

Theoretical calculations of resonant inelastic soft X-ray scattering based on semi-classical approximation -Application to methanol-

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In our laboratory, various types of X-ray spectroscopy calculations are performing for several liquids. In this study, we performed soft X-ray emission spectroscopy (XES) calculations and resonant inelastic soft X-ray scattering (RIXS) calculations for liquid methanol, which is a typical example as a liquid with simple hydrogen bonds.

In these spectroscopic calculations, especially the system including the second-row elements, it is important to consider the dynamic effects of the intermediate state, i.e., the core hole state. The Kramers-Heisenberg equation unifies the formation of the core excited state due to the absorption of incident photons and the emission of X-rays accompanying the transition of valence electrons to the core hole. In this study, we performed the calculations using the semi-classical Kramers-Heisenberg approximation.[1] By applying the semi-classical approximation, it is possible to perform the XES calculations that take vibrational effects into account while keeping the calculation cost down.

$$\sigma(\omega, \omega') = \frac{\omega' \Gamma_f}{\omega \pi} \sum_f \langle F_{if}^+(\omega, \omega' - \omega) F_{fi}(\omega, \omega' - \omega) \rangle \quad (1)$$

$$F_{fi}(\omega, \omega' - \omega) = -i\alpha \sum_n \frac{\tilde{D}_{ni}(R)}{\omega - E_{ni}(R) + i\Gamma} \left(\int_0^\infty dt' \tilde{D}_{fn}^+(t') e^{i \int_0^{t'} d\tau E_{nf}(\tau)} e^{-i[\omega - E_{ni}(R)]t'} e^{-\Gamma_f t'} e^{i\omega' t'} \right) \quad (2)$$

Molecular dynamics (MD) simulations of a liquid methanol with condition were performed, and several dimer model structures were extracted. Based on this dimer model, theoretical calculations of XES and RIXS spectra were performed, and the obtained spectra were compared with the results of previous studies.

The RIXS spectrum showed a blunt peak change near the first resonance excitation compared to the previous study [2], which is considered to be due in part to the difference in the dimer model.

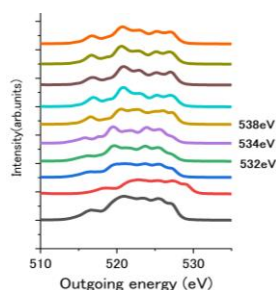


Figure 1. Calculated RIXS spectra of methanol dimers

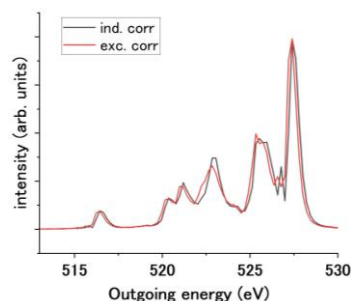


Figure 2. Calculated XES spectra of methanol dimers

REFERENCES

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2. M. P. Ljungberg, I. Zhovtobriukh, O. Takahashi and L. G. M. Pettersson, JCP, 2017.