

Laser Spectroscopic and Theoretical Study of the Structures of the Calix[4]arene Complexes

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Introduction: Calixarenes(CAs) are well known functional molecules in host-guest chemistry. We have been studying the structure of the Calix[4]arene(C4A) complexes by using supersonic molecular beam, and laser spectroscopy. We found that C4A can encapsulate variety of species in its cavity. Here, we investigate the structure of the C4A complexes with various guests, Ar, N₂, C₂H₂, H₂O and NH₃, and discuss the interactions working in the complexes.

Experiment: The molecular beam of C4A complexes are formed by an adiabatic expansion of gaseous mixture of C4A, guest molecule, and carrier gas (He or Ne). Electronic spectra are measured by laser induced fluorescence(LIF) and mass-selected resonant two-photon ionization(R2PI). Infrared spectra are measured by IR-UV double resonance(DR) and IR photodissociation(IRPD) spectroscopy.

Result and discussion: Figure1 shows the plots of the red-shift of the S₁-S₀ band origin of the C4A complexes against the polarizability of guest molecules. The red-shift of band origin of C4A-rare gas, and -CH₄ shows a smooth increase with an increase of the polarizability. On the other hand, C4A-H₂O, and -NH₃ show much larger red-shifts, indicating an importance of the dipole moment and/or hydrogen-bonding. Fig. 2 shows the IR-UV DR spectra of the (a) bare C4A and (b) C4A-NH₃ complex. The IR spectrum of bare C4A exhibits a strong and broad OH stretching band centered at 3160cm⁻¹. Also, the IR spectrum of C4A-NH₃ shows a strong OH stretching band at 3160cm⁻¹. The stable structures of C4A-NH₃ were calculated at M05-2X/6-31+G* level. We obtained two structures as shown in Fig. 3, (a) endo-complex and (b) exo-complex and the calculated IR spectra are shown in Fig. 2 (c) and (d). The stabilization energy and the IR spectra suggest that the observed C4A-NH₃ complex is the endo-complex. The structure is thought to be stabilized mainly by the dipole-dipole interaction. We will also discuss the structures of other complexes.

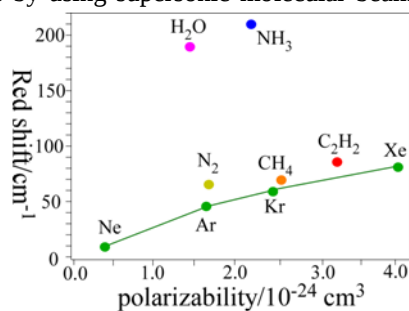


Fig. 1 plots of red-shifts of band origins of C4A complexes vs. polarizabilities of guest molecules.

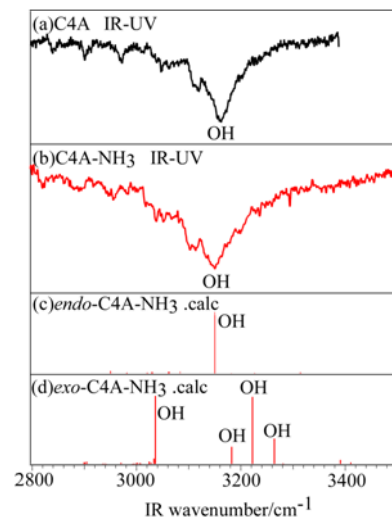


Fig. 2 IR-UV DR spectra of (a) bare C4A, (b) C4A-NH₃, and calculated IR spectra of (c) C4A-NH₃ endo-complex, (d) exo-complex

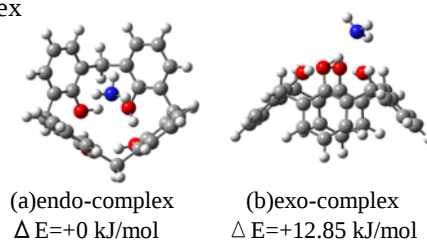


Fig. 3 Optimized structure of C4A-NH₃