

# Infrared Gas-Phase Studies of $K^+(\text{Tryptamine})(\text{H}_2\text{O})_{n=0-4}$

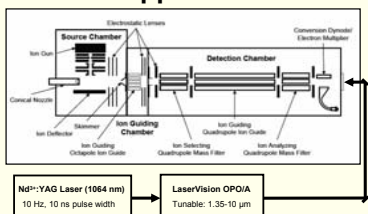
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## Introduction

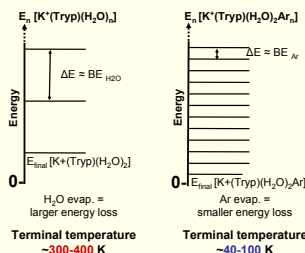
The stability of hydrated gas-phase cluster ions is determined by the balance between various competing electrostatic and hydrogen bonding interactions. In  $K^+(\text{Tryptamine})$  cluster ions, a favorable electrostatic interaction between the potassium cation and the tryptamine  $\text{NH}_2$  lone pair stabilizes the high-energy Gph(n) and Gpy(n) conformers of neutral tryptamine. Previous studies of  $\text{Tryptamine}(\text{H}_2\text{O})_n$  clusters indicate that the hydrating water molecules favor stabilizing the neutral minimum energy Gpy(out) tryptamine conformer. In this scheme, the first water molecule interacts directly with the  $\text{NH}_2$  lone pair and is located to the side of the tryptamine monomer. By incorporating a potassium cation, however, the minimum energy tryptamine-water configuration is disrupted in order to maximize the electrostatic interactions with the cation, shifting so that the tryptamine-water interaction includes a  $\pi$ -hydrogen bond between the water and the phenyl ring of tryptamine.

## Apparatus



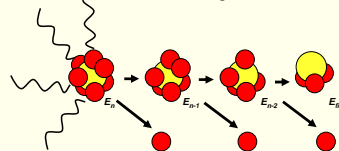
## Cluster Stabilization

- Cluster ions initially have excess internal energy and are stabilized through evaporative cooling
- Cooling efficiency determined by the evaporating ligands' binding energy
- Most weakly bound ligand evaporates to cool cluster, removes both mass and energy



- Cluster ions stabilized through loss of water have a higher terminal energy compared to those stabilized through loss of argon
- "Warm" spectra are obtained at biologically relevant temperatures
- "Cold" spectra have sharper spectral features

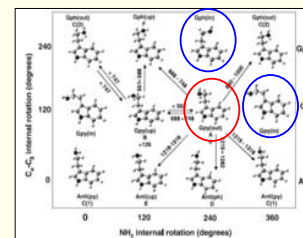
## Action Spectroscopy



- Electrostatic lenses guide cluster ions from the source chamber, through the ion guiding chamber and into the detection chamber
- Quadrupole 1 – mass selects parent ion of interest
- Quadrupole 2 – RF only; a photon from the tunable IR laser may interact with the cluster and cause fragmentation
- Quadrupole 3 – mass selects fragment ion of interest
- Infrared photodissociation (IRPD) spectra are recorded as a function of frequency

## Tryptamine Conformers

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



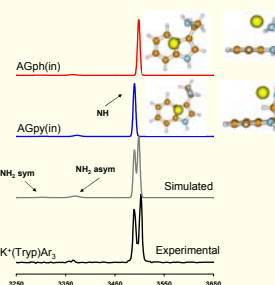
Dian, Clarkson and Zwier, *Science* 2004, 303, 1169-1173.

- Favored conformer in neutral gas-phase experiments
- Not observed in neutral gas-phase experiments

- The two conformers not observed in neutral gas-phase experiments both have unfavorable interactions between the lone pair electrons on the  $\text{NH}_2$  group and the  $\pi$  electrons above the aromatic rings
- The addition of two or more water molecules to neutral tryptamine locks in the Gpy(out) structure and results in the formation of a bridge between the  $\text{NH}_2$  and  $\text{NH}$  groups

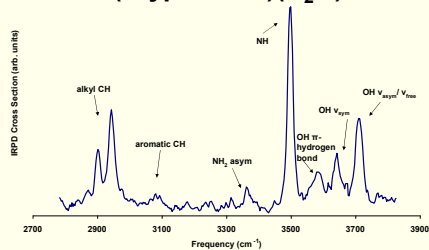
## $K^+(\text{Tryptamine})\text{Ar}_3$

- In the presence of  $K^+$ , the two lowest-energy  $K^+(\text{Tryp})$  isomers are built from those not seen in neutral experiments
- $K^+$  has favorable electrostatic interactions with  $\text{NH}_2$  lone pair and aromatic  $\pi$  electrons



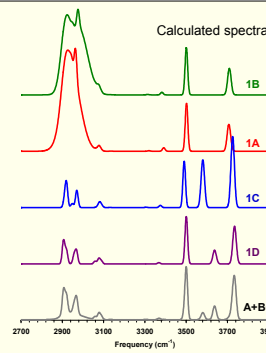
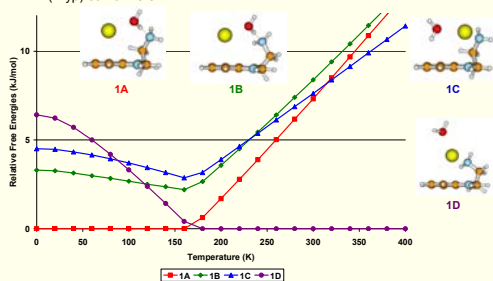
- Geometries and frequencies were calculated at the B3LYP/6-31+G\* level using Gaussian
- Calculated spectra (red and blue) are combined to form a simulated spectrum (gray) in good agreement with experimental spectrum (black)

