

UV and IR spectroscopic studies of metal ion-crown ether complexes in the gas phase and on gold surface

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Summary

In the gas phase

- UV and IR spectroscopy was performed in a cold, 22-pole ion trap.
- Host-guest complexes with good matching in size have multiple conformers with solvent, giving entropic advantages.

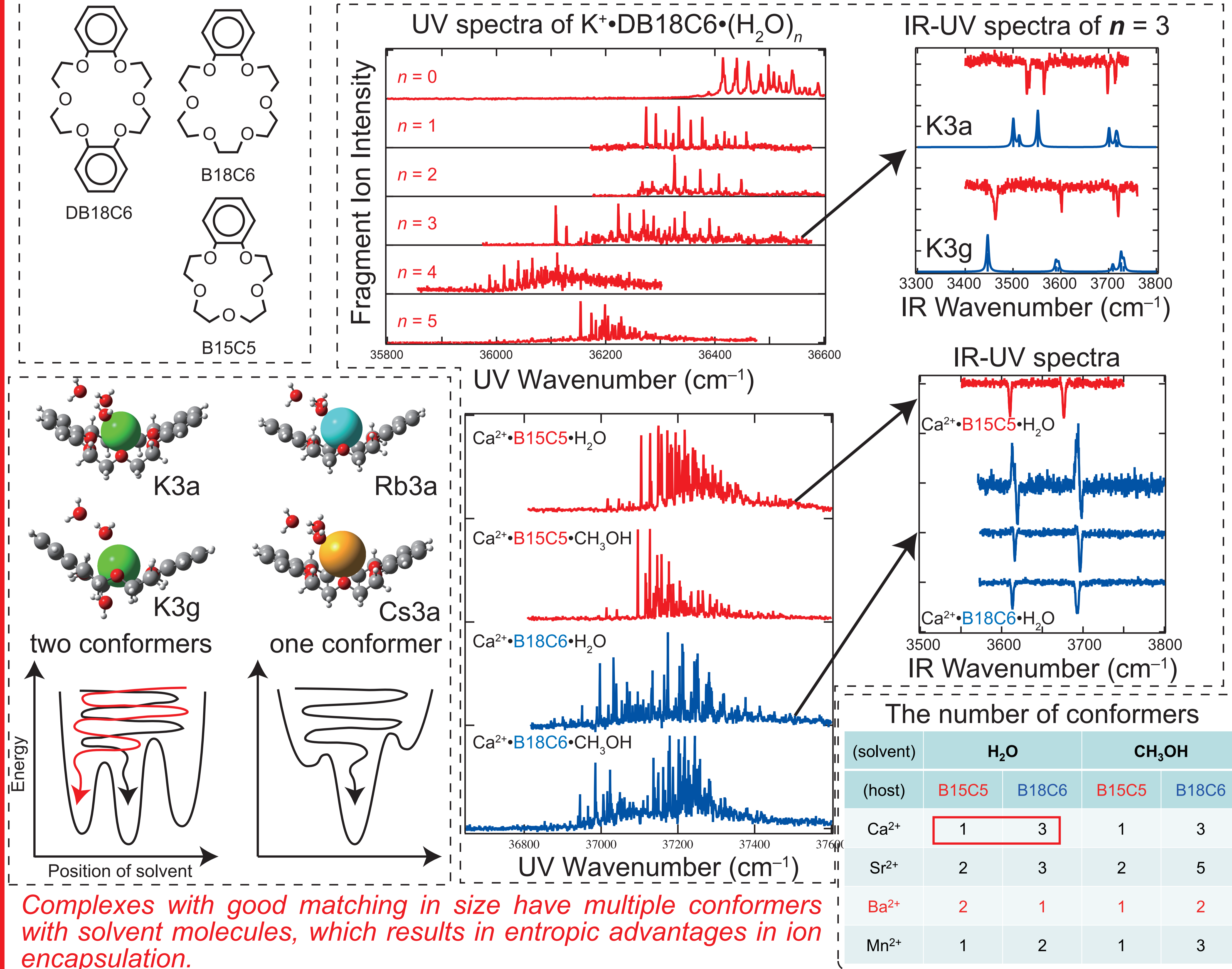
On gold surface

- SEIRA spectroscopy is used to detect ion complexes on gold surface.
- Concentration dependence of metal ions gives equilibrium constants and cooperativity of complex formation.

