Auger Electron Angular Distribution of Double Core-Hole States in the Molecular Reference Frame

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The Linac Coherent Light Source free electron laser is a source of high brightness x rays, 2×10^{11} photons in a $\sim$5 fs pulse, that can be focused to produce double core vacancies through rapid sequential ionization. This enables double core vacancy Auger electron spectroscopy, an entirely new way to study femtosecond chemical dynamics with Auger electrons that probe the local valence structure of molecules near a specific atomic core. Using 1.1 keV photons for sequential x-ray ionization of impulsively aligned molecular nitrogen, we observed a rich single-site double core vacancy Auger electron spectrum near 413 eV, in good agreement with *ab initio* calculations, and we measured the corresponding Auger electron angle dependence in the molecular frame.

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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) [1,2]. Core-level double vacancies have been observed in atomic systems via a single photon double ionization process [3–5]. 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 Linac Coherent Light Source (LCLS) xFEL to induce photoionization rates that exceed Auger relaxation rates. Sequentially produced double core vacancies represent a novel process [6–11] that has been proposed as a new tool for femtosecond-scale chemical analysis of molecular dynamics, because of an enhanced sensitivity to the valence environment [1,6,12].

Rapid sequential ionization results in two types of double core holes (DCHs) in a molecule. These can be described either as a fully depleted inner-shell orbital of a single atomic site (single-site) or as two inner-shell vacancies on different sites (two-site). The two-site DCH (tsDCH) is of interest for its valence sensitivity [6,12] 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; this is the basis for the widely applied technique of Electron Spectroscopy for Chemical Analysis [13,14]. Double core-hole PES and AES are expected to exhibit larger energy shifts than traditional PES or AES and therefore more strongly reveal the local electronic structure [1,6,12]. This enhancement may improve future studies of transient electronic structure. In

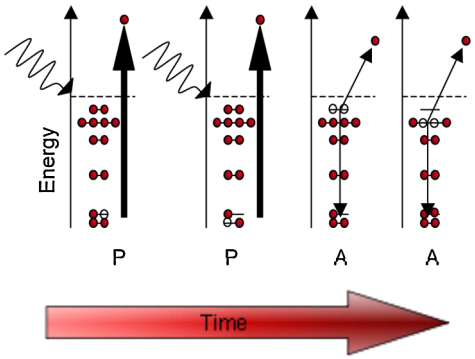

FIG. 1 (color online). Schematic diagram of sequential double photoionization (P) of core electrons by the LCLS, followed by Auger (A) relaxation in diatomic nitrogen. The horizontal arrow indicates the sequence of events. For the short LCLS pulses, sequential double ionization prior to Auger decay is the most likely path to molecular double core-hole excitations, either single-site or two-site.

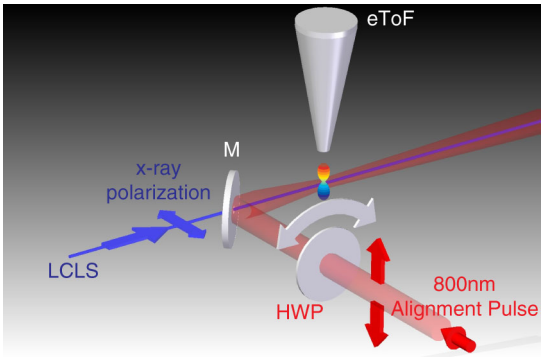

FIG. 2 (color online). Experimental setup. Linearly polarized x rays pass through a 2 mm hole in the mirror labeled (M) and then come to a ~3 μm diameter focus (FWHM) in the interaction region. A motorized half-wave plate (HWP) controls the linear polarization of a nonresonant molecular alignment laser. The mirror (M) reflects the IR laser into copropagation with the x rays. The IR laser comes to a ~75 μm 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.

addition, the angular distributions of Auger electrons carry 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 [15–20]. We use impulsive molecular alignment to fix the molecular axis in the laboratory frame in order to investigate the influence of the valence orbital structure on Auger relaxation of these novel doubly-excited ssDCH states. We present a study of the formation and decay of double core vacancies in N_2 in the molecular frame.

A linearly polarized, nonresonant (800 nm) ultrafast laser pulse aligned the molecular ensemble to its lab-fixed linear polarization direction. The ~100 fs square impulse created a rotational wave packet by impulsive rotational Raman scattering in the ~20 K N_2 ensemble that in turn exhibited field-free alignment revivals [21]. We measured AES at a rotational revival since otherwise the Auger process would suffer from laser-induced perturbation of the valence electrons. 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. [22] and estimate a field-free alignment of $\langle\cos^2\theta\rangle \sim 0.7$ [23]. Such an ensemble of molecules has an angular standard deviation $\Delta\theta \sim 30°$.