## $K^+(\text{Tryptamine})(\text{H}_2\text{O})$



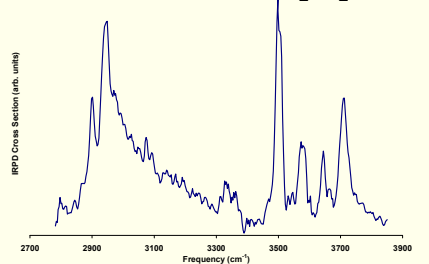
- With just one water molecule present, there are three unique features in the OH stretching region, indicating that there must be at least two isomers present in the experiment

Geometry and frequency calculations are combined with thermodynamics data to determine which isomers are expected near 300K. All four lowest-energy  $K^+(\text{Tryp})(\text{H}_2\text{O})$  isomers are built from the preferred  $K^+(\text{Tryp})$  conformers



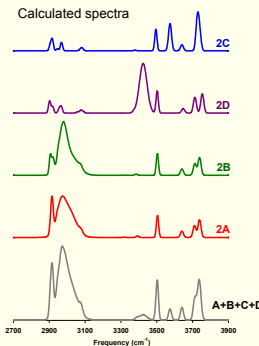
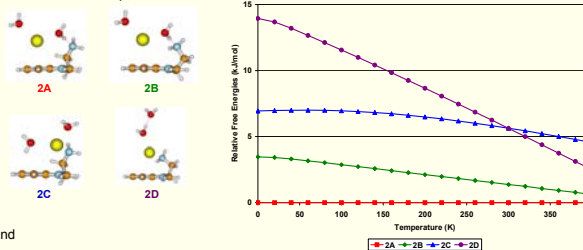
- Structures 1A and 1B have significant hydrogen bonding between 2900-3100  $\text{cm}^{-1}$
- Structure 1C exhibits  $\pi$ -hydrogen bonding near 3600  $\text{cm}^{-1}$
- Structure 1D is the only low-energy isomer with no hydrogen bonds
- Structures 1C and 1D best replicate the experimental spectrum
- From thermodynamics data, 1D is expected to be the major contributor, while 1A, 1B and 1C most likely all make small contributions to the spectrum
- The gray simulated spectrum is a weighted summation of all four calculated spectra

## $K^+(\text{Tryptamine})(\text{H}_2\text{O})_2$



- With the addition of a second water molecule, there is an increase in intensity of the  $\pi$ -hydrogen bond feature as well as a broad hydrogen bond feature between 2800-3300  $\text{cm}^{-1}$

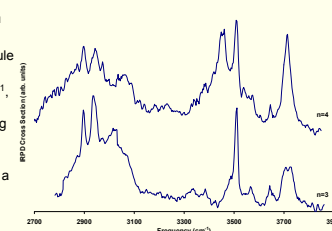
- From thermodynamics data, 2A and 2B are expected to be the major contributors near 300K
- Some amount of structures 2C and 2D must be present to account for the  $\pi$ -hydrogen bonding and the feature near 3330  $\text{cm}^{-1}$  in the experimental spectrum



- Structures 2A and 2B have significant hydrogen bonding between 2900-3100  $\text{cm}^{-1}$  from a water bound to the  $\text{NH}_2$  group
- Structure 2C exhibits  $\pi$ -hydrogen bonding near 3600  $\text{cm}^{-1}$
- Structure 2D has a new feature near 3430  $\text{cm}^{-1}$  arising from a hydrogen bond between two water molecules
- Structures 2A and 2B best replicate the experimental spectrum
- The gray simulated spectrum is a weighted summation of all four calculated spectra

## $K^+(\text{Tryptamine})(\text{H}_2\text{O})_{3-4}$

- The hydrogen bonding region below 3100  $\text{cm}^{-1}$  broadens with each additional water molecule
- At  $n=4$  a new feature appears near 3450  $\text{cm}^{-1}$ , most likely from water-water hydrogen bonding
- $\text{NH} \cdots \text{OH}_2$  hydrogen bonding – indicated in neutral experiments by a reduction in intensity at 3500  $\text{cm}^{-1}$  – is not observed through  $n=4$



## Conclusions

- The presence of  $K^+$  stabilizes the high-energy tryptamine conformers
- Multiple isomers are observed in every  $K^+(\text{Tryp})(\text{H}_2\text{O})_{n=0-4}$  experiment
- $K^+$ ,  $\text{Tryp}$  and  $K^+ \cdots \text{OH}_2$  interactions are favored over  $\text{Tryp} \cdots \text{OH}_2$  interactions, resulting in structures that are not observed in neutral clusters
- The presence of the  $\text{NH}$  stretching feature near 3500  $\text{cm}^{-1}$  indicates that the majority of cluster ions have not formed water bridges between the  $\text{NH}_2$  and  $\text{NH}$  groups of tryptamine, in contrast to the neutral  $\text{Tryp}(\text{H}_2\text{O})_n$  clusters that form a bridge with as little as two water molecules

## References

- Dian, Clarkson and Zwier, *Science* 2004, 303, 1169-1173.
- Zwier, *J. Phys. Chem. A* 2001, 105, 8827-8839.

## Acknowledgements

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