Introduction

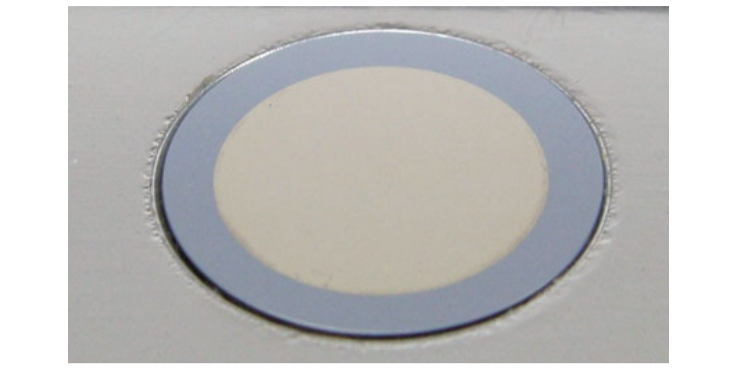
- Crown ethers show ion selectivity in solution.
- Mass spectrometric studies cannot explain ion selectivity, suggesting importance of solvent effect.
- We study “solvated” metal ion-crown ether complexes in the gas phase and on gold surface to discuss solvent effect on ion selectivity.

“Cold” spectroscopy in the gas phase

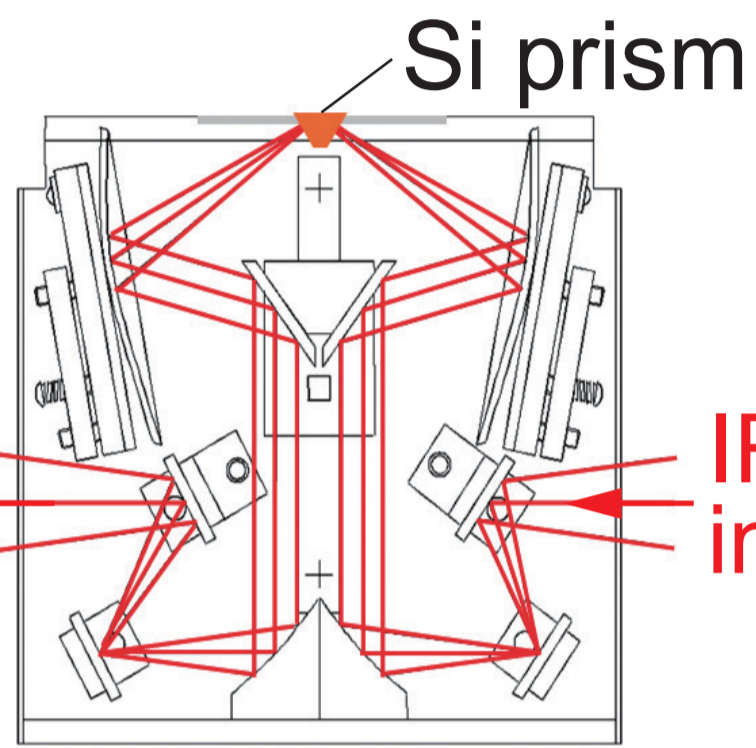


SEIRA spectroscopy on gold surface

SEIRA (Surface-enhanced IR absorption) spectroscopy with ATR configuration



Au surface on Si prism of ATR (~8 nm thickness)



