sup>10</sup> In this case, the experimental contraction from a much shorter ground-state value is much smaller than that in (3) but predicted in a series of DFT calculations on the isolated complex with different basis sets and functionals to be at least twice as large as the observed value of 0.154(13) Å and often considerably larger.<sup>10</sup> It is of interest that in the case of (4), qualitative information is also obtained for the displacement of the ligands (Figure 4). Such information could not be extracted in preceding studies of binuclear complexes.

The Cu(I) ammonium dimer (5) is only stable when incorporated in the anionic hydrogen bonding framework of the supramolecular THPE solid, so that no comparison with the contraction in isolated molecules is possible. A contraction is

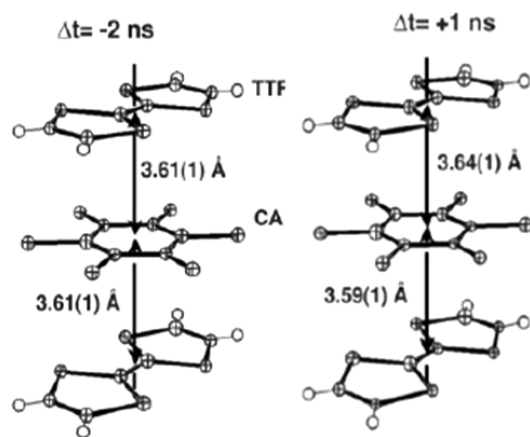


**Figure 4.** Structural changes upon excitation in complex (4). Ground-state (blue lines) and excited triplet state (green lines). From ref 10 (Reproduced with permission of the Royal Society of Chemistry).

again observed experimentally, this time from 3.025(1) to 2.72(1) Å.<sup>22</sup> The latter number may be compared with the theoretical value of 2.60 Å for the excited state of the isolated ion, which, unlike the ground state, shows a bonding minimum as a function of the Cu—Cu distance as the excitation corresponds to bond formation as in (2) and (3). A smaller than calculated molecular deformation was also observed for the tetrahedral Cu(I) complex [Cu(I)(dmp)(dppe)][PF<sub>6</sub>] [dmp = 2,9-dimethyl-1,10-phenanthroline; dppe = 1,2-bis(diphenylphosphino)ethane] (6), in which the expected flattening upon excitation from Cu(I) to Cu(II) is much reduced from a theoretical value of 8 to 3.2° for one and no distortion for the second of the two independent molecules in the asymmetric unit.

Thus, evidence is accumulating for the constraining effect of the crystal lattice on the photoinduced molecular deformations. How can it be confirmed experimentally? One, albeit approximate, approach is through QMMM (quantum mechanics/molecular mechanics) calculations, in which the environment of the photoexcited molecule is treated by MM methods or kept fixed upon excitation of the central species. In a first such study, the method was applied to the [bis(4-chlorothiophenyl)-1,10-phenanthroline]zinc(II) complex, in which the thiolate ligands show large displacements upon excitation according to isolated molecule theory. The QMMM calculation shows an excited state with a geometry very close to that of the ground state,<sup>28</sup> in agreement with experimental results which show none or only minor geometrical changes, thus supporting the evidence for the constraining effect of the environment. Further studies on some of the other complexes mentioned above are underway.

**Evidence is accumulating for the constraining effect of the environment on photoinduced molecular excitations in crystals even though structural changes observed can be as large as 0.8 Å.**



**Figure 5.** The structure of TTF-chloranil before (left) and after (right) application of the laser pump pulse inducing electron transfer and pair formation. From ref 29. Reprinted with permission from AAAS.

Electron transfer and its mechanism are of great relevance to both biologically and technologically important processes. The intermolecular electron-transfer phase transition of TTF-chloranil was discovered in 1981 by Torrance and co-workers, who applied pressure to induce the transition.<sup>37</sup> The neutral to ionic transition occurs thermally at 81 K upon cooling. It can be photoinduced both above the thermal transition temperature at 93 K (N—I)<sup>29</sup> and in the reverse sense below that temperature at 70 K (I—N).<sup>20</sup> The photochemical transition is cooperative and has a quantum yield much larger than 1. The molecules in the neutral phase are equidistant in the mixed stacks, but in the ionic phase, dimeric A—B pairs are formed with a reduced intermolecular distance. The charge transfer has been measured by accurate X-ray charge density methods to be 0.74(2) e below the thermal transition temperature and 0.21(2) e in the formally neutral phase.<sup>30</sup> At these temperatures, the intermolecular intrastack distances are changed by  $\sim \pm 0.2$  Å, which exceeds the values found in the photochemical experiments (Figure 5).

Unlike in the static charge density measurements described above, the charge density and the electron transfer cannot be quantitatively measured by TR X-ray methods because of the limited conversion achieved in the pump—probe experiments. However, fundamental information on the mechanism of the dynamic changes can be obtained from the structural information, which can then be used in subsequent theoretical treatments.

