

Report on the Workshop for Potential Users of the Argonne Linear Free-Electron Laser Facility (ALFF)

October 30-31, 2003
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1. Background

A recently developed high-gain free-electron laser (FEL) at Argonne is based on the injector linac of the Advanced Photon Source (APS) and a 20-m undulator installed in the low-energy undulator test line (LEUTL) tunnel. This LEUTL FEL has demonstrated the ability to deliver sustained operation over a tunable wavelength range from 660 nm to 120 nm [1,2] and was the first self-amplified spontaneous emission FEL in the world to reach gain saturation at visible and ultraviolet wavelengths, establishing the feasibility of such devices and underscoring their promise of one day achieving laser-like operations well into the x-ray spectrum [3,4].

At present, the LEUTL FEL is the only operating laser system in the world capable of providing intense light pulses that are broadly tunable in the vacuum ultraviolet (VUV) spectral region. A small number of proof-of-principle experiments designed to take advantage of these unique properties are being pursued at the LEUTL end station. However, beam time available for FEL user experiments is severely limited due to the fact that the linac is normally used exclusively for the APS running in top-up mode. Even when the linac is available, its use is shared with other activities. Funding is needed to turn this one-of-a-kind system into a robust, full-scale user facility capable of servicing a vibrant user science program. The proposed Argonne Linear FEL Facility (ALFF) would be the first high-gain FEL user facility in the U.S. and one of only two in the world [5].

There are three principal improvements required for turning the LEUTL FEL into the ALFF facility. First, the undulators need to have their gap increased and need to be tuned for operation in the wavelength range between 55 nm and 450 nm. This would involve a minimal amount of perturbation to the existing diagnostics and beam-guiding systems. Second, upgrades to the linac and gun components are imperative for interleaving operation and greater pulse stability. Interleaving involves dynamically sharing the beam from the linac between top-up of the APS storage ring and servicing ALFF, and will allow the linac to be 96% available for the FEL users compared to the current 3% availability. Finally, improvements to and expansion of conventional facilities are needed to support a full-time user experimental program in the end station. The performance parameters of the existing LEUTL and proposed ALFF are summarized in Table 1.

Vacuum ultraviolet radiation, with this unprecedented set of parameters, has the potential to address scientific challenges in a number of fields. As shown in Figure 1, the pulse energy level delivered by the ALFF represents a significant enhancement over what is presently available in the VUV range. Note also that the tuning ranges of the laboratory lasers in Figure 1 are rather limited in contrast to the broad tuning range of the FEL source. The pulse energy makes possible experiments requiring the saturation of absorption or photoionization steps. The peak brilliance attainable is ideal for driving nonlinear processes, and the pulse length is short enough to probe molecular motion, for example bond dissociation. Some examples of experiments that can be done at ALFF are listed in Appendix A.

The ALFF end station currently contains a state-of-the-art mass spectrometer, referred to as SPIRIT (single-photon ionization or resonant ionization to threshold), which is specifically designed to use the VUV beam from ALFF as a photoionization source. SPIRIT was built by a

core user group and is currently being used for experiments in trace isotope measurement, fundamental ion-solid interactions, and biomolecule photoionization. The SPIRIT instrument consists of a vacuum system with a state-of-the-art ion source and time-of-flight mass spectrometer, a microfocus ion probe, a microscope with integrated laser desorption, and an excimer laser for instrument testing and two-color experiments.

Table 1: Main FEL Parameters for the Existing and Proposed FEL Facilities at ANL

Parameter	Existing (LEUTL)	Proposed (ALFF)
Photon Energy Fundamental Tuning Range (wavelength)	2-10 eV (600-120 nm)	2.7-22 eV (450-55 nm)
Bandwidth (FWHM)	$\geq 0.4\%$	0.4-0.3%
Pulse Length (FWHM)	≤ 300 fs	≤ 300 fs
Photon Energy/Pulse Delivered to Experiment	30 μ J	> 200 μ J
Minimum Beam Diameter at Experiment	1.0 mm	20 μ m
Repetition Rate	6 Hz	30 Hz
User Beam Available (time relative to storage ring)	3%	96%

The ALFF also provides an excellent opportunity to perform beam physics research that will lead to improvements in both the accelerator and FEL performance. High-performance beam diagnostics devices coupled with excellent stability of the accelerator system will allow experimental techniques in FEL studies that have either been difficult or impossible. Several challenges in accelerator/FEL development research that are candidates for investigation are: electron beam brightness enhancements; extensions to the wavelength; creation of femtosecond pulses; generation of multiple arbitrary wavelengths in a single pulse; and seeding techniques to stabilize the output amplitude, improve its longitudinal coherence, reduce the bandwidth, and reduce the pulse duration. Although these are important topics and are an integral part of the ALFF proposal, they were beyond the scope of this workshop and so were only discussed in passing. A future workshop will be organized to address these beam physics topics in more detail.

A three-year upgrade plan has been developed that will allow groundbreaking user science experiments, instrument commissioning, and the accelerator/FEL development research to proceed in parallel. After the three-year period, ALFF will be operated in the same manner as the other APS beamlines, with beam time awarded based on peer-reviewed proposals. A majority of the accelerator and FEL system is already in place and functional. This includes operational and technical support by virtue of the need for the linac in normal APS operations. With this upgrade, at a small fraction of the cost of a new FEL facility, the user community would have a unique world-class VUV FEL at its disposal.

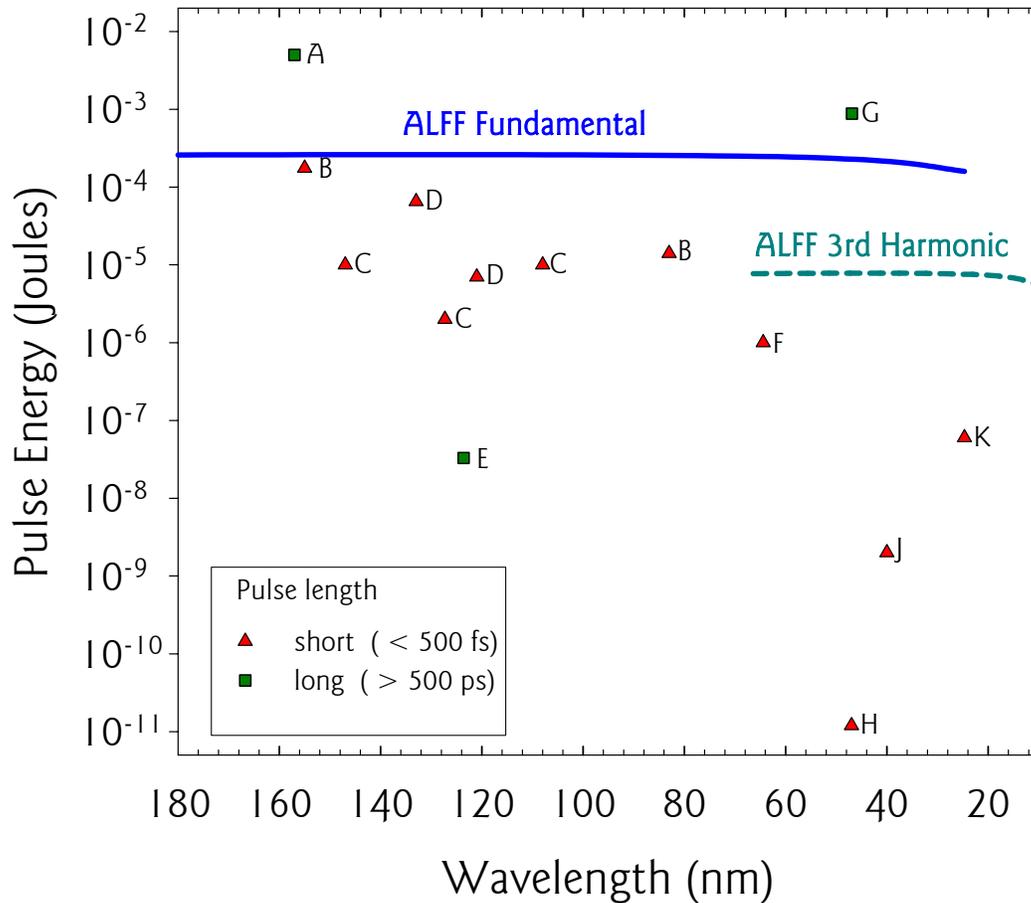


Figure 1: Argonne Linear FEL Facility: pulse energy compared to laboratory sources. Laboratory sources are primarily beams generated by nonlinear mixing or high harmonic generation in a gas. Tunability in narrow spectral ranges (1-5 nm) has been achieved in some cases. No broadly and continuously tunable source has been demonstrated throughout the VUV.

