Letter of Intent, Category A, for the LCLS Experimental Program

Gas–Phase and Cluster Science using the LCLS

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II. Scope of Proposed Investigations

1. Introduction

The development of high-field and femtosecond lasers brought advances in time-resolved investigations in the IR, visible and UV as well as enabling the capabilities of non-linear spectroscopies [1]. The revolutionary tool for observing molecular motion in real time has been pump-probe schemes. They were used, for example, for the study of bound states of small diatomic molecules [2], of elementary chemical reactions [3], in liquids [4], solids [5] and in biological specimens [1, 6].

The advent of ultrafast x-ray light sources, however, is timely, since, even with the major advances in the capabilities of lasers, we lack a detailed understanding of the mechanisms of the action of radiation at very short times following a broad range of energy depositions in an isolated system. We also lack understanding of the time-dependent energy dissipation from a quantum mechanical point of view. Comprehensive information on the interaction and decay pathways following energy deposition is much needed in gas-phase systems such as atoms, molecules, clusters, and their ions. Time-dependent studies of carefully selected systems and comparison with the results of forefront theoretical methods will provide the basic knowledge of the behavior of matter in the ultrafast and ultra-intense regime accessed by the LCLS.
We propose a multi-institution, multi-disciplinary collaborative experimental research program in high-field and ultrafast physics of atoms, molecules, clusters and their ions, benefiting from a strong connection with many theoretical groups, in order to better understand many body-processes in photoionization and their various dynamic manifestations. Specifically, we seek to understand the dynamics and competing mechanisms that lead to various phenomena when the inner-shell electrons of these complex systems are excited with ultrafast and ultra-intense linearly and circularly polarized light. The team members bring a variety of strengths and experiences in laser and synchrotron radiation photionization studies, and we expect the proposed research to uncover new phenomena, as well as to stimulate fundamental calculations. The unique capabilities that the LCLS promises will allow this team to assume a leading role in time-resolved and high-field studies in the proposed areas of research. Finally, the proposed research impacts many areas of science such as chemistry, physics, biology and material sciences.

2. Proposed Research Program

We plan to capitalize on the unique attributes of the LCLS, such as the extreme peak power and spatial and good temporal resolution of the photon beam, to investigate complexity in atoms and molecules, negative ions, atomic and metallic clusters, and biological molecules. The proposed studies will lead to significant advances in our understanding of the behavior of matter at the fundamental time scales of nuclear motion.

The extreme peak power of the LCLS beam will allow access to highly excited states of matter due to multi-photon excitation/ionization, such as inner-shell hollow target and multiply-charged targets. These previously inaccessible states will allow detailed investigations of collective tunneling effects [7], rescattering [8] of ionized electrons with the targets and most certainly new and unexpected phenomena that will reveal themselves, including non-linear phenomena and high-field dynamics. The spatial and temporal resolution of the LCLS beam will allow us to follow nuclear motions of molecules and clusters in real time using laser/LCLS pump-probe schemes.

We propose initially to investigate the inner-shell photoexcitation of simple targets such as atoms and small molecules. We will then increase the challenge by exploring bigger molecules, clusters and their negative ions with the LCLS beams. They are complex systems whose study is at their infancy, since they could only be preliminarily explored with third generation light sources. Finally, on a longer time scale, the single shot diffraction capabilities of the LCLS will be used to directly determine structures of size-selected metal and semiconductor clusters.

A. Basic Molecular Studies

Initial studies will involve the weak field and strong field interaction of x-rays at 800 eV and 8 keV with simple small neutral atoms and molecules, Ne, Ar, N₂, Cl₂, I₂, SO₂, etc., to probe inner shell ionization from neutrals and ions with one and two sequential photon
absorption processes. This experiment would be a single beam investigation, and the weak field measurements could be performed at the Advanced Light Source to establish a baseline of data for one photon processes on neutral beams. Similarly, using a positive ion beam at the LCLS, the second ionization step of the positive ion (ground state) can be interrogated initially in isolation. A detection system consisting of ion and electron angular imaging will be constructed and used to investigate the angular correlations of the ionization processes.

