

# Time-resolved X-ray Analysis of the Excited State of the Cu(I)(dmp)(diphos)<sup>+</sup> Complex at Atomic Resolution

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## Introduction

For a full understanding of the nature of photoinduced species, a detailed knowledge of the molecular distortions that occur upon photoexcitation is required. Recent advances in the field of photocrystallography (a combination of crystallographic and spectroscopic methods) make it possible to obtain such information experimentally for a molecule in a solid-state environment and to produce results that can be compared with theoretical calculations for an isolated complex. In time-resolved photocrystallography at atomic resolution, a pump-probe technique is used, in which a crystalline sample, kept at helium temperatures, is exposed to 5- to 25-kHz pulsed laser light, synchronized with the monochromatic x-ray probe pulses [1-5].

Cu(I)phenanthrolines and their derivatives are being extensively investigated because of their potential for harvesting solar energy [6, 7]. They have broad absorption bands in the visible region, with high extinction coefficients. The highly luminescent excited states have powerful reducing properties and can inject electrons into conduction bands of semiconductors when the complexes are tethered to the appropriate surfaces, indicating their potential for solar energy capture.

## Methods and Materials

A schematic drawing of the time-resolved diffraction station at beamline 15-ID at the APS is shown in Fig. 1. It includes (a) a rapidly rotating chopper wheel acting as a periodic shutter, (b) a high-frequency pulsed laser, (c) electronics for synchronizing the x-ray probe and laser pump pulses (the x-ray timing being adjusted by an auxiliary diode detector), (d) a luminescence detector for *in situ* monitoring of the crystal excitation, (e) an optical sensor (photodetector) for timing purposes, and (f) a He gas flow system for crystal cooling and heat dissipation (not shown in Fig. 1).

In the pump-probe experiment, each laser pump pulse was followed immediately by an x-ray probe pulse. In the reported experiment, a brass chopper wheel with a 12.8-cm diameter and with 64 1.3-mm-wide slots, rotated at 5000 rpm, was used to produce  $\approx 40$ - $\mu$ s-long x-ray pulses at a frequency of 5400 Hz. The x-ray pulse length was selected to be shorter than the 85  $\mu$ s (16K) lifetime of

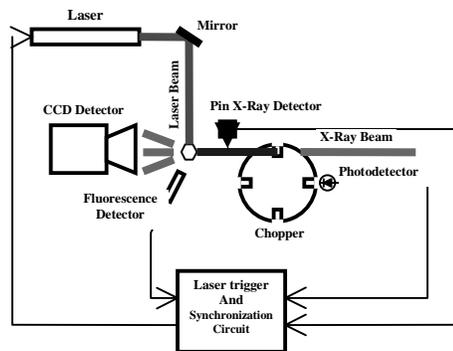


FIG. 1. Schematic diagram of the experimental arrangement for time-resolved diffraction studies at beamline 15-ID.

the first excited triplet state of Cu(I)(dmp)(diphos)PF<sub>6</sub> [where dmp = dimethylphenanthroline and diphos = 1,2-bis(diphenylphosphino)ethane], so that the diffraction pattern was recorded after each pulse, before most of the excited molecules returned to the ground state. The light from a Spectraphysics T80-YHP70-355Q tripled Nd:YAG pulsed laser ( $\lambda = 355$  nm) was focused on the sample by an optical system (to be described elsewhere). The laser produced 50-ns-long pulses at a time-averaged power of 1.4 W at 5 kHz. The number of photons per pulse ( $\sim 5 \times 10^{14}$ ) exceeded the number of molecules in the  $\sim 80$ - $\mu$ m single crystals used in the experiments. Monochromatic  $\lambda = 0.49594$  Å radiation was used for the data collection. Refinement was based on the response ratios  $\eta(hkl)$ , defined as follows:

$$\eta(hkl) = \frac{I_{on}(hkl) - I_{off}(hkl)}{I_{off}(hkl)} \quad (1)$$

$$= \frac{(F_{on}^2(hkl) - F_{off}^2(hkl))}{F_{off}^2(hkl)}$$

where  $F_{on}^2(hkl)$  and  $F_{off}^2(hkl)$  are the laser-on and laser-off squared structure factors, respectively.

