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MICHAEL GOODRICH
DEPARTMENT OF CHEMISTRY

Ion Delivery in Matrix Isolation Spectroscopy and the Characterization of Cryogenic Reactions

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Matrix isolation spectroscopy is a 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. The first portion of this seminar will discuss 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.

The second project that will be discussed is the characterization of a low temperature, matrix isolated equilibrium process. The separated CO_2 dimer anion, $(CO_2)(CO_2^-)$, trapped in an argon matrix is known to convert to an oxalate-like $C_2O_4^-$ upon annealing the matrix to 25K. We found that subsequently holding the matrix at 10K caused the $C_2O_4^-$ species to fully convert back to $(CO_2)(CO_2^-)$. Further analysis revealed that the two species reversibly interconvert between 19K and 23K, suggesting they 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 plot. Interestingly, studying the process in a krypton matrix revealed that the reaction is more endothermic than in argon, but has nearly the same entropy.

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