Chemical reactivity, bonding and structure of the nucleophilic substitution of p-chlorofluorobenzene ions by ammonia

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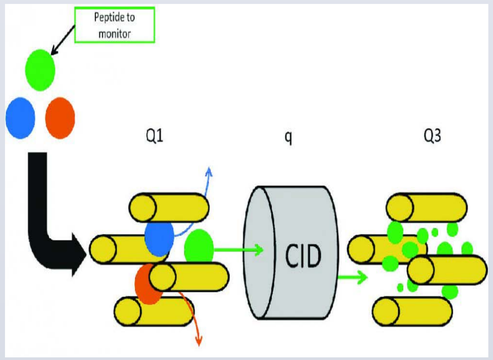
ABSTRACT

The chemical reactivity within gas phase p-chlorofluorobenzene-ammonia heterocluster cations $\{(ClFC_6H_4)_m\text{-}(NH_3)_{n=1\text{-}8}\}^+$ have been investigated via a triple quadrupole mass spectrometer and through DFT calculations. Collision induced dissociation (CID) experiments were performed in which mass selected cluster ions are accelerated into a cell containing argon gas and the resulting products then subsequently mass analyze. Two interesting reaction results are observed. The first is that the 1:1 peak is missing. Further investigation is underway to find out why this is the case. The second is survey from the CID experiments display the magic number for $(ClFC_6H_4)_6^+$ with helium gas. The reactions between p-chlorofluorobenzene cation and ammonia involve intra-cluster proton transfer of ammonia giving clusters of high stability.

OBJECTIVES

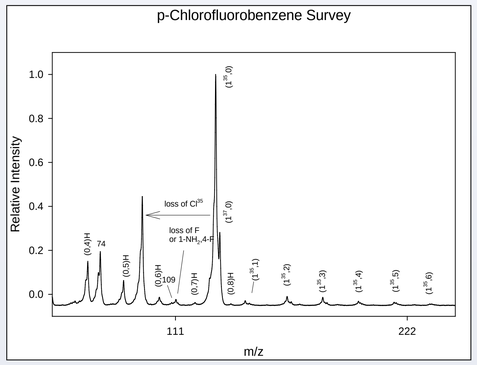
- Triple quadrupole mass spectrometer
- Collistion induced dissociation (CID)
- Metastable decay
- "Magic number" for $(ClFC_6H_4)_6^+$

Triple quadrupoles mass spectrometer



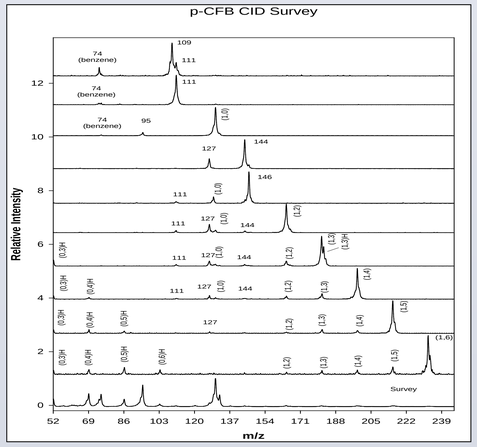
- Consist three quadrupoles
- Uses radio frequency to manipulate ions
- Ions form a continuous beam
- First and third quadrupole serve to identify and filter different masses
- Second quadrupole known as collision-induced dissociation which fragments the peptide into smaller cluster ions.

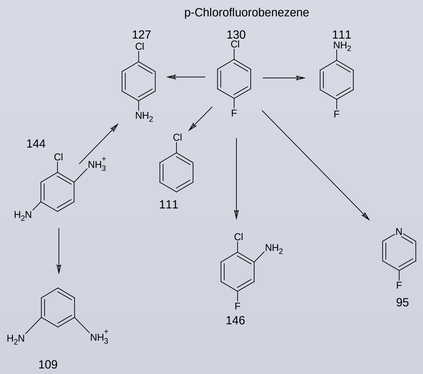
METHODDS



Collision-Induced Dissociation:

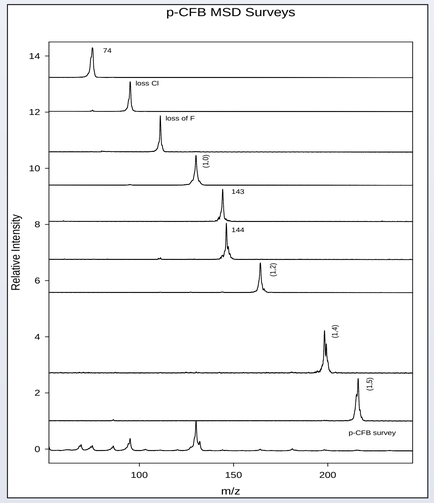
- Powerful technique to study parent ions and chemical reactions within mass-selected cluster ions
- A mechanism to fragment molecular ions in the gas phase
- fragment ions can be analyzed by a mass spectrometer
- Useful in determine partial or complete structure
- Achieve more sensitive and specific detection





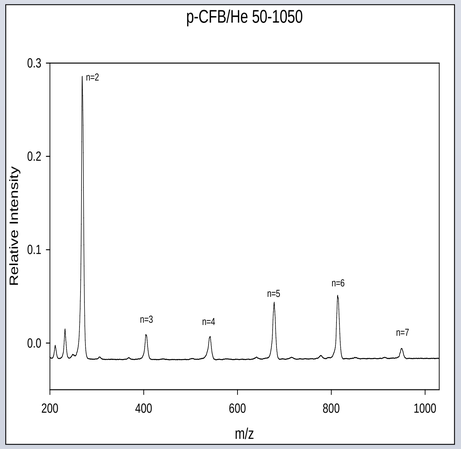
Metastable Decay

- To make a qualitative comparison with CID experiments for decomposition processes of individual cluster ions of the series
- Identical to those employed for the CID mass spectra except with no collision gas in the collision cell



"Magic number" for $(ClFC_6H_4)_n^+$

- Some cluster sizes, in particular n=6, are significantly more abundant than their nearest neighbors, n=3,4,5,7, such value of n is "magic number"
- Stabilization is due to an energetically favorable molecular arrangement
- Thermodynamically stabilized



RESULTS

The collision induced dissociated proton transfer reaction within the p-chlorofluorobenzene-ammonia cluster ions is size-restricted at $2 \le n \le 4$, for $n \ge 5$ clusters, ammonia monomers must be evaporated off at least n=4 for this reaction to occur

Metastable decay experiments confirm that the energetically favored reactions can lead to the formation of protonated $(ClFC_6H_4)_n^+$ clusters, in this case n=6, which is the "magic number"

ONGOING RESEARCH

To find out the reason why 1:1 peak on CID is missing

To study detail reactivity of "magic number" cluster size ion $(ClFC_6H_4)_6^+$

REFERENCES

Chiang, C.-T.; DeLeon, R. L; Kevin, S. S., Marek, F., Thomas F., Garvey, J. F.*J.Phys.Chem.*2008, 112,11565.

Kassner, J.L.; Hagen, D.E. Comment on "Clustering of Water on Hydrated Protons in a Supersonic Free Jet Expansion", *J.Chem. Phys.* 1976,64, 1860-1861

ACKNOLEDGEMENTS

McNair Conference at University of Maryland

Heather I. Welser, Ed.M.(Project Asistant)

Dr. Susan J. Ott (Director)

Dr. James F. Garvey(Faculty Mentor)

Kristin Butterworth (Grad Student)