金属イオン－カリックスアレーン錯体の極低温気相レーザー分光

（広大院理）

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Outline

1. Introduction
   Why ion guest-host complexes?
   Why cold gas-phase spectroscopy?

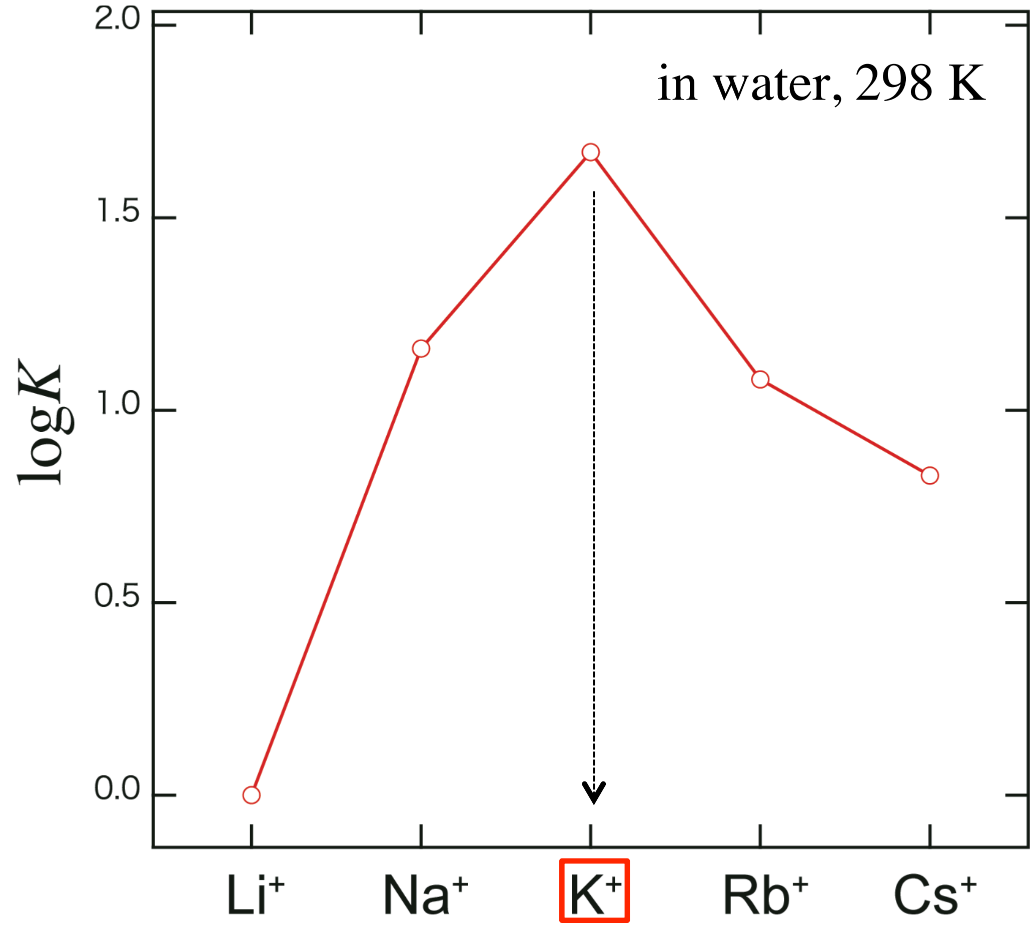
2. Construction of instrument
   Estimation of T_{ion} by UVPD spectroscopy

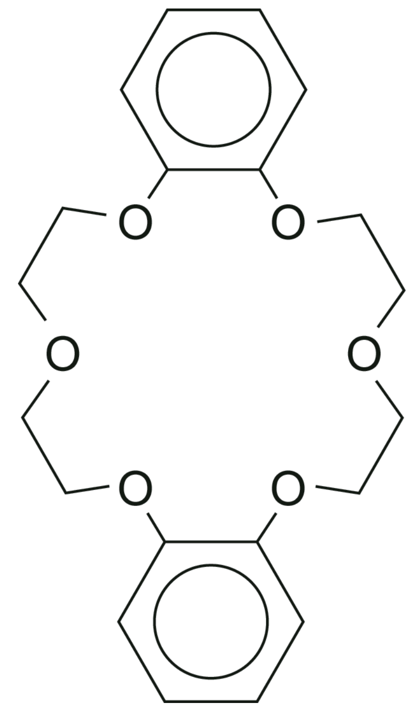
3. Application to ion complexes
   K^+•calix[4]arene complex
   Electronic and geometric structure

4. Future prospects

Guest selectivity of hosts

$$M^+ + \mathrm{DB18C6} \overset{K}{\rightleftharpoons} M^+ \bullet \mathrm{DB18C6}$$





DB18C6

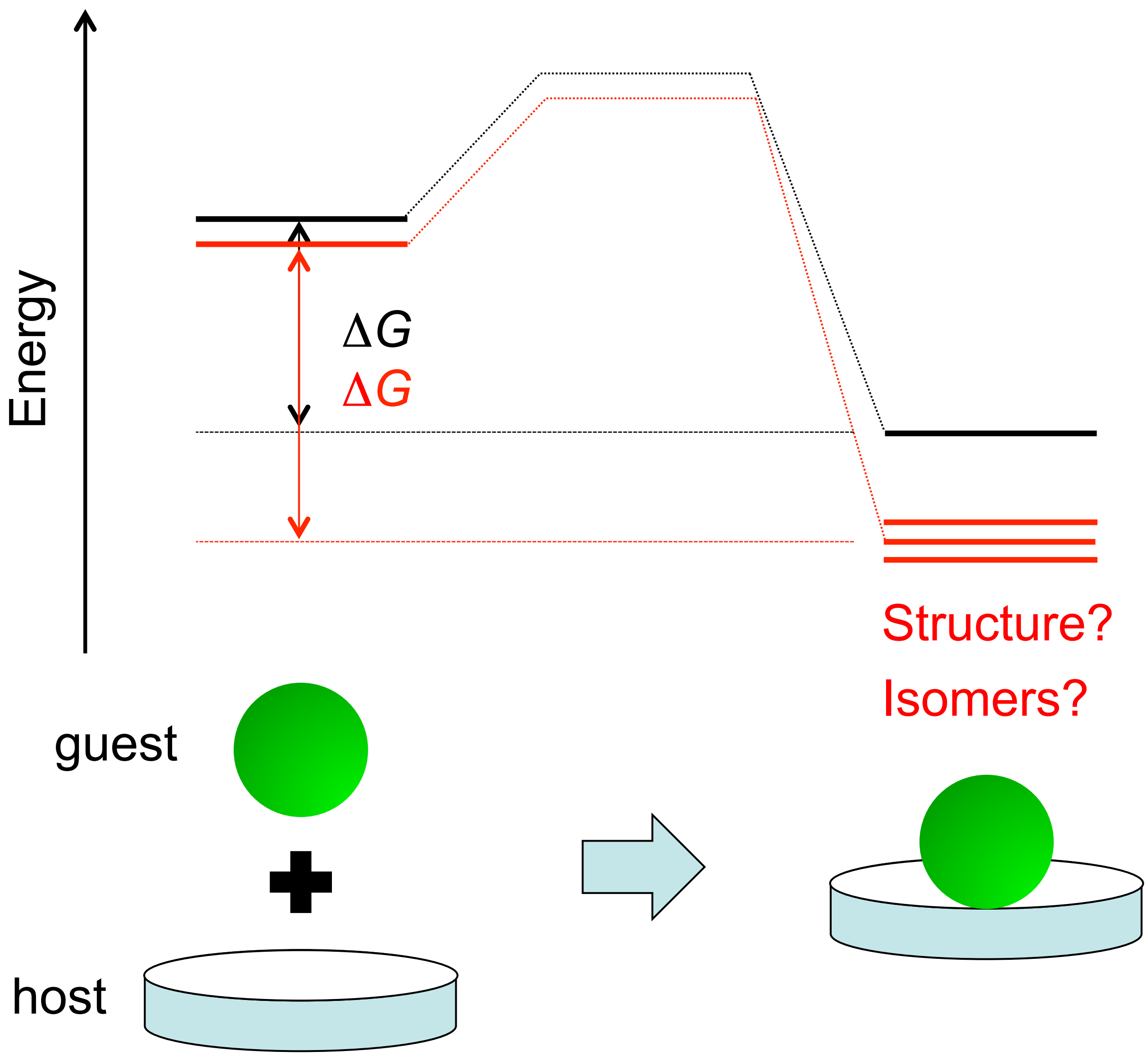
Izatt et al., Chem. Rev., 85, 271 (1985).

