Theoretical study of Auger decay in benzene and its derivatives using Feshbach-Fano approach with equation-of-motion coupled-cluster wave functions.

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X-ray based spectroscopies are used to probe the electronic structure of atoms and molecules. X-ray absorption creates electron vacancies in the core shell, leaving the molecule in a highly excited state. Such molecules with core vacancies predominantly decay via Auger process when comprised of light atoms. Auger decay is an autoionization process in which a valence electron fills the core hole and liberates sufficient energy to eject another electron to the ionization continuum. The theoretical modeling of Auger decay is challenging owing to the metastable nature of core-ionized or core-excited states and the continuum nature of the ejected electron. One of the recent theoretical approaches for computing Auger decay rates is based on Feshbach-Fano resonance theory combined with the equation-of-motion coupled-cluster (EOM-CC) framework [1, 2]. In this study, we use this approach to compute the Auger spectrum of the benzene molecule. The theoretical modeling of the Auger spectrum of benzene is difficult owing to its high symmetry and multiple core orbitals. Our theoretical spectrum can reproduce the main features of the experimental spectrum and shows the configuration mixing of decay channels. Our calculations also provide insights into the contribution of individual core-orbitals and decay channels to the Auger spectrum. In addition, we calculated the Auger decay rates of benzonitrile and phenylisonitrile to understand how electron-withdrawing substituents, additional core orbitals, and decrease in symmetry influence the Auger spectrum. Our studies indicate a shift and decrease in the intensity of peaks in these molecules compared to benzene owing to the removal of electron density from the aromatic ring. In our analysis, we discuss how the core orbitals on the substituents impact the Auger spectrum.

References:

1. Skomorowski, W.; Krylov, A. I. Feshbach–Fano approach for calculation of Auger decay rates using equation-of-motion coupled-cluster wave functions. I. Theory and implementation. *J. Chem. Phys.* 2021, 154, 084124.
2. Skomorowski, W.; Krylov, A. I. Feshbach–Fano approach for calculation of Auger decay rates using equation-of-motion coupled-cluster wave functions. II. Numerical examples and benchmarks. *J. Chem. Phys.* 2021, 154, 084125