## Results

The shift of the atoms in one of the molecules is illustrated in Fig. 2. The most pronounced shifts on excitation are observed for the Cu atoms, which move in the unit cell by  $0.27 \pm 0.01$  and  $0.25 \pm 0.01$  Å in the two independent molecules, respectively. The three atoms in each of the CuPP groups move in the same direction, as is evident also in the photodifference maps (not shown here), defined as  $\rho_{\text{light-on}} - \rho_{\text{light-off}}$ .

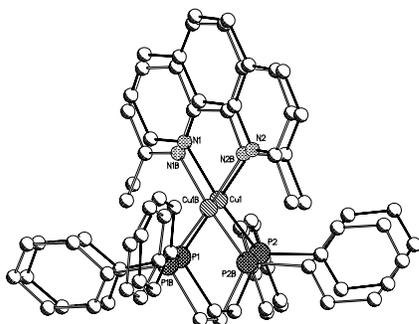


FIG. 2. Excited state of one of the two independent molecules (open lines) superimposed on the ground state of the complex (black lines).

As the molecules are constrained in the crystal matrix, the large distortions of the central atoms are necessary to accommodate the change in the molecular geometry within the crystal cavity. In order to describe the changes that occur upon excitation in the molecule-based coordinate system, the distortion angles  $\theta_x$ ,  $\theta_y$ , and  $\theta_z$ , which are  $90^\circ$  in the idealized  $D_{2d}$  symmetry of the Cu(I) diimine complexes, are defined as shown in Fig. 3. The values of both the ground state (GS) and excited state (ES) are compared with those from a parallel calculation for Cu(I)(dmp)(dmpe) [where dmpe = 1,2-bis(dimethylphosphino) ethane].

In both independent molecules in the crystal, the rocking distortion  $\theta_x$  decreases (by  $4.9^\circ$  and  $4.2^\circ$ , respectively) to values not significantly different from zero, in agreement with a decrease from  $2.7^\circ$  to  $0.6^\circ$  calculated for the isolated reference molecule. The wagging distortion similarly reduces to very small values in molecule 1 and in the isolated molecule from theory, but it reduces to a nonzero value of  $4.9 \pm 0.5^\circ$  in molecule 2. The flattening upon excitation (i.e., the deviation of  $\theta_z$  from  $90^\circ$ ), which is more than  $30^\circ$  in the isolated Cu(I)(dmp) $_2^+$  complex [8], is observed for molecule 1 at the modest value of  $3.2 \pm 0.5^\circ$ , compared with  $8^\circ$  for the isolated Cu(I)(dmp)(dmpe) $^+$  ion. It is

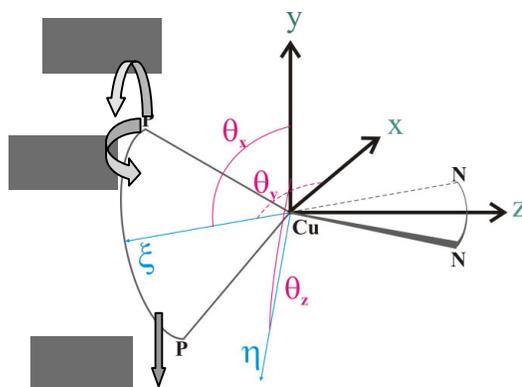


FIG. 3. Definition of the molecular distortion angles of the Cu(I) complex discussed in the text.

noteworthy that no flattening is observed for molecule 2, which in the GS already shows a flattening distortion of  $2.8 \pm 0.1^\circ$ , indicating a significant constraint of the molecular conformation even in the GS. This is in agreement with the much lower flattening upon excitation of both molecules in the crystal compared with the theoretical isolated molecule values.

## Discussion

The work described represents the first time-resolved excited state diffraction study in which both the heavy atom and ligand geometries have been determined. The results demonstrate the effect of the restraining crystal environment on the molecular changes that occur upon photoexcitation. As a result, the molecular reorganization energy upon excitation is much smaller than it would be in the liquid or gas phases, where environmental constraints are essentially eliminated.

## Acknowledgments

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