Ultra-intense X-ray Induced Non-linear Processes in Molecular Nitrogen

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Abstract.
Sequential multiple photoionization of the prototypical molecule \( \text{N}_2 \) is studied with femtosecond time resolution using the Linac Coherent Light Source (LCLS). A detailed picture of intense x-ray induced ionization and dissociation dynamics is revealed, including a molecular mechanism of frustrated absorption that suppresses the formation of high charge states at short pulse durations. The inverse scaling of the average target charge state with x-ray peak brightness has possible implications for single pulse imaging applications. Moreover, we investigate the creation of double K-shell holes in \( \text{N}_2 \) molecules via sequential absorption of two photons on a timescale shorter than the core-hole lifetime by using intense x-ray pulses from the LCLS. The production and decay of these states is characterized by photoelectron spectroscopy and Auger electron spectroscopy. In molecules, two types of double core holes are expected, the first with two core holes on the same N atom, and the second with one core hole on each N atom. We report the first direct observations of the former type of core hole in a molecule, in good agreement with theory, and provide an experimental upper bound for the relative contribution of the latter type.

1. Introduction
The development of femtosecond light sources covering the infrared to the extreme ultraviolet (EUV) has led to a revolution in time-resolved studies of physical and chemical processes [1]. However, even with the development of high-harmonic generation sources in the EUV and soft-x-ray regions, the relatively long wavelengths of these sources preclude the direct imaging of the motion of individual atoms. As a result, there has been a tremendous interest in “fourth generation” accelerator-based free electron lasers (FEL’s) [2, 3, 4, 5], which offer an unprecedented combination of spatial and temporal resolution. The Free Electron Laser in Hamburg (FLASH) [2, 3] pushed the wavelengths of these sources into the soft x-ray regime, while the recently commissioned Linac Coherent Light Source (LCLS) now accesses the hard x-ray regime [4, 5]. The intense, short pulse, x-ray FELs will allow the exploration of novel states of atoms, molecules and clusters, with potential impact on applications ranging from single-pulse imaging of biomolecules to high energy density materials [6, 7, 8, 9, 10, 11]. In this proceeding, we present (1) the first study of the response of a molecular system, the prototypical molecule \( \text{N}_2 \), to ultraintense femtosecond duration laser pulses at a wavelength of 1.1 nm (1100 eV). We observe intense x-ray induced ionization and dissociation dynamics leading to various charge states up to fully-stripped \( \text{N}^{7+} \) ions. A molecular mechanism of
frustrated absorption that suppresses the formation of high charge states at short pulse durations is revealed. We show that this phenomenon can be explained by a simple rate equation model that accounts for molecular valence electron dynamics during the sequence of ionization events. (2) The first experimental attempt to characterize the creating double core hole (DCH) states of a molecule, N₂, by sequential two-photon absorption from an x-ray FEL, the LCLS. The production and decay of these states are characterized by using photoelectron spectroscopy and Auger-electron spectroscopy. The experimental results are interpreted with the help of \textit{ab initio} calculations [12, 13, 14, 15, 16] of the singly, doubly, and triply ionized states and their corresponding Auger spectra [17]. These results will serve as a basis for understanding double- and multiple-core-hole states in more complex molecules.

The experiment was conducted using the LCLS Atomic Molecular and Optical (AMO) physics instrument [18]. We used a photon energy of 1000 and 1100 (±15) eV and pulse durations of 280 fs, 80 fs, \(\sim 7\) fs and \(\sim 4\) fs [19, 20]. The pulse duration of 280 fs and 80 fs were produced with electron bunches with 250 pC and the pulse duration of 7 fs and 4 fs were obtained with 20 pC. Unless otherwise noted, the pulse energies quoted here are nominal values measured upstream from the beamline optics. These values are reduced by \(\sim 65 - 85\%\) in the interaction region due to various photon beam transport losses [20]. The photon beam was focused by Kirkpatrick-Baez (KB) mirrors to an area equal to about \(2\ \mu\text{m}^2\). The details of the apparatus and x-ray facility are described in Refs [19, 21, 22]. The LCLS had a repetition rate of 30 Hz. It took about 5 minutes to measure one of the ion-time of flight spectra and about 2 hours to obtain one of the photoelectron spectra presented in this work.

