

Atomic and electron density shifts on excitation to fleeting triplet states

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Recent studies have produced experimental triplet excited state structures with lifetimes of nanoseconds to microseconds.¹ The structural changes observed can be fairly well reproduced with theoretical calculations taking into account the molecular environment in the crystal, and may differ between chemically equivalent, but crystallographically independent molecules in the asymmetric unit.^{2,3} A second issue of importance is the electronic change on excitation. However, *photodifference* maps, showing the total change on excitation, are dominated by the atomic shift, which have a much larger effect than the change in orbital shape and occupancy on excitation. *Excitation* maps, showing this electron shift can be calculated theoretically by projecting the excited state orbitals on the ground state structure thereby achieving a formal deconvolution of the atomic and electronic shifts. Examples of metal-to-ligand transfer in Cu(I) coordination complexes (MLCT), ligand to metal transfer in a coinage metal complex (LMCT) and cluster to ligand charge transfer in a functionalized CdS nanoparticle (CLMT) will be shown.⁴ A direct measurement of the electronic shift only is currently not feasible as the effect on the X-ray intensities is too small compared with that of the atomic shifts. However, accurate ultrafast time-resolved experiments could possibly reveal electron shifts before atomic motion takes place.

(1) Jarzemska, K.; Kaminski, R.; Fournier, B.; Trzop, E.; Sokolow, J.; Henning, R.; Chen, Y.; Coppens, P. *Inorg. Chem.* **2014**, *53*, 10594.

(2) Makal, A.; Benedict, J.; Trzop, E.; Sokolow, J.; Fournier, B.; Chen, Y.; Kalinowski, J. A.; Graber, T.; Henning, R.; Coppens, P. *J. Phys. Chem. A* **2012**, *116*, 3359.

(3) Coppens, P.; Sokolow, J.; Trzop, E.; Makal, A.; Chen, Y. *J. Phys. Chem. Lett.* **2013**, 579.

(4) Zhang L.; Coppens, P. *To be submitted*.