The initial goal would be to obtain basic information about the relative cross sections for release of a first high energy electron by the x-ray photon from the neutral molecule and then the second high energy electron from the ion or doubly charged ion by absorption of an x-ray photon. Intervening between these events will be a wide range of Auger and other decay processes, but these will produce electrons with characteristically different energies. Then experiments can be performed where the intensity of the LCLS will be increased substantially (single beam), and a sequential two-photon process will be driven at rates that are high enough so that electron-electron correlation effects on the energies and angular distributions can be introduced and observed. The initial photon absorption can leave the ion in various excited states, which will differ from the baseline data obtained on the ground state ion. The intense peak power of the LCLS beam will permit access to highly excited states of matter due to multi-photon excitation/ionization, such as inner-shell hollow target and multiply-charged targets due to multi-Auger processes, shake-off and electron-rescattering. These previously inaccessible states will permit detailed studies of collective tunneling effects [7], rescattering [8] of ionized electrons with the targets as well as unexpected phenomena that will reveal themselves, including non-linear phenomena.

The nature of these excited states and their effect on the electron angular distributions will need to be explored in the simplest possible systems first to make progress in this high-field multiphoton regime. The goal is to measure higher field physics with x-rays, similar to what has been done with visible and near infrared light, to explore the scaling laws and properties of ionization and cross section information in a first basic way.

B. Cluster Studies

Studies of the electronic and magnetic properties of clusters are important because they provide a link between quantum mechanically accessible atoms and molecules and the corresponding bulk forms of matter where band structure blurs out the available information. Clusters can also be used to model solvation effects in theoretically tractable systems. As such, they can provide unique information to fill the gap between the understandings of gas phase and condensed state physics. Although much progress has been achieved in the study of clusters in general, inner-shell studies of van der Waals and metal clusters are only recently developing, with studies carried out mostly in Europe [9]. Our proposed spin-resolved studies of metal clusters are unique at present. They will allow us to determine the magnetic moments of metal clusters as a function of cluster size, which, when compared to the bulk values or values obtained using low-field photons, may infer new information on magnetism and solid state effects.

a) Van der Waals Free Clusters
Noble gas clusters are the most weakly bound of all clusters and their interactions are well understood theoretically, making them ideal models systems for studying finite size-effects on electronic structure. Unlike valence shells which often extend over the dimensions of a molecule, core levels are highly localized on specific atoms within a cluster. Utilizing the binding energy shift observed between atoms on the inside and the outer surface of the cluster, the core-excitation can be used to provide insight into local properties in different regions within a cluster.

Over the past two years, we have built and used a supersonic expansion cluster source at the ALS [10] demonstrating the production of Ar, Kr and Xe clusters of up to 4000 atoms. This source was used with three different detector systems demonstrating successful performance in all three cases. Highly resolved photoionization data of Xe clusters measured with our hemispherical electron analyzer (Scienta) [11] are shown in Fig. 1. The source was also adapted to our electron time-of-flight (TOF) systems to detect electrons over wide kinetic energy regions as well as survey electronic relaxation mechanisms following specific shell excitation.

Fig 1: Xe 5p photoelectron spectrum of Xe clusters of approximately 1000 atoms measured using the Scienta electron spectrometer at \( h\nu = 30 \) eV. NOO Auger lines arising from photoionization from contaminating 3\textsuperscript{rd} order light (90eV) are apparent in the spectrum.

