FREISER LECTURE

Professor Michael A. Duncan

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"Infrared and UV-Visible Photodissociation Spectroscopy of Organometallic Cations"

Cold cations of metal ion-acetylene and metal ion-benzene complexes are produced in a pulsed supersonic molecular beam by laser vaporization. These ions are mass-selected and studied with infrared and UV-visible laser photodissociation spectroscopy and photofragment imaging. Infrared spectra are compared to the predictions of theory to elucidate the structures of these ions and their electronic states. Transition metal (Fe, V, Co, Pt) complexes with acetylene are studied in the C-H stretching region, revealing the formation of cation-p complexes or cycloaddition products.[1,2] The spectra reveal coordination numbers, ligand vibrational shifts as a function of cluster size, and the occurrence of intracluster cyclization reactions to form benzene. UV-visible laser spectroscopy reveal specific electronic states for Ag^+(benzene) and Mg^+(benzene) complexes, but continuous spectra for Fe+(acetylene), Fe^+(benzene) and U^+(benzene).[3-6] The threshold for photodissociation in the latter cases provide the determination of the bond energies.[3-6] Photofragment images also probe dissociation energies for Fe^+(acetylene), Fe^+(benzene) and Mg^+(benzene).[3-5] Computational studies at the DFT level complement all of these experiments.

References

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[3] J. E. Colley, N. J. Dynak, J. R. C. Blais, M. A. Duncan, "Photodissociation Spectroscopy and Photofragment Imaging to Probe the Dissociation Energy of the Fe^+(Acetylene) Complex," *J. Phys. Chem. A* **127**, 1244–1251 (2023).

[4] J. E. Colley, N. J. Dynak, J. R. C. Blais, M. A. Duncan, "Photodissociation Spectroscopy and Photofragment Imaging to Probe the Dissociation Energies of the $Fe^+(Benzene)_{1,2}$ Complexes," *J. Phys. Chem. A* **127**, 2795–2804 (2023).

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