

Calix[4]arene can recognize metals captured in the cavity by IR absorption

Calix[4]arene (C4A), composed of four phenols connected with methylene chains, has been used extensively as host molecules in supramolecular chemistry. C4A has a dominant, cone-type conformation formed by a strong hydrogen-bonded network with four OH groups (Fig. 1), and captures guest species such as molecules and ions in the cone.

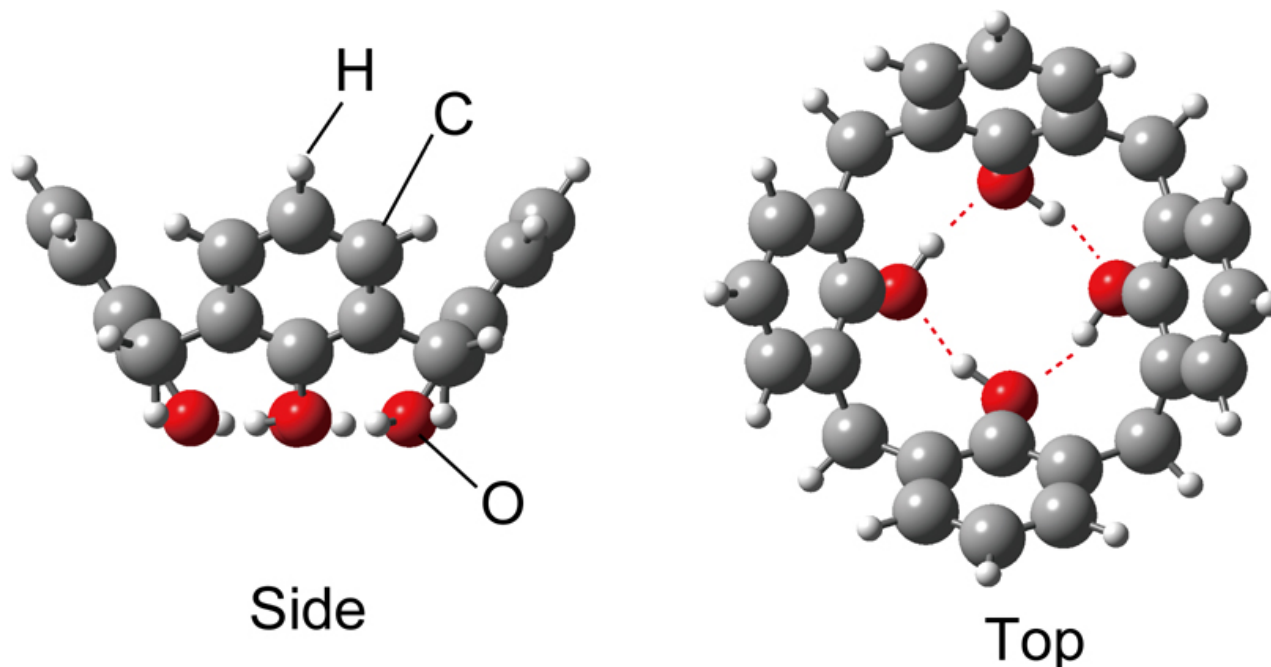


Fig. 1. Side and top views of cone-shaped C4A. Red, dotted lines in the top view indicate the OH...O hydrogen bonds.

We observe IR spectra of C4A complexes with K^+ , Rb^+ , and Cs^+ ions in the 3200–3700 cm^{-1} region under cold (~ 10 K) gas-phase conditions using a vacuum chamber equipped with an electrospray ion source, cold ion trap, and time-of-flight mass spectrometer (Fig. 2). All the complexes show two bands, which can be assigned to the stretching vibrations of the hydrogen-bonded OH groups in the C4A part. The frequency of the OH stretching vibrations decreases with increasing the ion size from K^+ (3357 and 3513 cm^{-1}), Rb^+ (3323 and 3463 cm^{-1}) to Cs^+ (3279 and 3379 cm^{-1}), but it is substantially higher than that of C4A (3158 cm^{-1}).