Sequential formation of DCHs requires the extremely high photon flux of the LCLS. Low bunch charge mode (20 pC) produces x-ray pulses shorter than 10 fs containing $\sim 10^{12}$ photons, or $\geq 10^{18}$ photons/cm^2 when focused [24]. 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 [25]. The shot distribution of x-ray pulse energies was centered around 150 μJ with a FWHM of 100 μJ as measured upstream of the transport and focusing optics. Based on rough loss estimates, we estimate that roughly 25 μJ, or $\sim 2 \times 10^{11}$ photons, were focussed to a ~3 μm diameter focal spot.

One core-level excitation unique to LCLS is the two-site double core hole since it can only be created via sequential photoionization [1]. We predict a range of ~342–353 eV for the main tsDCH Auger electron energy based on our *ab initio* calculations. The measured energy should lie a few eV above this prediction since the calculations underestimate the relaxation energy of final states with core vacancies [26]. The Auger decay of dication states (N_2^{2+}) formed by shake-off ionization [27,28] 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. [29]. Although the main tsDCH spectral features are not clearly distinguished from other doubly ionized and singly ionized Auger processes, Fig. 3 may 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 will require further analysis and additional experiments which either employ near-edge excitation to help suppress the shake-off peaks or coincidence detection to distill the tsDCH electrons.

Single-site double core holes are predicted to show ~80 eV larger binding energy than single core holes in nitrogen [12]. Our calculations predict that the Auger decay of ssDCH states will emit electrons with energies a few eV above the calculated 408 eV, and indeed Fig. 4 shows a peak centered at ~413 eV, 5 eV above the pre-

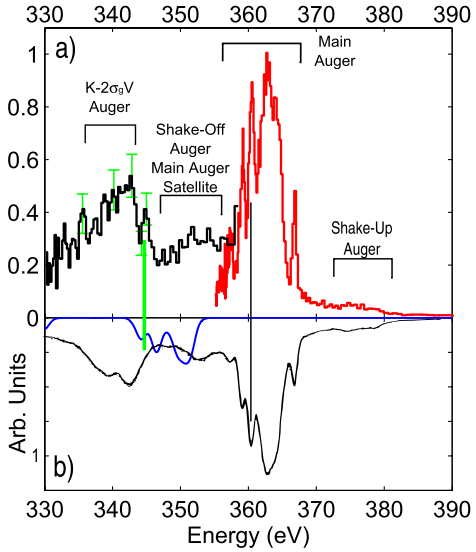

FIG. 3 (color online). Panel (a) Auger electron energy spectrum from isotropic N_2 for two retarding voltages, 350 V (red) and 300 V (black), adjusted for eTOF spectrometer transmission. The spectra are normalized with respect to the largest peak (main Auger feature). Panel (b) We replicate the Auger electron spectrum of Ref. [29] (black, inverted, bottom) as a reference along with the calculated Auger electron spectra for the tsDCH (blue) with arbitrary relative intensity. We call out some known features above the experimental spectra where $K - 2\sigma_g V$ 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 360 eV (black bar) and a previously unobserved feature (green bar) as discussed in the text.

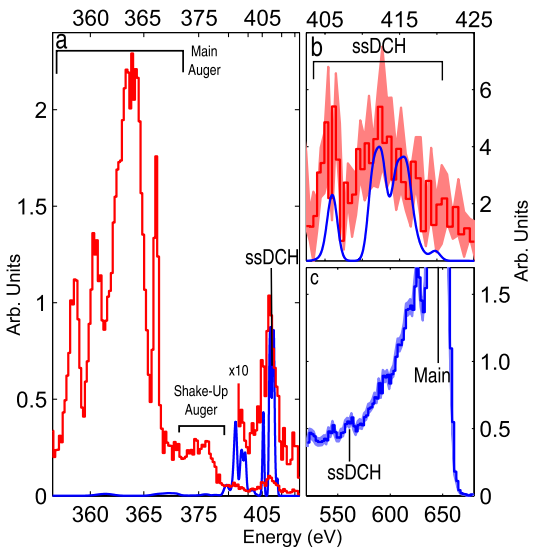

FIG. 4 (color online). Transmission-corrected Auger electron spectrum from N_2 aligned along the detector axis for a retardation voltage of 350 V. Panel (a) shows the Auger electron time-of-flight spectrum (reversed) with the abscissa relabeled in energy units. Various features are called out above the spectra, e.g., ssDCH denotes the Auger relaxation feature from a single-site double core hole. The calculated ssDCH Auger electron spectrum is shown in blue (dark gray), shifted by 5 eV as discussed in the text. Panel (b) shows the fine details of the Auger electron spectrum of the ssDCH as a red band with a width of 2 times the standard deviation. Panel (c) shows the photoelectron spectrum recorded with the data shown in panel (a).

dicted value. We assign Auger electrons near this energy to relaxation of the ssDCH state. As mentioned above, this excitation can be produced by either two-photon sequential ionization or one-photon nonsequential ionization although the probability for the nonsequential process is quite low [5]. The yield of ssDCH Auger electrons compared to SCH Auger electrons is ~4%, nearly an order of magnitude greater than the expected ~0.5% [5] for the nonsequential process. Therefore, a majority of our ssDCHs are produced by the sequential two-photon ionization process. This is further supported by the appearance of a ~4% spectral enhancement ~80 eV below the main photoelectron peak in Fig. 4(c). The energy of this feature coincides with photoionization of the N_2^+ $(1s^{-1})$ state, ordinarily suppressed by Auger decay in lower intensity x rays.

