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Double Core-Hole Spectroscopy for Chemical Analysis with an Intense X-Ray Femtosecond Laser

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Theory predicts^{1,2,3} that double-core hole (DCH) spectroscopy can provide a new powerful means of differentiating between similar chemical systems with a sensitivity not hitherto possible. Although double core-hole ionization on a single site (DCHSS) in molecules was recently measured with double^{4,5} and single^{6,7} photon absorption, double core holes with single vacancies on two different sites (DCHTS), allowing unambiguous chemical analysis, have remained elusive. Here we report the direct observation of DCHTS, produced via sequential two-photon absorption, using short, intense x-ray pulses from the Linac Coherent Light Source (LCLS)⁸ Free-Electron Laser (FEL) and compare it with theoretical modeling. The DCH states exhibit unique signatures probing the chemical environment in molecular species^{1,2,3}, proving the validity of the methodology². Our findings exploit the ultrashort pulse duration of the FEL to eject two core electrons on a time scale comparable to that of Auger decay^{2,3} and demonstrate *x-ray control* of physical inner-shell processes.

Advances in the understanding of the structure and dynamics of matter using lasers⁹ and synchrotron radiation¹⁰ were made possible by x-ray photoelectron spectroscopy (XPS) based on single core hole (SCH) ionization. However, this widely used technique has limitations when it comes to investigating molecules with nearly equivalent atoms such as carbon, oxygen or nitrogen atoms in hydrocarbons¹, aromatic molecules² or nucleobases such as uracil¹¹.

Double core hole (DCH) ionization, not easy to produce due to their short lifetime, can remove such ambiguity. As schematically shown for CO in Fig. 1, in a molecular system, two types of DCHs are expected¹. About two decades ago, Cederbaum *et al.*¹ demonstrated by calculating SCH and DCH binding energies that DCHTS spectra should show an enhanced chemical shift, allowing site-specific identification of nearly equivalent atoms with different chemical environments. They predicted¹ that the ability to distinguish binding energies associated with DCHTS will provide a sensitive probe of the local chemical environment of the atoms in molecules. This is a substantial development of the general principle of Electron Spectroscopy for Chemical Analysis (ESCA), which until now has been mostly limited to SCH ionization.

Santra *et al.*² extended Cederbaum's original idea¹ by calculating the inner-shell double ionization spectrum of para-aminophenol which was found to be more sensitive to chemical effects than the inner-shell single ionization spectrum. They suggested² that intense, ultrashort pulses could allow such investigations via a non-linear two-photon absorption process. Such experimental observations were not possible until the recent^{8,12} advent of ultrafast x-ray FELs, which are revolutionizing spectroscopy^{4,5,13-15} and imaging¹⁶.

Here, we report the first measurements of DCHTS using CO as the showcase, and support them by calculations³. Although recently DCHSS in molecules were measured with the LCLS^{4,5} FEL and synchrotrons⁶⁻⁷, DCHTS spectra have remained elusive. The work described here demonstrates an important enhancement of ESCA using FELs such

as the LCLS⁸ and illustrates unambiguously the ability for *x-ray control* of inner-shell processes. The breakthrough in our investigation is the novel capability to manipulate inner-shell ionization processes, in particular to modify and control femtosecond Auger decay processes to probe the chemical environment in a highly sensitive way. This population control is achieved by tuning the x-ray pulse intensity and duration. We chose intense x-ray pulses with duration comparable to the intrinsic Auger decay time of the atoms constituting the molecular species. The intensity of the pulse ensures that the fluence is high enough to allow two core electrons to each absorb a photon in order to create two core holes. By choosing the ultrashort x-ray pulse duration to be shorter than the typical SCH state lifetime, the Auger cascade decay is suppressed and the formation of DCH versus SCH state is, thus, actively controlled. We characterize the production and decay of these states by photoelectron and Auger electron spectroscopy.

Observation of DCHTS and DCHSS states in CO using photoelectron spectroscopy

The interaction of intense ultrashort x-ray pulses with matter is dominated by core-shell excitation and by the competition between Auger relaxation and *multiple* inner-shell ionization. In order to unravel the SCH and DCH ionization processes in molecular CO and its fragments C and O we use photoelectron spectroscopy (see methods section). The x-ray laser pulse duration is comparable to the core lifetimes of C and O (4-7 fs) and this allows a second photon to be absorbed by the singly charged ion, prepared by the first photon, before Auger decay sets in. The latter process would favor multiple valence ionization leading to high charge states and spectral congestion. In order to have

sufficient x-ray laser pulse intensity to enable DCH ionization, we carried out the present measurements with ~ 10 fs pulse duration.

