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What can time-resolved diffraction tell us about transient species?: excited-state structure determination at atomic resolution

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The author describes his work for which he coined the word 'photocrystallography', a technique which consists of using a laser to pump, or excite, a molecular crystal while the X-ray diffractometer probes its structure at the atomic level. The technique is being used to study highly reactive excited molecules that exist for just millionths or even billionths of a second using very intense light sources at the National Synchrotron Light Source at Brookhaven National Laboratory and the Advanced Photon Source at Argonne National Laboratory.

Introduction

In a mature science the assumptions on which the field is based are often so generally accepted that they are no longer challenged. This is especially true for X-ray structure analysis, the success of which has revolutionized disciplines from solid state physics to molecular biology. Among the basic assumptions of the method are 1) that each element has a well-defined specific scattering power and 2) that the experiments lead to the time-averaged image of the ground state structure of the system. That the former assumption is only approximate becomes evident when accurate data sets are collected as done in *X-ray charge density analysis*,[1] which shows that the electron distribution and thus the scattering power is a function of the chemical bonding of each atom. This assumption is also no longer valid when a wavelength close to the absorption edge of one of the constituent elements is used. Because of resonance effects the scattering at a specific wavelength becomes dependent on the valence state of the resonating atom, which is exploited in *valence-specific diffraction*.[2]

'Photocrystallography'

The breakdown of the second assumption is the focus of this article. It can be achieved by exposing a crystal by an external perturbation followed by a rapid measurement on a time-scale that may be as short as picoseconds, or by freeze-trapping the transient species generated by the perturbation. After we decided in the early nineties to concentrate on developing such methods, our attention was drawn to a series of transition metal nitrosyl complexes which at that time were believed to have light-generated excited states with very long lifetimes at liquid nitrogen temperature and below. To study such states it is necessary to expose the crystals *in situ* on the diffractometer to an external light source, generally under

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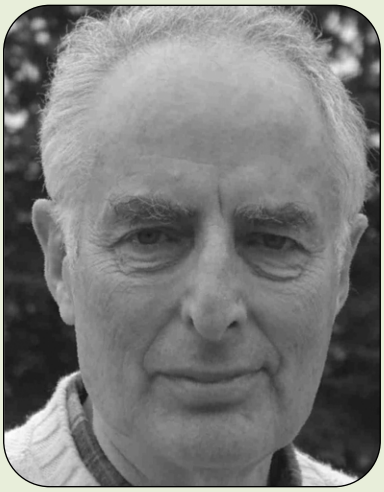

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cryogenic conditions, either before or during data collection. We coined the word *photocrystallography* to describe the field. After data collection an initial confirmation of the effect of the illumination is obtained by a *photodifference map*, which shows the change in electron density, and thus indirectly nuclear positions, upon exposure to light.[3] Application of these methods showed that the new nitrosyl species were at that time unknown metastable linkage isomers, formed after relaxation of a photo-induced excited state, but not excited states.[4] Other recent studies of low-temperature stable species include those on side-bound transition-metal dinitrogen and sulfur dioxide complexes,[5] and an investigation of the geometry change upon formation of a light-induced radical pair of a hexaarylbiimidazolyl derivative.[6] However, while these photocrystallographic studies reveal novel species and binding modes, they do not deal with short-lived transient states that exist on sub-millisecond time scales.