2. Multiple photon ionization and intense x-ray induced frustrated photon absorption [21]
The x-ray photons used in this study interact predominantly with the N₂ 1s electrons, representing an entirely different regime than previous FEL-based experiments in the EUV [23]. Absorption of the first photon produces a single 1s inner shell vacancy in N₂. The core hole state undergoes Auger decay into N²⁺ with two valence-shell holes within 6.4 fs [24]. The subsequent decay of N₂²⁺ occurs on a range of timescales; most dissociates to N⁺ + N⁺ and N²⁺ + N on a femtosecond timescale, but some of the N₂²⁺ is metastable [25, 26, 27]. The high peak brightness of the LCLS opens the possibility of DCHs by sequential two-photon absorption within the core-hole lifetime [19]. These DCH states of N₂ can have both holes on a single N atom, or a single hole on each atom. DCH states decay via Auger processes on timescales that are shorter than the corresponding SCH lifetimes, accelerating multiple ionization. Cyclic photon absorption and core-hole decay sequences produce ions of increasing charge states, eventually reaching the extreme case where all electrons are removed.

If the x-ray pulse duration is shorter than the Auger decay time, absorption will effectively terminate after the ejection of the two K-shell electrons in atomic N, or after the ejection of four K-shell electrons in N₂ (assuming that absorption by the other shells is negligible). In contrast, if the x-ray pulse is long relative to the Auger decay time, \textit{sequential multiple photoionization} sets in. One or more additional photons from the same laser pulse can be absorbed by the products of the Auger decay of N₂⁺ (dominantly N, N⁺, and N²⁺). For these fragments, a second photoelectron-Auger (PA) cycle will result in N²⁺, N³⁺, and N⁴⁺ ion charge states, respectively. The Auger relaxation timescale for this second PA cycle will be longer than that of the first cycle because there are fewer valence electrons available that can participate in the Auger decay [36]. The N²⁺ and N³⁺ fragments can undergo a third and still slower PA cycle, producing N⁴⁺ and N⁵⁺ ions. These ions can absorb additional photons, but now Auger decay is no longer possible due to the lack of valence electrons. Absorption of five or more photons will result in the production of fully stripped N⁷⁺ ions. A time-of-flight (TOF) mass spectrometer [18] was used to analyze ions produced in the interaction of the sample with the LCLS pulses as shown.
in Fig. 1. The relative ion yields have been corrected for the spectrometer-specific acceptance efficiency. The "bare" ions above were indeed observed for long (280 fs) pulses with high pulse energies (2.2 mJ), represented by the gray curve in Fig. 1.

The tremendous interest in single-pulse imaging and structure determination has raised questions about radiation damage and the ability to extract information before the sample is degenerated or destroyed. Previous calculations and experiments have focused on the idea of "inertial delay" of the Coulomb explosion during scattering from a pulse that is significantly shorter than the disassembly timescale for the object [6, 28, 29, 7]. We examine another effect that might have an even larger impact than inertia based distortion limitations: PA cascades induced by sufficiently short x-ray pulses are subject to frustrated absorption. As a result, the effective total photoionization cross section is reduced and Coulomb-repulsion effects in the sample during exposure to an imaging light pulse might be minimized.

Figure 1 shows ion time of flight spectra for three different pulse durations (∼7 fs, 80 fs and 280 fs) at similar pulse energies (0.26 mJ). Over the range of parameters investigated, longer pulses generally result in the observation of the highest charge states (red curve) whereas shorter pulses lead almost exclusively to lower charge states. Highly charged N5+ and N6+ ions are clearly observed for 80 fs and 280 fs pulse lengths. In contrast, the ∼7 fs spectrum shows only charge states up to N4+. The intensity of the N3+, N4+, and N5+ peaks decreases monotonically from 280 fs pulse duration to ∼7 fs pulse duration. This indicates that molecular N2 and its fragments cannot absorb photons as efficiently for short pulses as for longer pulses. The effect shown in Fig. 1 can be explained by frustrated absorption after the removal of K-shell electrons with a short pulse. The finite Auger relaxation time determines how fast the K-shell can be replenished with electrons, and thereby limits the number of photons that can be absorbed in a given time interval. This leads to a reduction of multiple ionization events with increasing peak power and therefore a suppression of the production of higher charge states for short pulses.