Figure 2 reveals various ionization mechanisms. The inset in Fig. 2 shows the photoelectron spectra recorded at 700 eV photon energy obtained with an electron time-of-flight (e-TOF) spectrometer aligned at 54.7° with respect to the polarization axis of the LCLS x-ray beam. The yellow (solid line) spectrum was taken with synchrotron x-rays¹⁷ and is shown for comparison. The dark green filled spectrum corresponds to the measurement carried out with the highest x-ray laser pulse intensity, 10^{18} W/cm² (focus, see methods) while the light green filled spectrum corresponds to the weakest pulse intensity, 3×10^{15} W/cm² (defocus). The red filled spectrum corresponds to the difference between the dark and light green spectra and this spectrum is shown separately in the main plot. We display the measurements in this fashion because the focused spectra are very rich in SCH and DCH structures. Subtracting the defocused from the focused spectrum emphasizes the DCH ionization processes, shown clearly in the red filled spectrum. Predicted electron energies for several SCH and DCH photo-processes are indicated in the figure by vertical lines.

The electron spectrum in Fig. 2 (red filled) reflects a sequence of ionization events produced by Auger decay and fragmentation of CO and its ions as well as multiple ionization of C and O fragments, in a *single pulse*. We observe:

1) SCH ionization of neutral molecules and molecular ions with a valence hole (the inset of Fig. 2). While the SCH CO peak results from single photon processes, the SCH CO⁺ peak results from sequential absorption of two photons, where the first photon ionizes a valence electron and the second photon ionizes a core electron. The calculated positions of these peaks are shown in the main panel of Fig. 2 as a thin black dotted-dashed line (CO⁺) and a thin black dashed line (CO).

2) SCH ionization from atomic C^{q+} fragments (initial state with q valence holes). These peaks correspond to multiple photon processes. The initial atomic ions are prepared by fragmentation following either Auger decay or direct valence ionization or by further ionization/Auger decay of atomic ions. The calculated energies are indicated by the group of solid purple lines.

3) DCH ionization from atomic C^{q+} (1s) (with a single core hole and the remaining holes in the valence shells). This process involves sequential ionization faster than Auger decay. The calculated energies of these multiply ionized states are shown by the group of solid blue lines.

4) DCH ionization of CO molecules. Photoelectrons from core-shell ionization of CO^{+(1s)⁻¹} with a single hole in the 1s orbital of the C atom, DCHSS_C, and the second electron ejected from the same atom (as depicted in Fig. 1). These energies are indicated by the solid thick black line.

The most intense peak in Fig. 2 corresponds to the DCHTS with its energy indicated by the dashed thick black line. This was the goal of our investigation and the experimental finding agrees very well with our calculations as shown in Table 1. In order to check our DCHTS results, we used a different method. We carried out two measurements with two pulse intensities (focused) and with photon energies above (700 eV) and below (500 eV) the O K-edge. After subtraction of the two spectra (to remove single-photon ionization events), shown in panel (a) of Fig. 3, we obtain consistent observation of the DCHTS when compared to panel (b) of Fig. 3.

Observation of DCHTS and DCHSS states in CO using Auger electron spectroscopy

Figure 4 shows Auger electron spectra. The inset displays the focused (red curve) and defocused (blue curve) spectra, along with synchrotron data (purple) for comparison¹⁷. The black curve shows their difference, also displayed in the main plot along with our calculation³. The yellow shaded area represents the total calculation (all processes). While the red solid and dashed curves represent DCHTS Auger and secondary Auger processes, respectively, the blue solid and dashed curves represent DCHSS Auger and secondary Auger processes. The Auger data confirm the presence of the DCHTS signal for C and O and also show clearly the DCHSS signal. The agreement between the measurements and the calculations is again very good, although our theory may underestimate the relative intensity of the DCHTS features. Auger decays of highly charged SCH states may contribute to the discrepancy between the experimental and the theoretical results.