Relation between *K*, Δ*G*, Δ*H*, and Δ*S*

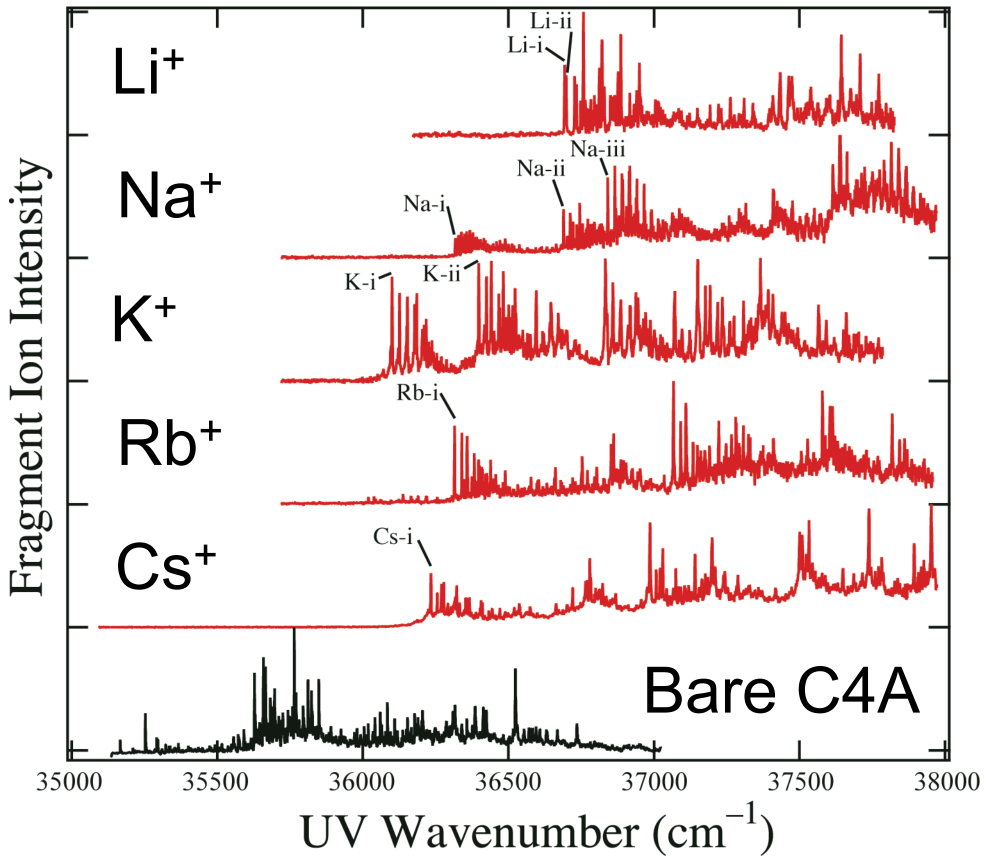
$$K = \exp\left(-\frac{\Delta G}{RT}\right)$$

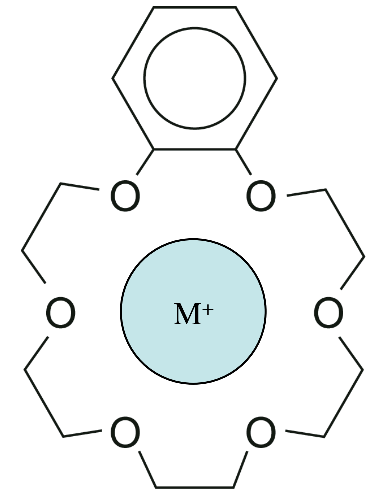
$$\Delta G = \Delta H - T\Delta S$$

Complex properties reflect selectivity?



Cold gas-phase spectroscopy is useful





M^+•benzo-18-crown-6
(M^+•B18C6)
T_{vib} = ~10 K

sharp vibronic bands ⟶ conformer-specific experiment

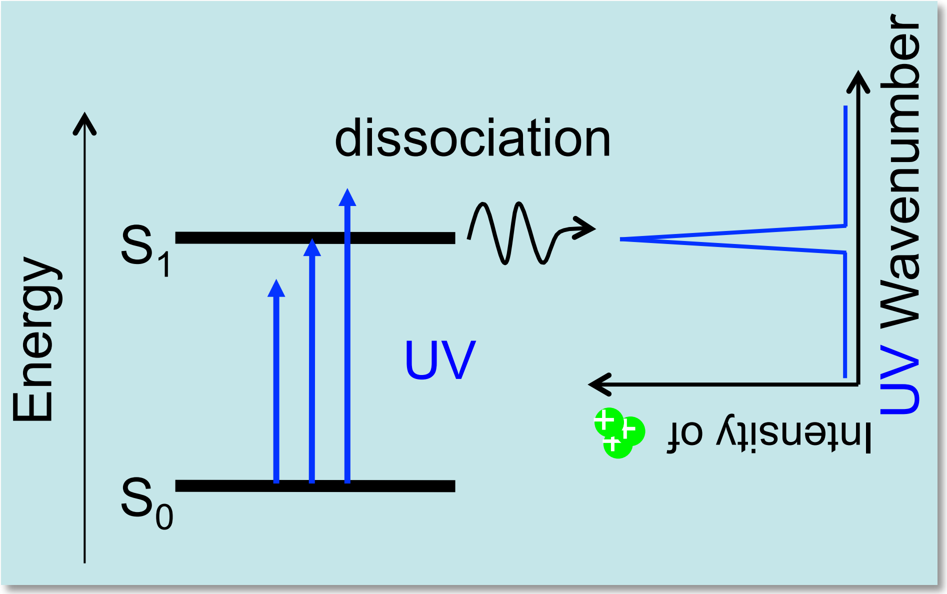
Inokuchi et al., J. Phys. Chem. A, 116, 4057 (2012).

