X-Ray FEL Induced Double Core-Hole and High Charge State Production

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Abstract. We report novel results on multiple photoionization of the N\textsubscript{2} molecule by femtosecond x-ray pulses from the Linac Coherent Light Source free electron laser. Ion spectroscopy reveals the ionization and dissociation dynamics, including a molecular mechanism of frustrated absorption that suppresses the formation of high charge states at short pulse durations. Auger and photo-electron analysis of double core hole production (through absorption of two photons on the time scale shorter than the Auger decay) agrees well with theory for the case of both K-shell holes on the same N atom, and gives an experimental upper bound for the relative contribution in case of one core hole on each N atom.

Keywords: FEL, X-ray, Photoionization.

PACS: 33.20.Rm, 33.80.Eh, 41.60.Cr

1. Introduction

A great many new avenues in different experimental scientific fields became available with the development of free-electron lasers (FELs) operating in VUV and X-Ray regime. For several years now the Free Electron Laser in Hamburg (FLASH) has been operating in the soft x-ray regime, while users of the Linac Coherent Light Source (LCLS) in Stanford, which successfully started its operation in fall 2009, can now benefit from FEL pulses with photon energy from below the oxygen K-edge up to the hard x-ray regime. Atomic and molecular physics is at the forefront of applications of this new laser technology. Combination of high intensity short pulses with unprecedented spatial and temporal resolution of accelerator based FEL facilities offer great capabilities, ranging from a single-pulse imaging of clusters and biomolecules to studying the exotic ionization and fragmentation pathways of the molecules and the time-resolved motion of individual atoms.

Infrared lasers and even high-harmonic generation sources in the EUV and soft X-ray regions interact predominantly with the outer (valence) electrons, whereas VUV and X-ray FEL beam has much higher cross-section to interact with the inner-shell electrons. Given the very high fluence of the X-ray laser pulses this interaction and ionization of inner-shell electrons can happen several times during the laser pulse duration per molecule or per atom. This multiple ionization process typically competes with the Auger decay of the inner-shell vacancies. Multi-step cascading, often involved in
this decay, can quickly lead to the formation of very high charge states of the target matter. The observed high charge states, often all the way up to fully-stripped atoms, are very unique and specific to the type (photon energy, duration and fluence) of the X-ray beam pulse. On the other hand, if the pulse energy is high enough in combination with short pulse duration, second inner-shell ionization (core ionization in particular) can happen before the first vacancy had time to Auger decay. The different atomic sites in molecules introduce multiple possibilities for the double core hole (DCH) production configurations, e.g., DCHs with both vacancies on a single site (DCHSS) and DCHs with single vacancies on two different sites (DCHTS).

In this report we present the results of the first study of the charge state formation in the response of a molecular system, N\textsubscript{2}, to intense laser pulses, as well as characterization of its DCH states production after sequential two-photon absorption. We will also present the preliminary findings for the charge states of SF\textsubscript{6} molecule similarly subject to the X-ray FEL pulses. All of these studies were carried out by our collaborative group \cite{1,2,3} as a part of the research conducted during the first round of pioneering experiments at the LCLS Atomic Molecular and Optical (AMO) physics instrument.

2. Experiment

The experimental setup consists of the electron and ion time-of-flight spectrometer (see E-TOFs and I-TOF below) placed in the high-field-physics (HFP) chamber of the AMO hutch of the LCLS FEL facility. The N\textsubscript{2} data was collected at the 1000 and 1100eV photon energy (±15eV) of 280, 80 ~7 and ~4fs pulse duration, while 800eV and 1000eV 280fs pulse was used for sulfur hexafluoride run. The X-ray pulse energies measured upstream from the focusing optics were .26mJ and 2.2mJ. These values are reduced by ~65%–85% in the interaction region due to photon beam transport losses. The photon beam was focused by Kirkpatrick-Baez (KB) mirrors to an area equal to about 2µm\textsuperscript{2}. Molecular target was introduced into the instrument via a 100 µm pulsed nozzle.

2.1. E-TOF setup

Five identical electron TOF spectrometers (see Fig.1) are positioned at unique angles, including magic angles with respect to the polarization plane. These allow for highly resolved electron angular distribution measurements. Two major parts of the e-TOF system are a lens stack and a drift tube. A specially designed electrostatic lens system is used to apply required retardation voltage while providing for electron trajectory bending to optimize collection efficiency even for the lowest difference between electron energy and retardation potential. Due to the specific voltages applied to the lenses the maximum transmission is typically reached at electron energies 10-15% above the retardation voltage and is defined by the first aperture (acceptance angle of ±1.6°) and the target gas jet diameter. Typical maximum transmission is in the range 1/2500 – 1/5000 of the 4π solid angle. A conversion function is used to obtain electron energy from its time-of-flight. A Long drift tube distance is essential for high electron time-of-flight and thus energy resolution. Properly calibrated conversion together with the most optimal retardation, for example, was found to resolve the Ne Auger line with sub 100meV accuracy.

