

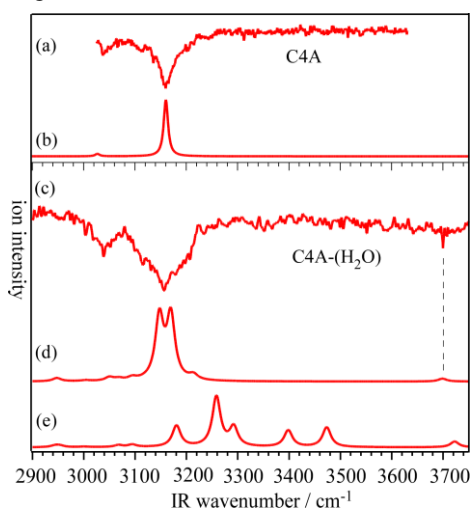
## Structure of the Calix[4]arene-(H<sub>2</sub>O) Cluster -The World's Smallest Cup of Water-

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**Introduction:** Calixarene (CA) is well known as the encapsulation molecule and its complex (cluster) structure has been studied extensively in condensed phase. In the present work, we investigate its cluster formation by different method. We form the CA-guest complex in a supersonic beam, and investigate the structure by laser spectroscopy and quantum chemical calculation. We choose calix[4]arene (C4A) as a host and water as a guest.

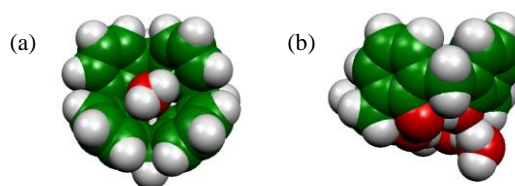
**Experiment:** The supersonic beams of calix[4]arene(C4A) and its clusters are obtained by an adiabatic expansion of the gaseous mixture of CA, water vapor, and carrier gas in a vacuum chamber. Electronic spectra are measured by mass-selected resonant two-photon ionization (R2PI). Vibrational spectrum of each species is measured by IR-UV double resonance (DR) spectroscopy. Dissociation energy of the C4A-(H<sub>2</sub>O) → C4A + H<sub>2</sub>O is measured by IR photodissociation (IRPD). In addition, possible stable structures are obtained by quantum chemical calculation at the MP2/aug-cc-pVQZ level.

**Results and discussion:** Figure 1 shows IR-UV DR spectra of (a) C4A and (c) C4A-(H<sub>2</sub>O). The IR spectrum of C4A exhibits a strong and broad H-bonded OH stretching band centered at 3160 cm<sup>-1</sup>. In the spectrum of C4A-(H<sub>2</sub>O), a strong H-bonded OH stretching band is also observed at 3160 cm<sup>-1</sup>. However, its bandwidth is broader than that of C4A. In addition to the strong band at 3160 cm<sup>-1</sup>, the IR-UV spectrum of C4A-(H<sub>2</sub>O) exhibits a weak band at 3700 cm<sup>-1</sup>, which is assigned to the asymmetric or free OH stretching vibration of H<sub>2</sub>O. We then performed calculation to determine the structure of C4A-(H<sub>2</sub>O) cluster at MP2/aug-cc-pVDZ. We obtained two isomers, one is endo-isomer (water inside the C4A cavity) (figure 2b) and the other is exo-isomer (water hydrogen bonded to the rim of C4A) (figure 2b). High-level



**Fig. 1** IR-UV double resonance spectra,  
IR spectra calculated (MP2/aug-cc-pVDZ)

electronic structure calculations at the MP2/aug-cc-pVQZ suggest that the endo-isomer is ~1100 cm<sup>-1</sup> more stable than the exo-isomer. Figure 1 shows the calculated IR spectra of (d) endo-isomer and (e) exo-isomer. The calculated IR spectrum of endo-isomer shows a very good agreement with the observed one. Therefore we concluded that structure of the observed C4A-(H<sub>2</sub>O) is endo-isomer.



**Fig.2** Optimized structure of C4A-(H<sub>2</sub>O)  
(a) endo-isomer, (b) exo-isomer