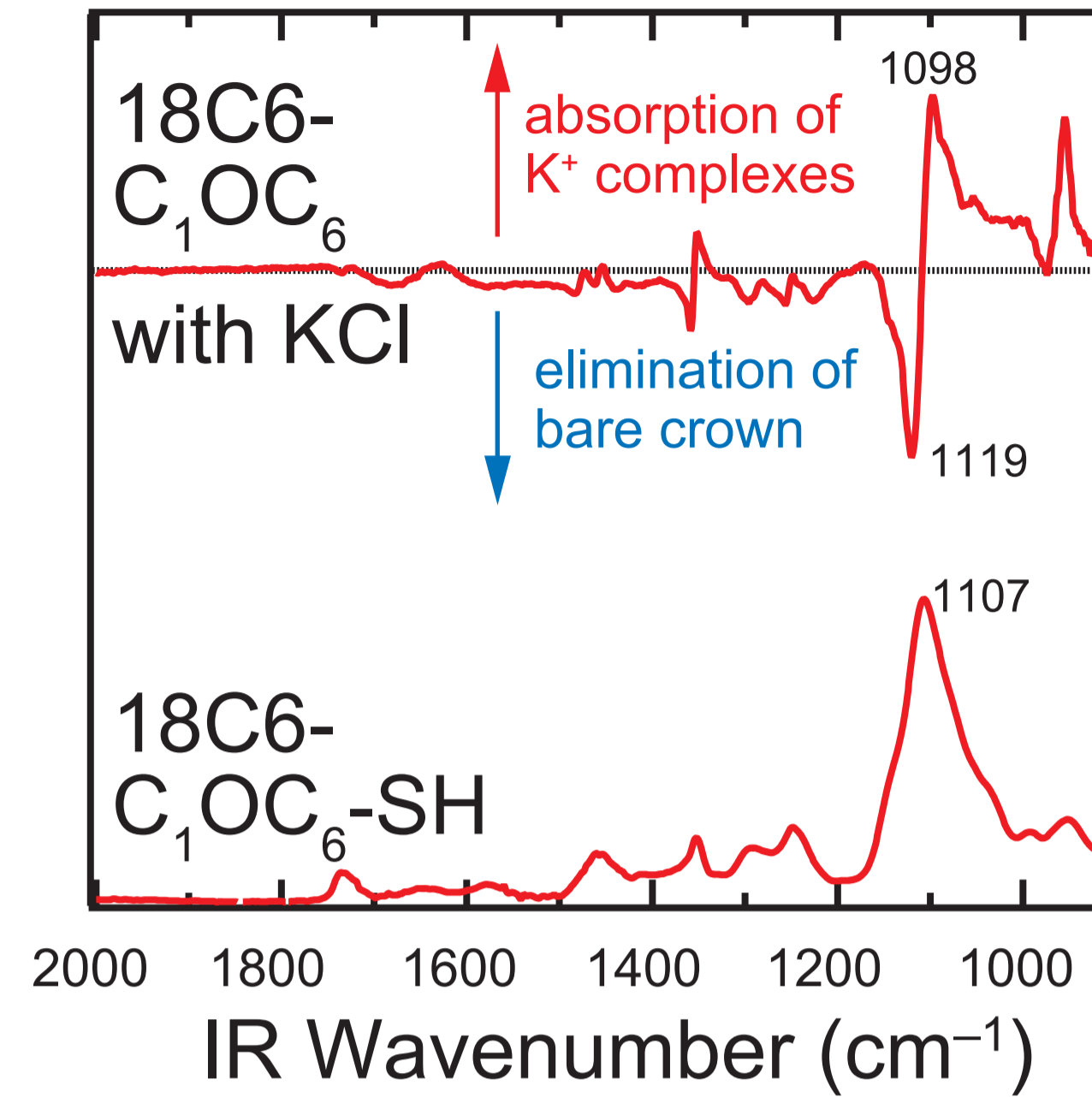
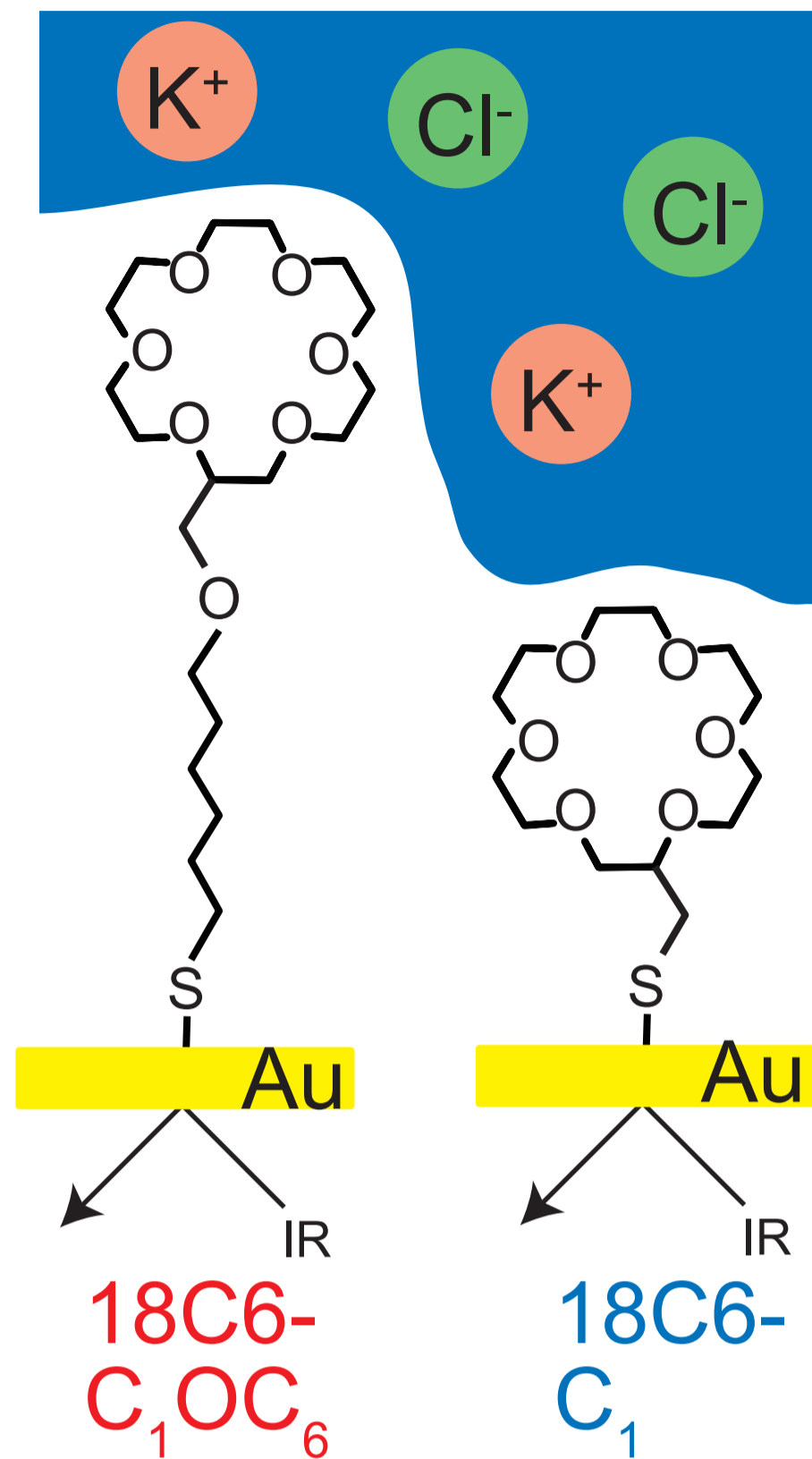
(1) Au surface (~8 nm) is formed on an ATR (attenuated total reflection) element by vacuum deposition.

(2) Thiol derivatives of crown ethers are chemisorbed on the Au surface with S-Au bonds.

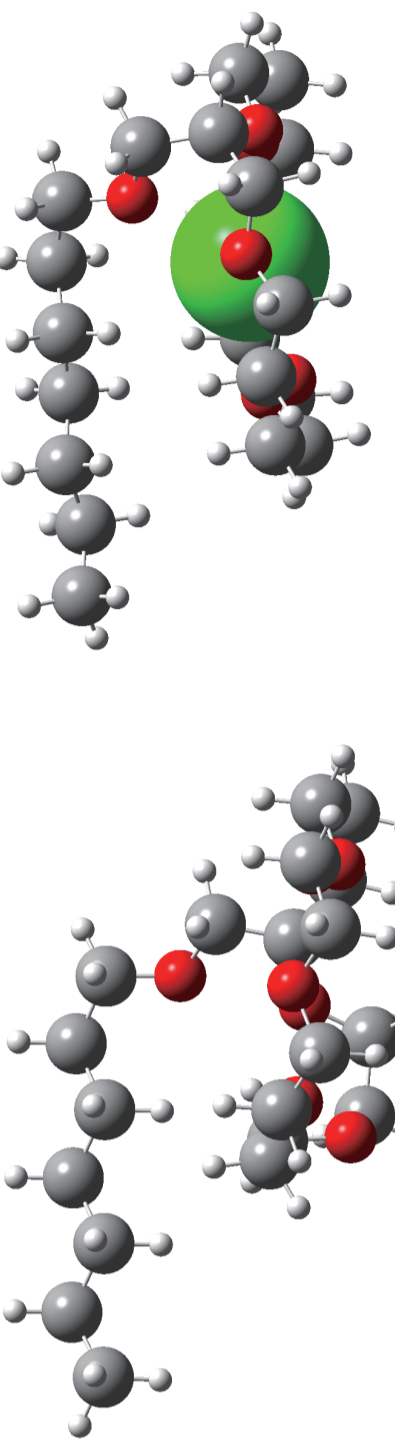
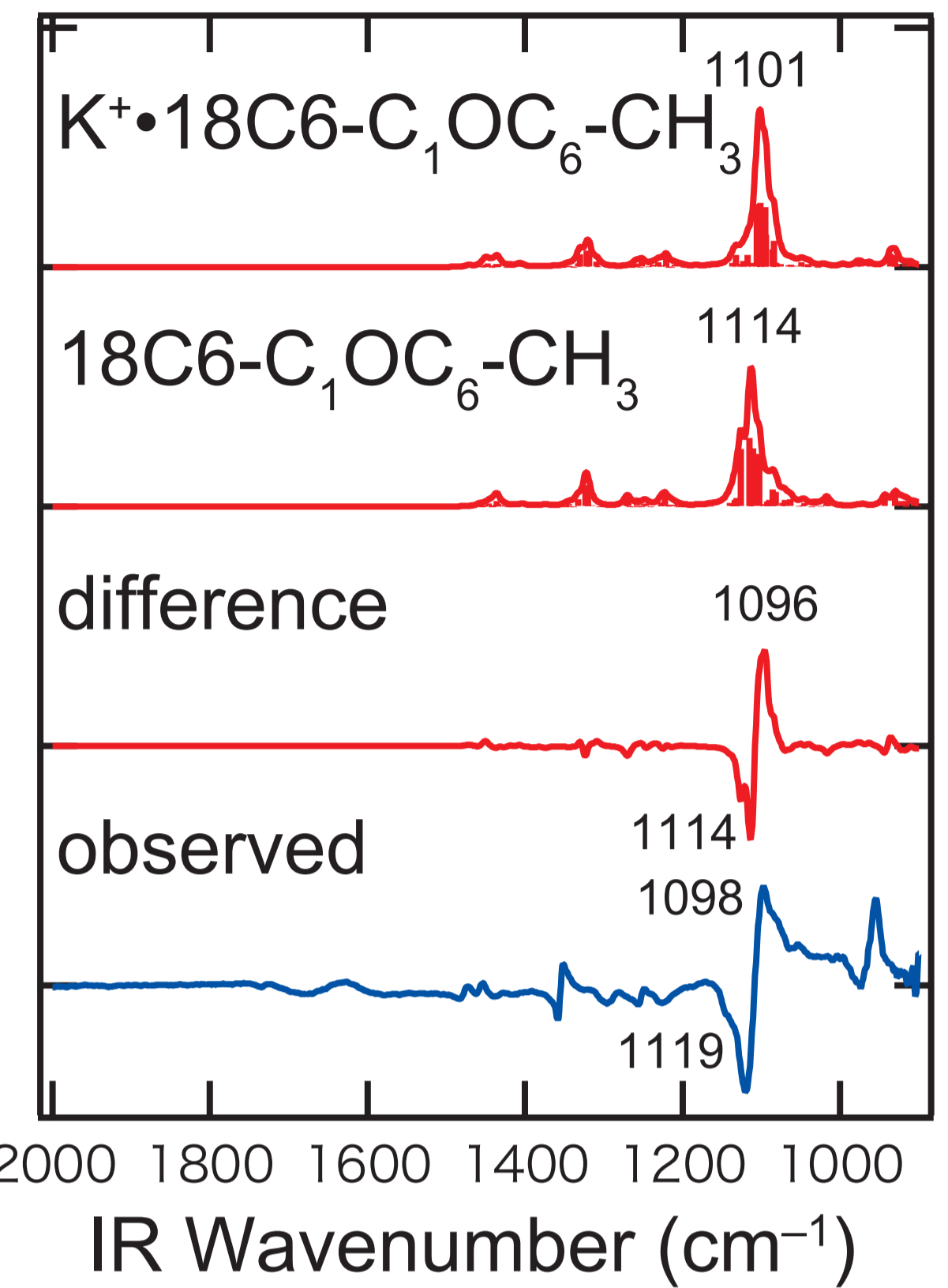
(3) Aqueous solutions of metal salts are put on it to form complexes.