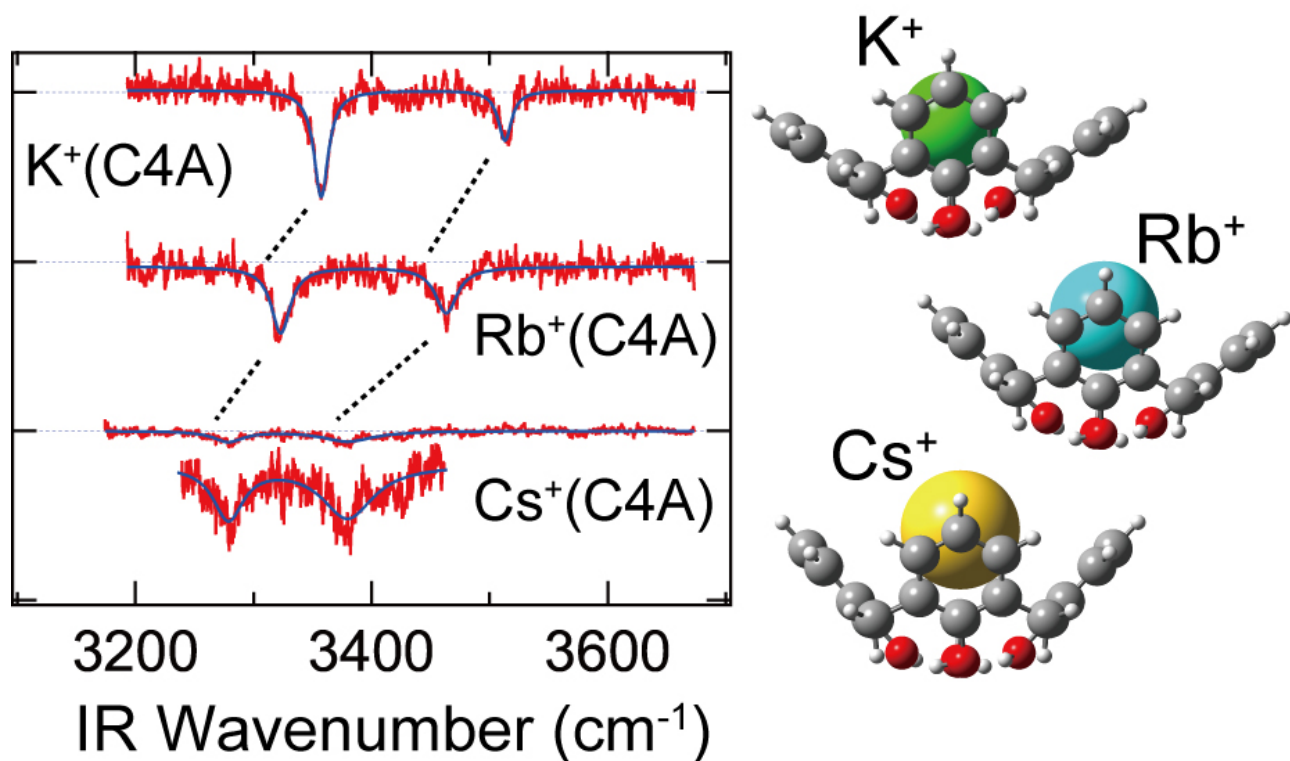


Fig. 2. The IR spectra of the $M^+(C4A)$ ($M = K, Rb, \text{ and } Cs$) complexes. Stable structures of the $M^+(C4A)$ complexes predicted by quantum chemical calculations.

These results suggest that C4A encapsulates the metal ions by distorting the cone cavity, and that the distortion of the cone conformation is reduced more and the hydrogen bond between the OH groups becomes stronger with increasing the ion size from K^+ to Cs^+ . The Cs^+ complex has the smallest distortion on the C4A cavity among the alkali metal ion complexes. This can be one origin for the predominant encapsulation of Cs^+ ion by C4A over smaller alkali metal ions in solution.

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Publication

[Conformation of alkali metal ion-calix\[4\]arene complexes investigated by IR spectroscopy in the gas phase](#)

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