DEPARTMENT OF CHEMISTRY

LEHIGH UNIVERSITY.

Graduate Student Dissertation Defense

Tuesday, April 25, 2017

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"Matrix Isolation Studies of Ionic CO_2 Clusters and Improvements on the Counter Ion Co-Deposition Technique"

Matrix isolation spectroscopy is method which allows for the study of reactive species by trapping them in the inert environment of a cryogenic rare gas matrix. Matrix isolation studies involving ions are limited due to the requirement that charge of the matrix remain neutral. A focus of the research in the Moore group was developing improved methods of ion delivery for matrix isolation experiments. We present on the development and implementation of an ion delivery method which allows for two mass selected beams of oppositely charged ions to be simultaneously deposited into a matrix. Preliminary results from the simultaneous deposition of Cu^- and SF_5^+ in a CO-doped argon matrix will be presented. To our knowledge, these experiments are the first time multiple mass selected beams of ions have been successfully deposited into a cryogenic matrix.

A low temperature, matrix isolated equilibrium of two CO_{2}-- dimer anion clusters was identified. The separated CO_2 dimer anion, $(CO_2)(CO_2^-)$, reversibly interconverts with the oxalate-like $C_2O_4^-$ species between 19K and 23K, suggesting the two structures are in thermodynamic equilibrium. The associated van't Hoff plot has a linear trend and indicates the reaction is endothermic and driven by a large increase in entropy. An independent kinetic analysis of the system confirms the thermodynamic values found from the van't Hoff analysis. Our findings suggest the thermodynamically stable structure is $(CO_2)(CO_2^-)$, which is in contrast to existing computational studies on the system. We believe a solvating effect by the matrix stabilizes the separated structure. These results may provide insight into understanding the nature of ion core switching trends in larger CO_2 anion clusters.

2:00 PM · STEPS · Room 101