

Time-resolved Photocrystallography of Short-lived Molecular Excited States

Philip Coppens, *Chemistry Department, State University of New York at Buffalo, Buffalo, NY 14260-3000, USA.* E-mail: coppens@buffalo.edu

Time-resolved photocrystallography is capable of providing atomic-resolution information on the nature of very short-lived transient species [1]. In its comprehensive application diffraction studies are combined with absorption and emission spectroscopy and parallel theory calculations. Several recent single-crystal results on triplet excited states, including large contractions up to 0.85 Å in a binuclear Rh-Rh complex and in a Cu(I) pyrazolate crystal, the latter leading to excimer formation through transient intermolecular Cu^{III}-Cu bonding, will be presented. Parallel theoretical calculations give insight into the electronic nature of the excitations. It is evident from the completed studies that the effect of the crystalline environment has a constraining influence when large shape changes are predicted, but is much less severe when intramolecular contractions occur. As may be expected, the crystal structure becomes the determining factor when intermolecular excitations are taking place.

The field is to be extended to include study of excited singlet states with nanosecond lifetimes and monitoring of irreversible chemical reactions in crystalline materials. Modifications in the techniques needed to accomplish such studies will be discussed.

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