Simulating Time-Resolved X-ray Photoelectron Spectra of $Fe(CO)_5$ Along its Photodissociation with Multireference Algebraic Diagrammatic Construction Theory

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The photodissociation of $Fe(CO)_5$ at 266 nm remains a prototypical problem for benchmarking new computational methods in electronic structure theory.[1,2] Leveraging the efficiency of the open-source Prism package for Multireference Algebraic Diagrammatic Construction (MR-ADC) theory,[3,4,5] we simulated X-ray photoelectron spectra (XPS) of $Fe(CO)_5$ across its dissociation pathway. This allows the prediction of XPS spectra for various transition metal complexes. Using MR-ADC(2) and MR-ADC(2)-x, we calculated ionization energies and spectral intensities for Fe $3p^{-1}$ and CO $3\sigma^{-1}$ ionization at each step of the photodissociation process. To accurately capture these transitions, spin-orbit couplings were incorporated through SOC-MR-ADC(1). Both formulations accurately predicted binding energy shift directions, with slight underestimations of their magnitudes. MR-ADC results further support the involvement of a C_{2v} $Fe(CO)_4$ geometry arising from equatorial ligand dissociation within the pathway, confirming a complete singlet dissociation mechanism.

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[5] https://www.github.com/sokolov-group/prism