Biology and Environmental Working Group

Three projects were presented and discussed at the Biology and Environmental working group that were suggested to be conducted at the proposed ALFF facility. All three projects described user projects that would utilize the free electron laser to tackle problems centered in other scientific areas. Most of the work and discussion focused on the use of the FEL for single photon ionization (SPI) applied to problems in mass spectrometry. Many of the underlying issues regarding FEL performance requirements were covered in a separate working group and were therefore not discussed here. In the following, the suggested projects will be briefly summarized.

Analyzing Nanoscale Organic Surfaces – From Conducting Polymers to Biomaterials (Luke Hanley)

Organic and polymeric films are used in a wide array of applications including biomaterials and molecular electronics. Chemical analysis of these films is limited by their frequent lack of order, chemical diversity, and sensitivity to radiation damage. Several problems in organic film analysis were presented. X-ray photoelectron spectroscopy is perhaps the primary analysis method of these films, but it often does not provide sufficient chemical resolution to distinguish different species or determine their molecular weight. A typical example is shown below [1]: several polythiophene and non-polythiophene films are produced by surface polymerization by ion assisted deposition (SPIAD). These films display very different optical properties, yet their C 1s x-ray photoelectron spectra are nearly identical.

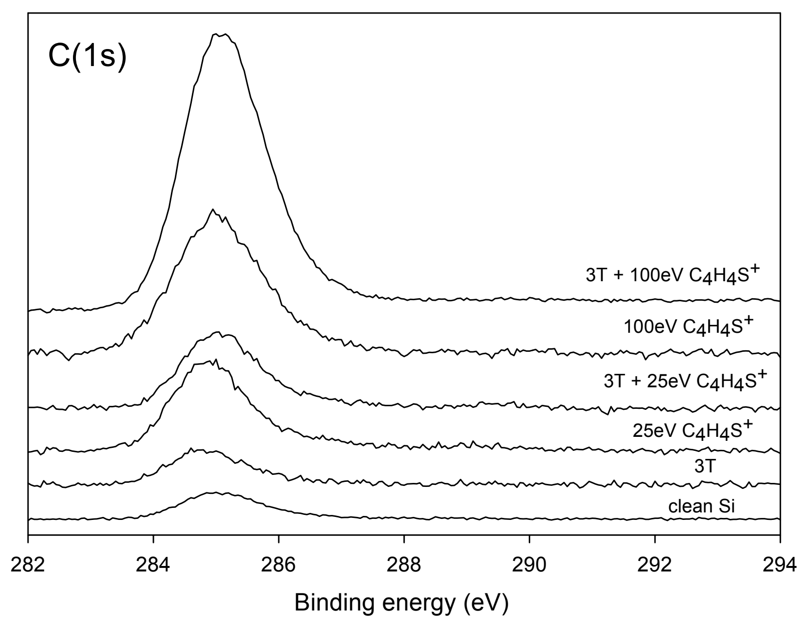

Figure 1: C 1s x-ray photoelectron spectra of several polythiophene and non-polythiophene films are produced by surface polymerization by ion assisted deposition (SPIAD) on silicon [1].

Single photon ionization of ion or laser desorbed neutrals has previously been shown to be extremely useful for the analysis of such materials [2-4]. However, previous work has relied upon 118 nm radiation produced by 9th harmonic generation from the 1064 nm fundamental of a Nd:YAG laser. This method is very inefficient, experimentally difficult for widespread application in mass spectrometry, and does readily not allow tuning of the photoionization wavelength. Use of the FEL overcomes these difficulties and therefore displays great promise for organic and polymeric film analysis.

Analysis of organic film electronic structure is also important, especially in the valence band. For example, many useful optical and electronic properties of conducting polymers are determined in part by their highest occupied and lowest unoccupied molecular orbitals. However, complete analysis of these orbitals is not possible by traditional (single photon) ultraviolet and x-ray photoemission. Two photon photoemission has been shown to be a superior method for their analysis [5]. However, this method at limited by an inability to produce intense radiation at wavelengths below 200 nm. The FEL will readily permit such experiments.

Study of Atmospheric Aerosols by Laser Post Ionization Time-of-Flight Mass Spectrometry at the Argonne Free Electron Laser Facility (Martina Schmeling)
The radiative properties of atmospheric aerosols play a critical role in modeling important climatic phenomena such as global warming. A system was described for the collection of these aerosols for elemental analysis by x-ray fluorescence. The chemical content of atmospheric aerosols has begun to be probed by mass spectrometric techniques. However, these methods tend to combine laser desorption and ionization in a single step, greatly complicating the mass spectral analysis of these highly heterogeneous particles. A new protocol was described whereby collected aerosol particles will be analysis by single photon ionization mass spectrometry on the SPIRIT instrument. These aerosol mass spectrometry experiments will determine surface and bulk composition of single particles which will provide insight into internally vs. externally mixing of the particles, their surface coating, and their reaction potential. Together with bulk chemical composition, this information will be used to estimate radiative properties.

Analysis of Biological Samples (with no matrix) Using Large Gold Cluster Bombardment and an Orthogonal TOFMS (J. Albert Schultz and Amina Woods)
Large molecule mass spectrometry has become a routine tool in the fields of medicine, biology, biochemistry, and chemistry. Matrix assisted laser desorption ionization is one of the standard tools for such analyses, which are typified by the determine of protein and peptide primary structure [6,7]. Secondary ion mass spectrometry using atomic ions does not compare in performance to matrix assisted laser desorption ionization for the analysis of peptides, but polyatomic projectiles have been shown promise in this regard [4]. Results were presented here on the use of large gold clusters (Au_{400}^{+}) as projectiles for desorption of peptides for mass spectrometric analysis. Large enhancements were observed with gold cluster deposition, indicating that this method might be extended into the analysis of a wide variety of high molecular weight biopolymers. These experiments would be further enhanced by combination with single photon ionization of the desorbed neutrals.

Other Mass Spectrometric Applications (Group Discussion)

The group discussion illuminated a variety of potential mass spectrometric applications of single photon ionization. These included noncovalent complexes of biomolecules (peptide-peptide, peptide-lipid, peptide-surface) as well as covalent complexes (DNA-small molecule adducts). Single photon ionization would also be useful for reionization in drift cell experiments which are now being applied as a type of gas phase chromatography of biomolecules. One point was made that many experiments in single photon ionization for biological mass spectrometry could be performed in the SPIRIT apparatus and perhaps one or two other instruments to be permanently installed on the FEL. Such shared instrumentation would allow widespread application of single photon ionization to a variety of complex mass spectrometric analyses.

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