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2. ALFF Workshop Overview

2.1 Summary

On October 30-31, 2003 over 60 scientists gathered at ANL to discuss potential science that could be done with a fully operational user facility dedicated to delivering widely tunable, short pulse, high peak power vacuum ultraviolet light. The charge given to the workshop by J. Murray Gibson, ANL Associate Lab Director for the Advanced Photon Source, included the following two points:

1. What are the scientifically important experiments that can only be done with the proposed ALFF facility?
2. Are the combined ALFF characteristics of pulse energy, tunability, pulse length, and coherence sufficiently unique to justify establishing a user facility at this time?

To fulfill this two-point charge, special emphasis was placed by the workshop committee on two goals. First, scientists were invited who work in areas where the lack of powerful, tunable VUV is a limitation to speak about their current research and to speculate on the science that would be uniquely possible with the ALFF. Second, while many of the same scientists have expertise in using lasers and other VUV sources, it was considered crucial to invite scientists explicitly working on the development of tabletop VUV systems. In addition to addressing the second charge question, the purpose of inviting people with expertise in VUV source development was to raise awareness of the state of the art in tabletop VUV and soft x-ray sources, and to provide a discussion on potential combinations of FEL and tabletop sources (for example, in seeding and pump-probe arrangements).

This report briefly summarizes the talks presented at this workshop and highlights some of the user needs that this facility can fulfill. The full presentations may be accessed online at

www.aps.anl.gov/conferences/ALFFworkshop.

The workshop was organized around four working groups to focus the discussions among scientists with similar backgrounds. These groups were: Atomic, Molecular, Optical (AMO) and Chemical Physics; Cosmochemistry and Geochemistry; Materials Science; and Biology and Environmental Science. A plenary session included a background talk on the LEUTL followed by a lecture from one scientist in each of these areas. The background, presented by Steve Milton, delineated the existing FEL capabilities as well as the nature of the proposed upgrade, specifically the interleaving operations that will allow for a large number of user beam hours, similar to the level that the APS storage ring users now enjoy. A higher repetition rate and a shift in tuning range to shorter wavelengths was also proposed.

Don Burnett (CalTech) presented a talk highlighting interesting questions in cosmochemistry and geochemistry that could be addressed with ALFF. Small particles referred to as dust or grains have been recovered from meteorites and are being collected by high flying aircraft, as well as one NASA sample return mission that has passed through the tail of a comet. These grains sometimes have *extrasolar* compositions that yield information about stellar

evolution. Another sample return mission, Genesis, is collecting the solar wind in coupons that will be archived in Houston. All of these samples require instruments with exquisite sensitivity and precision in isotopic measurements. Although state of the art microprobe instruments may be adequate for measuring transition metals present in these grains, a number of cornerstone scientific discoveries, including validation of the x-wind theory, will await a better measurement of light elements and molecules, which can be ionized in the VUV with ALFF. The high pulse energy and tunability of ALFF will maximize the ability to quantify the composition of these tiny dust particles.

Nick Lockyer (UMIST) showed a set of studies applying cluster ion beam/secondary ion mass spectrometry to problems of biological interest. These studies could be performed with an instrument such as SPIRIT, which is now operational at the LEUTL end station. Using C_{60} ion beams to analyze biological materials is a novel approach that greatly reduces damage due to the primary ion beam on freeze-fractured or freeze-dried tissues, allowing for much more of the sample to be analyzed. This technique in principle allows depth profiling of biological specimens, for example single cells. ALFF could dramatically extend this technique by allowing for selective, efficient photoionization of biological molecules using the VUV beam.

Robert Gordon (UIC) presented work from his group on using light for dissociation and to control the motion of molecules. Velocity-map imaging can be used to help understand the photodissociation of small molecules such as C_6H_5I , but currently multiphoton techniques are used since powerful, tunable VUV lasers do not exist near the ionization energies of interest. A specific example of looking at iodine photodissociation from 90-100nm with ALFF was suggested, and using pump-probe photoelectron-photoion coincidence to determine the product channels. Furthermore, by accessing high Rydberg states in molecules with the ALFF beam, it may be possible to deflect molecules in a coherent beam by using their dynamic polarizability. Finally, control of branching ratios by tuning the phase of mixed beams has been demonstrated and could be applied in the single-photon regime at ALFF, which may be simpler than the multiphoton regime due to the well-defined electronic structure.

Bruce King (U of Newcastle, Australia) highlighted work performed on fundamental studies of sputtering with SPIRIT, representing the Materials Science working group. Sputtering occurs when an energetic (usually keV) ion beam impinges on a solid, creating a *collision* cascade that causes the ejection of a few secondary particles, usually neutral atoms but sometimes dimers or clusters. Sputtering of alloys is not completely understood, and a result obtained with SPIRIT showed a surprising matrix effect in a Au-Al system, the first such effect seen in a purely metallic system. This result is discussed in detail in section 3.3.1.

Two of the other results from the first year of experiments with SPIRIT that were presented included the first measurement of a nucleobase adduct by VUV photoionization and the first polypeptide soft ionized by a free-electron laser. In the first experiment, guanine was sputtered with an ion beam from a cinnamic acid matrix. The LEUTL beam was able to efficiently ionize the guanine, along with the matrix, and a number of interesting reaction products between the two. A guanine-phenyl adduct was among the species identified by mass spectrometry (see Figure 2). The high sensitivity of this technique, coupled with the ability to identify specific adducts, has important implications in measuring carcinogens and understanding the mechanisms by which they cause cancer.

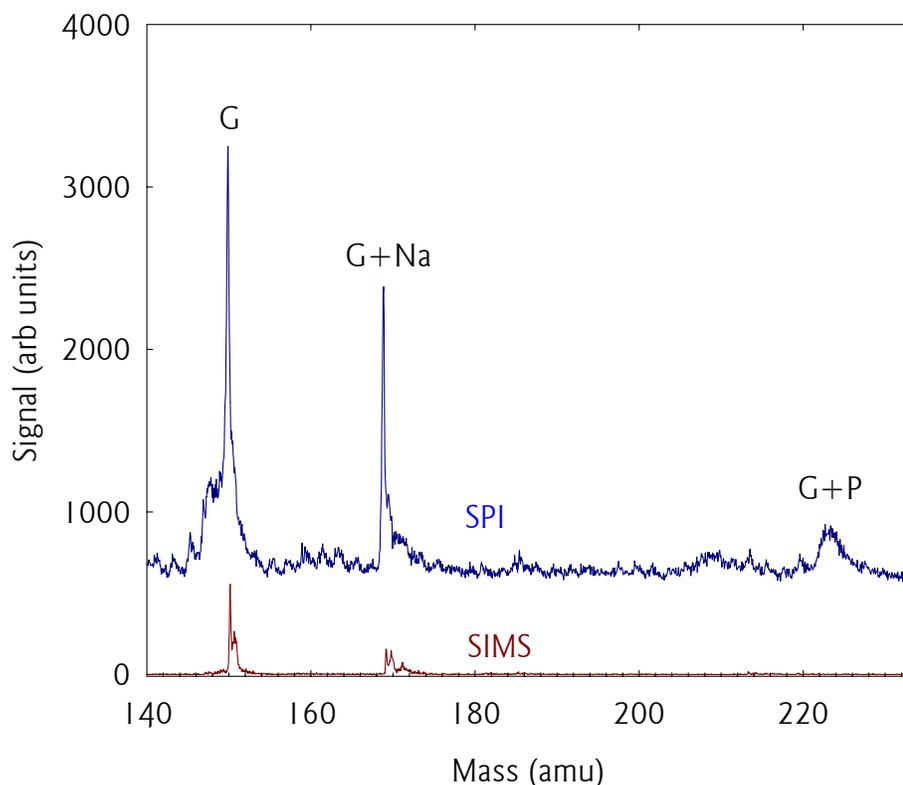


Figure 2: Single photon ionization (SPI, top) time-of-flight mass spectrum of guanine (G) with sodium (G+Na) and phenyl (G+P) adducts. The guanine was desorbed with an ion beam and photoionized with the LEUTL beam tuned near 157 nm. The detection of the G+P adduct is at least 100 times more sensitive with the SPI compared to secondary ion mass spectrometry (SIMS, bottom). The SPI spectrum has been offset for clarity.

