

An efficient first principles method for molecular pump-probe NEXAFS spectra: Application to thymine and azobenzene

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Pump-probe near edge X-ray absorption fine structure (PP-NEXAFS) spectra of molecules offer insight into valence-excited states, even if optically dark. In PP-NEXAFS spectroscopy, the molecule is “pumped” by UV or visible light enforcing a valence excitation, followed by an X-ray “probe” exciting core electrons into (now) partially empty valence orbitals. Calculations of PP-NEXAFS have so far been done by costly, correlated wavefunction methods which are not easily applicable to medium-sized or large molecules. Here we propose an efficient, *first principles* method based on density functional theory in combination with the transition potential and Δ SCF methodology (TP-DFT/ Δ SCF), to compute molecular ground state and PP-NEXAFS spectra. We apply the method to $n \rightarrow \pi^*$ pump / O-K-edge NEXAFS probe spectroscopy of thymine (for which both experimental and other theoretical data exist), and to $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ pump / N-K-edge NEXAFS probe spectroscopies of *trans*- and *cis*-azobenzene.

References

1. C. Ehlert, M. Gühr and P. Saalfrank, *J. Chem. Phys.* **149** (2018), 144112.