Auger electron angular distribution of double core hole states in the molecular reference frame

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The LCLS x-ray free electron laser enables an entirely new way to study chemical dynamics: double core vacancy Auger electron spectroscopy. The LCLS produces double core vacancies through rapid sequential ionization. Such novel excitations are of interest for x-ray investigations of femtosecond chemical dynamics because Auger electrons probe the local valence structure of molecules near a single atomic core. We used the LCLS to study sequential x-ray ionization in molecular nitrogen. We observed a rich single-site double core vacancy Auger electron spectrum and measured the Auger electron angle dependence in the molecular frame. We also measured the shift in the Auger electron energy spectrum due to the reduced screening of the double core vacancy. This shift confirms our theoretical prediction for molecular Auger relaxation following sequential multiple core-level excitations. In addition, we observe another new feature in the Auger electron spectrum that only appears for intense x-ray sequential excitation.

The sequential creation of core-level double vacancies was not possible until the unprecedented x-ray peak intensities of an x-ray free electron laser (xFEL) [1]. Core-level double vacancies have been observed in atomic systems via a single photon double ionization process [2–4]. However, the sequential formation of double core vacancies, shown schematically for N_2 in Fig. 1, relies on the extremely high peak intensity of the the Linac Coherent Light Source (LCLS) xFEL to induce photoionization rates that exceed Auger relaxation rates. Sequentially produced double core vacancies represent a novel process that can be used as a new tool for femtosecond-scale chemical analysis of molecular dynamics [1, 5].

Rapid sequential ionization results in two types of double core holes (DCHs) in a homonuclear diatomic molecule that can be described as follows: a fully depleted inner-shell orbital of a single atomic site (single-site), or two inner-shell vacancies, one on each atomic site (two-site). The two-site DCH (tsDCH) is of interest for its valence sensitivity [5] while the single-site DCH (ssDCH) represents one *hollow* constituent with a neutral partner.

Core electrons are highly localized around the nucleus with a Z^2 scaling of core binding energies that provides element specific spectroscopic information. The local molecular environment is revealed by the photoelectron spectra (PES) and Auger electron spectrum (AES) through shifts in the line shape or position, which is the basis for the widely applied technique of Electron Spectroscopy for Chemical Analysis [6, 7]. Double core hole PES and AES will exhibit large energy shifts that reveal the local molecular structure [1, 5]. The angular distributions of Auger electrons carry additional information regarding the shape of core and valence orbitals. A wealth of angle resolved measurements already exists for the decay of single core holes (SCHs) in molecules [8**?**
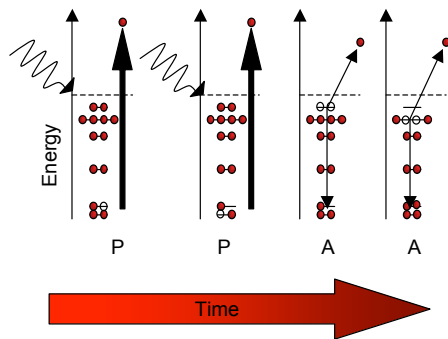
FIG. 1: Schematic diagram of sequential double photoionization (P) of core electrons by the LCLS, followed by Auger (A) relaxation in diatomic nitrogen. The horizontal arrow indicates the sequence of events. For the short LCLS pulses, sequential double ionization prior to Auger decay is the most likely path to molecular double core-hole excitations, either single-site or two-site.
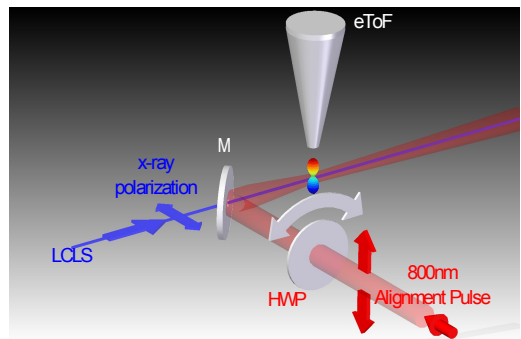

FIG. 2: Experimental setup. Linearly polarized x rays pass through a 2 mm hole in the mirror labeled (M) and then come to a $\sim 3\mu$m diameter focus (FWHM) in the interaction region. A motorized half-wave plate (HWP) controls the linear polarization of a non-resonant molecular alignment laser. The mirror (M) reflects the IR laser into co-propagation with the x rays. The IR laser comes to a $\sim 75\mu$m diameter focus in the interaction region. Auger electrons are collected with an electron time-of-flight (eTOF) spectrometer that is oriented perpendicular to the plane containing the x-ray polarization and propagation vectors.