To support the interpretation of our measurements within the concept of frustrated absorption, we have developed a theoretical description of the interaction of intense x-rays with nitrogen molecules based on a parameterized rate equation model. As shown in the following, these x-ray induced chemical dynamics are of fundamental importance to understand charge formation in samples that consist of more than a single atom. The model presented here is based on a complete set of atomic ionization cross sections and relaxation rates. The effects of valence electron dynamics on the measured partial ion yields are modeled by including valence charge exchange between different atoms. Experimental parameters such as the pulse shape and the light intensity distribution across the focal volume have been included.

Fig. 2a-d show the measured charge state distributions for four different x-ray pulse durations
along with the results of the parameterized rate equation model. The average charge states $q_{av}(\tau)$ shown in Fig. 2e are derived by $q_{av}(\tau) = \sum_{i=1}^{7} N_i(\tau) q_i / \sum_{i=1}^{7} N_i(\tau)$ (1). Here, $N_i$ are the relative abundances of the charge states $q_i$ detected in the partial ion yield measurement. The frustrated absorption effect is clearly seen as a drop of the average charge towards short pulse durations and it is well reproduced by the model calculations. The brown band in Fig. 2e indicates the variation of the model calculations when adjusting the pulse energy between 17% and 21% of the nominal pulse energy (0.26 mJ). The good agreement of the band with the measured data indicates that the fundamental physics of the frustrated absorption effect is captured in the model. The extent of the theory band is a measure for the precision with which the pulse energy at the sample can be determined within the rate equation model. The effect of frustrated absorption on the average charge state is well reproduced by the parameterized rate equation model based entirely on available spectroscopic data, ab-initio calculations, and experimental parameters provided by LCLS.

To demonstrate the importance of molecular valence charge dynamics in the modeling of charge formation, the results of a rate equation model that is entirely based on an independent atom picture are included in Fig. 2 a-d as dashed lines. By comparing the atomic and molecular model, it shows that the inclusion of molecular valence electron dynamics in the theoretical description is instrumental to describe charge formation, and therefore damage formation, on the microscopic scale.

Beyond the fundamental importance of modeling a new regime of x-ray induced chemical dynamics, the ability to describe atom-specific transient charge formation in molecular samples will be vital to model damage mechanisms induced by the LCLS with an Angström spatial resolution and femtosecond time resolution. Fig. 3 provides a demonstration of how the findings described above can be employed to estimate charge-induced distortion effects in single-shot imaging of molecular samples. These distortion effects are directly related to the Coulomb repulsion between charged atoms within the molecular complex and thus to the time-dependent charging of the sample. In contrast to the asymptotic charge distributions that define the partial ion yields described in Fig. 2, only those charges that are present at the moment that the photons pass through the sample are of interest for imaging applications. An important benchmark for the achievable image quality is therefore the photon flux weighted charge as defined by $Q(\tau) = \int_{-\infty}^{+\infty} q(t) I_\tau(t) dt / \int_{-\infty}^{+\infty} I_\tau(t) dt$ (2). Here, $q(t)$ is the transient average charge in the molecule
and $I_\tau(t)$ is the time dependent intensity of the x-ray pulse with a pulse envelope width $\tau$. The illuminated charge $Q(\tau)$ represents the average charge that is encountered by an imaging photon while it traverses the sample. $Q(\tau)$ is significantly more affected by frustrated absorption than the asymptotic average charge $q_{av}(\tau)$ (Fig. 2 and 3). The illuminated valence charge is of particular interest since valence charges are predominantly responsible for distortion effects in the regime of low average charge. Core electrons contribute only little to molecular bonding. In addition, Coulomb repulsion between core holes that are shielded by a number of valence electrons is expected to be significantly smaller than the repulsion between valence charges. Thus, the results presented in Fig. 3 suggest that the relatively modest frustrated absorption effect presented in Fig. 2e might reduce the Coulomb forces that are ultimately responsible for target distortion during imaging applications by about one order of magnitude.