2.2. I-TOF setup
The ion TOF spectrometer used in the experiment is depicted in Fig. 2. This so called “integrating” spectrometer has a 1mm by 10mm slit aligned perpendicular to the X-ray beam and separating the interaction region from the second acceleration segment and the drift tube. This type of slit serves for the most efficient alignment of the FEL laser focus to the spectrometer center. It also cuts a very thin slice out of the momentum sphere and thus lowers the transmission of the spectrometer – the higher the kinetic energy release (KER) of the ions the lower the transmission. This slit cuts down to an even higher degree the detection probability of ion-pairs that come from the same parent molecule thus hindering any sort of coincidence or even covariance measurements of the molecular fragmentations. This I-TOF spectrometer was still found to be a very effective instrument for measuring the ionic charge states as well as for the extraction of basic ion momentum information.

![SIMION representation of the I-TOF spectrometer of AMO instrument.](image)

Figure 2. SIMION representation of the I-TOF spectrometer of AMO instrument.

3. Results and discussion

3.1. N₂ charge state production

As single-pulse measurement experiments become more feasible, a fundamental question about the technique arose: would the radiation damage destroy or degrade the sample before information is extracted [4]. The study of N₂ charge states production as a function of FEL pulse duration addresses this issue. The extensive analysis of different contributions into I-TOF plot (see Fig.3) (as a function of spectrometer acceptance efficiency for different ion charges and energies) confirms the trend of frustrated absorption that suppresses the formation of high charge states at short pulse durations. This also agrees well with the results of the specially developed rate equation model, which gives much more physical result than isolated atom-based rate equations [1].
3.2. \( \text{N}_2 \) DCH production

The production of the DCH and the spectroscopy of the associated electrons is believed to be a much richer and more sensitive tool to provide unique spectral signatures of the chemical environment of the core holes [6,7,8]. Figure 4 shows the results of the analysis of DCHSS creation in \( \text{N}_2 \) revealed by the

\[ \text{Figure 4.} \] Experimental and theoretically calculated Auger spectra. Thick solid curves: Auger spectra recorded at 1.0keV and 1.1keV. The 1.1keV spectrum is offset vertically for clarity. Solid green curve: Auger spectrum recorded with synchrotron source [5]. Dashed curves: calculated Auger spectra (scaled) of various initial states, including SCH (green), DCHTS (grey shaded curve), DCHSS (yellow [light grey] shaded curve). Black stems indicate predicted energies of DCHSS shakeup Auger electrons. Dotted curve: spline fit to background.
Auger spectrum. There is a very good agreement with the theoretical calculations of the position and the strength of the DCHSS peaks. On the other hand, the determination of the DCHTS is difficult due to spectral congestion from other states which only allowed us to infer an experimental upper bound estimate of the effect. This was found to be 4% relative to the \( N_2(1s^1) \) main photoline. Even higher pulse intensity, improved stability of the photon energy and a more discriminating experimental technique will be required to resolve the DCHTS features and thus realize the full potential of DCH spectroscopy.

3.3. SF\(_6\) multi-photon ionization

Very stable and highly symmetric molecule of sulfur hexafluoride along with its technological importance [9,10,11] made it a subject of extensive studies over last several decades. Preliminary data on the SF\(_6\) ionization and dissociation pathways by the 800eV and 1000eV, 280fs FEL pulses reveals a very rich structure (see Fig. 5). Several types of molecular ions are identified as well as atomic sulfur fragments up to charge states 14+ (ionization of the S(1s) is energetically forbidden at these photon energies), and atomic fluorine ions with rather high kinetic energy. Further analysis of the SF\(_6\) data is under way and will be published elsewhere [3].

![Figure 5. SF6 TOF spectrum. Green numbers represent sulfur charge states, blue – fluorine charge states.](image)

4. Conclusions

We conducted an extensive study of the light-molecules interaction in the case of the prototypical target, \( N_2 \) molecule, with the LCLS FEL x-ray laser. Ion spectroscopy revealed a trend of frustrated absorption as a function of pulse duration. Electron spectroscopy established the first experimental result on the characterization of DCH states. We also presented a preliminary ion TOF spectrum for the SF\(_6\) dissociation after multiple photoionization by the intense x-ray pulse.

Acknowledgments
We thank all authors of the papers in references [1,2] and acknowledge their contribution to the work and the analysis presented. This work is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division.

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