Summary

The seminal prediction of Cederbaum *et al.*¹ has set in motion the idea to measure DCHTS and its realization, to achieve unambiguous chemical analysis. A substantial development of ESCA with FELs has commenced and our work starts the beginning of a new phase of chemical analysis of matter using DCH spectroscopy. Our reported photo- and Auger-electron spectra demonstrate the feasibility of this new method². Our work unveils the possibility to probe very sensitively the chemical environment by measuring the binding energies associated with DCHTS. The measurements are accomplished with the unique ability to *control* the brightness and short pulse duration of the LCLS x-FEL. The physical phenomena are general and should be possible with any intense, x-ray femtosecond laser. Furthermore, this technique is expected to be applicable to many systems, including bio-molecules² and solids. Finally, these results will serve as a basis for producing selective configurations with single or double core holes on specific atoms in any molecule, ultimately controlling how these states decay and how the molecule fragments.

Methods Summary

The experiment was conducted using the Atomic Molecular and Optical instrument^{14,15,18} and the LCLS⁸ at SLAC National Accelerator Laboratory. Five e-TOF

spectrometers were used to record the spectra reported. The electron energy spectra were recorded by e-TOFs located at selected polar and azimuthal angles with respect to the polarization and propagation directions of the x-ray beam. For the present experiment, the LCLS produced pulsed x-ray laser radiation at 500 and 700 (+/-10) eV at a repetition rate of 60 Hz, with a pulse energy of 0.05 mJ (500 eV)/ 0.2 mJ (700 eV) and ~10 fs pulse duration.

Single ionization potentials (IPs) and double core hole ionization potentials (DIPs) were calculated³ using the complete active space self consistent field (CASSCF) method. The influence of the chemical environment on these DIPs was evaluated³ for DCHSS and DCHTS states. Electron energies of the sequential Auger emissions following the double core-hole creation were obtained from *ab initio* energies of triply charged states with one core hole and two valence holes and quadruply charged states with four valence holes. Auger intensities were estimated from the *ab initio* Auger rates and the initial-state populations obtained by solving rate equations.

Experimental and Theoretical Methods:

1) Experiment

The molecular CO sample was introduced via a 100 μm pulsed nozzle into the interaction region where it crossed the LCLS photon beam. The photon energies were generated by 40 pC compressed electron bunches to acquire the ~7-10 fs pulse duration data. The pulse duration is difficult to determine for ultrashort pulses (<10 fs) with compressed electron bunches¹⁹. We used indirect estimates based on measurements of the

peak electron current to derive x-ray pulse durations⁸. Absolute pulse energy calibration is problematic, since the LCLS AMO chamber does not have a direct method to measure the energy. All pulse energy values given in this paper are the nominal accelerator values measured upstream from the beamline optics. The actual pulse intensities are estimated to be about 65%-85% smaller than the nominal values due to photon transport losses in the AMO beamline^{14,15}. All pulse energy values given in this paper are the nominal accelerator values measured upstream from the beamline optics except where explicitly stated otherwise.

For the measurements in the “focused” conditions, the LCLS photon beam was focused by Kirkpatrick-Baez (KB) mirrors to an elliptical profile with FWHM lengths of the major and minor semi axes of 2.2 μm and 1.2 μm ²⁰, respectively. The focus profile was determined during the commissioning phase of the LCLS by solid target depletion experiments²⁰. This focal size results in an x-ray beam intensity of about 10^{18} W/cm². In order to produce the very short pulses (< 10 fs), only the very last 16-17 LCLS undulators, out of a total of 33 undulators were used. This configuration should not change the spot size based on accelerator data⁸. For the measurements in the “defocused” condition, the stage of the KB mirrors was moved 20 mm away from the optimal “focus” position resulting in an intensity of $\sim 3 \times 10^{15}$ W/cm² and an estimated elliptical profile with FWHM lengths of the major and minor semi axes of 37.5 μm and 20.6 μm respectively.

The photoelectron spectra shown in Fig. 2 and Fig. 3 were measured at an e-TOF positioned in the plane perpendicular to the x-ray propagation, at the so called magic angle (where the signal intensity is independent of the angle of detection) to optimize the detection of photoelectrons. The Auger spectra shown in Fig. 4 were