3. Double core hole formation and decays [30]
One intriguing possibility enabled by intense x-ray sources is the ability to produce atoms and molecules with multiple electron vacancies in core orbitals through the sequential absorption of multiple photons on a timescale faster than Auger decay, and it has been suggested that DCHs could provide the basis for richer, sensitive, spectroscopies than conventional inner-shell photoelectron spectroscopy [31, 32]. The different atomic sites in molecules introduce multiple possibilities for the DCH configurations, e.g., DCHs with both vacancies on a single site (DCHSS) and DCHs with single vacancies on two different sites (DCHTS). For such states, the presence and location of the first hole is predicted to affect the energy to produce the second hole, as well as the decay mechanisms and fragmentation patterns of the resulting DCH states [31]. The magnitude of the energy shifts of these states will provide unique spectral signatures as well as new information on the chemical environment of the core holes [33, 32]. While the intensity of conventional x-ray sources is too low to produce observable DCHs through sequential absorption processes, DCH states have been observed as a result of electron correlation in single-photon absorption. Unfortunately, these processes have a very low yield [34, 35], and only DCHSS states have been observed in this manner. At the intensities of the new x-ray FELs, photoabsorption should compete effectively with Auger decay [19, 21], allowing the production of both types of DCH states through sequential two-photon processes.

Figure 4 shows photoelectron spectra recorded at 1.0 keV and 1.1 keV photon energy and the
theoretically predicted electron energies for the relevant photo-processes. The electron energies in the 1 keV spectrum have been shifted by 100 eV to higher kinetic energies. The labels indicate the energies of photoelectrons resulting from a number of different processes based on the calculations [17, 36]. These include: (1) Photoelectrons from single core-shell ionization of molecular N2, N2+, and N22+, where the initial state electron vacancies are located in the valence shells (dot-dashed blue lines). (2) Photoelectrons from core-shell ionization of atomic Nm+ (initial state with m valence holes) (dashed black lines). (3) Photoelectrons from core-shell ionization of atomic Nm+(1s), with a single core hole and the remaining holes in the valence shells (dotted green lines); the processes responsible for these photoelectrons result in atomic DCH production. (4) Photoelectrons from core-shell ionization of N2+ (1s) with a single hole in the 1s orbital of one N atom, where the second electron is removed either from the same atom, i.e., the DCHSS process (purple solid line), or from the other N atom i.e., the DCHTS process (red solid line). Most of the spectral features are the result of multiple photon absorption by a single molecule. In particular, processes (3) and (4) present sequential two-photon inner-shell double ionization events on timescales that are fast compared to Auger decay. For the higher charge states, the reduced number of valence electrons increases the Auger lifetime, and thus increases the probability of producing atomic DCH states. The peak identification is particularly clear for N1+ (1s), N5+(1s), and N6+(1s) ionization, because no other photoelectrons are expected at energies below \( \sim 550 \) eV, and the observed peaks are in good agreement with the predicted line positions [36].

Fig. 5 shows the corresponding Auger spectra for N2, where the solid curves are the experimental data and the dashed curves are our theoretical results. Above \( \sim 400 \) eV, no Auger electrons of N2 have been observed with conventional x-ray sources. In contrast, the new spectra shown in Fig. 5 exhibit two new features lying 50-80 eV above the main SCH Auger peaks and with kinetic energies of 413 eV and 442 eV. These signals are clearly associated with Auger processes since the kinetic energies of the peaks do not vary with the photon energy. Contributions from photoelectrons observed in Fig. 4 are strongly suppressed in Fig. 5 due to the selected electron emission direction perpendicular to the light polarization. Our calculation shown in Fig. 5 (yellow shaded curve) predicts peaks at \( \sim 410 \) eV, which are produced by the Auger decay of the main DCHSS state of N22+ involving mainly 2\( \sigma_u \) and 1\( \tau_u \) electrons. In light of the expected underestimate in theory of 2-4 eV due to partially unaccounted electron relaxation in the final states [37], the prediction agrees very well with the observed peak position. We conclude that the newly observed Auger electron signal at \( \sim 410 \) eV kinetic energy stems from the decay of DCHSS states and is associated with so-called Auger hypersatellites [34, 35]. We estimate the DCHSS signal intensity to be \( \sim 1\% \) of the main Auger peak signal between 355 eV- 370 eV (\( \pm 5 \) eV). Experiments have also been performed at the LCLS to characterize the angular distribution of these hypersatellite electrons [38].