–12]. In order to investigate the influence of the valence orbital structure on Auger relaxation of atomic-like ssD-CHs, we fix the molecular axis with respect to the laboratory frame. Here we present a study of the formation and decay of both single-site and two-site double core vacancies in molecular nitrogen in the molecular frame.

A linearly polarized, non-resonant (800 nm) ultrafast laser pulse produced impulsive stimulated rotational Raman scattering, aligning the molecular ensemble to the polarization direction, thus fixing the molecules in the lab frame. The $\sim$100 fs square impulse created a rotational wavepacket in the $\sim$20 K N_2 ensemble that in turn exhibited field-free alignment revivals [13]. We measured AES only at the field-free alignment revivals since the Auger process will reflect any laser-induced perturbation of the valence electrons. The direction of the optical laser pulse polarization determined the alignment axis of the molecular ensemble, and by rotating the polarization, we investigated three different orientations of the molecular axis with respect to the detector (Fig. 2): 0°, 45°, and 90°. We fit a model to the transient alignment signal as in Ref. [15] and estimate a field-free alignment of $\langle \cos^2\theta \rangle \sim 0.7$. Such an ensemble of molecules has an angular standard deviation $\Delta\theta \sim 30°$.

The sequential formation of DCHs requires an extremely high photon flux from the LCLS. This is achieved in low bunch charge mode (20 pC), which produces x-ray pulses shorter than 10 fs containing $\sim 10^{12}$ photons, $\geq 10^{18}$ photons/cm^2 when focused [17]. Such short intense pulses help to ensure that a significant number of double photoionization events occur within the Auger lifetime, ≤ 7 fs, as depicted in Fig. 1 [18]. The shot-distribution of x-ray pulse energies was centered around 150 μJ with a FWHM of 100 μJ before the transport and focusing optics. Based on the predicted losses in the transport and focusing optics, we estimate roughly 25μJ,

or $\sim 2 \times 10^{11}$ photons, in a ~ 3 μm diameter focal spot.

One core-level excitation unique to LCLS is the two-site double core hole since tsDCHs can only be created via sequential photoionization [1]. The main tsDCH Auger electron energy is predicted by our *ab initio* calculations to appear in the range $\sim$342–353 eV. This is expected to be a few eV below the measured energy since the calculations underestimate the relaxation energy of final states with core vacancies [19]. The Auger decay of dication states (N_2^{2+}) formed by shake-off ionization [20, 21] also appear in this range, 348–355 eV, along with satellites of the main Auger feature. Figure 3 shows the rich AES of isotropic N_2 along with a third generation synchrotron reference spectrum from Ref. [14]. Although the main ts-DCH spectral features are not clearly distinguished from other doubly ionized and singly ionized Auger processes, Fig. 3 does reveal a previously unobserved peak near 345 eV with a statistical significance of 2σ. This peak is not present in the reference spectrum and must be due to some high intensity process initiated by the LCLS pulse, such as the tsDCH formation or similar multiple photoionization-Auger decay sequence. Firm identification requires further calculation and additional experiments that employ near-edge excitation to help suppress the shake-off peaks.