This study

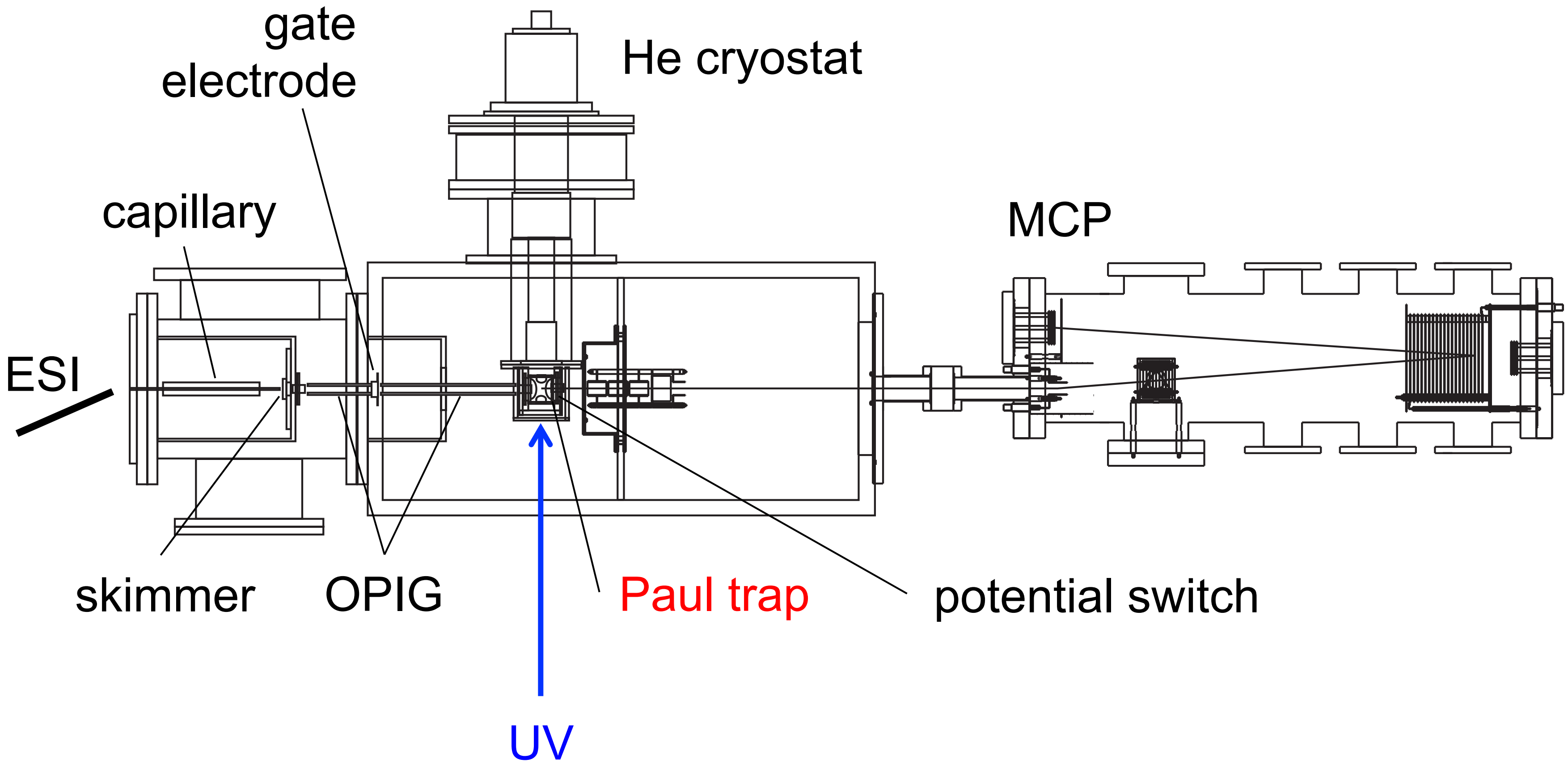
- Construction of instrument
  Estimation of T_{ion} by UVPD spectroscopy

- Application to ion complexes
  K^+•calix[4]arene complex
  Electronic and geometric structure

UV photodissociation spectroscopy



UV photodissociation spectroscopy

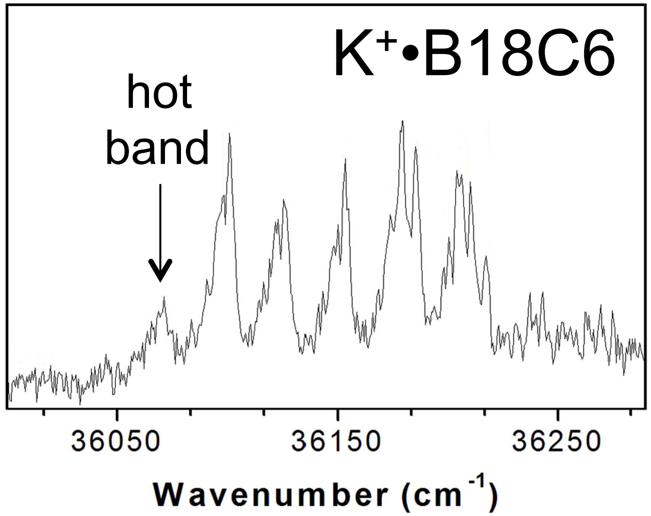


Laser spectroscopy with cold quadrupole Paul trap

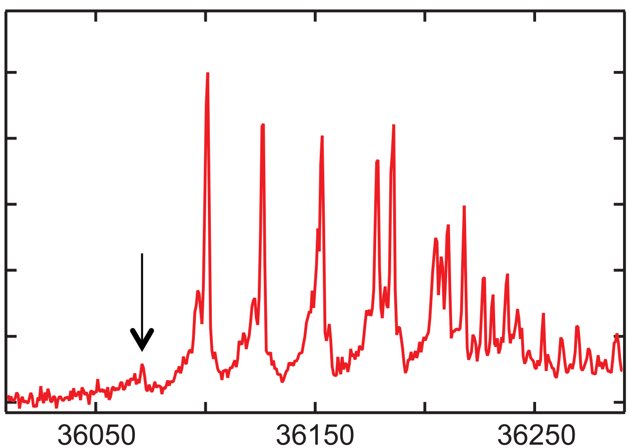
Jouvet, Zwier, Johnson, Kim, Grégoire, Ishiuchi (3P014)…

Ions in cold Paul trap are not so cold?

Collisional activation (heating) of ions in RF ion trap?