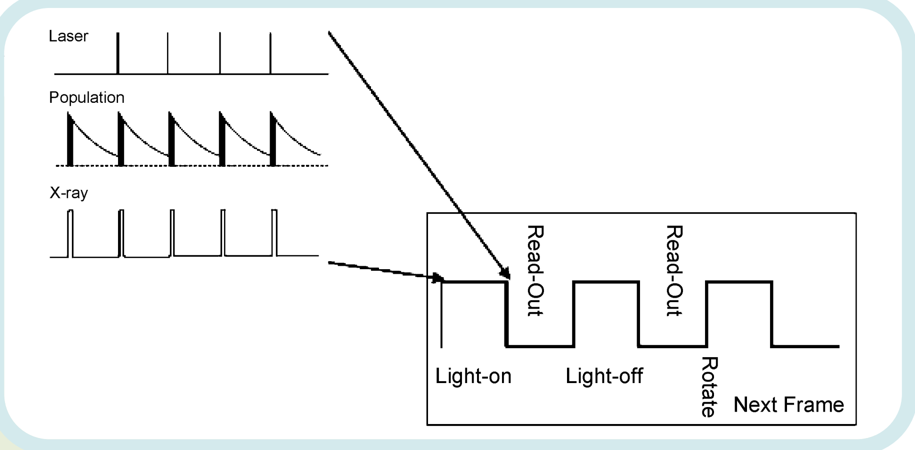

Fig. 1 Time-structure and data collection strategy of the stroboscopic diffraction experiment. Top left: the relative timing of the laser and X-ray pulses and a schematic of the light-induced population; bottom right: the alternation of the light-on and light-off measurement periods of typically 1–5 seconds duration. Each period is followed by the time required for detector read-out.

Stroboscopic diffraction

The appropriate approach for non-equilibrium structure determination is the use of pump-probe techniques in which a perturbing pump pulse is followed by a probing, in this case X-ray pulse. With a laser pump source the incident-photon to molecule ratio must be significantly larger than one to reach a measurable conversion percentage. To prevent evaporation or burning of the crystal exposed to such an intense pulse, experiments must be performed in a cold helium-gas stream. An important distinction is between reversible and irreversible processes. When a process is reversible, as is the case for many molecular excitations, the diffraction pattern can be accumulated in a stroboscopic experiment, illustrated schematically in Fig. 1.

On the other hand, for irreversible processes in crystals, such as fast moving chemical reactions, read-out limitations of current detectors dictate that only one measurement can be made at a selected delay time, there is no second change until the sample is changed and the experiment repeated. But, unlike spectroscopic methods for excited state structure determination, such as time-resolved EXAFS[7] and Franck-Condon analysis of vibrational fine structure,[8] the diffraction method has the potential of giving information on the full geometry of the excited state structure.

Results of stroboscopic experiments on molecules of chemical interest are now becoming available. A prime example is the geometry change upon reversible intramolecular charge transfer in the molecule of 4-(dimethylamino)benzonitrile (DMABN), which was studied by powder diffraction on a picosecond timescale by Techert, Schotte and Wulf at the ID09 beamline at the European Synchrotron Radiation Facilty.[9] They concluded that the light-excitation caused an increase in the torsional angle around the exocyclic C–N bond on charge transfer. We performed the first single-crystal diffraction experiment on an excited state at the X3 beamline at the National Synchrotron Light Source at Brookhaven National Laboratory. Spectroscopic studies have indicated that dinuclear platinum and rhodium ‘paddlewheel’ complexes show a pronounced shortening of the metal–metal bond upon excitation.[10] The diffraction results confirm this conclusion (Fig. 2),[11] which theoretical calculations attribute to a promotion of an electron from a *d*-orbital, which is antibonding in the metal-metal region, to a *p*-orbital which is slightly bonding. The project illustrates the crucial interplay between observation and calculation. While all our DFT calculation support the shortening upon excitation to the shortest triplet state, quantitatively the shortening varies greatly with the choice of functional and relativistic treatment in the DFT calculation.[12] The experiment can thus be used to calibrate theoretical methods, the most successful of which can in turn be exploited to calculate quantities no accessible experimentally, such as the excited state spin density, which turns out to be concentrated on the Pt atoms, explaining the excited complex’s ability to abstract hydrogen and halogen atoms from a wide range of substrates.[13,14] A second study by Ozawa *et al.*[15] on the excited state of $[Pt_2(pop)_4]^{4-}$ confirms the earlier results.

