The need for inter- and intra-data set scaling in time resolved photocrystallography

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Recent studies have produced experimental triplet excited-state structures of crystals with phosphorescence lifetimes from nanoseconds to hundreds of microseconds.[1] The measurements were performed using the pink-Laue technique, which allows a more efficient use of the synchrotron beam and therefore limits the necessary "pump-probe" cycles, and the Ratio method,[2] which is based on the ratio of the laser-on and laser-off intensities. The measurement strategy and the data processing have been summarized and discussed in a recent article.[3]

The relative scaling of multi-crystal data sets is crucial because of the eventual decomposition of the crystals in the laser beam, which prevents complete data collection, and the need to maximize completeness of the merged data set. Two different methods have been developed: the simpler AASR method which is based on the average absolute system response for each data set, and the more sophisticated WLS method based on a non-structural weighted least squares refinement of the ratios similar to methods applied previously to Weissenberg data.[4] In addition *intra-data-set* scaling is required to correct for the existence of molecular excitation anisotropy in the crystal, which can be pronounced.[5] Appropriate tools for visualization and analysis of the angular dependence of the observations are also presented. This dependence can affect the reliability of excited-state models.

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