In the second experiment, substance P was laser desorbed from a cinnamic acid matrix, and photoionized with a VUV pulse (140 nm) from the FEL. Remarkably, the molecule was softly ionized, indicated by the lack of fragmentation in the mass spectrum. Soft ionization allows the possibility of measuring the intact mass of biological molecules, which is important for identification, and measuring low abundances of molecules above a substantial background.

The plenary talks were followed by a presentation on state of the art tabletop sources in the VUV to soft x-ray spectral range. Margaret Murnane (JILA) summarized two promising technologies: high-harmonic generation (HHG) in a capillary waveguide, and a capillary discharge driven laser plasma. The HHG sources are driven by high power, short pulse Ti:Sapphire lasers, and offer kHz repetition rates and modest pulse energy. The capillary discharge laser provides a nanosecond scale pulse with substantial energy, but is not tunable and operates at low repetition rates. Four and six-wave mixing schemes were also presented, and an explanation was given for persistent limitations of power scaling such methods. Essentially, the phase matching conditions that allow for high conversion efficiencies are very difficult to achieve in the VUV relative to the UV, visible, or even EUV wavelengths.

Following Prof. Murnane's presentation, a panel discussion ensued regarding whether existing lasers could potentially deliver beam with comparable parameters to ALFF. The consensus of the expert participants was that while there were interesting developments in VUV sources, ALFF offers significant and unique capabilities in the combination of pulse energy, short pulse duration, and tunability, which are essential for some important experiments.

Working groups met for several hours to allow scientists within each group to give more detailed topical presentations. Each working group leader prepared a brief presentation summarizing the talks and discussions in that group, which was then delivered at a final closeout session of all workshop participants. The working group leaders also met with the workshop committee following the closeout session, and prepared short reports on their group. These reports are included in section 3.

2.2 Conclusions

One of the expectations of the workshop was to learn from the potential users what qualities they sought in the ALFF facility. The parameter table distributed to the participants (see Figure 1 in section 1) was largely validated. The pulse energy and tunability sparked the most interest. Availability was clearly desirable, and it was recognized that interleaving operations is crucial to achieving the stated levels of beam time. The pulse repetition rate was considered adequate for most of the proposed science, although this could be limiting for some cosmochemistry experiments requiring long averages for measuring isotope ratios. Nearly everyone was satisfied with the pulse duration. The bandwidth was considered too broad for some experiments requiring exciting atomic transitions, and this criticism initiated a discussion of FEL seeding methods that could be used to narrow the bandwidth and reduce wavelength jitter significantly.

There was also significant discussion of parameters not listed in the table. Timing stability would be important for any pump-probe type experiments. Methods for synchronizing a secondary laser to less than the pulse width (300 fs) are being developed elsewhere and it is expected that they could be implemented at ALFF in the proposed timescale. Pump-probe experiments that use the split FEL beam with a delay line (single color or with a harmonic) would also be an option for certain experiments.

Several users expressed concern about harmonic purity. The existing beam transport will provide an effective cutoff of wavelengths shorter than 40nm with standard coatings. Given that the most intense harmonic (3rd) will have about 1% of the intensity of the fundamental, for experiments requiring a fundamental wavelength shorter than 120nm, the harmonic intensities should be negligible (10^{-4} or less). For wavelengths longer than 120nm, cutoff windows can be used effectively with some beam intensity loss. Another intriguing possibility is to modify the undulator structure so that harmonic output is reduced.

It became clear that a number of different apparatuses could be used at ALFF. The existing SPIRIT instrument is appropriate for many materials analysis, cosmochemistry, and geochemistry applications. As described in section 3.1, the atomic, molecular, optical (AMO) and chemical physics experiments require a specialized instrument with different capabilities than SPIRIT. Al Schultz (Ionwerks) proposed installing an ion mobility-mass spectrometer that

would be ideal for many biological and environmental samples, as it would allow for an ambient pressure or low vacuum sample environment. Dave Keavney (ANL) has a photoemission microscope system that would be required for his experiments on magnetic domain imaging. A number of other experiments would require more modest space and power requirements. The existing space is not adequate for serving a full-time beamline with the number and diversity of users represented by those attending the workshop. A modest building extension was therefore proposed (Figure 3). The building structure, a second end station laboratory, and beam transport to that lab can be constructed from the funding request of \$5 million to DOE-BES. Completion of the offices, workshop and storage will require additional funding.

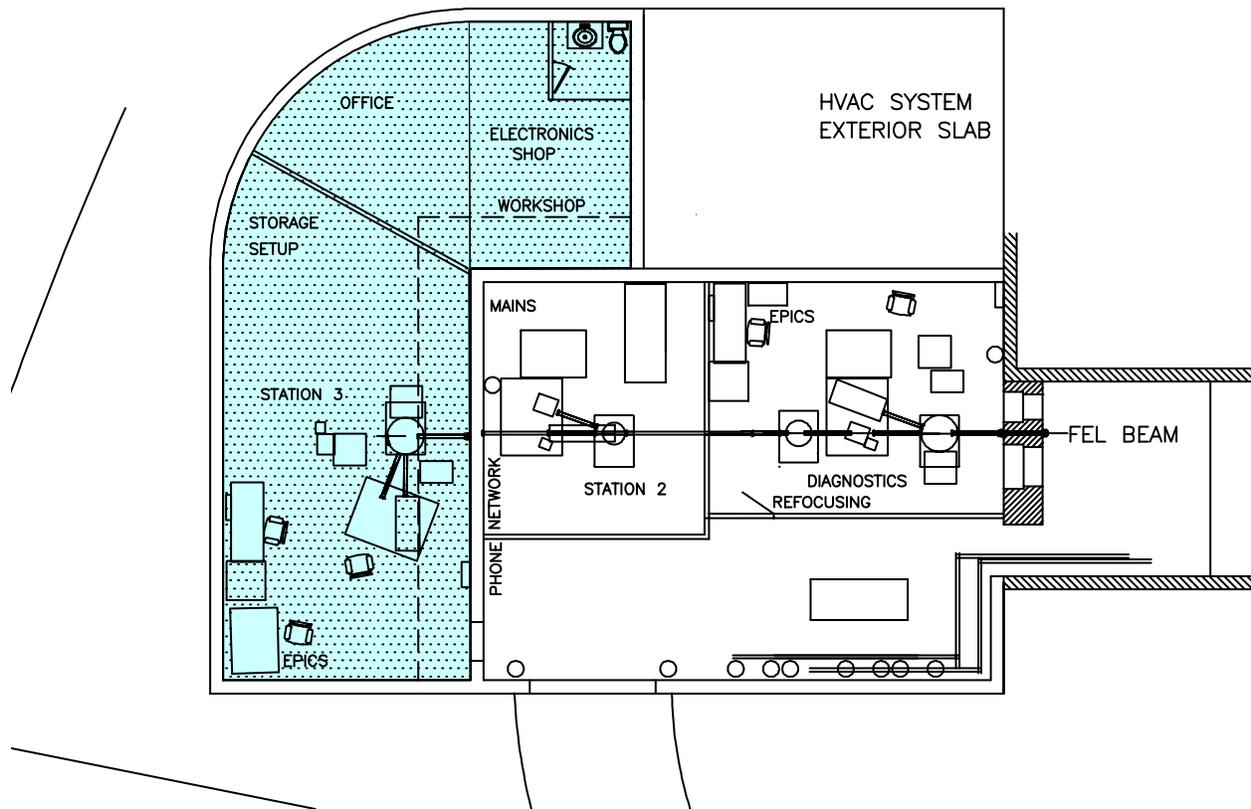


Figure 3: A proposed expansion of the end station at ALFF (shaded area). The existing laboratory would be complemented with two additional experimental stations, setup and storage areas, a workshop, restroom and office space, and a meeting area. Parking is not shown but would be available.

3. Working Group Summaries

3.1 AMO and Chemical Physics

Working Group Chair: Cheuk Ng, University of California at Davis

Photoionization is a basic phenomenon that sensitively depends on the electronic structure of an atom, cluster, or molecule. Understanding the mechanism of photoionization is intrinsically important and finds applications in many fields of physics and chemistry. Often, the results of a photoionization experiment can be corroborated with quantum mechanical calculations. Some examples of photoionization using ALFF for each type of species were addressed in this working group.