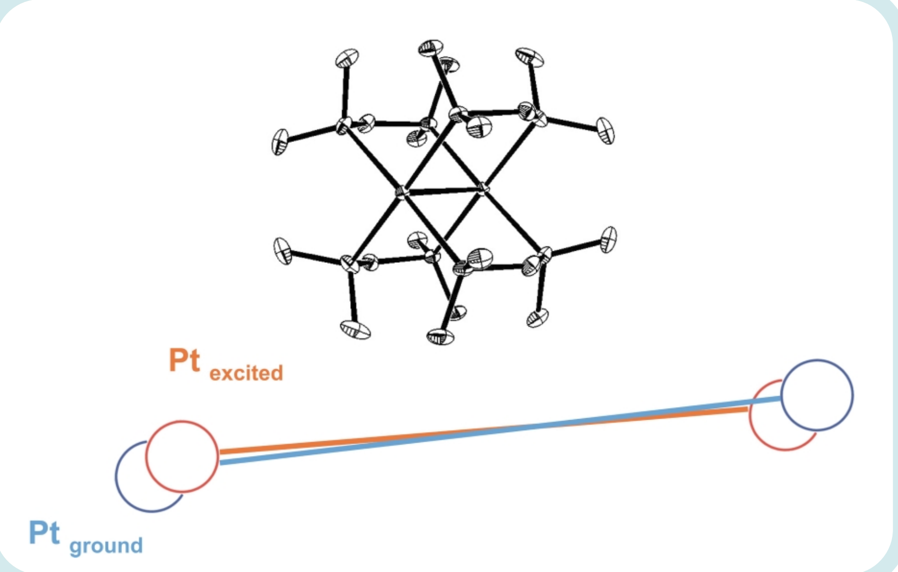

Fig. 2 Top: The $[Pt_2(pop)_4]^{4-}$ ion. Bottom: Schematic of the relative positions of the ground (blue) and excited state (red) Pt atoms according to the diffraction results. Note both the shortening and the rotation of the central bond.

Photoelectron transfer

Another intriguing application of excited state photocrystallography is the study of geometry changes on photoelectron transfer. Intramolecular metal-to-ligand charge transfer (MLCT) is often accompanied by large structural changes. Our theoretical calculations on the prototype ion $Cu(I)(dmp)_2^+$ (dmp = dimethylphenanthroline) predict a very significant opening of the dihedral angle between the two ligand planes upon excitation (Fig. 3).[16] As $Cu(I)(dmp)_2^+$ has a lifetime of a microsecond or less (depending on the counterion) even at helium temperatures, we have performed measurements on $Cu(I)(dmp)(diphos)^+$ (diphos=1,2-bis(diphenylphosphino)ethane), which has a 60 μsec lifetime at 17K. A redesigned optical system (Fig. 4)[17] installed at the 15-ID beamline of the third generation Advanced Photon Source at Argonne National Laboratory was used. The distortion of $Cu(I)(dmp)(diphos)^+$ upon excitation from a recent series of measurements is illustrated in Fig. 5.[18] The distortion is considerable, though significantly less than calculated for $Cu(I)(dmp)_2^+$. The difference is not a result of the experiment being performed on the molecules in the crystals, while the calculation is on the isolated molecule, as shown by theoretical calculations on $Cu(I)(dmp)(diphos)^+$, which similarly indicate a much smaller flattening in the latter complex.

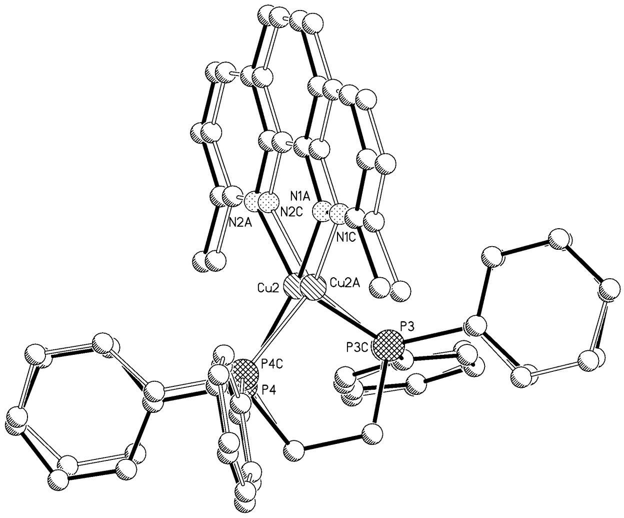

Fig. 5 Distortion of one of the $Cu(I)(dmp)(diphos)^+$ ions in $Cu(I)(dmp)(diphos)PF_6$ (dmp=dimethylphenanthroline, diphos=1,2-bis(diphenylphosphino)ethane) upon excitation to its lowest triplet state. Full lines: ground state; open lines: excited state. From ref. 18.