We propose with this LOI to investigate time-resolved and high-field phenomena in particular cluster targets with the LSLS. Specifically, we would like to:

Investigate high-field effects by carry out inner-shell systematic studies of the electronic response of van der Waals clusters to intense LCLS radiation, as a function of cluster size and LCLS intensity. Our understanding from the LCLS team is that plans to incorporate an attenuator can reduce the field by as much as four orders of magnitude. Experiments of interest to us initially are Ar K-shell excitation at 3206 eV, Kr L\textsubscript{i}, L\textsubscript{II} and L\textsubscript{III} at 1921 eV, 1731 eV, and 1678 eV respectively and Xe L\textsubscript{i}, L\textsubscript{II} and L\textsubscript{III} at 5453 eV, 5104 eV and 4782 eV respectively. Laser work has shown that these clusters Coulomb explode when
irradiated with an intense laser field up to $8 \times 10^{15}$ W cm$^{-2}$ giving rise to a charge state distribution that doesn’t seem to be fully understood, although many scenarios have been reported [12]. It will be thus interesting to carry out similar experiment with x rays, which are shell specific and which may provide new information. We will use the temporal resolution of the LCLS to follow the dissociation of the clusters and record fragment motions in real time using pump-probe schemes. We would like to study the fragmentation processes since the electronic relaxation of inner-shell excited cluster states, which occurs on a fs time-scale is followed by substantial ionic dissociation of the cluster. Systematic studies of the relaxation processes as a function of the rare gas, cluster size, and thus structure, will highlight size effects in multiphoton excitation processes.

We plan to use two complementary spectroscopy methods for these experiments; electron and ion- TOFs will allow us to map the photoelectrons and photoion kinetic energies as a function of the incident photon intensity/energy as well as assist in identifying regions of interest. Our ultimate goal will be to do these experiments in coincidence using multihit capable electron and ion momentum detection.

b) Metal Clusters

Studies of a variety of metallic clusters have been pursued aggressively [13] and many of them are modeled quite well by the jellium approximation [14]. The behavior of transition metals clusters deviate significantly from the predictions of that model, however, making them interesting targets for studies of electronic structure and dynamics. We will initially investigate high-field effects as a function of the LCLS intensity using Ti and Fe, exciting them at their K-edge at 4966 eV and 7112 eV respectively. We would also like to extend our investigations to the dynamics of semiconductor clusters as a function of cluster size when irradiated with intense short pulses. Our long term goal will be to carry out spin-resolved experiments in metal clusters as a function of cluster size to understand how the magnetic dipole moment changes from the atom to the bulk, in the presence of the intense fields from the LCLS. This type of experiment will undoubtedly demonstrate new phenomena that are relevant to magnetism.

We have already used our cluster source [10] with our electron-spin resolving Mott-detector apparatus [15], using circularly polarized light from beamline 4.0.1 of ALS resulting in a clear demonstration of spin-resolved data for Xe clusters of about 1000 atoms.

C. Negative Ions Studies.

Studies of negative ions are interesting because they provide new information about electronic dynamics, structure and their photo-processes, which are both qualitatively and quantitatively different from similar photo-processes in neutral and positive ions targets. They represent an ideal testing ground for correlation phenomena, exposing inaccuracies or discrepancies in fundamental ab-initio calculations and thus provide detailed insight
into strongly correlated systems in general. In addition to its fundamental interest, negative ion research impacts plasma physics and astrophysics since these ions play an important role in weakly ionized gases.

Although there is much sophisticated negative ion laser photodetachment work [16], there is no information on inner-shell photodetachment and fragmentation of molecular negative ions to date. Inner-shell studies of negative atomic ions were initiated simultaneously at the ALS and in Europe [17, 18] only three years ago. At the ALS, we have focused on inner-shell spectroscopic studies of fundamental negative atomic ions such as He− [19], Li− [18], B−, C− [20] and on small clusters such as of B2−, B3−, Si2−, Si3−.

