Estimating Vertical Transition Energies for X-ray Absorption and Non-resonant X-ray Emission with *Ab Initio* Composite Approaches

Abdulrahman Y. Zamani and **Hrant P. Hratchian**

Department of Chemistry and Biochemistry
Center for Chemical Computation and Theory
University of California, Merced, Merced, CA, USA

X-ray spectroscopy provides a great deal of information for analyzing chemical reactivity and characteristic properties of matter by probing the interactions of molecules with their local environment. The nature of core orbitals and elemental specificity of core-level transitions provide an advantage for resolving spectroscopic signatures with continually advancing experimental X-ray techniques. The research presented examines the applicability of practical *ab initio* composite methods for modeling X-ray absorption and non-resonant X-ray emission.[1,2] Vertical K-edge excitation and emission energies, with relativistic corrections, are obtained from core-electron binding energies calculated using spin-projected Hartree-Fock / Møller-Plesset perturbation theory[3] and outer-core ionization potentials / electron affinities calculated with electron propagator theory.[4] An assessment of the combined methodologies against experiment is performed for a set of small molecules containing second-row elements. Methods for obtaining transition intensities are applied for reconstructing non-resonant X-ray emission spectra.[5] Results from the models examined indicate that sub-electron-volt accuracy can be obtained for core-level energetics while maintaining a satisfactory balance between accuracy and computational cost.

[1] A.Y. Zamani and H.P. Hratchian, *J. Chem. Phys.* 159, 224109 (2023)
[2] C. Liegener and H. Ågren, *Theor. Chim. Acta* 89, 335–362 (1994)
[3] H. B. Schlegel, *J. Phys. Chem.* 92, 3075–3078 (1988)
[4] J. V. Ortiz, *Int. J. Quantum Chem.* 105, 803–808 (2005)
[5] R. Manne, *J. Chem. Phys.* 52, 5733–5739 (1970)