Paul trap (~10 K)[a]
T_{vib} = 50 K

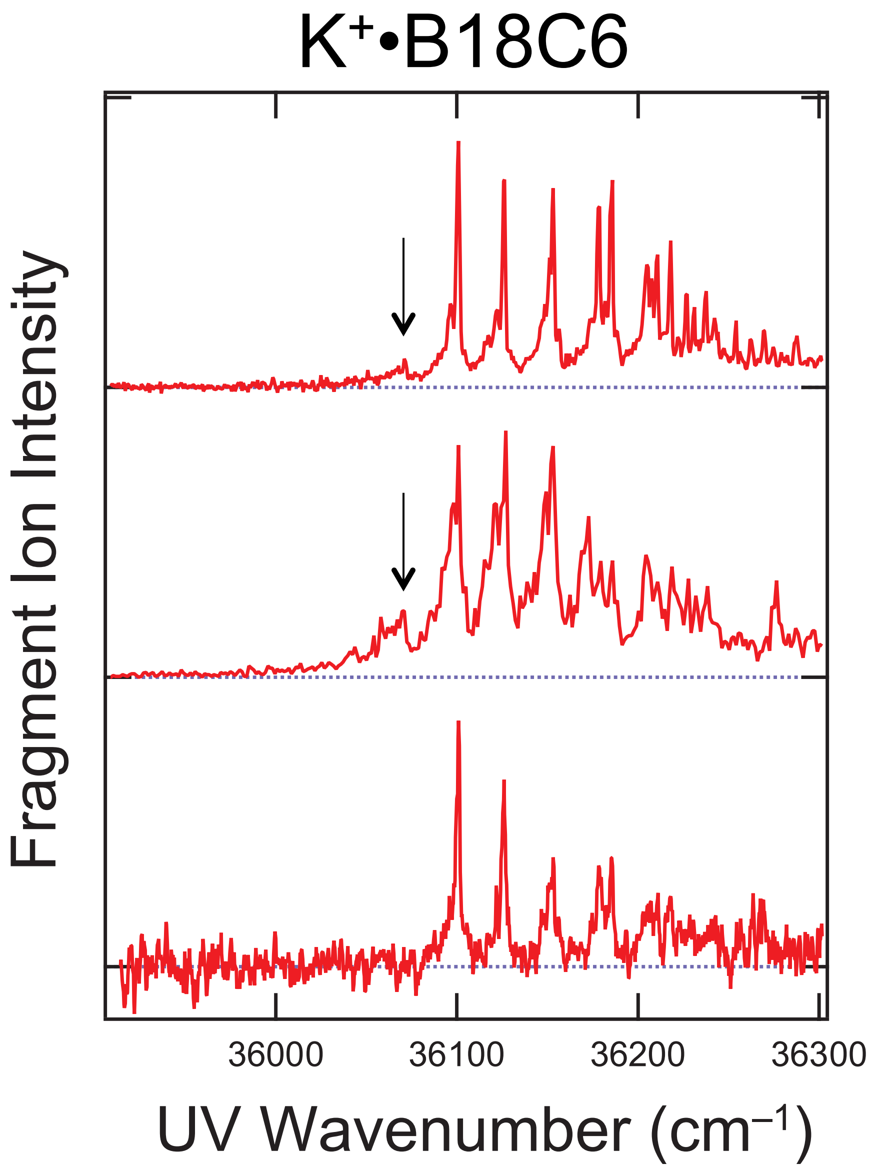


22-pole trap (~6 K)[b]
T_{vib} = ~10 K

[a]Choi et al., Chem. Phys. Lett., 593, 150 (2014).

[b]Inokuchi et al., J. Phys. Chem. A, 116, 4057 (2012).

Ions can be cooled to ~10 K even in Paul trap



22-pole trap (~6 K)[a]
T_{vib} = ~10 K

Paul trap (~6.5 K)[b]
T_{vib} = 35 K

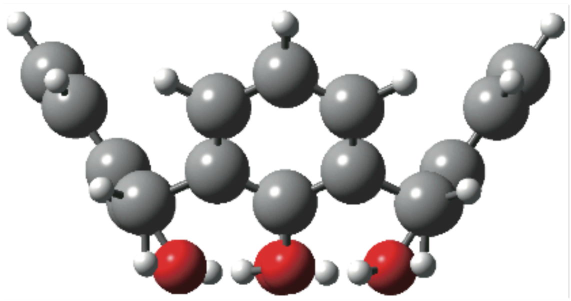
Paul trap (~4.3 K)[b]
T_{vib} = ~10 K

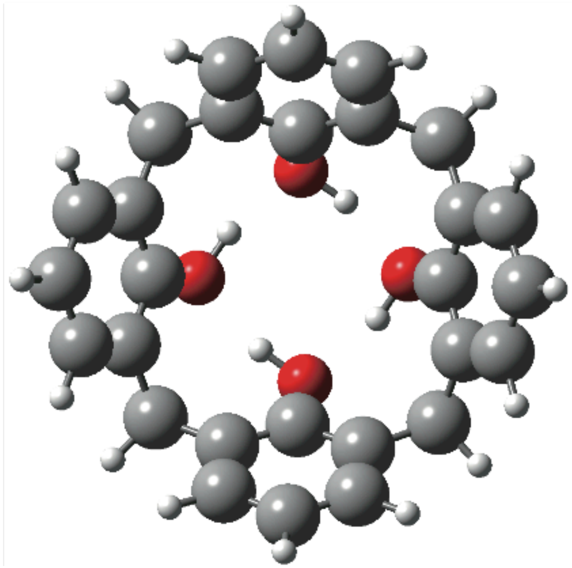
[a]Inokuchi et al., J. Phys. Chem. A, 116, 4057 (2012).

[b]Inokuchi et al., J. Phys. Chem. A, 119, 8512 (2015).

Calix[4]arene (C4A)

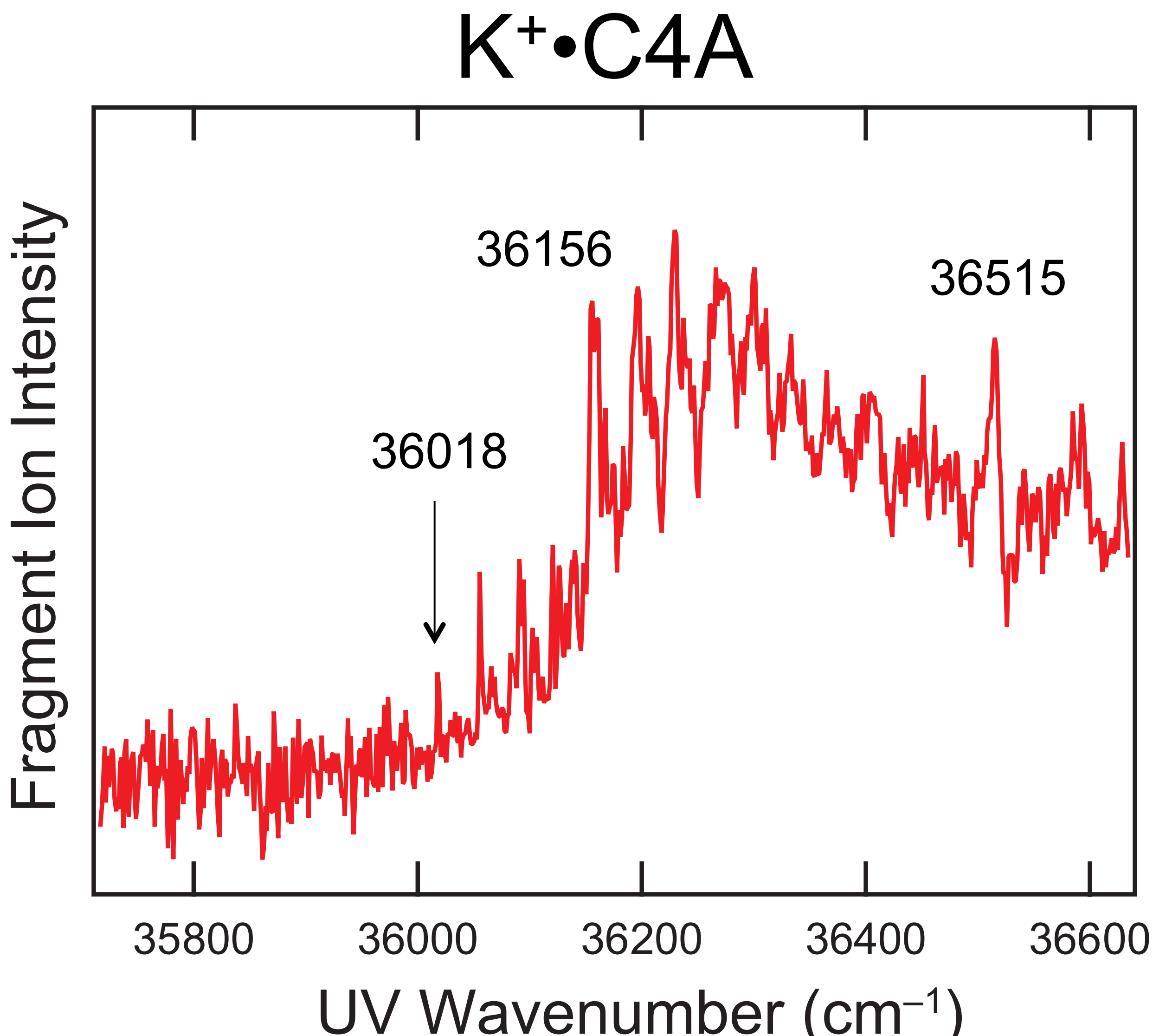
Four phenols are connected by $–CH_2–$ chains.
Four OH groups form a rigid H-bonded ring.





