Theoretical Study on Decay Processes Following Core Excitation

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This study focused on spectroscopic techniques that incorporate decay processes following inner-shell excitation, which have evolved into methods for analyzing electronic and molecular structures. We improved the theoretical calculation methods for X-ray emission spectroscopy (XES) and Auger electron spectroscopy (AES). Inner-shell hole states have lifetimes of several femtoseconds, and nuclear dynamics during this brief period significantly influence the spectral shape, particularly in molecules containing light elements. Therefore, establishing highly accurate and efficient theoretical methods is essential for the precise interpretation of experimental spectra in general.

For XES theoretical calculations, we propose an improved method based on Slater transition state theory (STS) used to evaluate ionization potentials (IP) [1]. Instead of removing 1/2 electrons from each orbital, as is conventionally done, electrons are uniformly removed from the entire valence electron orbital. This method reduces the number of required SCF calculations from multiple (based on the number of valence electron orbitals) to one. When applied to water molecules, it reproduces experimental peak positions with higher accuracy than the Koopmans' theorem. Furthermore, incorporating the molecular dynamics (MD) of the inner-shell hole state brings the peak intensities closer to the experimental values.

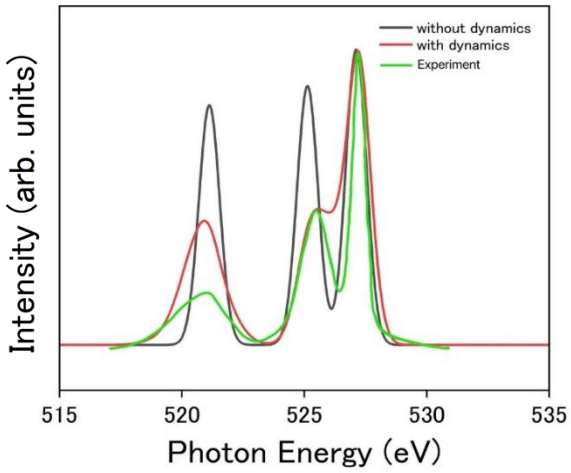

FIGURE 1. XES theoretical spectrum of one molecule of H_2O [2].

Next, for the AES theoretical calculations, we introduced the semiclassical Kramers-Heisenberg (SCKH) equation, which treats inner-shell excitation and Auger decay as a single scattering process, replacing the previously dominant two-step model. This allows the direct incorporation of correlations between the two processes, establishing a framework in which the energy-time evolution from MD is naturally reflected in the spectral width via Fourier transformation. Considering the computational cost and accuracy, the CI method was adopted for the electronic state calculations.

For single water molecule, 20 fs MD simulations of the inner-shell hole state were performed to investigate the required number of velocity and initial structure samples. The results showed that the spectrum converged with approximately 20 velocity samples, while maximizing the number of initial structure samples was crucial. The AES spectrum calculated under the final conditions of 20 velocity samples and 50 initial structure samples successfully reproduced the experimental peak positions. However, an overestimation of the peak intensity originating from the bound orbitals was observed, indicating that expanding the initial structure sampling remains a challenge for future studies.

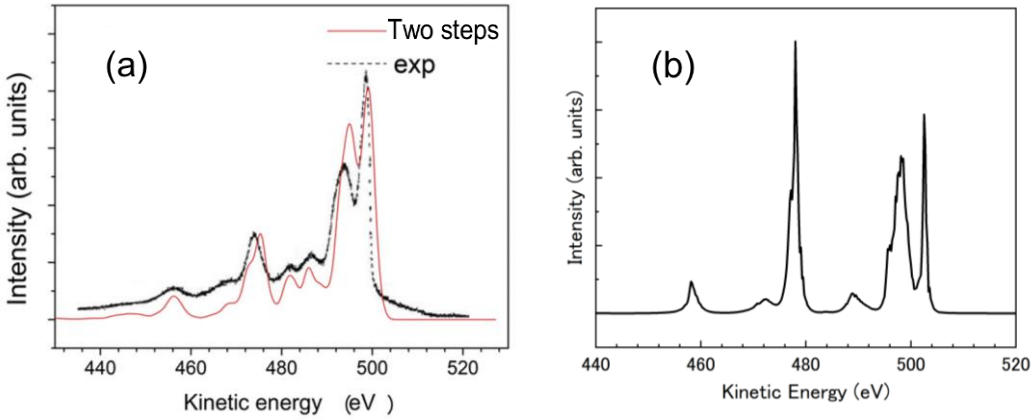

FIGURE 2. AES spectrum of single molecule of H_2O.
(a) Theoretical (two steps model) and experimental spectra[3],
(b) Theoretical spectrum with SCKH method.

In summary, this study established a method for XES that significantly reduces the computational cost while maintaining high accuracy. For the AES, the introduction of the SCKH formula enabled a physically reasonable spectral description. These results provide a new framework for the theoretical analysis of spectroscopic methods, including inner-shell collapse processes, that balances practicality and precision.

REFERENCES

1. Hirao et al. *J. Chem. Phys*., **155**, 034101 (2021).
2. Rubensson et al., *J. Chem. Phys*., **55**, 2317(1985)
3. Takahashi et al. *J. Phys. B: At. Mol. Opt. Phys*., **48**, 204001 (2015)