The other core-level double excitation that should be observed in molecules is the single-site double core hole. Our calculations predict that the Auger decay of ss-DCH states will emit electrons with energies centered near 408 eV, again expected to be a few eV below the measured energy. Figure 4 shows a peak centered at $\sim$413 eV, 5 eV above the predicted value. We therefore
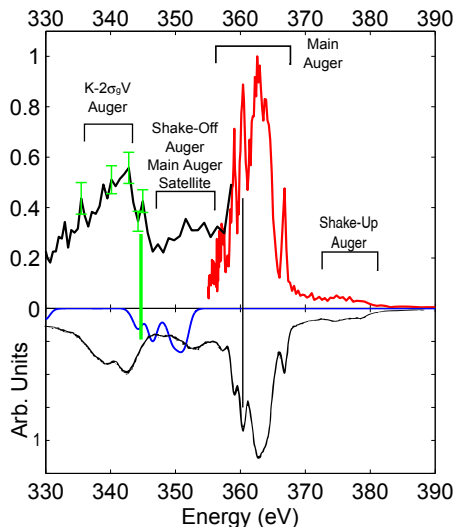
FIG. 3: Auger electron energy spectrum from isotropic N_2 for two retarding voltages, 350 V (red) and 300 V (black), adjusted for eTOF spectrometer transmission (top). Both spectra are normalized with respect to the largest peak (The main Auger feature). We replicate the Auger electron spectrum of Ref. [14] (black, inverted, bottom) as a reference, also shown is the calculated Auger electron spectra of the ts-DCH(blue), the relative intensity is arbitrary. We call out well known features above our experimental spectra, K-$2\sigma_g$V is the Auger decay of a single core hole involving valence and $2\sigma_g$ electrons. In addition, we call out two features with vertical bars: the SCH reference peak near 360eV (black bar) and a previously unobserved feature (green bar) as discussed in the text.
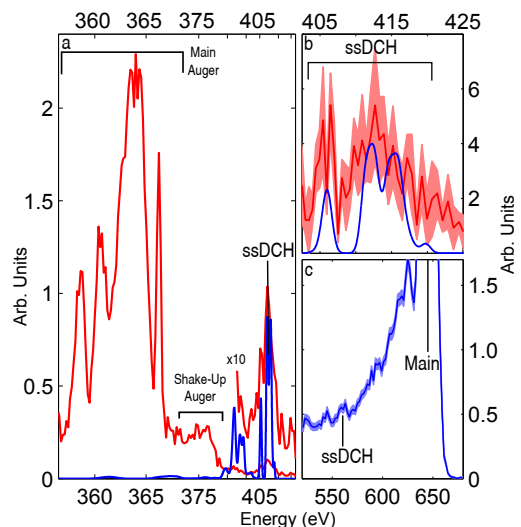
FIG. 4: Transmission-corrected Auger electron spectrum from N_2 aligned along the detector axis for a retardation voltage of 350 V. Panel (a) shows the Auger electron time-of-flight spectrum (reversed) with the abscissa relabeled in energy units. Various features are called out above the spectra, e.g. ssDCH denotes the Auger relaxation feature from a single-site double core hole. The calculated ssDCH Auger electron spectrum is shown, shifted by 5 eV, in blue with an intensity fit to the ten times magnified observed Auger electron spectra. Panel (b) shows the fine details of the Auger electron spectrum of the ssDCH as a red band with a width of two times the standard deviation. Panel (c) shows the photoelectron spectra recorded with the data shown in panel (a).

assign Auger electrons near this energy to relaxation of a ssDCH state. As mentioned above this excitation can be produced through either two photon sequential ionization or one photon non-sequential ionization, however the probability for the non-sequential process is very low [4]. The yield of ssDCH Auger electrons compared to SCH Auger electrons is $\sim 4\%$, which is much higher than the expected $> 1\%$ [4] if the ssDCHs were produced through a non-sequential process. Therefore a majority of our ss-DCHs are due to the sequential ionization porcess, which is verified by the appearance of the second peak in the photoelectron spectra shown in Fig. 4 (c).

The shift in energy between the main AES and the ss-DCH spectrum reveals the change in electron binding energy induced by the removal of the second core electron. A cross-correlation of the features finds a 51 ± 7 eV shift. For comparison, the shift between the highest computed ssDCH Auger electron energy and the highest computed normal Auger electron energy is $\sim$49 eV.