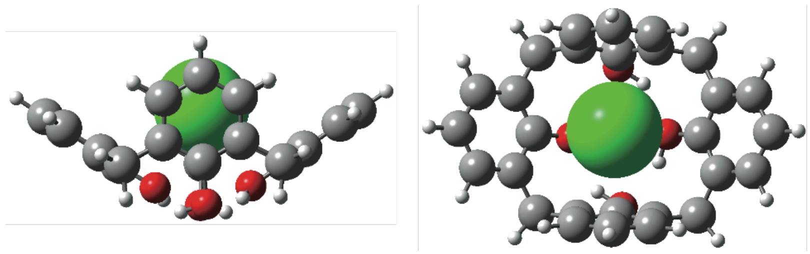
Ikeda and Shinkai, Chem. Rev., 97, 1713 (1997).
Ebata et al., J. Chem. Phys., 126, 141101 (2007).

K^+•C4A shows sharp UV bands



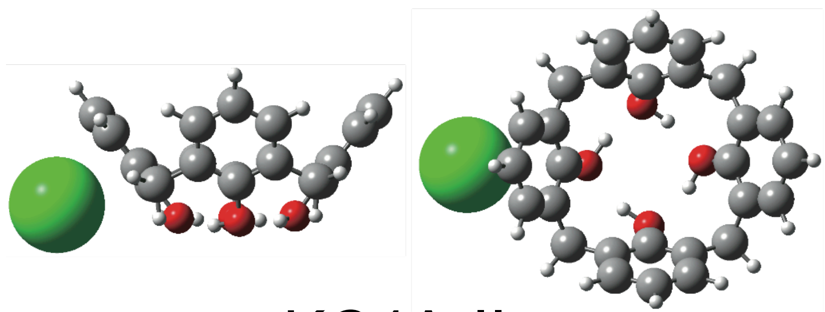
Inokuchi et al., J. Phys. Chem. A, 119, 8512 (2015).

Isomers of K^+•C4A



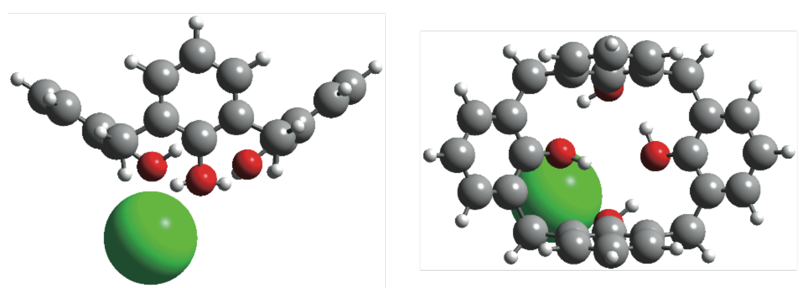
KC4A-I

endo



KC4A-II

exo
+97 kJ/mol

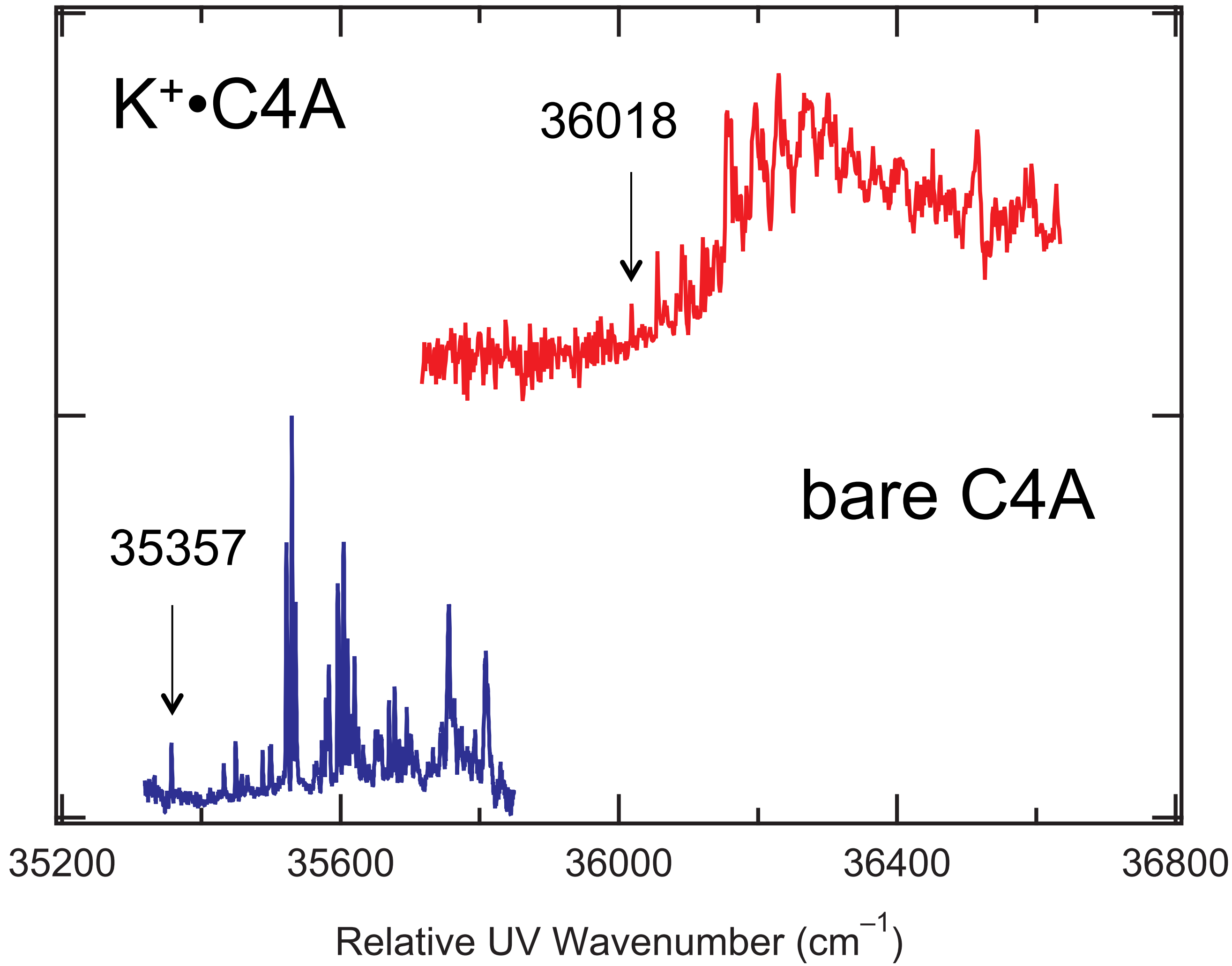


KC4A-III

exo
+101 kJ/mol

Gaussian09 M05-2X/6-31+G(d)

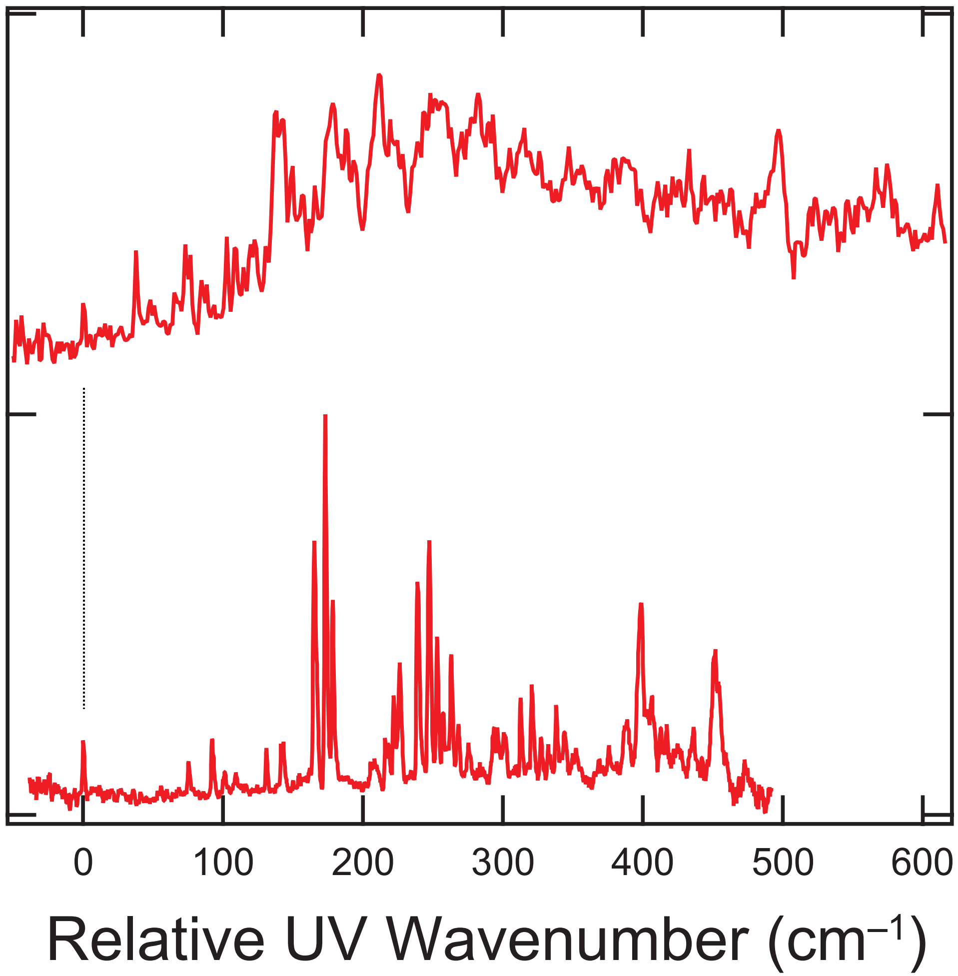
K^+ ion shifts the UV band to the blue



Ebata et al., J. Chem. Phys., 126, 141101 (2007).

UV spectra are similar for K^+•C4A and C4A

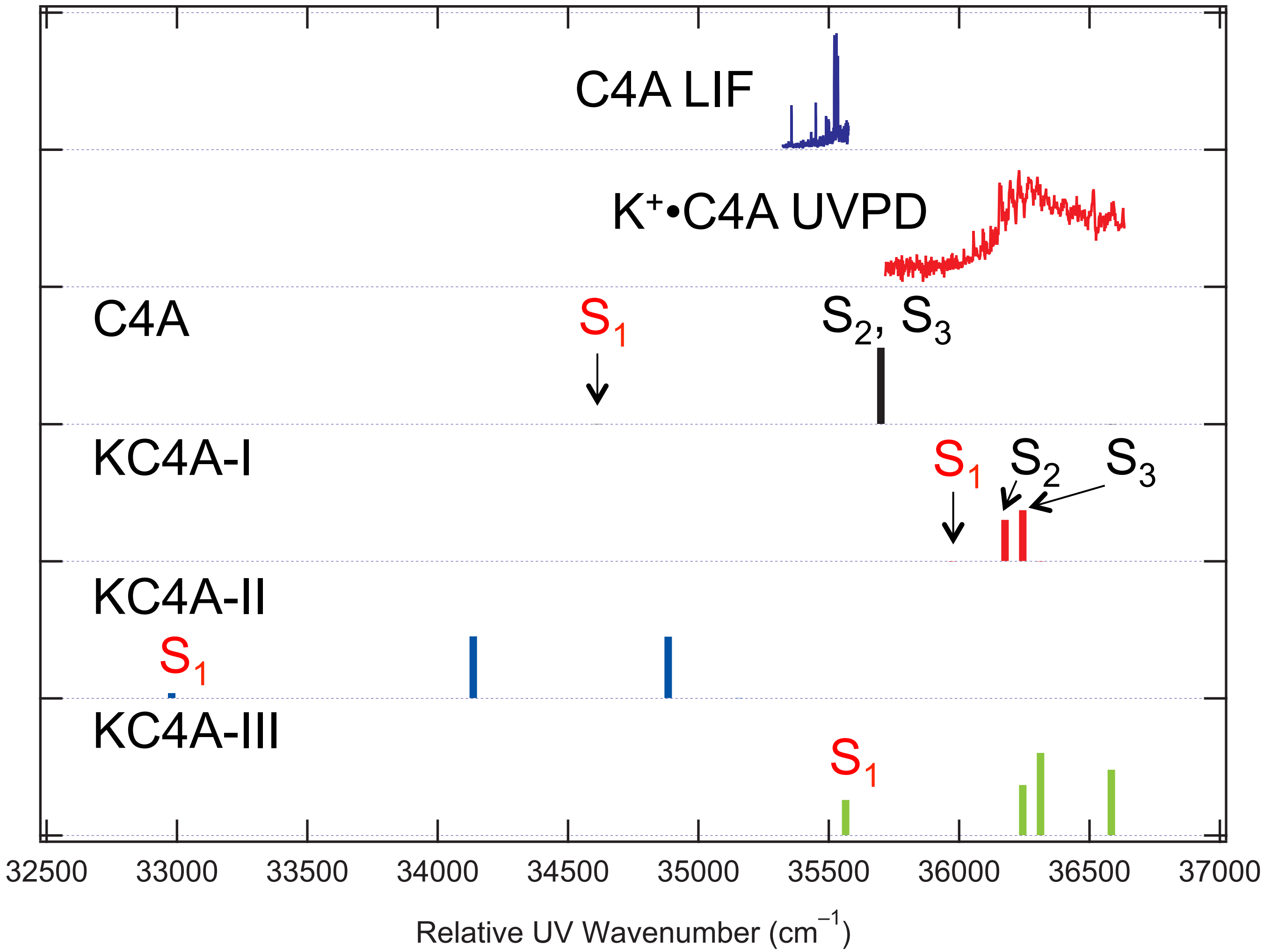
Weak origin band, followed by strong bands.