ATOMS

It is of considerable interest what happens to the bound electrons of an atom in the intense fields of a laser beam. Effects such as tunneling ionization or rescattering have been observed, but not much work has been done in the high-frequency regime (VUV wavelengths). The photoionization mechanism can be estimated to be dominated by multiphoton effects for the given ALFF parameters from Table 1, assuming a 10- μm focal spot. This indicates that the field is still relatively low and tunneling is not a likely factor. In this case, it is speculated that nonsequential double ionization may be possible, and that inner-shell holes may be generated through multiple steps.

One example of this nonsequential double ionization was described by Steve Pratt (ANL) for the case of a Kr atom. A pulse of 88.6-nm photons from ALFF may cause the following sequential excitations by three successive absorbed photons: (1) an excitation of a valence electron to a high Rydberg state, (2) a valence-valence transition, and (3) photoionization of the second electron. Field ionization then removes the electron in the $n \sim 35$ state. The photoelectrons can be examined by velocity imaging in the apparatus described below.

CLUSTERS

Clusters, consisting of two or more bound atoms (normally of the same element) represent the simplest form of condensed matter. Cluster formation is fundamentally related to chemical bonding, thin film growth, and phenomena such as phase equilibria and heterogenous nucleation. Measurement of the ionization potential (IP) of metal clusters shows a clear dependence on the cluster size, with the tendency of the IP to decrease and approach the work function of the bulk metal as the size increases. Reactions of metal clusters such as Nb₇₋₂₀ with Ar have also been studied using conventional UV lasers, as described by Mark Knickelbein (ANL) in his presentation.

The availability of ALFF will allow for IP measurements and reaction studies at photon energies above 6.4 eV. Therefore, essentially any size or composition of cluster or complex could be studied (provided that it can be formed). Dissociation of clusters induced by photoionization may also be studied at ALFF. Ultrafast pump-probe experiments were suggested, where a femtosecond UV laser dissociates a molecule, followed by the 300-fs ALFF

pulse for product detection by photoelectron spectroscopy. Finally, measurement of the optical response of clusters and nanoparticles in the VUV could be performed using action spectroscopies.

MOLECULES

Laurie Butler (University of Chicago) presented work on using VUV to study the ground state unimolecular dissociation channels of polyatomic radicals. In this experiment, a molecular sample in the form of a supersonic beam is intersected by a dissociation laser. The photofragments thus formed are sampled by VUV photoionization and detected by velocity ion imaging scheme. By selecting the VUV photoionization energy, structures of photoproducts, including isomeric radicals, can be determined. The velocity map imaging technique allows the determination of product angular distributions and translational energy distributions, from bond dissociation energies and potential barriers for dissociation can be deduced. By momentum matching, correlated product pairs can be unambiguously identified. Wavelength bandwidths for these experiments of 3-4% are acceptable. Experiments that were done with the pink beam at beamline 9.0.2 at the Advanced Light Source were presented. The time-averaged flux and brightness from ALFF will be comparable.

Experiments at the DUV-FEL, presented by Xijie Wang (BNL) have also demonstrated the utility of ion-pair imaging spectroscopy, in which velocity map images can be used as a direct measure of the internal energy in a dissociated species. Methyl fluoride dissociation at 13.5-14.0 eV was shown as an example. This type of experiment makes use of the high degree of linear polarization of FELs based on a planar undulator. The higher pulse energy available from ALFF will be valuable for further studies of this type.

The VUV ALFF source will be unique for ultrafast pump-probe studies due to the wide tunability of the ALFF source. The detailed photodissociation dynamics or energy transfer processes induced by photoexcitation using a femtosecond laser can be followed by a delayed VUV photoionization using the ALFF source. In this type of experiment, the resulting photoions or photoelectrons are detected. The photoelectron distribution provides information about the state of the excited molecular complex along the dissociation coordinate and the wave-packet dynamics for the fragments.

Two specific spectroscopic methods that could exploit the characteristics of ALFF were suggested by Cheuk Ng. In the first, two-color IR-VUV photoionization, the IR laser frequency is scanned with the VUV photoionization fixed below the ionization threshold of a molecular species. In this way, the IR spectrum of the neutral molecules can be measured with high sensitivity by detecting the photoions formed due to IR laser excitation. To obtain the absorption spectrum, the photoelectron signal at the ionization threshold can be monitored as the excitation laser frequency is scanned. Since the VUV ALFF is used as the probing photoionization light source, high optical resolution is not needed.

The second approach, two-color VUV-IR photoionization, is suitable for studies of the infrared spectroscopy of ions. In this experiment, the low resolution VUV ALFF source is used to excite the molecular to high- n Rydberg states prior to IR excitation of the ion core to discrete rovibrational states. The detection of the electron or ion resulting from the IR excitation

provides spectroscopic information on the corresponding ion. It has been demonstrated that the IR spectrum is independent of n over a wide range of n -values. Thus, a high-resolution VUV source is not needed. However, the high VUV intensity offered by the VUV ALFF source is expected to make the IR-VUV scheme highly sensitive.

APPARATUS

In order to carry out these experiments, the working group proposes to construct a portable, multi-purpose experimental apparatus as shown in Figure 4. The apparatus consists of a pulsed molecular beam production system, a time-of-flight (TOF) mass spectrometer, and a TOF electron detector. The molecular beam production system can be used to prepare metal clusters by laser ablation and radicals by laser photodissociation.

Furthermore, ion and electron multichannel plate (MCP) detectors can be replaced by ion and electron imaging detectors for the velocity imaging experiments described below. The types of experiments described in the following subsections can be performed using the molecular beam photoion-photoelectron apparatus of Figure 4.

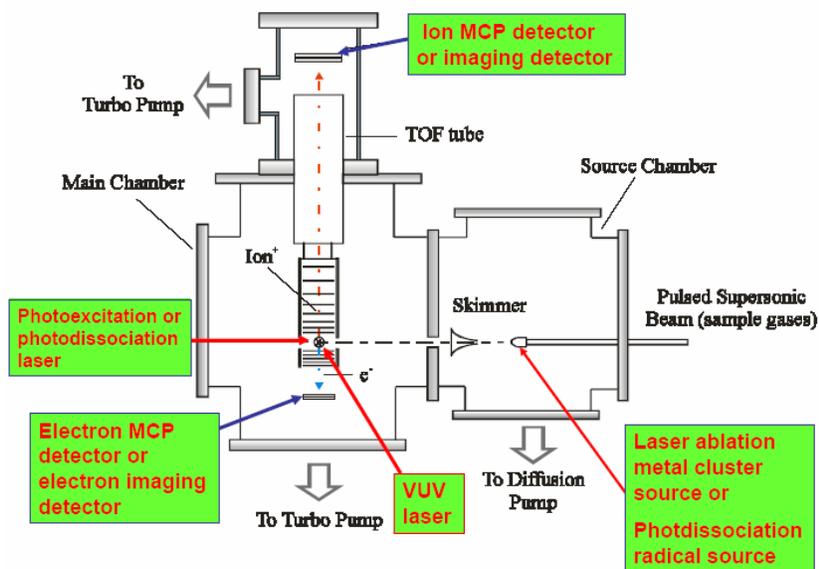


Figure 4: Molecular beam photoion-photoelectron apparatus.

3.2 Cosmochemistry and Geochemistry

Working Group Chair: Robert N. Clayton, University of Chicago

There are many unique opportunities for research in cosmochemistry and geochemistry that take advantage of the combination of brightness, tunability and access to short wavelengths. For many of these, the SPIRIT end-station is an essential part of the measurements. The

applications outlined here represent only a fraction of those possible, limited by the interests and expertise of those attending the workshop on October 30 and 31.

3.2.1. Resonant-ionization mass spectrometry (RIMS) of carbon, nitrogen, oxygen, and noble-gas isotopes in special samples

In a very successful collaboration between the Argonne National Laboratory and the University of Chicago, the RIMS technique has been developed for isotopic analysis of metallic elements in “stardust”: micrometer-sized mineral grains extracted from meteorites. These grains are found in the expanding or exploding envelopes of stars that preceded our own Sun, and carry the isotopic record of nuclear processes occurring in their parent stars. The RIMS technique involves a multi-photon photoionization of atoms that have been sputtered or ablated from a sample surface. For metallic elements, such as Ca, Ti, Fe, Sr, Zr, Mo, and Ba (which have been studied), the necessary resonant photons are in the energy range accessible by conventional lasers. For the non-metallic elements, C, N, O, Ne, the energy required for the initial excitation step is in the range 7–12 electron-volts, which is beyond the range of tunable conventional lasers, but which will be readily attainable by ALFF.

One of the most important potential applications of RIMS to isotopic analysis of small quantities of C, N, and O is in the measurement of the isotopic composition of the solar wind. The Genesis spacecraft is currently orbiting the L1 La Grange point between the Sun and Earth, collecting implanted solar wind ions in specially selected and prepared solid surfaces (of silicon, gold, and diamond). Analytical techniques for isotopic analysis of these precious samples are under development, but will not be ready when the sample is returned to Earth in 2004. A RIMS measurement using selective multi-photon ionization by ALFF, and isotopic analysis by SPIRIT has all of the needed characteristics to provide the prescribed accuracy of isotope ratio measurements (one part per thousand) for carbon, nitrogen, and oxygen, which are the first priority of the Genesis mission.

Other cosmochemical applications that require the combined capabilities of ALFF and SPIRIT include the following: (1) neon isotopes in Genesis samples, which are being collected on different surfaces for the different energy regimes of the solar wind; (2) oxygen isotopes in iron meteorites, essential for establishing genetic relations between iron meteorites and stony meteorites, and thus for understanding the formation of iron cores in asteroids and planets; (3) microscopic distribution of nitrogen isotopes in iron meteorites, for which bulk analyses show wide, unexplained variations; (4) nitrogen isotopes in minerals from the Earth’s mantle, which is probably the principal reservoir for nitrogen on Earth (although at a concentration of about one part per million by mass); the result is necessary both for the degassing history of the Earth and for identifying the origin of essential volatile elements (H, C, N) on Earth.

3.2.2. Single-photon ionization of geochemical and cosmochemical elements and compounds

Geochemists have long sought an analytical technique that would provide simultaneous quantitative analysis of all elements in a rock or mineral. The first approach to this goal was emission spectroscopy, in which a sample is excited by an electric arc, and a visible-light spectrum is recorded on a photographic plate. This was the dominant technique in the 1920’s–

40's, but has limited accuracy, and requires internal standardization. A successor technique was spark-source mass spectrometry, in which ions produced in the spark discharge are measured mass spectrometrically. However, ionization efficiencies vary widely from one element to another, again requiring internal standards. Secondary-ion mass spectrometry (SIMS) is a useful variant for microanalysis, in which sample ions are produced by bombardment by a focused primary ion beam. However, SIMS has limited sensitivity, and produces mass spectra that are made very complicated due to the presence of molecular ions, which may "interfere with" the atomic ions of interest. It is hoped that non-selective photoionization might provide a new analytical technique that is both highly sensitive for all elements and also capable of producing simple mass spectra. Photoionization provides greater sensitivity than any existing microbeam technique.

Preliminary experiments at Argonne National Laboratory have been carried out with a fluorine laser (monochromatic light at 157 nm), and have not shown the desired uniformity of sensitivity across a broad range of elements. The tunability and wider range of available photon energies of ALFF may improve the usefulness of this technique.

If the ALFF-SPIRIT combination proves satisfactory for trace-element analysis, the appropriate applications will be those for which small sample size is the limitation. These include:

- (1) presolar "stardust" grains, with dimensions on the order of one micrometer, and element abundance on the order of one ppm;
- (2) cometary dust particles, such as those to be returned to Earth by NASA's "Stardust" mission, with sub-micrometer dimensions and unknown elemental abundances;
- (3) meteorites or geologic materials in which micrometer-scale spatial resolution is important;
- (4) samples from experimental petrology, especially those from very-high-pressure diamond anvil cells, which are necessarily very small.

3.2.3. Organic molecular analysis

In both terrestrial and extraterrestrial natural materials, there is a great need for identification and quantification of organic molecules, both biogenic and abiogenic. In meteorites, particularly in carbonaceous chondrites, there is a great need to identify the level of complexity and variety achievable in natural, abiogenic processes. In ancient terrestrial rocks, chemical or isotopic signatures of biological processes are often ambiguous, so that even less diagnostic features, such as morphology, are called upon. New, microbeam techniques are required for excitation and detection of organic molecular species, with minimal fragmentation. The ALFF radiation is in the appropriate energy range for single-photon ionization, and its tunability is an invaluable asset in allowing molecular identification by tuning above and below specific ionization thresholds.

3.2.4. Astronomical applications

The understanding of chemical processes in the interstellar medium and in molecular clouds depends fundamentally on knowledge of the abundances of the major reactive elements, particularly hydrogen, carbon, nitrogen, and oxygen. The techniques for determining these abundances depend on the absorption of ultraviolet light from background stellar sources. These elements are so abundant that allowed electronic transitions are optically thick, and are, therefore, not very useful for accurate abundance determinations. Electronic transitions are known for the key species: C^+ ions, N atoms, and O atoms, for which the f -values (transition probabilities) are low enough that the lines are ideal for quantitative analysis. However, the very fact that the f -values are small makes them difficult to measure experimentally. The great enhancement in brightness of ALFF, relative to third-generation synchrotron radiation, makes it possible to determine these crucial f -values.

3.3 Materials Science

Working Group Chair: Andreas Wucher, University of Duisburg-Essen, Germany

During the sessions of the Materials Science working group, five projects have been presented and discussed that are suggested to be conducted at the proposed ALFF facility. These can be coarsely divided into i) user projects that utilize the free electron laser to tackle problems centered in other scientific areas and ii) developer projects that focus on the characterization and improvement of the FEL itself. It was found that the work to be performed in both categories is strongly interrelated in the sense that a proper characterization or even control of beam properties like wavelength, intensity and coherence of the emitted radiation is of utmost importance for the success of many suggested user projects. Four of the presentations belonged to the first category, the scientific scope ranging from fundamental studies of particle-solid interaction processes, laser ablation mechanisms, spin dynamics at magnetic nanostructures to more applied fields like the development of mass spectrometric surface characterization methods utilizing desorbed atomic and molecular surface species. One presentation described a project belonging into the second category. In the following, the suggested projects will be briefly summarized.

3.3.1 Fundamental studies of sputtering processes

(Bruce King, Andreas Wucher)

Sputtering is the release of particles from a solid surface into the gas phase by ion bombardment. This process is widely employed in thin film deposition and forms the basis for mass spectrometric surface analysis techniques that are used for the chemical characterization of solid surfaces. Although the phenomenon has been extensively investigated for more than three decades, there are still many open questions that need to be understood in order to make efficient use of the process in the applications mentioned above. Since most of the sputtered particles leave the surface in the neutral state, a proper characterization of sputtered fluxes ultimately requires the ionization and mass spectrometric detection of these neutral atomic or molecular species. One ionization mechanism that is particularly suited in this context is photoionization induced by the absorption of one single photon. The great advantage is that in this case the measured photon flux dependence of the ionization efficiency is linear and therefore easy to

interpret, which is very much in contrast to non resonant multiphoton ionization studies conducted on sputtered particles. For the identification of desorbed molecular species, single photon ionization offers the unique possibility to efficiently ionize a molecule without inducing significant photofragmentation. In both cases, it is necessary to irradiate the sputtered particles with photons of an energy greater than the ionization potential. The corresponding wavelengths reside in the UV, VUV and XUV regime that is targeted in the proposed ALFF. In order to obtain quantitative information about photoionization efficiency and, hence, about the desorbed particle fluxes, it is important to have enough photon flux available to drive the photoionization process into saturation. In particular for sputtered molecular species, it is moreover extremely important to be able to tune the wavelength of the ionizing laser in the regime around the ionization potential. Due to the high internal excitation of sputtered molecules, it may be advantageous to operate at or even slightly below the IP in order to minimize the excess energy and therefore the photon induced fragmentation. The combination of both requirements is clearly beyond the capabilities of currently available tabletop VUV laser systems and can only be achieved with the proposed ALFF facility.

As an example of new and surprising results that may still arise from fundamental sputtering experiments, Figure 5 shows single photon ionization mass spectra of neutral atoms and molecules sputtered from pure Au and an AuAl₄ alloy surfaces that were taken with the time-of-flight mass spectrometer located at the existing Low Energy Undulator Test Line (LEUTL) at Argonne. Interestingly, the emission of Au atoms, which constitute the major sputtered species for a pure gold surface, is apparently blocked for the alloy surface. This phenomenon has not been observed before and is currently under further investigation.

