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Fleeting Excited States by Synchrotron and In-House Pump-Probe Diffraction

P. Coppens¹

¹University at Buffalo, SUNY, Buffalo, NY, USA

While the geometry of the initial state of chemical reactions is now being studied by electron diffraction methods [1] with further efforts underway at XFEL's, the properties of longer lived molecular excited states remain of crucial importance for the design of photoluminescent devices [2] and as precursors in photochemical reactions and electron transfer into semiconductor nanoparticles. Triplet lifetimes in crystals are temperature dependent, but typical in the ns-ms range. If high luminescence is of importance, the lower part of this range is preferable, for other applications longer lifetimes may be desirable. In the former case time-resolved (TR) synchrotron experimentation, preferable with Laue techniques, is the method of choice, whereas for lifetimes above about 10 μ s monochromatic in-house TR methods are increasingly feasible due to the continuing increase in the brightness of commercial X-ray sources and in the efficiency of detectors. The in-house method implemented in our laboratory uses a fast mechanical shutter synchronized with up to 100 kHz high repetition-rate lasers, corresponding to a pulse separation of 10 μ s, as discussed in detail in a presentation by Kaminski. A number of synchrotron [3] and in-house experiments on mono- bi- and tetra-nuclear organometallic complexes have been completed and are compared. New methods for inter-sample scaling of multi-sample data sets and for visualization of the geometrical changes increase the sensitivity of the TR methods and allow examination of geometry changes on excitation at conversion percentages of only a few %. Further details will be presented in separate presentations. Research funded by the National Science Foundation (CHE1213223). BioCARS Sector 14 at APS is supported by NIH (RR007707). The Advanced Photon Source is funded by the Office of Basic Energy Sciences, U.S. Department of Energy, (W-31-109-ENG-38).

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