The Auger electron yield for a given alignment of the molecules is a convolution of the Auger emission angle dependence with the photoionization angle dependence. However, for energies far above the N_2 K edge, photoionization is insensitive to the orientation of the molecular

axis relative to the x-ray polarization [14]. At $\sim$1.1 keV, ~ 700 eV above the nitrogen K edge, the photoionization cross-section is nearly independent of molecular orientation. Any anisotropy in the Auger electron yield is therefore due to the angular dependence of the Auger decay process itself.

Figure 5 (a) shows the relative yields of the ssDCH Auger electrons for the three different orientations investigated. A comparison of our observed single core hole decay at 360 eV (marked in Fig. 3) to a previous coincidence experiment [8] validates our molecular frame measurement. The yield of ssDCH Auger electrons is maximal along the molecular axis and the yield is comparable at 90° and 45°, as shown if Fig. 5 (a). The centroid and RMS width of the ssDCH feature are independent of angle within the error of our observation. The observed anisotropy can be partially understood by appeling to a two-center interference model. An electron with an energy of $\sim$415 eV has a deBroglie wavelength of 0.6 Å, approximately half of the 1.1 Å nitrogen-nitrogen separation in N_2. The resulting interference pattern after convolving with a distribution of molecular orientations, will reach a maximum for emission along the molecular axis and comparable yields at 45° and 90°.
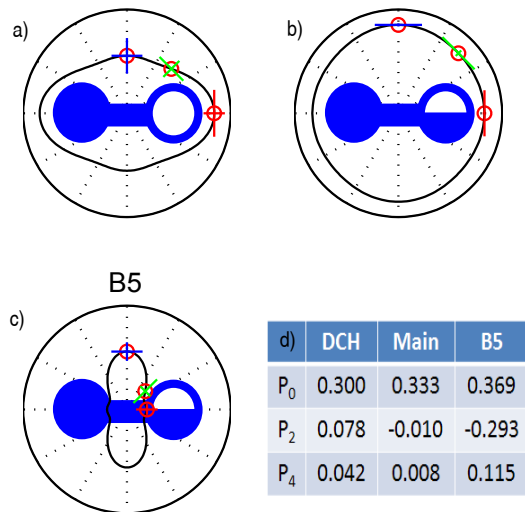
This is the first sequential production of single-site

B5

d)	DCH	Main	B5
P_0	0.300	0.333	0.369
P_2	0.078	-0.010	-0.293
P_4	0.042	0.008	0.115

FIG. 5: Angular yield of Auger electrons for: $90°$, $45°$, and $0°$ with respect to the molecular axis. Panel (a) shows the Auger electron yield of the ssDCH features. Panel (b) shows the Auger electron yield integrated over the primary SCH Auger lines. Panel (c) shows the Auger electron yield for the 360 eV reference peak which was previously studied in Ref. [8]. Panel (d) shows the coefficients of the fit of the 3 lowest even-Legendr polynomials.

double core holes observed in the molecular frame via angle-resolved Auger electron spectroscopy. The line shape of the ssDCH AES appears qualitatively similar to the primary molecular AES and agrees with *ab initio* calculations. We measured the angular anisotropy for the energy integrated ssDCH AES. The yield of ssDCH Auger electrons is maximal along the moleuclar axis. We measure the energy shift due to the reduced screening of these novel states to be 51 eV, consistent with *ab initio* calculations. In addition, previously unobserved structure in the shake-off region of the SCH AES is attributed to a process initiated by the intense LCLS x-ray pulses such as a two-site double core vacancy formation.

As discussed earlier several theoretical studies have raised the possibility of using tsDCH spectroscopy as a tool for femtosecond-scale chemical analysis of molecular dynamics. This spectroscopy can employ either photo-electrons as in the scheme for x-ray two photon photo-electron spectroscopy [1] or Auger electrons. We have shown that the tsDCH Auger electrons are not easily discernible from other Auger processes, and great care must be taken in implementing tsDCH spectroscopy. However, we easily identify the ssDCH because of the large energy shift from the main Auger electron peaks. Clearly, the chemical shifts associated with the ssDCH deserve further investigation for their use as a spectroscopic tool. Future studies at short pulse x-ray FELs may resolve the

angular pattern for the individual features of the DCHs. This would develop the field of molecular-frame multi-core Auger electron spectroscopy.

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