Chemistry 501 Seminar

Thursday, February 9, 2012
3:45 p.m. Buehler 415
Seminar Webcast
Refreshments in Buehler 412 at 3:30 p.m.

Dr. Michael A. Duncan

Franklin and Regents' Professor
University of Georgia

Hosted by Dr. Robert Compton

"Infrared Spectroscopy of Cold Ions and their Clusters: Inorganic and Organic Chemistry in the Gas Phase"

Biography

Michael A. Duncan is Franklin Professor and Regents' Professor of Chemistry at the University of Georgia. A native of Greenville, SC, he attended Furman University (B.S. Chemistry, 1976), where he worked with Lon B. Knight in matrix isolation spectroscopy of metal radicals studied with electron spin resonance (ESR).Duncan began graduate school at Rice University in the fall of 1977, where he worked with Prof. Richard E. Smalley. At Rice, he and his partners developed laser ionization and pulsed nozzle/laser vaporization for the production of metal-containing clusters in the gas phase. He received the Ph.D. in Physical Chemistry in 1982. The molecular beam machine built during his graduate work was used in 1985 by the Smalley group to discover C_{60}, which led to the Nobel Prize for Smalley, Curl and Kroto in 1996. Duncan received a postdoctoral fellowship from the National Research Council (NRC) to work at the National Bureau of Standards (NBS) and the Joint Institute for Laboratory Astrophysics (JILA) in Boulder, CO with Professor Stephen Leone. At JILA (1981-83), he worked on laser spectroscopy of molecular ions to study their collisional energy transfer processes. He joined the University of Georgia in the fall of 1983. At Georgia, Duncan uses laser vaporization, molecular beams, time-of-flight (TOF) mass spectrometry and laser spectroscopy to study a variety of metal containing clusters. This work includes "solvated" metal cations (Mg^+-H_2O, Ca^+-H_2O), metal ion π complexes (Ni^+-C_2H_2, V^+-benzene) and novel metal carbonyls. Other studies focus on exohedral metal fullerene clusters (Fe_x-C_{60}), metal oxide clusters and metal-carbides (Ti_8C_{12}). New work includes the synthesis of ligand-coated nanoparticles in macroscopic quantities using a laser vaporization flowtube reactor. In addition to this metal cluster work, Duncan has developed new methods to study protonated molecular ions and their clusters ($H^+(H_2O)_n$, $H^+(CO)_n$), as well as small carbocations ($C_3H_3^+$, $C_6H_7^+$), both of which are studied with infrared laser spectroscopy. Duncan is a Fellow of the *American Physical Society* (2001) and the *American Association for the Advancement of Science* (2004). Since 1998, he has been a Senior Editor of the *Journal of Physical Chemistry*. He is recipient (2007) of an Alexander von Humboldt Fellowship for work done at the Fritz Haber Institute in Berlin. He is the inaugural recipient (2011) of the *Experimental Physical Chemistry Award* given by the Physical Chemistry Division of the American Chemical Society. He also received the 2011 *Lamar Dodd Award* at the University of Georgia.

Abstract

Cold cations of metal-molecular complexes or of small hydrocarbons (aka "carbocations") are produced in a pulsed supersonic molecular beam by laser vaporization or pulsed discharge sources. These ions are mass-selected and studied with infrared photodissociation spectroscopy. Infrared spectra are compared to the predictions of theory (DFT and/or MP2) to elucidate the structures of these ions and, in the case of metal ions, their electronic states. Transition metal (Co, V, Mn, Cu) carbonyls or carbon dioxide complexes are studied in the C-O and CO_2 stretching regions. The spectra reveal coordination numbers, ligand vibrational shifts as a function of cluster size, and the occurrence of intracluster reactions. Ligand shifts compared to the predictions of density functional theory provide the spin state on the transition metal cation and how it changes upon progressive ligand addition. Carbocations ($C_2H_3^+$, $C_3H_5^+$, $C_3H_3^+$, protonated benzene, protonated naphthalene) are studied in the C-H stretching and fingerprint regions of the spectrum. Several of these species exhibit more than one structural isomer, allowing investigation of the multiple minima on their potential surfaces. Unusual vibrations are detected for non-classical structures with bridging hydrogens. Protonated naphthalene has spectral lines relevant for the Unassigned Infrared Bands seen in interstellar gas clouds.

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