K^+•C4A

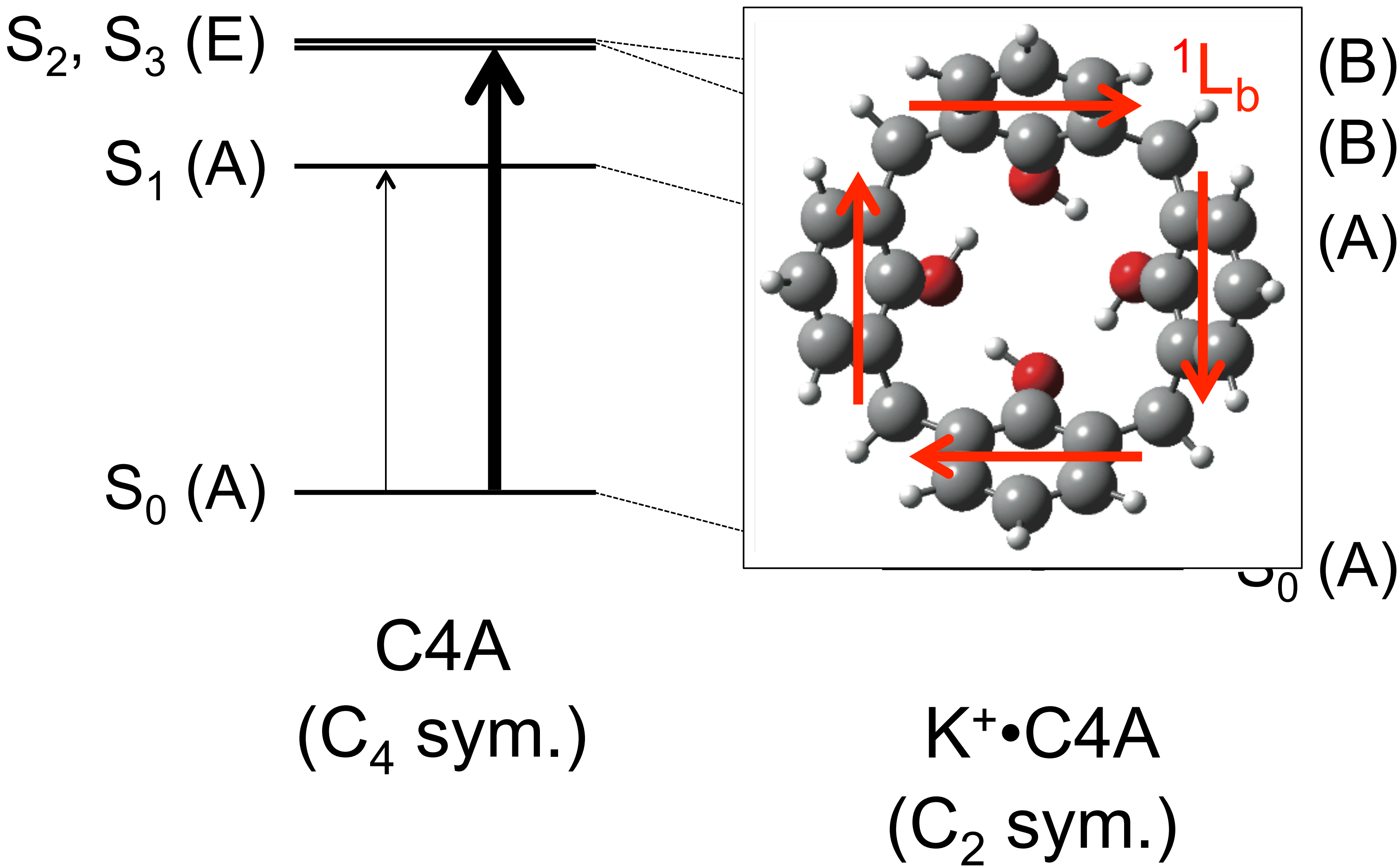
C4A

KC4A-I reproduces UVPD spectrum

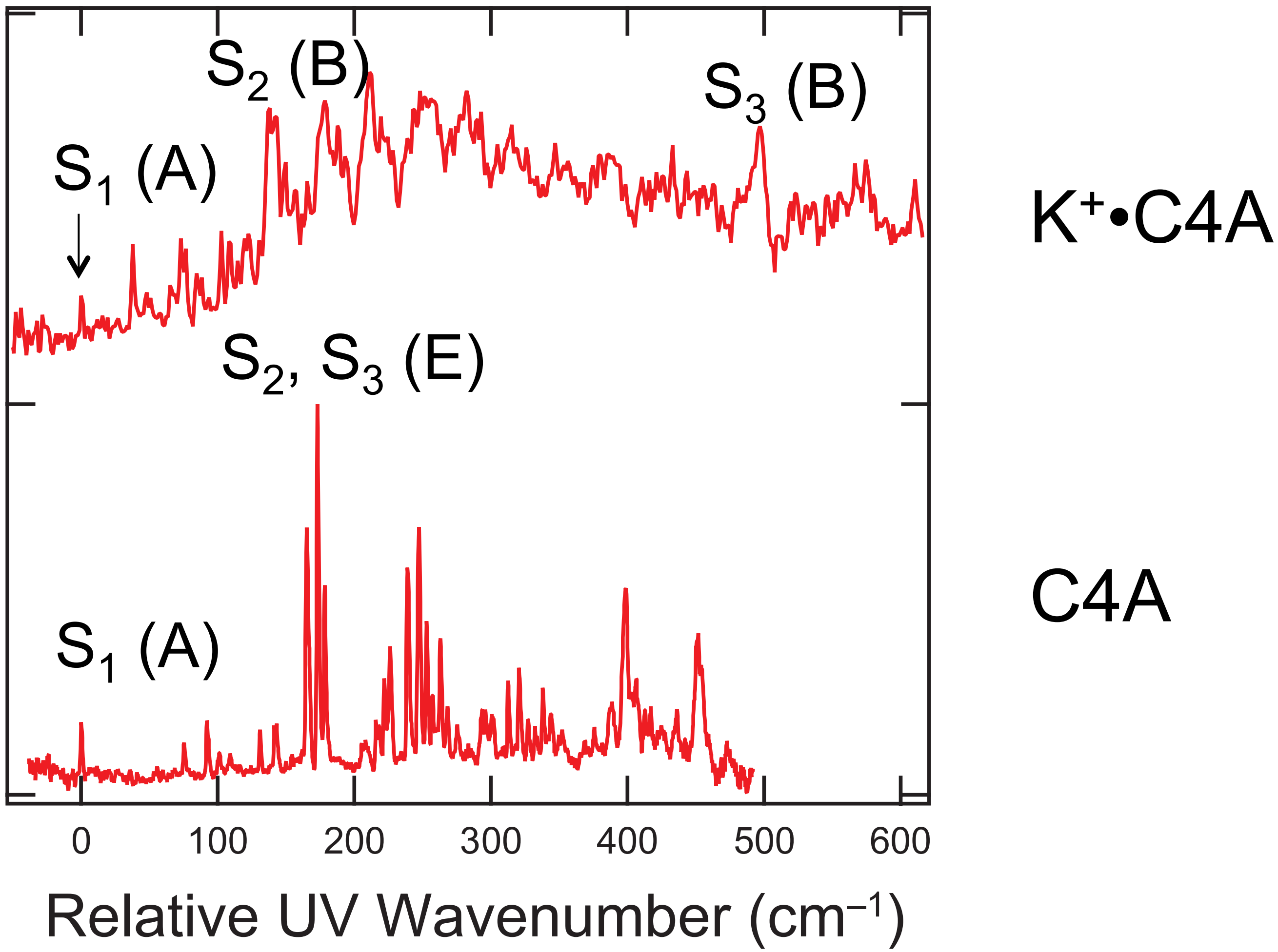


Gaussian09 M05-2X/6-31+G(d), S.F. = 0.843

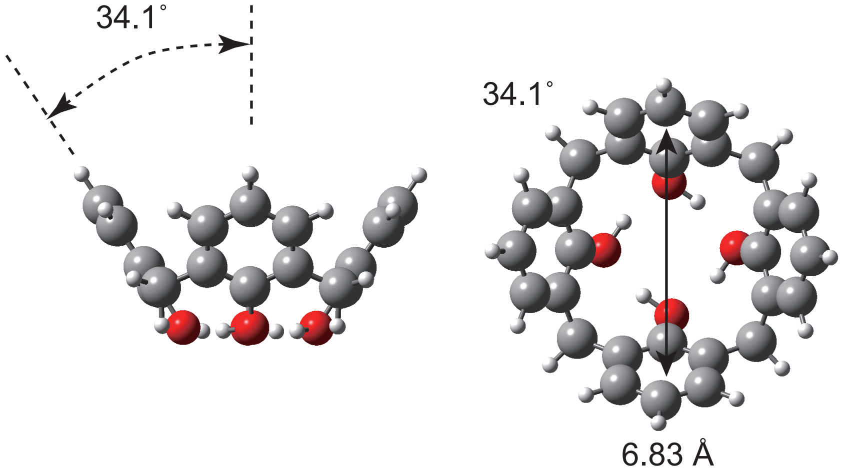
C4A and K$^+$•C4A have high symmetry



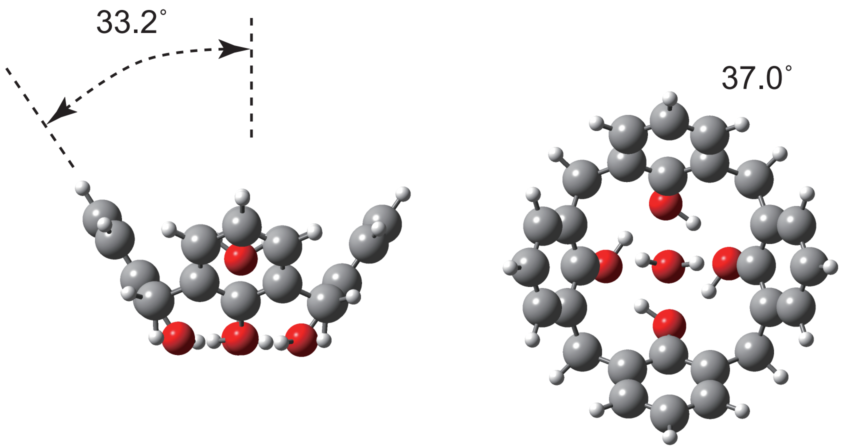
C4A and K^+•C4A have high symmetry



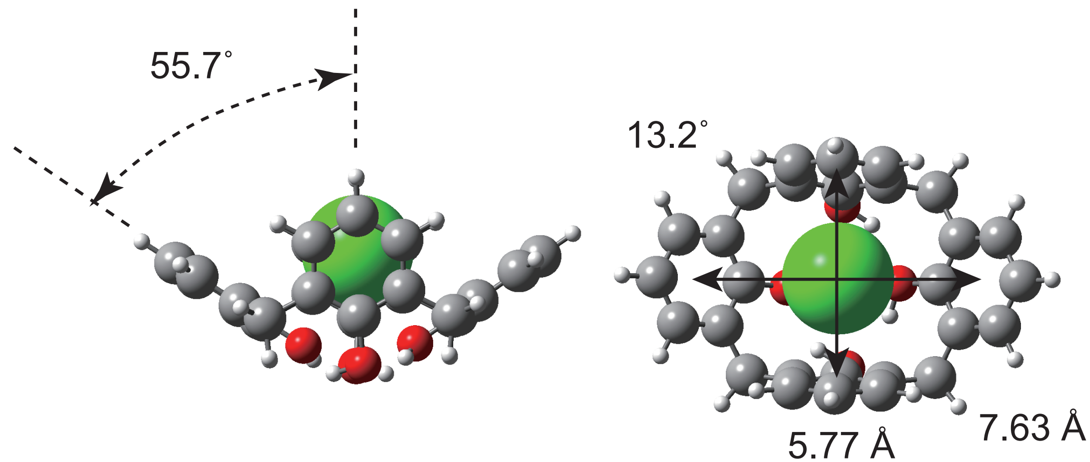
C4A in K^+•C4A is highly distorted



bare C4A



H_2O•C4A



K^+•C4A

Future prospects

■Cold gas-phase spectroscopy

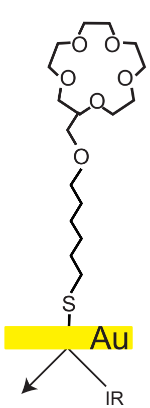
Host-guest complexes

Organometallic complexes

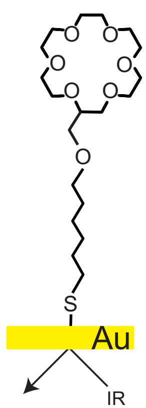
Hypervalent compounds

Inokuchi et al., J. Phys. Chem. A, 119, 8512 (2015).