(4) IR spectra are measured with and without the metal salts and we obtain IR difference spectra.

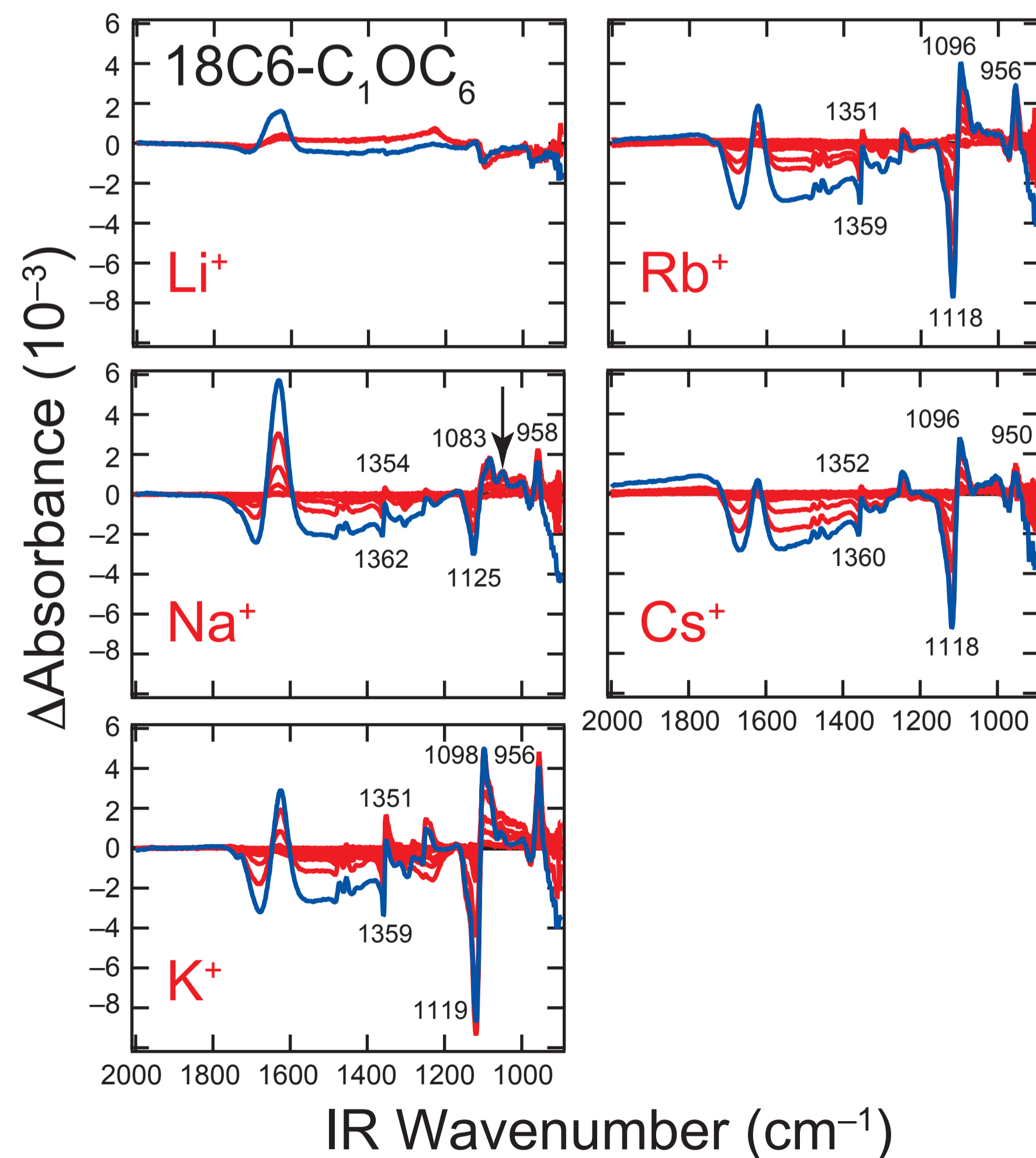
