

The electronic structure of 18-crown-6/acetonitrile/metal salt observed by soft X-ray absorption spectroscopy

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Crown ethers are a class of cyclic polyethers known for their ability to selectively encapsulate metal ions based on their molecular size and structure. It is well established that 18-crown-6 preferentially binds potassium ions (K^+), as the ionic diameter of K^+ (0.26 nm) closely matches the cavity size of the ether (0.3 nm). However, this selectivity is primarily observed in aqueous solutions; in the gas phase, complexes formed with smaller metal ions exhibit higher stability. Jing et al. investigated the potential energies of complex formation between 18-crown-6 and alkali metal ions (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) in both aqueous and gas phases using molecular dynamics (MD) simulations and quantum chemical calculations [1]. They reported that while the binding free energy is lowest for K^+ in water—supporting size-match selectivity—the potential energy in a vacuum is lowest for Li^+ , indicating that smaller ions are trapped more strongly in the absence of solvent. This discrepancy arises because, in a vacuum, the ether ring distorts to wrap around the ion, maximizing stability for the smallest ion, Li^+ (0.14 nm). In contrast, in aqueous environments, the strong hydration energy of Li^+ prevents the formation of stable 18-crown-6 complexes. These findings demonstrate that the metal ion selectivity of crown ethers cannot be explained solely by the cavity size of 18-crown-6; it requires a comprehensive consideration of total energetic stability, including the solvent environment and the structural role of solvent molecules.

This study aims to elucidate the origin of ion selectivity from the perspective of electronic states. We experimentally investigated the molecular structures and electronic states of crown ether complexes in various solutions. Specifically, soft X-ray spectroscopy was performed on 18-crown-6 systems containing mixtures of different metal ions to observe how variations in ionic composition affect the electronic state of the host molecule. In addition, crystallized samples were also used to confirm the molecular structure.

Soft X-ray absorption spectroscopy (XAS) measurements were performed at SPring-8 BL17SU and UVSOR BL3U. At SPring-8, the generated crystals were placed under vacuum, and absorption spectra were measured using the fluorescence yield method. At UVSOR, measurements were conducted on the supernatant solution pumped into a liquid flow transmission cell.

Theoretical absorption spectra were calculated via Density Functional Theory (DFT) using the deMon2k code. To evaluate the dependence on the encapsulated ion, calculations were performed by substituting the metal ion type while maintaining an identical host geometry (FIGURE 1).

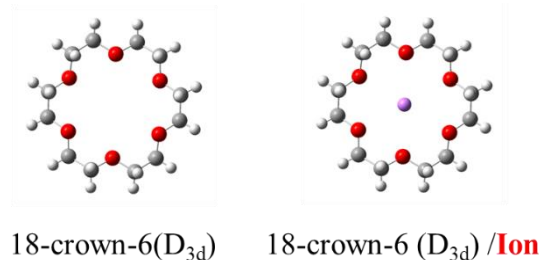


FIGURE 1. Structure of the 18-crown-6/metal ion complex used in the calculation.

The left panel of Figure 2 shows the soft X-ray absorption spectra at the oxygen K-edge for each crystal measured at SPring-8 BL17SU. In addition to the samples containing the four metal salts, a reference spectrum of an 18-crown-6/AN mixed crystal without metal salts is included. Resonance peaks were observed in all samples, exhibiting peak shifts dependent on the valence of the mixed metal ions. However, given the high deliquescence of the crystals and the limited soft X-ray penetration depth ($\sim 1 \mu\text{m}$), the possibility remains that the spectra reflect 18-crown-6 in a liquid phase on the crystal surface.

The right panel of Figure 2 presents the calculated absorption spectra. The onset position of the main peak shifts to higher energies in the order: metal-free < encapsulated monovalent ion < encapsulated divalent ion. This trend is in qualitative agreement with the experimental shifts, suggesting that the observed peak shifts likely originate from interactions between 18-crown-6 and the metal ions. However, regarding the peak observed near 532 eV in the experiment, only the structure with Mg ions reproduced this feature, while other structures did not. This implies that the ion-containing structures of the 18-crown-6 being measured is not uniform like the structure in Figure 1.

In this presentation, we will report DFT results exploring candidate structures for 18-crown-6/metal ion complexes that account for the 532 eV peak observed at SPring-8. Additionally, we will present results from UVSOR measurements of absorption spectra for 18-crown-6 interacting with ions in the liquid phase.

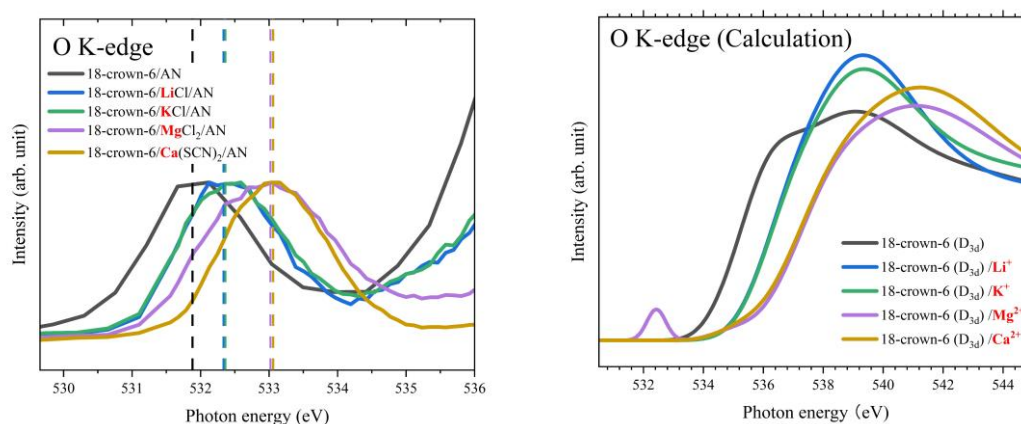


FIGURE 2. Oxygen K-edge soft X-ray absorption spectra of 18C6/AN mixture and 18C6/AN/metal salt mixture (left panel) and calculation results of oxygen K-edge soft X-ray absorption spectra (right panel).

REFERENCES

1. Z. F. Jing *et al.* *J. Mol. Liq.* **311**, 113305 (2020).