

# Femtosecond X-ray absorption reveals excited state structural dynamics in cobalamins

*Monday 14 September 2020 16:45 (30 minutes)*

The fate of a photoactive molecule is determined by the electronic and structural rearrangements that follow excitation. Femtosecond (fs) X-ray free electron lasers (XFELs) have made it possible to use X-ray absorption spectroscopy to probe changes in electronic configuration and atomic structure as a function of time, beginning from the initial excited state. Both ‘movies’ of coherent or ballistic motion and ‘snapshots’ of local minima or kinetic intermediates are possible. Polarization anisotropy, long exploited in ultrafast optical measurements, permits decomposition of the X-ray transient difference signal into contributions along the direction parallel to the transition dipole initially pumped, and perpendicular to this transition dipole. This decomposition allows the analysis of asymmetric sequential structural changes of photoexcited molecules in isotropic solution.

We have used femtosecond X-ray absorption near edge structure (XANES) at the Co K-edge to characterize the excited state dynamics of cobalamins, B12 coenzymes and analogues. The initial subpicosecond dynamics are found to be ballistic rather than kinetic, with sequential structural changes in the plane of the corrin ring followed by expansion of the axial bonds perpendicular to the ring. A change in electronic configuration accompanies the axial bond elongation as the molecule evolves from the initial ‘bright’ state to a ‘dark’ state within a few hundred femtoseconds. Subsequent structural intermediates prior to bond dissociation or ground state recovery are also identified and characterized. The Finite Difference Method Near Edge Structure (FDMNES) program is used to calculate the XANES spectrum for both the ground and excited states. These simulations are used to extract more detailed static and dynamical information from the time- and polarization-resolved XANES difference spectra.

## Acknowledgments

This work was supported by the NSF through NSF-CHE 1464584 and NSF-CHE 1836435. Use of the Linac Coherent Light Source (LCLS), SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. In addition, many collaborators at Michigan (A. Deb, K.J. Kubarych, A. Kanishiro, J. Meadows, L. B. Michocki, N. A. Miller, J.E. Penner-Hahn, D. L. Sofferman) the University of Louisville (B. Garbato, M. Toda, P.M. Kozlowski) and at LCLS (R. Alonso-Mori, A. Britz, D. DePonte, J. M. Glowacki, J. Koralek, S. Song, T.B. van Driel, D. Zhu) contributed to the success of this work.

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**Session Classification:** Session 3 - Femto-chemistry & Catalysis