The shift in energy between the main AES and the ssDCH spectrum reveals the change in valence electron binding energy induced by the removal of the second core electron. A cross correlation of the features shows a 51 ± 7 eV shift. The *ab initio* calculated shift between the highest ssDCH Auger electron energy and the highest normal Auger electron energy is ~49 eV, a good agreement with the measurement.

The Auger electron yield for a given alignment of the molecules represents a convolution of the Auger emission angle dependence with the photoionization angle dependence. However, for energies more than 50 eV above the N_2 K edge, photoionization is insensitive to the orientation of the molecular axis relative to the x-ray polarization [29]. At 1.1 keV, ~700 eV above the nitrogen K edge, any anisotropy in the Auger electron yield is 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 qualitative agreement between our observed single core-hole decay at 360 eV (marked in Fig. 3) with a previous coincidence experiment [15] validates our molecular frame measurement. We find that the yield of ssDCH Auger electrons is maximal along the molecular axis but similarly low for both 90° and 45°, as shown in Fig. 5(a). The centroid and root mean square (RMS) width of the ssDCH feature are independent of angle within the error of our observation. The observed anisotropy can be partially understood by appealing to a two-center interference model [30]. An electron with an energy of ~415 eV has a de Broglie wavelength of 0.6 Å, approximately half of the 1.1 Å bond-length in N_2. The resulting interference

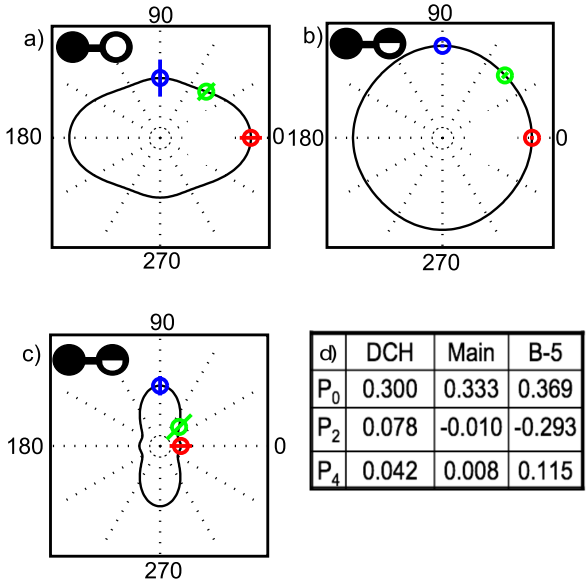

FIG. 5 (color online). Angular yield of Auger electrons for: 90°, 45°, and 0° with respect to the molecular axis. Panel (a) shows the Auger electron yield of the ssDCH features. Panel (b) shows the Auger electron yield integrated over the primary SCH Auger lines. Panel (c) shows the Auger electron yield for the 360 eV reference peak which was previously studied in Ref. [15]. Panel (d) shows the coefficients of the fit of the 3 lowest even Legendre polynomials shown in each panel as a solid line.

pattern, convolved with the distribution of molecular orientations, will reach a maximum for emission along the molecular axis with lower but similar yields at 45° and 90°, in agreement with our data. This interference predicts a relative angular yield of Auger electrons within 0.8σ of our measured result.

We report the first sequential production of single-site 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 and find that the yield is maximal along the molecular axis. We measure the energy shift due to the reduced screening to be 51 eV, also consistent with *ab initio* calculations. In addition, we have indication of previously unobserved structure in the shake-off region of the SCH AES due to a process initiated by the intense LCLS x-ray pulses such as a two-site double core vacancy formation.

Several theoretical studies have raised the possibility of using tsDCH spectroscopy as a tool for femtosecond-scale chemical analysis of molecular dynamics [1,12]. This spectroscopy could in principle employ either photoelectrons as in the scheme for x-ray two-photon photoelectron spectroscopy [1] or Auger electrons. We have shown that the tsDCH Auger electrons are not easily discernible from other Auger processes and that great care must be taken in implementing tsDCH spectroscopy. The low repetition rate of the LCLS greatly limits the ability to perform high statistics studies, but we nevertheless 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 local-valence sensitive spectroscopic tool. Furthermore, future studies at short pulse x-ray FELs could resolve the angular pattern for the individual features of ssDCHs and could develop a field of molecular-frame multicore Auger electron spectroscopy.

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