Although calculations of the Auger decay of DCHSS shakeup states have not been performed
Figure 5. Auger spectra from the LCLS and synchrotron experiments, and from theoretical calculations. Thick solid curves: Auger spectra recorded at 1.0 keV and 1.1 keV. The 1.1 keV spectrum is offset vertically for clarity. Solid green curve: Auger spectrum recorded with synchrotron source [39]. Dashed curves: calculated Auger spectra (scaled) of various initial states, including SCH (green), DCHTS (grey shaded curve), DCHSS (yellow shaded curve). Black stems indicate predicted energies of DCHSS shake-up Auger electrons. Dotted curve: spline fit to background. (See text for details).

explicitly, the energy splitting between the DCHSS main Auger peak and the DCHSS shake-up Auger peaks can be estimated by the energy difference between the calculated DCHSS photoline and the DCHSS shake-up photoline. The predicted energies of the DCHSS shake-up Auger electrons are indicated by black stem lines in Fig. 5. The good agreement of the calculated positions with the peak at 442 eV suggests that this peak might correspond to the Auger decay of the DCHSS shake-up states.

The detection and assignment of electrons associated with the production of the uniquely molecular DCHTS states requires improved energy resolution, which is achieved by increasing the retardation voltage in the photoelectron spectrometer to 480 V, as shown in Fig. 6. The spectrum is analyzed by taking into account the contributions from single-photon shake-up/off (SUO) processes as previously determined by Svensson et al. [40] and Kaneyasu et al. [41], and convoluting them with the experimental energy resolution of the current study (blue shaded area in Fig. 6). To disentangle the major contributions generated by multiple photon ionization, a nonlinear least-squares fit is performed based on five spectral components with identical peak shapes and independent amplitudes and center energies (green and red shaded areas).

Within the model of identical, apparatus-limited peak shapes, the fit result is globally unique as determined by a Monte-Carlo based sampling of the available fit starting parameter space by $\sim 10^5$ independent fit cycles. One spectral component is consistently found exactly at the position of the expected DCHTS photoline (574 eV). As indicated by the red area, the estimate of the total multiple photon ionization signal at 574 eV varies between zero and 8% of the main photoline intensity. Given the uncertainty in the contributions from overlapping spectral components, we can provide only an upper bound for the DCHTS signal rather than an absolute value. The upper limit of the DCHTS contribution is mainly defined by the minimum contribution of the $N^+(1s^22s^12p^3)$ ionization signal. This leads to an upper bound for DCHTS contributions in the photoelectron spectrum of 4% relative to the intensity of the $N_2(1s^{-1})$ main photoline. This value is in qualitative agreement with the $\sim 1\%$ DCHSS signal described above and an estimated ratio of $\sim 1.65$ between DCHTS and DCHSS signal intensities. An independent estimate of
the intensity of the DCHTS process by examination of the Auger spectrum is not possible at this stage. The nature of these states marked by a single core hole per atom leads to Auger electron energies that are embedded in the SCH Auger spectrum, as indicated by the grey shaded structure near 350 eV kinetic energy in Fig. 5.

4. Conclusion

In summary, the results presented here highlight some of the new frontiers in molecular physics that can be explored with high-intensity x-ray FELs. We present a microscopic picture of charge formation on a femtosecond time-scale and frustrated absorption in molecules that includes the decisive x-ray induced valence electron dynamics. The inclusion of molecular valence charge dynamics is fundamental for a correct description of frustrated absorption and time-dependent distortion effects in molecules. The present results are a significant step towards understanding ultra-intense x-ray induced physical processes and chemical dynamics in molecules. The predicted suppression of Coulomb repulsion effects in ultrashort x-ray pulses by one order of magnitude might have far reaching implications for single shot imaging applications, which are amongst the most promising fields of research at 4th Generation Light Sources. We also present the first experimental results on the characterization of DCH states produced by sequential two-photon absorption in molecules. The observation of DCHSS states is supported by photoelectron and Auger-electron spectra, as well as by theoretical calculations. In contrast, the observation of the uniquely molecular DCHTS states remains ambiguous, and only an upper bound to their production can be determined. Higher intensity (afforded by improved beam transport optics), improved stability of photon energy, higher electron energy resolution, and detailed studies of the intensity dependence of the electron spectra will thus be required to fulfill the potential of DCH spectroscopies.

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6. References

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