Determining Topologies of Alkylammonium Complexes of Cucurbit[6]uril Using multiCRAFTI Techniques in an FTICR Mass Spectrometer

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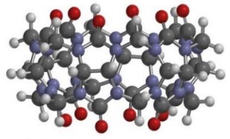
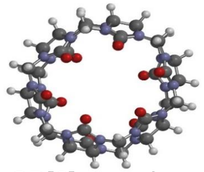
Introduction

- **Cucurbit[6]uril** (CB[6]) is known to form singly charged (1:1) and doubly charged (1:2) complexes with alkylmonoammonium ions, detected in the gas phase using FTICR.
- The alkyl chains may bind inside or outside the cage or with a part of the alkyl chain protruding. **Multi-CRAFTI** technique can be used to determine the relative collision cross-sections and hence the structures of these complexes.

Cucurbit[6]uril (CB[6])
$C_{36}H_{36}N_{24}O_{12}$
Mol. Wt. 996.295



CB[6]-Side view



CB[6]- top view

Theory

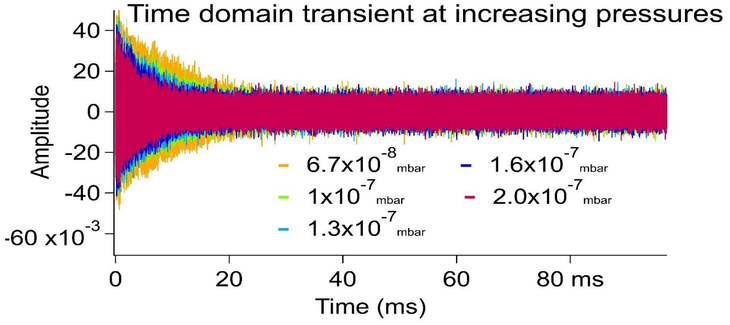


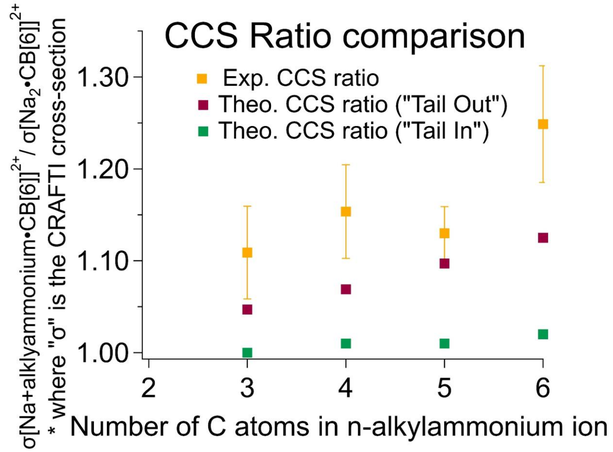
Figure 1. A time domain transient at different Ar pressures for $[Na+Butylammonium•CB[6]]^{2+}$ complex.

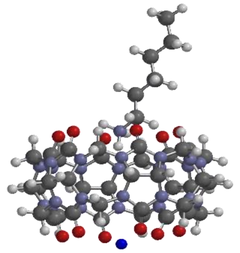
- Larger ions collide with the neutral collision gas easily: resulting in a shorter time domain transient, which when Fourier transformed, gives a peak with larger width.

Methods

- MMFF94 force field and IMoS were used to calculate structures and compute hard sphere collision cross sections in Ar collision gas via projection approximation.
- Experiments were performed in a Bruker APEX 47e FTICR mass spectrometer controlled using a PREDATOR data system. Multi-CRAFTI excitation wave forms were generated such that the ions of interest are excited to the same center-of-mass kinetic energy.
- Linewidths of the ions of interest are extracted as a function of collision gas pressure and kinetic energy, enabling the measurement of relative cross sections as a function of collision energy.

Results I: Na forces the alkyl tail out.



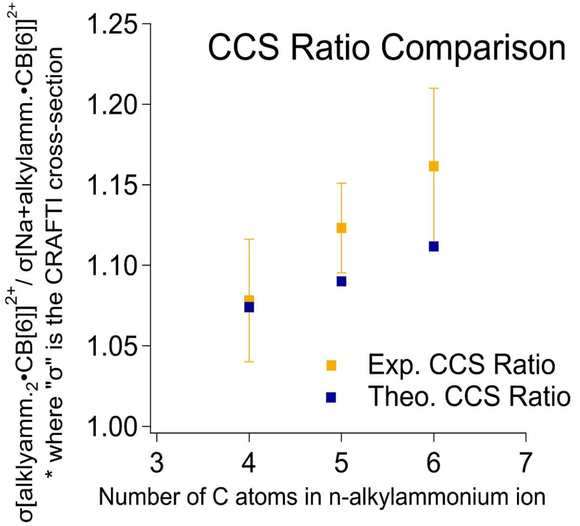


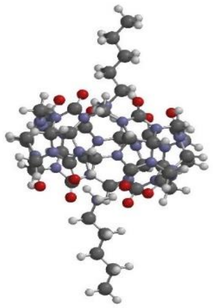
[Na+hexylamm•CB[6]]$^{2+}$

Figure 2. Experimental and computational cross-section ratio comparison: $[Na+alkylammonium•CB[6]]^{2+}$ / $[Na_2•CB[6]]^{2+}$.

*Theoretical ratios are calculated for models with alkylammonium tails in and out of the CB[6] cavity.

Results II: "Tail-Out" complexes.





[(pentylamm)$_2$•CB[6]]$^{2+}$

Figure 3. Experimental and computational cross-section ratio comparison: $[(alkylammonium)_2•CB[6]]^{2+}$ /$[Na+alkylammonium•CB[6]]^{2+}$ * Theoretical ratios are calculated for models with both alkylammonium tails out of the CB[6] cavity.

Conclusions

- Metal ions like Na^+ forces the alkylammonium tail out of the CB[6] cavity.
- Both alkylammonium tails are forced out of the cavity when a CB[6] molecule binds with two of them.
- Further research is ongoing to confirm the structure of the complexes.

Acknowledgments

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