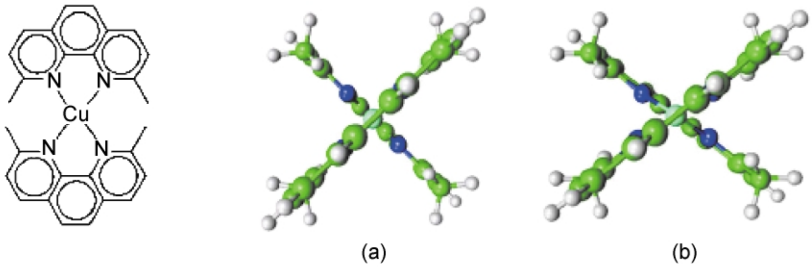

Fig. 3 Ground (a) and excited (b) state structure of Cu(I)bis(2,9-dimethyl 1,10-phenanthroline according to theory. From ref.16.

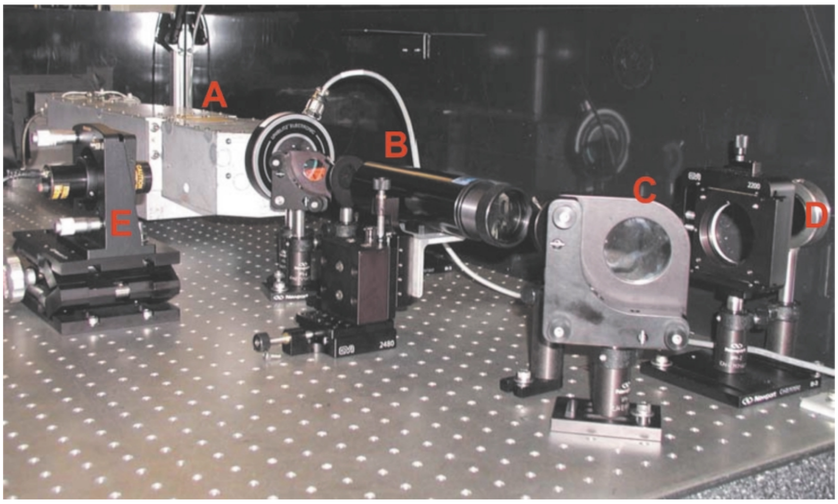

Fig. 4 The optical system at the 15-ID beamline at the Advanced Photon Source: A: high-frequency pulsed laser, B: diffuser, C: mirror directing the beam towards the diffractometer-mounted sample (outside the picture to the right), D: focusing lens, E: small laser used for alignment purposes.

Chen at Argonne National Laboratory has performed picosecond time-resolved spectroscopic and time-resolved EXAFS solution measurements on $Cu(I)(dmp)_2^+$, and finds a blue shift of the photo-generated absorption band on a picosecond time scale. Our DFT calculations confirm that the opening up of the dihedral angle correlates with an increase of the HOMO-LUMO gap of the lowest excited state, and thus support the explanation.[19] It is clearly necessary to combine different techniques including diffraction, spectroscopy and theoretical calculations to achieve a comprehensive insight in the nature of excited states of complex molecules.

Future outlook

What is to be done to further advance excited state diffraction so that it can become a broadly applied method? The use of highly intense X-ray sources is crucial to reduce not only the time the sample has to be exposed to the intense laser beam, but also to allow use of smaller samples, which contain fewer active centers so that a large laser-photon to active molecule ratio can be achieved.

Picosecond and sub-picosecond diffraction techniques must be further developed so the photoexcitation dynamics can be monitored at the atomic level. The ID09 beamline at the European Synchrotron radiation facility is particularly suited for sub-nanosecond studies.[20] In the future new sources such as the Sub-Picosecond Photon Source (SPPS) now under construction[21] will undoubtedly play an important role in such studies. Unlike the procedure in macromolecular time-resolved crystallography, in which the white beam Laue technique is used,[22] our experiments so far have been conducted with monochromatic radiation to maximize the accuracy of the results. But a golden compromise may be possible by use of a narrow band path 'pink' beam, which would still allow use of monochromatic crystal-rotation techniques, but speed up data collection and thus reduce the time the crystals have to be exposed to the high-intensity laser light. Such changes must be explored and are sure to lead to much broader application of photocrystallography of transient species in the coming years.

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