Visualizing ultrafast coherent molecular structure in solution using free electron laser X-radiation

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A profound understanding of chemical processes in complex environments like liquid solutions requires significant experimental insight into the many degrees of freedom systems. The advent of free electron lasers, providing very intense X-ray pulse at the time scale of atomic motion, provides a new tool that allows to bring X-ray methods with atomic length scale sensitivity to the femtosecond time-scale. We have studied electronic and nuclear structural changes during the spin transition of Iron complexes in solution by measuring ultrafast changes in the X-ray near K-edge absorption spectrum using femtosecond pulses from the Linac Coherent Light source (LCLS, United States). The molecular complex was optically excited into a short lived electronic charge transfer state whose characteristic spectral changes could be temporally resolved. The consequent transition to a high spin configuration of the 3d electrons could be detected through changes related to motion of the nuclei caused by the new electronic configuration. This structural signal revealed an oscillatory relaxation indicating a coherent relaxation of the probed ensemble. Using reference measurements and XANES signal simulations, the results could be related to the so called breathing vibrational mode of the molecule, overlaid with the electronic signal from the initial charge transfer state.