Experimental systems and IR results



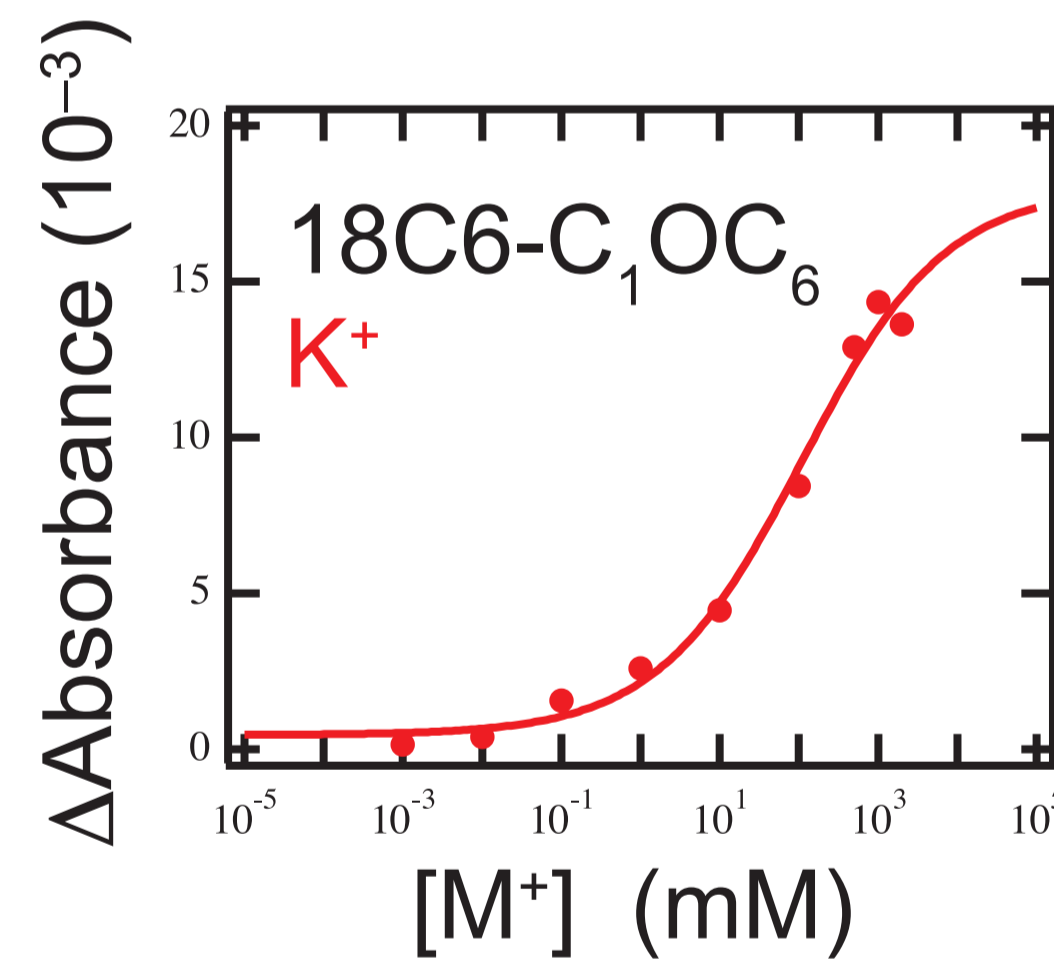
Simulation with DFT calculations