*Time-Resolved Diffraction in Structural Biology.* Biological TR diffraction using the Laue method has been an active field of research since the early 90s.<sup>31</sup> It has made rapid advances due to the great improvement in source brightness, laser techniques, and electronics in the past decade.<sup>32</sup> Macromolecular crystals have a molarity which is typically in the millimolar range and thus much lower than that for most small-molecule chemical systems as the molecules are much larger and embedded in an extensive solvent mantle. Dynamic changes in macromolecular crystals are therefore much less constrained by the crystal environment. On the other hand, because of poorer crystal quality and ubiquitous disorder, diffraction is limited to low resolution so that atomic resolution in the chemical sense is elusive. Studies published deal with photon-triggered release and recombination of ligands such as CO in CO-myoglobin.<sup>33</sup>

Conformational changes such as those that occur in the signaling protein of marine organisms, photoactive yellow protein, are a further example. They have been studied at 47 time points between 1 ns and 1 s.<sup>34</sup>

With the increasing use of the Laue technique in chemical TR diffraction and the improving flux at monochromatic beamlines, both techniques are converging. Methods developed in either can undoubtedly be used profitably in the other field. For example, the RATIO method, which eliminates uncertainties due to spectral distribution and wavelength-dependent absorption and detector response effects,<sup>12</sup> should have advantages in macromolecular studies as it also eliminates the effect of all but short-term intensity fluctuations.

**Femtosecond TR Diffraction.** An important experimental limitation in the synchrotron work results from the close to 100 ps length of the synchrotron pulses. This is too long to track the progress of chemical reactions at the atomic level and that of many electron-transfer and electron-recombination processes which typically have to be monitored on femtosecond time scales and, in addition, be initiated coherently by very short light pulses. Zewail and co-workers achieved femtosecond resolution by using electron diffraction in the gas phase and molecular beams to elucidate the mechanism of a number of bond-breaking small-molecule reactions.<sup>2</sup> For studies of more complex systems and, in particular, crystals, plasma X-ray sources have been developed in which a short pulse train from a Ti:sapphire laser both serves as a pump source and, through a delay line, generates X-ray probe pulses from a plasma induced on a moving (to avoid radiation-damaged regions) copper tape. Such laboratory-based sources cannot compete in intensity with synchrotron-type sources but do allow femtosecond TR resolution.<sup>35</sup> Elsaesser and Woerner report a pioneering study on a powder of (small unit cell) orthorhombic ammonium sulfate, in which observed charge density changes up to  $\sim 0.8 \text{ e } \text{Å}^{-3}$  indicate migration of one of the hydrogen atoms of an ammonium ion to a position halfway between two oxygen atoms of adjacent  $\text{SO}_4$  groups, the bond breaking and migration occurring within the first 100 fs after excitation.<sup>35</sup> More intense femtosecond sources are needed for more general application of this field.

**What Is Next?** It is clear from the above that the goal of following the progress of chemical reactions at the atomic structure level in fast dynamical processes such as isomerizations, dimerizations, and bimolecular reactions has not yet been reached. Such processes do take place in crystals (see, for example, references given in ref 22). It is again imperative that very small crystals be used if only to ensure coherence of the light-triggered reaction. The prospect for such experiments is increasingly bright with the advent of X-ray free electron laser (XFEL) facilities like the Linear Coherent Light Source (LCLS) at SLAC. However, the experiments require a drastically new methodology. A method in which a stream of nanocrystals, carried in a continuous liquid water jet, is exposed to the femtosecond light flashes and a very large number of single orientation diffraction patterns are collected and interpreted has been developed.<sup>36</sup> The method is still in its infancy but offers great promise for achieving the goal of time-resolved tracking of dynamic processes in Chemistry.

**The goal of following the progress of chemical reactions at the atomic structure level in fast dynamical processes such as isomerizations, dimerizations, and bimolecular reactions has not yet been reached. However, the prospect for such experiments is increasingly bright with the advent of X-ray free electron laser (XFEL) facilities like the Linear Coherent Light Source (LCLS) at the Stanford Linear Accelerator Center.**

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: coppens@buffalo.edu.

## BIOGRAPHY

**Philip Coppens** received his Ph.D. from the University of Amsterdam in 1960 and is currently SUNY Distinguished Professor of Chemistry and Henry M. Woodburn Chair at the University at Buffalo. After extensive work on electron density mapping by accurate X-ray diffraction, he returned to his earlier interest in photoinduced chemical changes in molecular crystals, now including photochemical reactions in supramolecular solids and time-resolved studies of fleeting species by pulsed laser pump/X-ray probe experiments. For more information, see harker.chem.buffalo.edu.

## ACKNOWLEDGMENT

I am grateful to my many co-workers over the last 15 years, without whose work this Perspective could not have been written, as is evident from the bibliography. This work was supported by the National Science Foundation through Grant CHE0843922. Additional support is listed in the cited publications.

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