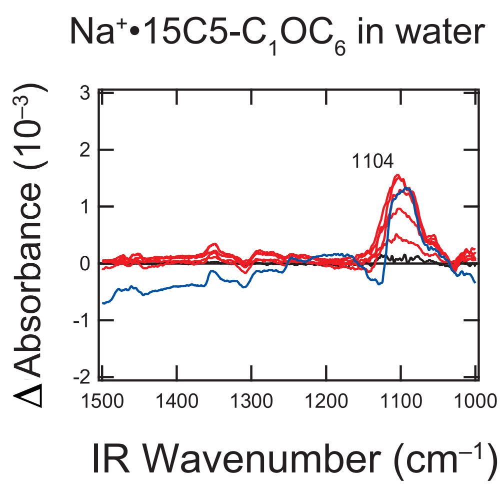
■SEIRA spectroscopy on metal surface

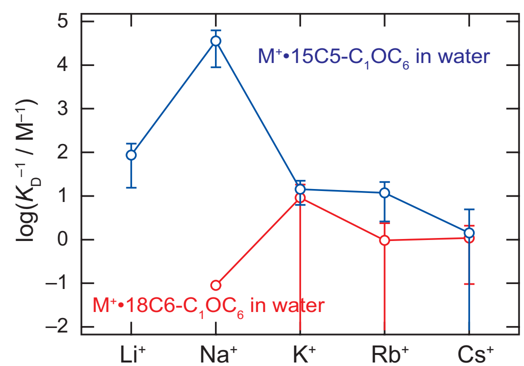


15C5-C_1OC_6



18C6-C_1OC_6





Inokuchi et al., Chem. Phys. Lett., 592, 90 (2014).

Inokuchi et al., New J. Chem., 2015, DOI: 10.1039/c5nj01787d .

Summary

■ We have constructed a mass spectrometer for UVPD spectroscopy with a cold, quadrupole Paul ion trap.

■ We have estimated T_{vib} in the trap to be ~10 K by the UVPD spectrum of K^+•B18C6.

■ The UVPD spectrum of K^+•C4A was measured; it shows sharp vibronic bands.

■ The spectral features and theoretical results suggest that K^+•C4A has an *endo* form with C_2 symmetry.