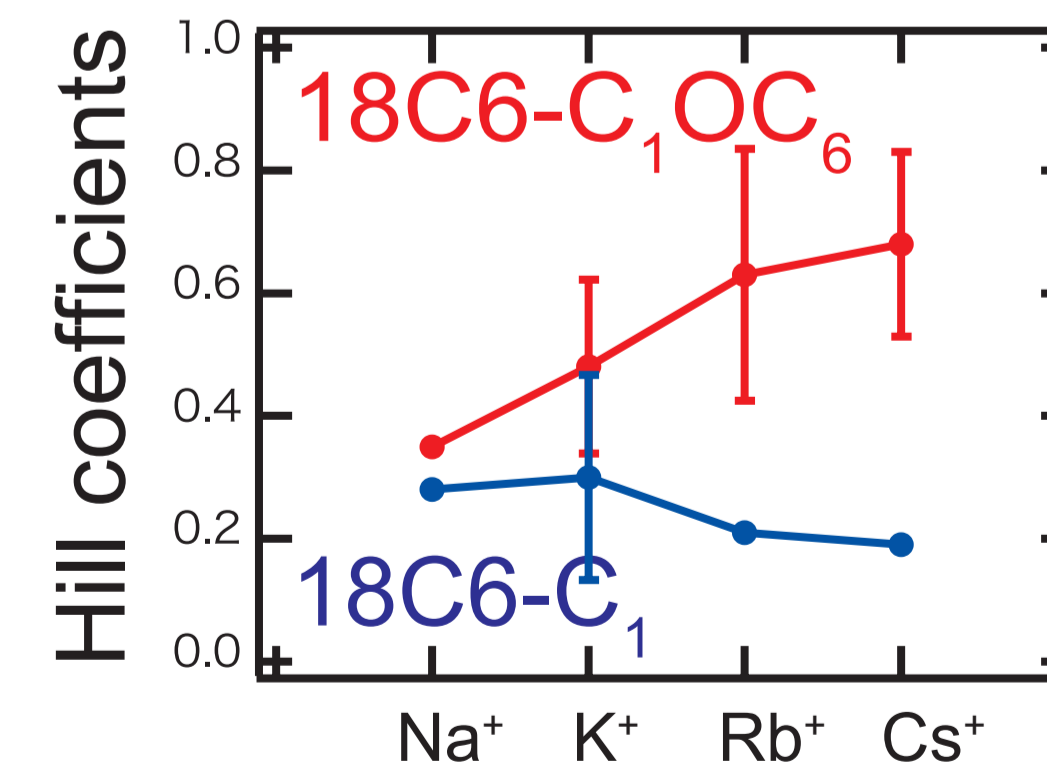
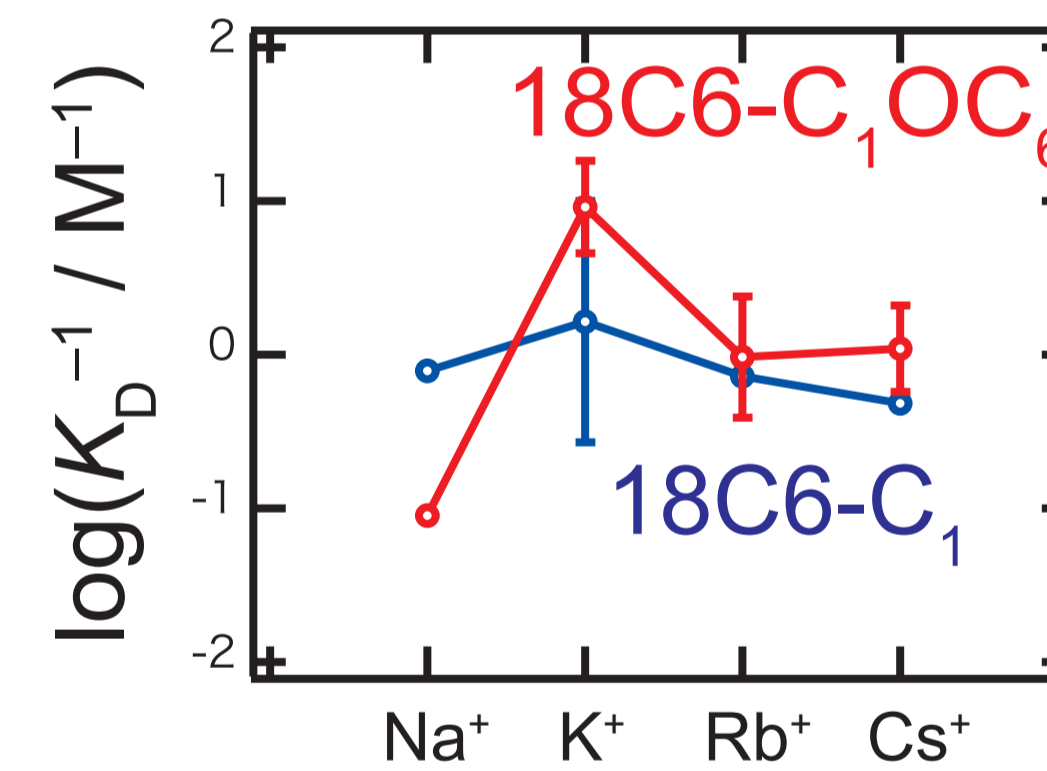
IR difference spectra