We propose in this LOI to investigate time-resolved and high-field studies of particular targets with the LSLS. Specifically, we would like to:

i) Study the effect of inner-shell photodetachment in the presence of intense LCLS fields in single beam experiments to understand the effects of multi-photon ionization and of the ponderomotive potential on negative atomic ions. Some of us have explored ponderomotive effects [21] but for valence electrons only using two-color lasers. We would like to propose investigating fundamental targets such as H−, He− and Li− and investigate threshold behavior photodetachment phenomena as well as multiply charged ion formation due to strong field multiphoton ionization.

ii) Investigate the effects of high-field photodissociation dynamics of small clusters following inner-shell photodetachment of K- and L-shell targets of interest. Targets of interest to us are: a) carbon chain clusters such C2− to C12− and fullerenes such as C60−, C72−, etc. b) semi-conductor or transition metals as well as metal hydride such as MH−, MH2−, MH3− and MH4 (M= Sc → Cu) to systematically study the effect of filling the 3d shell, c) and small main group clusters such as Br−, Br2−, B2−, B3−, and Si2−, Si3−.

Fig. 2 shows the results of an experiment conducted at one of the best 3rd generation synchrotron radiation beamlines (10.0.1 of the ALS). It depicts, in the top panel, the double photodetached signal (B+) for the K-shell photodetachment of B−. The middle panel shows the two decay pathways in the case of B2−; photodetachment of the molecule (B2+) and its photodissociation fragment (B+), and the bottom panel shows the photodetachment and photodissociation decay pathways for B3−. These results demonstrate the feasibility of using our ion source to produce small clusters and of the types of experimental systems that can be studied to detect the photodetached signals. They also show the need for more intense photon beams to conduct detailed photodetachment experiments, with good statistics. To extend the method and follow the motion of the fragments in real time to understand the dissociation mechanisms, we will use typical approaches based on pump-probe schemes.

The measurements will be conducted using a movable ion beamline, recently funded by a DOE grant from the Material Sciences Division, which is presently being designed. This ion beamline will be used in both merged and cross beam geometry. We propose to design and build a photoelectron spectrometer for the above proposed work since the
increased differentiation will provide partial photoionization cross sections and angular distribution of all photo-processes.

**Fig. 2** Photodetachment of atomic $B^-$, $B_2^-$, and $B_3^-$ around the B K-edge measured with 400 meV photon bandwidth. Insets: higher resolution data which clearly show that the structures are composed of two peaks. In the case of the photodetachment of $B_2^-$ and $B_3^-$, the atomic fragment, $B^+$ resulting from photodissociation is the most intense signal.

### D. Diffraction studies of size-selected clusters

Metal and semiconductor clusters have attracted much interest for many years owing to their ability to "bridge the gap" between isolated atoms/molecules and bulk materials. Photoelectron spectroscopy of negative cluster ions and ion mobility studies of positive and negative ions have hinted at profound structural changes as the size of a cluster is varied; examples include the evolution of carbon clusters from linear to cyclic to fullerenes as the number of carbon atoms increases [22], and silicon clusters from spherical to prolate structures at around Si$_{25}$ [23]. However, direct structural probes of these clusters are sorely lacking. We propose to use the single-molecule X-ray diffraction capabilities of the LCLS to determine the structure of size-selected metal and semiconductor clusters in the size range of 10-100 atoms, using the same scheme put forth by Hajdu and co-workers [24] to probe biomolecule structure. Positively or negatively charged cluster ions will be generated by laser ablation, mass-separated by time-of-flight, and crossed by the LCLS X-ray pulse. The cluster ion density is such that for each pulse of ions produced by the laser ablation source, at most one cluster will interact with the X-ray pulse. Hence, collecting data over a series of pulses will provide the orientational sampling necessary to determine the structure of the cluster of interest.
E. Photoionization Dynamics of Biomolecules

The molecular structure of many biological molecules – DNA, RNA, peptides & amino acids – are very well known, in light of 50 years of research that have elapsed since Watson and Crick’s original postulation for the structure of DNA. However, fundamental aspects (photoionization dynamics) of “nuts and bolts” molecules that are the building blocks of life are not yet understood. Both intramolecular properties (how a molecule interacts with itself) and intermolecular properties (how a molecule interacts with its surroundings) are unknown for a great majority of biomolecules. The dynamics and reactivity of peptides, proteins, and nucleic acids must also be probed to understand biology and medicine at the molecular level. Investigation of complexes of increasing size can mimic the transition from the isolated molecule to solution or bulk, pointing the way from in vacuo to in situ.