measured with e-TOF spectrometers positioned perpendicularly to the photon polarization direction to minimize the contribution of photoelectron peaks relative to Auger peaks. The synchrotron reference data shown in Fig. 2-4 were taken at the ELETTRA synchrotron light source, Gas Phase beamline. We carried out the measurements in the “focused” and “defocused” conditions in order to directly take into account SCH ionization, including shake up and shake off (SUO) excitations. These effects proved to be problematic in a previous work⁴ since using synchrotron based-ionization was not adequate in accounting for SUO or removing structures from highly charged states produced by FEL radiation. The subtraction of the focused-defocused spectra allowed us to generate clean spectra demonstrating unambiguously the production of the DCHTS. The experimental values listed in Table 1 were obtained by Gaussian fitting the spectral peaks. The theoretical values are from Ref 3. We also carried out measurements with photon energies above and below the O K-edge to take into account the SCH/multiple ionization structures. The subtraction of the spectra led to the confirmation of the observation of the DCHTS since it appeared at the same position when we compared the below-above O K-edge (top panel of Fig. 3) with the focused-defocused method (bottom panel of Fig. 3).

Theory

The IPs and DIPs of single and double core-hole states of CO were computed by means of the CASSCF method to evaluate the impact of the chemical environment on the respective ionization processes and provide guidance for the x-ray two photon photoelectron² (XTPPS) experiment reported here. Spectral distributions of the sequential

Auger emission following the DCH creation were also computed as a guide of the present experiment and to interpret the present experimental spectra. For this purpose, we calculated the energies of triply charged states with one core hole and two valence holes (CVV) and quadruply charged states with four valence holes (VVVV), by the complete active space configuration interaction (CASCI) method with the orbitals obtained from the CASSCF calculations. The intensities of the Auger emissions from DCHTS and DCHSS states to the CVV states and subsequent Auger decay from CVV to VVVV states were evaluated from the atomic populations and the relative populations of the initial DCH states obtained by solving the rate equation where the FEL conditions were imposed.

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Author Contributions

NB, LF, BM, TO, KU, EK, RF, PvdM, PS, HTS, RDT, ML, RR, KCP, JDB, CB, SW, MP performed the experiment. MT and ME performed the calculations. NB wrote the paper incorporating comments from all the authors.

Additional Information

The authors declare no competing financial interests.

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Figure Caption

Fig. 1. Schematic illustration of (a) the electronic structure of the CO molecule, (b) the SCH ionization at the C K-edge (SCH_C) and the SCH ionization at the O K-edge (SCH_O), and (c) the DCHSS ionization at the C K-edge (DCHSS_C), the DCHSS ionization of the O K-edge (DCHSS_O) and the DCHTS ionization.

Fig. 2. Photoelectron spectra of carbon recorded at 700 eV photon energy, ~10 fs pulse duration. Calculated state energies and intensities are marked by vertical thick lines with head markers: DCHTS (dashed line), DCHSS (solid line) and SCH of CO⁺ with a valence

hole (dash-dotted). The calculated energies for atomic ions are marked by a group of solid vertical lines without head markers. The spectra are calibrated to the known experimental binding energy value of the CO SCH which is marked by the thin dashed line (see text and methods for details).

Fig. 3. Photoelectron spectra demonstrating consistent structures measured with two experimental methods. a) Top panel, photoelectron spectrum resulting from the subtraction of spectra measured above and below the O-K-edge. b) Bottom panel, represents Fig. 2 (red filled part) and is compared to the top panel to demonstrate the observation of DCHTS in the photoelectron spectrum.

Fig. 4. Auger spectra compared to theoretical DCH Auger spectra. Main panel: Measurements taken at different x-ray intensities with a focused beam (red curve in inset) and a defocused beam (blue curve in inset). The purple curve was taken with synchrotron radiation and is shown for comparison. The difference of the two x-ray intensities is shown as the black curve. Theoretical Auger spectra are shown in the main panel: overall calculation (yellow shaded area); DCHSS (solid blue curve); DCHTS (solid red curve); DCHSS secondary processes (dashed blue curve); DCHTS secondary processes (dashed red curve).

Table 1: Calculated electron binding energies³ and the corresponding experimental binding energies. BE indicates binding energy. The experimental values are calibrated by adjusting the BE_SCH value to a known value^{3,21}.

Theory ³ (2010)		Experiment
BE_SCH	298.2 eV	296.5 eV±0.5 eV
BE_DCHSS	369.6 eV	371.4 eV±3.5 eV
BE_DCHTS	314.2 eV	312.8 eV±0.7 eV
BE_diff_DCHSS_SCH	71.4 eV	74.9 eV±4.0 eV
BE_diff_DCHTS_SCH	16.0 eV	16.3 eV±1.2 eV