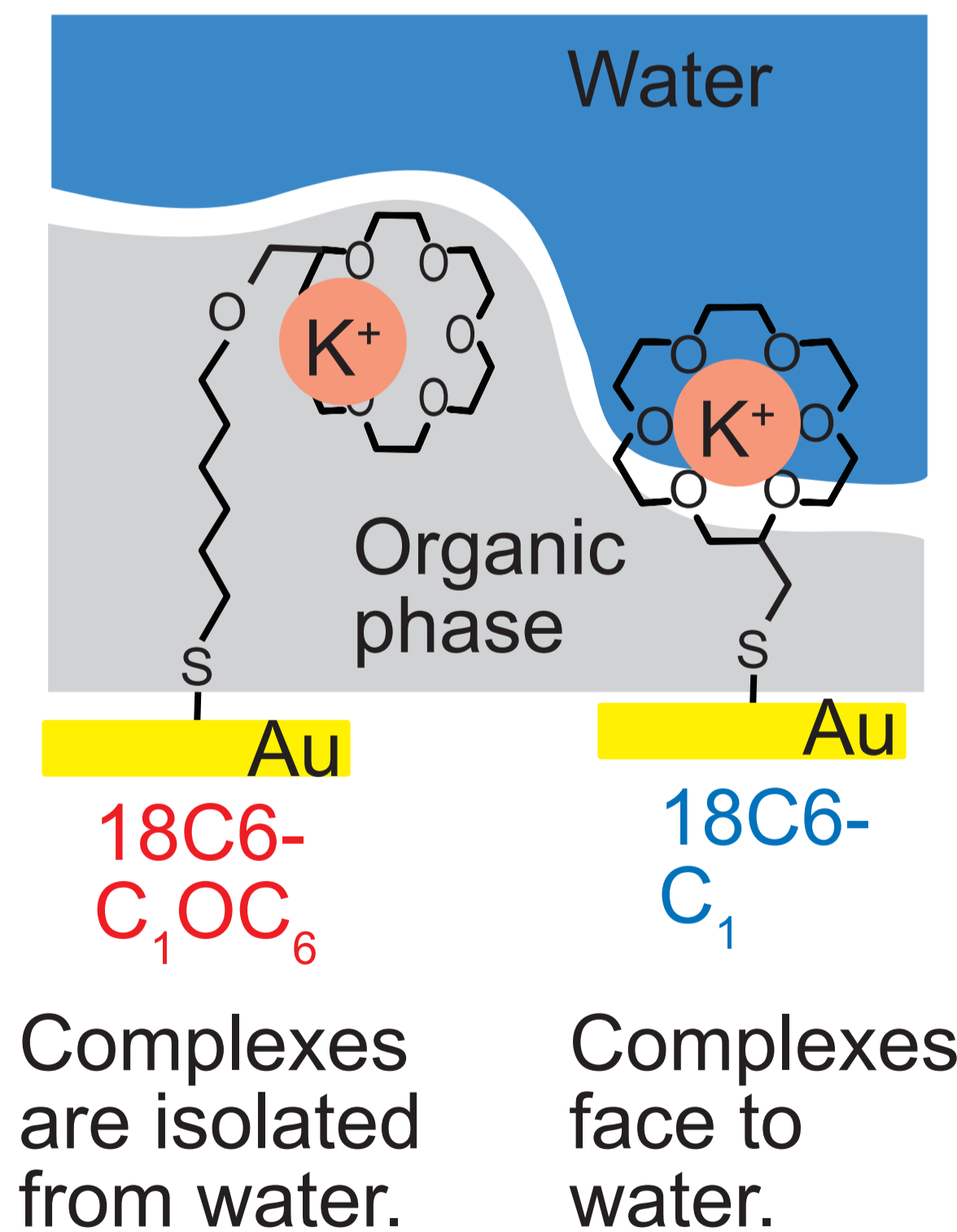
Ion concentration dependence



- Ion selectivity is not so obvious for C_1 .
- For C_1 , ion complexes on gold surface inhibit successive complex formation more than C_1OC_6 .



Proposed structure



- SEIRA spectroscopy is applicable to ion encapsulation processes of crown ethers on gold surface.
- Ion encapsulation depends on the chain length and its chemical properties.
- We have to examine dependence of the chain, solvent, crown density, etc.