We propose generating isolated biomolecules in the gas phase using laser desorption (small molecules) and nanospray (large particles) techniques. These will be interrogated with the LCLS X-ray pulse. Two kinds of experiments are envisioned, one immediately and the other when the LCLS is fully optimized for pump-probe work. The first would be to study the fragmentation dynamics of biomolecules in the time scale and intensities of the LCLS beam. Starting with small biomolecules (DNA bases, amino acids) and ascending through a range of polypeptides, we will end with large biological particles (proteins, viruses etc.). Coincidence techniques, as shown in Fig. 3, will be used to unravel different fragmentation channels when size selection is not possible. For larger particles, size selection will be performed with differential mobility analyzers. The results of these experiments would be crucial in designing future experiments at the LCLS where structural studies on single particles and biomolecules will be performed [25]. One of the ideas being discussed to protect proteins from radiation damage is to use tamperers like helium or water. [26] We can prepare biomolecules in these environments in a systematic way with a judicious choice of source parameters. The second experiment would be to perform core-level photoelectron imaging of isolated biomolecules and use pump-probe techniques to look at chemical shifts on ultrafast time scales. This would allow us to follow chemistry (bond breaking and bond forming) as it happens.

III. Collaboration

The team members listed in (I) plan to cooperate and collaborate for the above proposed work. Dr. Musahid Ahmed has been adapting various molecular beam sources in conjunction with pulsed lasers at the chemical dynamics beamline (ALS) to produce neutral carbon and metal clusters and interrogating them with synchrotron radiation. Dr. Steve Leone is an expert in laser-based time-resolved studies. Dr. Dan Neumark is an expert in valence shell photodetachment of negative ions using fs lasers. Drs. John Bozek, and Nora Berrah have been collaborating in inner-shell atomic, molecular and recently in cluster photoionization as well as pioneered inner-shell negative ions studies at the ALS. Each P.I. brings indispensable expertise for the proposed work outlined above. The team will utilize existing instruments such as a movable ion beamline, cluster sources, ion imaging detectors, and photoelectron spectrometers.
IV. Preliminary Budget

1) For the proposed cluster research, we will need funds to build a laser ablation and desorption source as well as a scattering chamber with provision for Ion & electron TOF imaging capabilities. This team is confident in their ability to build this source since Musahid Ahmed has already been successful at the chemical dynamics beamline in producing small neutral carbon clusters and has desorbed a number of DNA bases intact into the gas phase. We are already building the ion imaging detector using a DOE, BES equipment grant but we would also need to purchase a differential mobility analyzer and an electrospray source of about $50K. (The electrospray can be used to put nanoparticles into the gas phase, not just biological proteins). The approximate cost of the laser system, expansion cooling system and chamber amounts to about $300 K. With the LCLS intense ionizing power, we will have to work in the low $10^{-8}$ regime, requiring at least three differential pumping regions. A reasonable 100 hz solid state YAG laser with harmonics required for the experiment will cost around $100-120K.

2) We would like to design and build a photoelectron spectrometer optimized for the negative ion work. The approximate cost will be about $150K.

3) We will need to hire three posdocs to assist with the research work $300K/Y for 2 years.

4) We plan to be able to use the LCLS laser systems for the pump-probe proposed work.

DoE, BES is the expected source of funding for our equipment and posdocs requirements. An estimated amount of $1,220,000 will be needed.
References: