



# Gas-Phase Cluster Spectroscopy: Probing Non-Covalent Interactions on the Molecular Level

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## Introduction

Our research group uses infrared spectroscopic techniques to investigate the properties of size-selected cluster ions. We are especially interested in trying to characterize the weak interactions involved in solvated metal-ion systems, such as **hydrogen-bonding**.



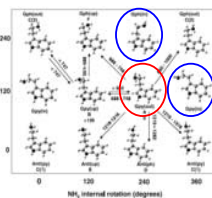
## Ionophores

- Complex ions in solution *selectively*
- Useful for ion extraction in industrial and environmental processes
- ion-ionophore
- solvent-ionophore
- ion-solvent
- solvent-solvent



A common example: Crown Ethers

## Hydrated Biomolecules



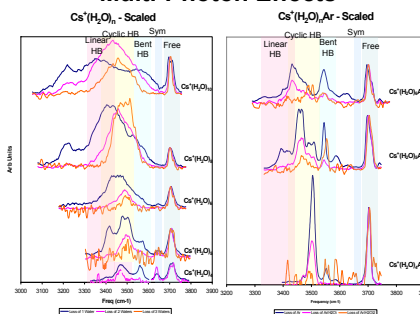
Tryptamine has nine conformers which differ in side chain orientation and lone pair position

Favored conformer in neutral gas-phase experiments

Not observed in neutral gas-phase experiments

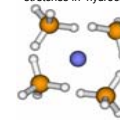
Zwiler, Science Vol. 303 pg. 1169, 2004

## Multi-Photon Effects



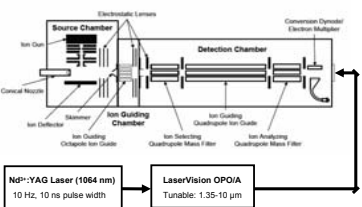
## Metal Ion—Hydrocarbon Studies

The goal of these experiments is to not only identify the structures of these clusters, but to try to understand how the strong electrostatic interaction from alkaline metal cations, Li+ in this case, affects the vibrational features of the C-H stretches in hydrocarbons.

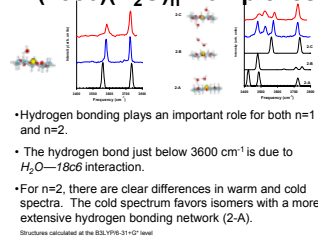


An example of four methane molecules in lithium's first solvent shell.

## Apparatus



## K+(18c6)(H2O)n Complexes



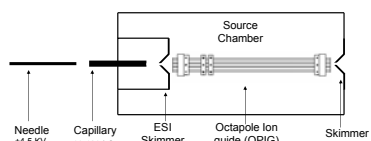
- Hydrogen bonding plays an important role for both n=1 and n=2.
- The hydrogen bond just below 3600 cm<sup>-1</sup> is due to H<sub>2</sub>O—18c6 interaction.
- For n=2, there are clear differences in warm and cold spectra. The cold spectrum favors isomers with a more extensive hydrogen bonding network (2-A).

Structures calculated at the B3LYP/6-31+G\* level

## Solvation of Multivalent Metal Ions

- Although most studies involved singly charged metal ions—significant number of metals **do not exist in +1 state** in the condensed phase or biological systems.
- Challenge:** generating sufficient number densities of multiply charged metal ions for spectroscopic experiments is **not easy**
- Solution: Electrospray Ionization (ESI) Source and Octapole Ion Guide (OPIG)

## ESI Source and OPIG



•Solutions are fed through needle by a syringe pump (2-6 μL/min). At the tip of the needle, **charge separation** is achieved and gaseous charged droplets emerge.

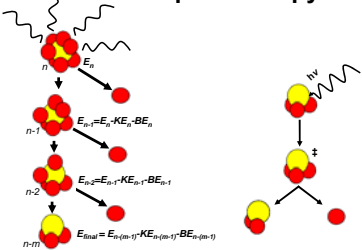
•These **charged droplets undergo a series of evaporative steps** while in the atmosphere and passing through capillary.

•Clusters emerging from capillary are **sampled by ESI skimmer**.

•Upon entering source chamber, clusters are **collected and guided** through the chamber by OPIG. A **skimmer extracts clusters** from OPIG and are passed to mass spectrometer.

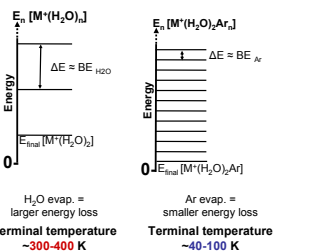
•Also developing a Sonic Spray source for use in generation multivalent metal ion and biological complexes.

## Cluster Stabilization and Action Spectroscopy



## Evaporative Pathways

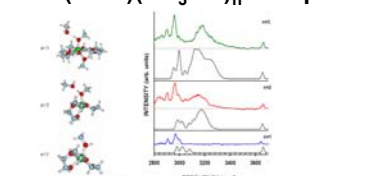
- Cooling efficiency determined by the evaporating ligands' binding energy
- Most weakly bound ligand evaporates to cool cluster; removes both mass and energy



H<sub>2</sub>O evap. = smaller energy loss  
Terminal temperature ~300-400 K

Ar evap. = larger energy loss  
Terminal temperature ~40-100 K

## Mn2+(18c6)(CH3OH)n Complexes

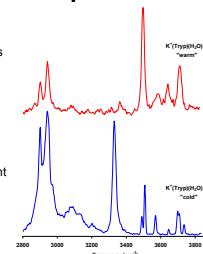


- Extensive hydrogen bonding is observed at n=2.
- The dominant hydrogen bonding observed is due to CH<sub>2</sub>OH—CH<sub>2</sub>OH interactions.
- In the C—H stretch region (below 3000 cm<sup>-1</sup>) significant perturbations of C—H stretches of the 18c6 macrocycle indicate that the crown ether backbone is greatly distorted by the dication.

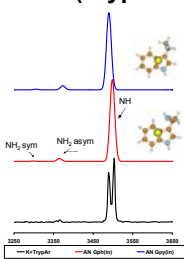
## Temperature Dependence

"Tagging" the cluster ions with an argon atom reduces the internal energy

By changing the effective temperature of the cluster ions, different isomers may be thermodynamically favored, resulting in different spectral features



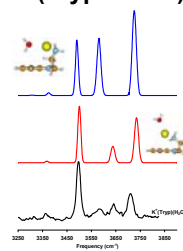
## K+(Tryptamine) spectra



In the presence of K<sup>+</sup>, the two lowest-energy K<sup>+</sup>(Tryptamine) isomers are built from those not seen in neutral experiments

Experimental spectrum shows presence of both isomers, in good agreement with the calculated spectra

## K+(Tryptamine)(H2O) spectra

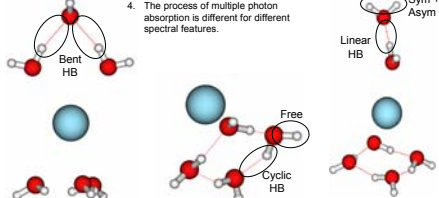


Two calculated spectra show good agreement with the features in the experiment

The relative intensities of the features in the experimental spectrum provide information about the abundance of each of the calculated isomers

## Initial Interpretation

1. Features associated with cyclic hydrogen bonds show significant intensity in channels with loss of more than one moiety. As expected, this is less pronounced in the argonated clusters because they start with less internal energy.
2. Features associated with bent and linear hydrogen bonds are suppressed in channels with loss of one moiety. This is because these H-bonded features break upon absorption of one photon.
3. The technique of monitoring multiple loss channels can therefore serve as a diagnostic tool.
4. The process of multiple photon absorption is different for different spectral features.



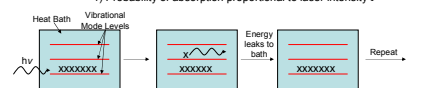
## Multi-Photon Absorption

Water Binding Energy ~ 30-40 kJ/mol  
Argon Binding Energy ~ 5 kJ/mol  
Photon Energy = 37-45 kJ/mol

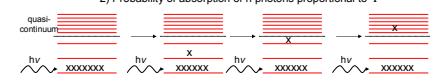
Multiple Photon Absorption Necessary to Lose Multiple Moieties

### Two Traditional Pictures of Multi-Photon Absorption

1) Probability of absorption proportional to laser intensity I



2) Probability of absorption of n photons proportional to I<sup>n</sup>



## A New Type of Multi-Photon Absorption?

If the photon absorptions are random, uncorrelated events, then they can be modeled with a Poisson Distribution:

$$P(x; \sigma F) = \frac{(\sigma F)^x e^{-\sigma F}}{x!} \quad \sigma F = -\ln(1 - D)$$

Frag.	% Fragmentation				Poisson Calculations							
	Loss of H <sub>2</sub> O	Loss of Ar	Loss of H <sub>2</sub> O/Ar	Total Depletion	σF	P(0)	P(1)	P(2)	P(3)	P(4)	P(5)	
CaH <sub>2</sub> OAr	3704	60.8	8.7	0.8	70.1	1.2	25.9	36.1	21.8	8.8	2.8	0.8
CaH <sub>2</sub> OAr	3808	52.3	17.8	2.8	73.0	1.3	27.0	35.4	23.1	10.1	3.3	0.9
CaH <sub>2</sub> OAr	3868	41.9	18.0	5.2	63.1	1.0	26.9	34.0	23.4	8.7	1.6	0.3

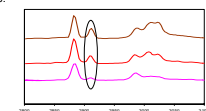
Conclusions: Small non-argonated clusters dissociate one water molecule per photon (red box). Argonated clusters require more than two photons to lose a water molecule (blue box). Future Directions: Use multi-photon analysis to identify spectral features and magic and anti-magic number clusters. Use IR/MS analysis to characterize internal energy distributions and dissociation rates in the multi-photon process.

## Discussion

•The peaks on all the spectra between 2980 cm<sup>-1</sup> and 3000 cm<sup>-1</sup> signify the asymmetric C-H stretches of the methanes.

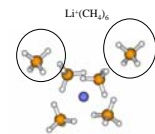
•Clearly, due to electrostatic interactions, strong peaks appear in the C-H symmetric stretch region between 2860 cm<sup>-1</sup> and 2890 cm<sup>-1</sup>. The symmetric C-H stretch of methane would otherwise be IR inactive.

•A new peak appears at n=5 and increases in intensity as n increases. This would seem to provide evidence of second shell methanes.



## Calculations

Here is a calculation example of Li<sup>+</sup>(CH<sub>4</sub>)<sub>6</sub> at the B3LYP/6-31+G\* level. The first solvent shell around Li<sup>+</sup> fills with 4 methanes. The next two methanes make up the second shell. It seems that the two second shell methanes would give rise to the peak near 2909 cm<sup>-1</sup> for n=5-7. Future work on second shell solvent molecules, methanes in this case, will allow us to further study the effects of the electrostatic interaction from the Li<sup>+</sup> cation.



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Professor Jim Lisy