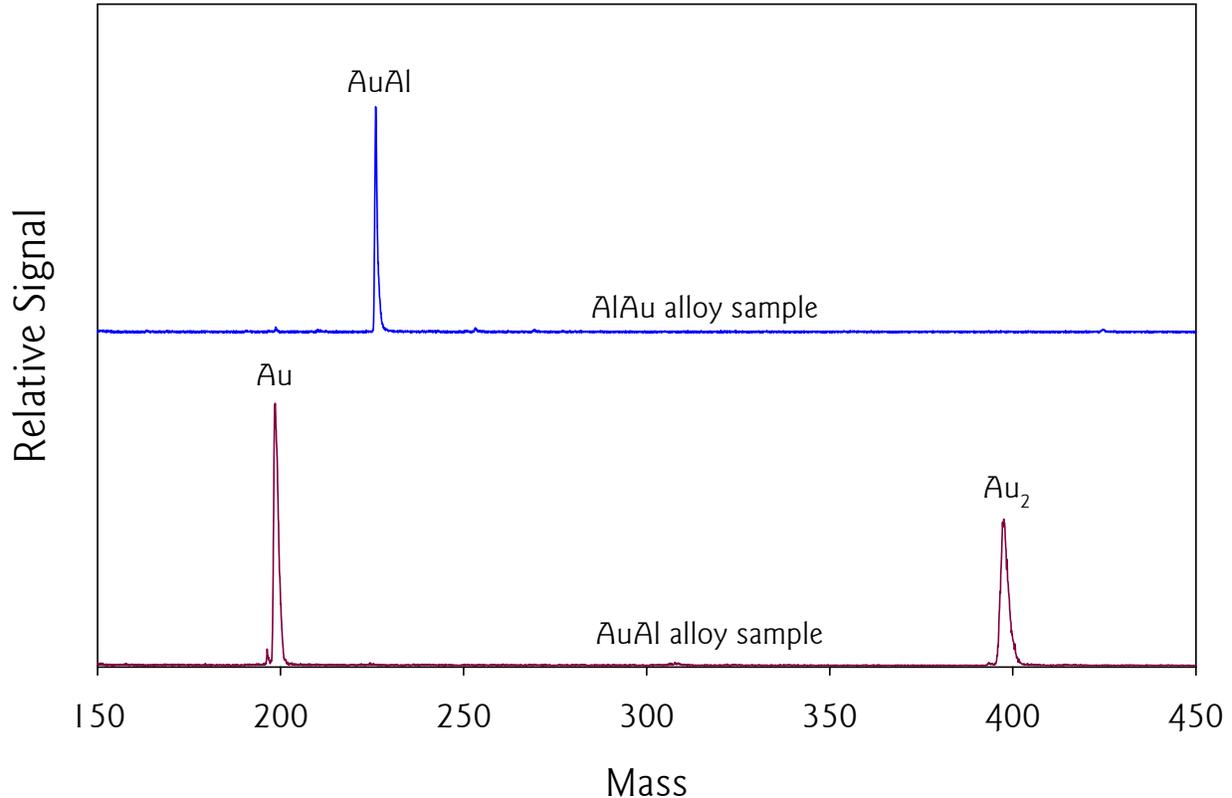


Figure 5: Anomalous sputtering observed in the gold-aluminum alloy system. In the gold rich alloy (bottom), gold and clusters are detected. In the aluminum rich alloy, most of the gold is sputtered as molecules.

3.3.2 Surface analysis by single photon ionization of atoms and molecules (Andreas Wucher, Igor Veryovkin)

This presentation reported on the ongoing activities that take place at the existing Low Energy Undulator Test Line (LEUTL) facility at Argonne National Laboratory. Over the last few years, a highly sensitive surface analysis instrument called SPIRIT has been designed, built and installed at the LEUTL end station which is based on time-of-flight mass spectrometry of post-ionized sputtered neutral particles. In order to allow the detection of virtually every desorbed atom and molecule released from the surface, the neutral particles are subjected to a non resonant single photon ionization process initiated by either a fixed frequency VUV laser operated at a wavelength of 157 nm or the tunable output of the LEUTL. The instrument has been optimized for utmost detection sensitivity and was recently demonstrated to be able to detect sputtered neutral atoms released from a metal surface with a total efficiency (“useful yield”) of up to 25% (see Figure 6). In order to optimize this quantity for different atomic and molecular species, the single photon ionization process must be thoroughly characterized and optimized for each detected particle desorbed from the investigated surface by either ion sputtering or laser ablation techniques. Probably the most important parameter in this context is the single photon ionization cross section and its dependence on the wavelength of the ionizing radiation. SPI cross sections of sputtered atoms have been measured to be in the range 10^{-18} to 10^{-16} cm² which have been

determined from the saturation behavior of the ionization process at a fixed wavelength of 157 nm. As stated above, tunability of the ionization laser in connection with achievable pulse energy densities of the order of J/cm^2 constitute an extremely important prerequisite for these experiments which form the basis of many of the proposed applications of the technique in the field of cosmochemistry and biology (cf. the reports of the corresponding working groups).

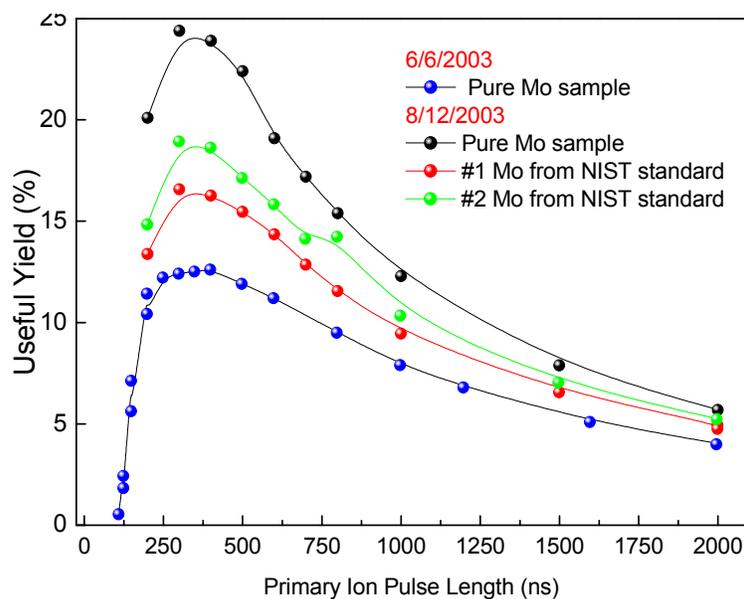


Figure 6: Useful yield for detection of Mo atoms sputtered from a pure Molybdenum surface and post-ionized with $\lambda = 157$ nm radiation vs. pulse duration of the primary ion beam.

3.3.3 Materials processing by laser ablation (Libor Juha)

Surface modification of materials by means of laser ablation constitutes an important step in many structuring technologies of modern materials science. The fundamental processes behind the ablation mechanism, however, are still poorly understood. In view of ever decreasing structure dimensions, the VUV wavelength region between 40 nm and 200 nm is particularly interesting for upcoming nano-patterning techniques since it extends the diffraction limit of conventional UV lasers down into the regime of a few tens of nanometers. Moreover, it is expected that the formation of laser induced periodic surface structures that are commonly observed in laser ablation experiments is strongly wavelength dependent and will therefore be significantly altered in this wavelength range. Unfortunately, next to nothing is known about the fundamental characteristics of the ablation mechanism at VUV wavelengths. From preliminary studies, it was found that the dependence of the ablation rate on the fine structure of the irradiated material may be much less pronounced than in the UV range accessible to conventional excimer lasers. Combining VUV wavelength with ultrashort laser pulse duration, it appears feasible to change the ablation characteristics from a mainly thermal process to non-thermal processes. Using the TESLA free electron laser at Hamburg, ablation rates have been measured at a wavelength of 86 nm and a pulse duration of 150 fs and compared to those obtained with nanosecond laser pulses (see Figure 7). These studies need to be continued in the future, but the TESLA facility is currently being upgraded and will afterwards not operate in the

VUV wavelength range any more. The proposed ALFF will therefore be the only available facility generating tunable, short pulse radiation in the wavelength range needed to pursue these investigations.

