Semiclassical Kramers-Heisenberg Calculations of Soft X-ray Emission Spectroscopy at the First Resonant Excitation

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In our laboratory, various X-ray spectroscopic calculations have been performed on liquid systems. In this study, we performed resonant inelastic soft X-ray scattering (RIXS) calculations for liquid methanol, which serves as a prototypical hydrogen-bonded liquid.

In soft X-ray spectroscopy, particularly for systems containing second-row elements, it is essential to consider the dynamic effects of intermediate core-hole states. The Kramers-Heisenberg approximation describes the RIXS process by unifying the absorption of an incident photon and the subsequent X-ray emission associated with valence-core transitions. To account for vibrational effects while keeping the computational costs low, we used the semiclassical Kramers-Heisenberg (SCKH) approximation [1].

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

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

To model the liquid methanol, we performed classical molecular dynamics simulations and extracted 20 representative molecular cluster models. We then calculated the electronic structures of these clusters and the RIXS spectra using the SCKH method.

The spectrum near the first resonant excitation obtained by theoretical calculations reproduced the peak structure in the experimental values from previous studies [2], confirming the validity of the calculation model.

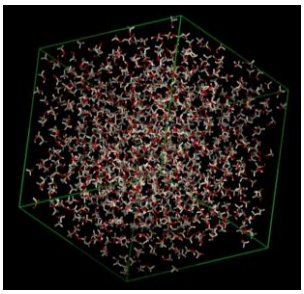

Figure. 1. Liquid methanol model based on MD simulation

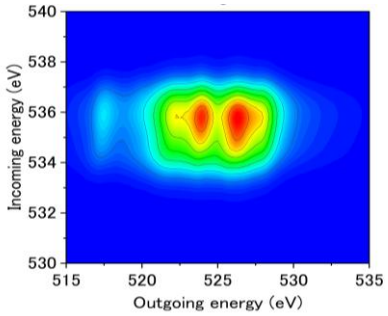

Figure2. RIXS map of the 20-mer in liquid methanol.

REFERENCES

1. M P. Ljungberg, Phys. Rev. B 96, 214302 (2017).
2. S Schreck *et al*, Struct. Dyn.1, 054901 (2014).