Glenn T. Seaborg Center Seminar

Imaging Mass Spectrometry and Electronic Structure of Organic Molecules

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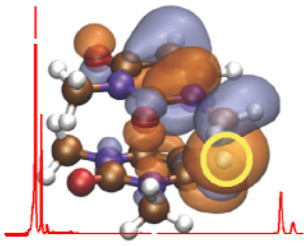
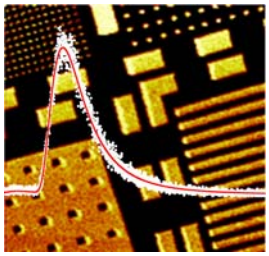
Wednesday, October 03, 2012
4:00 - 5:00 pm
Building 70A, Room 3377

Vacuum ultraviolet (VUV) photoionization performed at the Advanced Light Source in conjunction with theoretical calculations are being used to gain insight into proton transfer mechanisms, solvation and electronic structure in organic molecules and clusters relevant to biofuel production and biochemical processes. A major focus is on the effects of non-covalent interactions, i.e., hydrogen bonding, stacking, and electrostatic interactions, on the ionization energies of the individual molecules and the changes in electronic structure (i.e., hole localization) upon clustering and solvation induced by these interactions.

Proton transfer is ubiquitous in chemistry and biology, but has always been described in the context of hydrogen-bonding networks ("proton wires") acting as proton conduits. Efficient intra-molecular ionization-induced proton transfer for a system with no hydrogen bonds,1,3 dimethyuracil dimer, has been demonstrated by our group and will be discussed.[1] Micro-hydration of 1, 3-dimethyluracil shuts down this proton transfer and a new pathway arises at higher ionization energies where proton transfer occurs via the water network. This provides a window into following proton transfer in experimentally localized and theoretically tractable systems.



VUV photoionization mass spectra of dimethyluracil dimer and molecular orbital of its ion. (1)



VUV LDPI image of a polymer photoresist and TOF of laser desorbed adenine. (2)

The evolution and manipulation of natural systems requires detailed knowledge of complex heterogeneous chemical reactions that typically cannot be understood by simple bulk analysis. Chemical imaging methods provide simultaneously information of a sample's chemical composition and spatial heterogeneity. Laser desorption (LD) coupled with vacuum ultraviolet photoionization (PI) provides unique insight into the fragmentation dynamics of organic molecules.[2] Knowledge gained from these fundamental studies are being applied to imaging plant biomass, following molecular transformations in soil organic matter, and establishing the chemical composition and structure of biological material. I will discuss recent progress in elucidating the chemical structure of melanin – a material that has potential for novel optical and electronic applications.

1. A. Golan, K. B. Bravaya, R. Kudirka, O. Kostko, S. R. Leone, A. I. Krylov, and M. Ahmed "*Ionization of stacked dimethyluracil dimers leads to facile proton transfer in the absence of H-bonds*". Nature Chem. (2012), **4**, 323
2. O. Kostko, L. K. Takahashi, and M. Ahmed "Desorption Dynamics, Internal Energies and Imaging of Molecules from Surfaces with Laser Desorption and Vacuum Ultraviolet (VUV) Photoionization", Chem. Asian. J. (2011) **6**, 3066

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