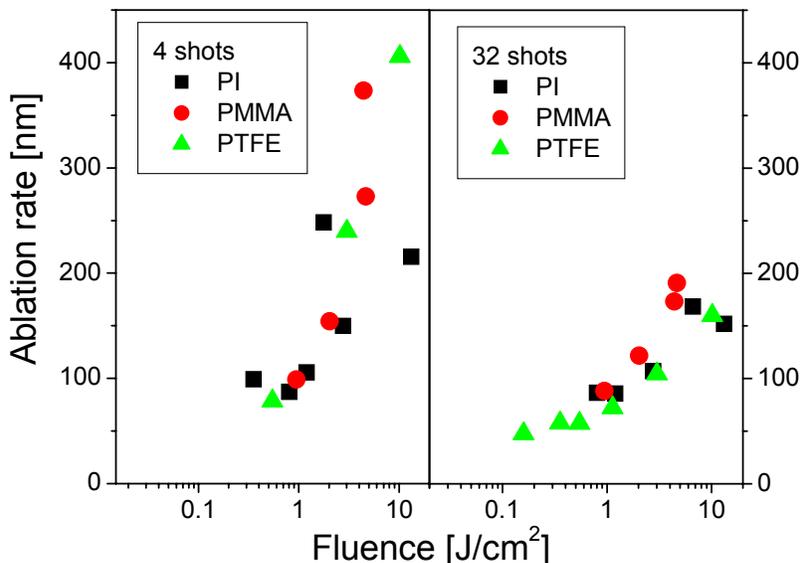


Figure 7: Ablation rate of different polymer surfaces measured using a capillary discharge laser at $\lambda = 46.9$ nm vs. laser power density.

3.3.4 Sub-ps magnetic domain imaging (Dave Keavney)

Modern concepts of magnetic storage media and MRAM chips feature nanoscale magnets that are often realized as patterned microarrays of magnetic nanostructures at solid surfaces. In order to optimize the design and performance of such devices, it is necessary to study the magnetization dynamics of magnetic nanostructures with both high lateral and temporal resolution. At present, photoemission electron microscopy (PEEM) in connection with soft X-rays obtained from the APS is used to record images of magnetic microarrays with about 100 nm lateral resolution and good magnetic contrast (see Figure 7). By means of pump-probe experiments triggered by an electrical pump pulse, the dynamics of magnetic domain modifications can be traced on a 100 ps time scale. In the future, the structure size is expected to significantly drop below the currently achieved lateral resolution, which in turn is mainly determined by chromatic aberrations induced by the width of the kinetic energy distribution of the emitted electrons. It is known that this width may be significantly reduced by changing the irradiating photon energy from the soft X-ray regime (500-3000 eV) to the VUV range (< 10 eV) (see Figure 8). Connecting the PEEM to the proposed ALFF facility would therefore greatly enhance the achievable lateral resolution, thus making it possible to image magnetic nanoarrays with structure sizes even below 20 nm. At the same time, the short pulse width of the free electron laser opens entirely new possibilities with respect to the time resolution that could be achieved in such experiments. Using pump-probe schemes, it is envisioned to study the correlation of ultrafast spin dynamics occurring on a sub-picosecond time scale within an array of magnetic nanostructures at surfaces.

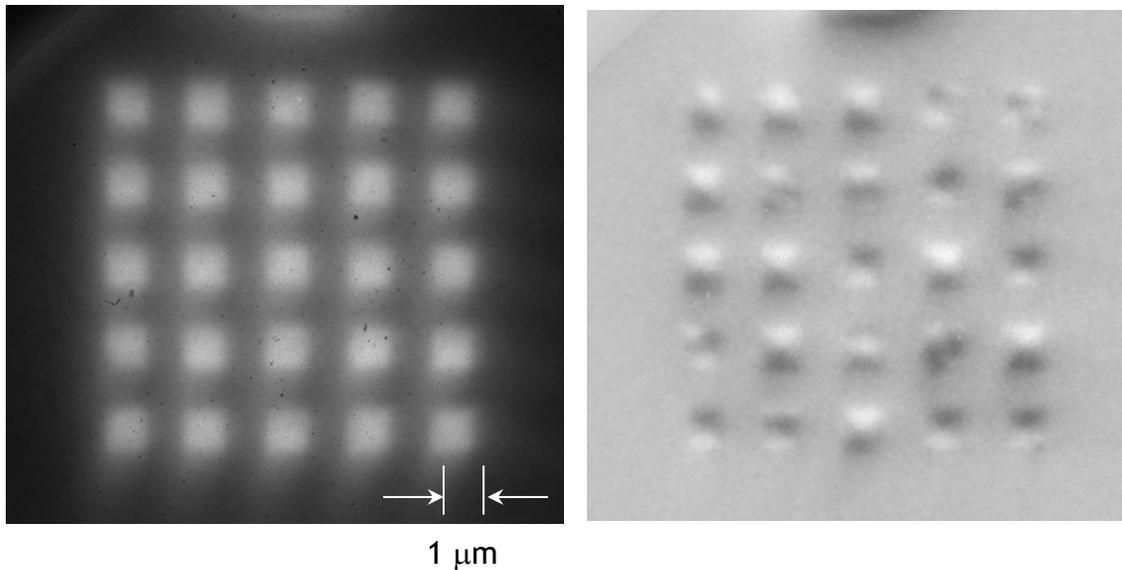


Figure 8: X-ray induced PEEM images of magnetic Co nanostructures on an Al buffered Si surface using a) chemical and b) magnetic contrast at an irradiating photon energy of 778 eV.

3.3.5 Spatial coherence measurement (David Paterson)

Many of the experiments that are planned to be conducted at ALFF heavily rely on the spatial coherence of the incoming VUV radiation. In order to interpret the results of experiments like LIPSS formation in laser ablation or make experiments like coherent control of chemical reactions even possible, it is of great importance to exactly know the coherence properties of the free electron laser beam and maybe use this input to drive a feedback mechanism that keeps those properties constant over time. In the proposed project, it is envisioned to measure the spatial coherence by recording a diffraction pattern of a so-called Uniformly Redundant Array (URA, see Figure 9), i.e., a one or two dimensional array of features that exhibit evenly distributed spacings and, hence, mimics many Young's double slit experiments with different slit spacing. Recording the diffraction pattern of such a device with a VUV sensitive CCD camera allows to determine the complete spatial coherence function on a single shot basis (see Figure 10 for an example). This information is extremely valuable for the interpretation of user experiments, since it is expected that the properties of the SASE beam may exhibit significant fluctuations from shot to shot. Moreover, it is conceivable that the information can be inserted into a feedback mechanism stabilizing the beam.

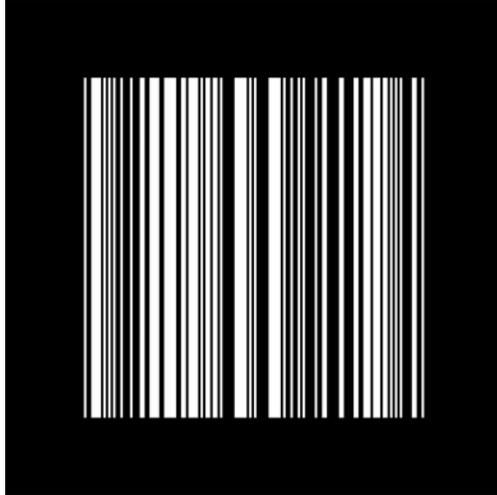


Figure 9: Uniformly Redundant Array used to determine the spatial coherence function

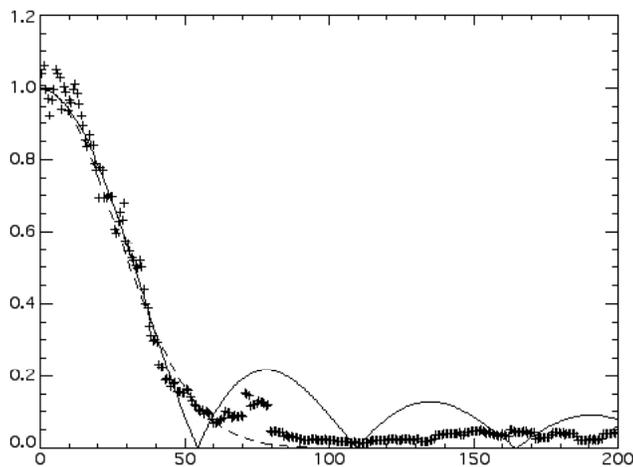


Figure 10: Measured spatial coherence function of soft X-ray radiation ($h\nu = 1500$ eV) emitted from APS Beamline 2-ID-B.

3.4 Biology and Environmental

Working Group Chair: Luke Hanley, University of Illinois at Chicago

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.

3.4.1 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 in Figure 11; 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.

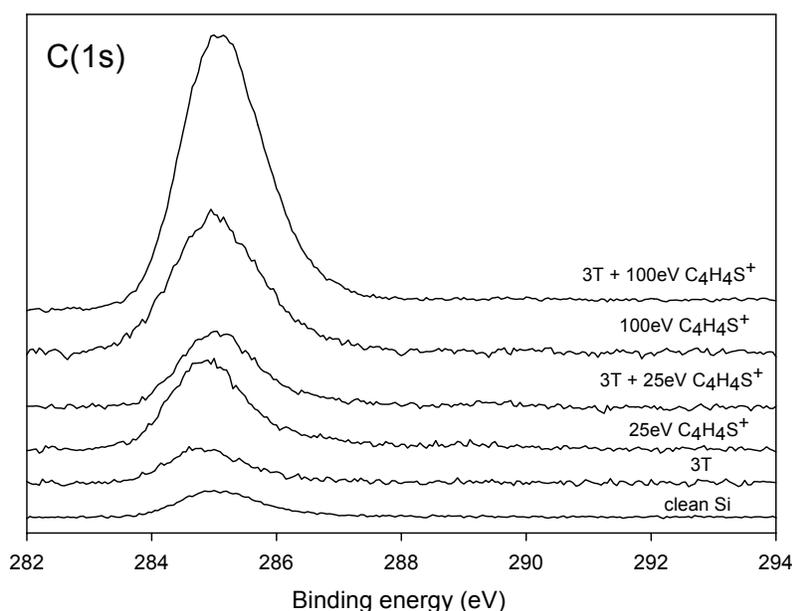


Figure 11: C 1s x-ray photoelectron spectra of several polythiophene and non-polythiophene films are produced by surface polymerization by ion assisted deposition (SPIAD) on silicon [1].

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 is limited by an inability to produce intense radiation at wavelengths below 200 nm. ALFF will readily permit such experiments.

3.4.2 Study of atmospheric aerosols by laser postionization 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.

3.4.3 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 determination 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.

3.4.4 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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Appendix A: Proposed Experiments

P.I./ Affiliation	Experiment Title	Tunable Wavelength Range (nm)	Minimum Pulse Energy (μJ)	Maximum Pulse Length (fs)*	Maximum Spot Size (mm)	Maximum Bandwidth (%)	Second Laser/other
	ALFF proposed parameters (for reference)	55-450	0-200	200-500	30-10000	0.3-2.5	N ₂ , F ₂ , others provided by users*
Laurie Butler/ U of Chicago	Photodissociation of radicals	65-180	200	500 or longer	0.5	1.0	ArF
C. H. Winston Chen / ORNL	VUV Ionization of Nanoparticles & Biopolymers	120-160	10	--	1	1.0	--
Chun-yen Chen / Academia Sinica, Taiwan	Nuclear Astrophysical Origin of Stardusts from comets and meteorites	82-200	100	--	3	2	N ₂
M. Paul Chiarelli/ Loyola University Chicago	Photoionization of MALDI-generated aromatic DNA adducts (polyaromatic hydrocarbon diol-epoxides and aromatic amines)	120-180	20	--	1	3	N ₂ , F ₂
M. Paul Chiarelli/ Loyola University Chicago	Photoionization of proteins for photodynamic therapy (tryptic fragments of hemoglobin modified by dye molecules)	120-180	20	--	1	3	N ₂ , F ₂

P.I./ Affiliation	Experiment Title	Tunable Wavelength Range (nm)	Minimum Pulse Energy (μJ)	Maximum Pulse Length (fs)*	Maximum Spot Size (mm)	Maximum Bandwidth (%)	Second Laser/other
Robert Clayton / U of Chicago	RIMS of carbon, nitrogen, oxygen, and noble-gas isotopes in special samples	50-120	100	500	1	1.0	N ₂ , F ₂
H. Gnaser/ Dept. of Physics, Kaiser-slautern University of Technology	Desorption and VUV ionization of organic/bioorganic molecules from nanocrystalline TiO ₂ films	100-280	15	--	3	3	N ₂ , F ₂
Luke Hanley/ UI-Chicago	Analyzing nanoscale biomaterial surfaces with single-photon ionization	110-180	50	--	2	1.0	--
Luke Hanley/ UI-Chicago	Two-photon photoemission as an electronic structure probe of conducting polymers	55-200	100	500	0.5	0.3-1.0	--
Libor Juha/	Materials Processing by Laser Ablation	40-200	20	300	1	2	--
Dave Keavney/ ANL	Sub-ps magnetic domain imaging	50-120	100	500	1	1.0	PEEM setup; Ti:sapphire

P.I./ Affiliation	Experiment Title	Tunable Wavelength Range (nm)	Minimum Pulse Energy (μJ)	Maximum Pulse Length (fs)*	Maximum Spot Size (mm)	Maximum Bandwidth (%)	Second Laser/other
Bruce King	Sputtering of nanoparticles: where are the limits to the collision cascade theory	110-160	50	--	2	1.5	F ₂
Mark Knickelbein/ANL	Photoabsorption of clusters	55-200	100	500	5	2.5	ArF
Nick Lockyer/UMIST	VUV post-ionization of prostate cancer cells (high sensitivity measurement of atomic/molecular species desorbed from cell lines or tissue)	100-200	10	--	2	1	Sync to ion beam and/or N ₂ laser
Nick Lockyer/UMIST	Spectroscopic study of polyatomic sputtering mechanisms: SPI of C ₆₀ -sputtered metals/bionols. Probing internal energy levels, threshold SPI, comparing poly and atomic sputtering and laser desorption (MALDI).	100-200	10	--	2	1	Sync to ion beam and/or N ₂ laser
Jerry Moore/ANL	Velocity and internal energy measurements of desorbed peptides	120-160	10	--	3	2	N ₂

P.I./ Affiliation	Experiment Title	Tunable Wavelength Range (nm)	Minimum Pulse Energy (μJ)	Maximum Pulse Length (fs)*	Maximum Spot Size (mm)	Maximum Bandwidth (%)	Second Laser/other
Cheuk Ng/ UC Davis	Spectroscopy of radicals and ions	55-200	200	200-500	2	0.3-2.5	IR-OPO
David Paterson/ APS	Spatial coherence diagnostic – beam characterization with a single shot	Any	0.1	Any	Any	1.0	none
Steve Pratt /ANL	Double photoionization of Kr	10-100	200	<300	<0.5	0.3-1.0	
Martina Schmeling / Loyola University of Chicago	Single particle analysis of atmospheric aerosols with depth resolution (comparative with bulk XRF). Significant implications in climate research.	120-200	20	--	3	2	F ₂ , N ₂
J. Albert Schultz/ Ionwerks	Combined ion mobility and photoionization analysis of peptides. Laser desorption from intact tissues located in mobility cell followed by postionization of desorbed neutrals.	110-160	50	--	2	1.5	Ion mobility cell; ortho-TOF experiment

P.I./ Affiliation	Experiment Title	Tunable Wavelength Range (nm)	Minimum Pulse Energy (μJ)	Maximum Pulse Length (fs)*	Maximum Spot Size (mm)	Maximum Bandwidth (%)	Second Laser/other
Amina Woods/National Institute on Drug Abuse Intramural Research Program NIH	Measuring non-covalent complexes of biomolecules (dynorphin – NMDA receptors) (part 1) addressing issues related to neurotoxicity in stroke and applications paralysis prevention.	100-200	10	105	3	2	N ₂ , F ₂
Amina Woods / NIDA IRP NIH	Measuring non-covalent complexes of dynorphin-NMDA receptors (part 2) improving the understanding of R-R communication. n.b.Very difficult to ionize these complexes by electrospray or conventional lasers.	100-200	10	--	3	2	N ₂ ,F ₂
Amina Woods / NIDA IRP NIH	Photoionization of complexes to study receptors – drugs of abuse interactions. Fundamental to understanding drug addiction.	100-200	10	--	3	2	N ₂ ,F ₂
Andreas Wucher	Fundamental studies of sputtering processes	80-180	50	--	2	1	F ₂
Igor Veryovkin	Surface analysis by SPI of atoms and molecules	100-170	40	--	3	0.3-1.5	F ₂

* no value indicates not a limiting factor, typically 10-ns pulse length is acceptable for these experiments.