Chemical Analysis: Double Core-Hole Spectroscopy with Free-Electron Lasers

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Abstract

Free-electron lasers with their femtosecond pulse duration, high pulse energy and tunable photon energy in a regime from XUV to hard-x-ray have opened up several research avenues in physics, chemistry and biology. We have exploited the attributes of these new lasers by exploring intriguing non-linear effects such as double core-hole formation via multiphoton absorption. We have carried out x-ray two-photon photoelectron spectroscopy for molecular chemical analysis using the Linac Coherent Light Source. Our experimental work aimed to probe the chemical environment of specific atomic sites in several molecules and validate the theory of two-photon photoelectron spectroscopy. This work demonstrates that our methodology will be very effective with the future intense, high repetition rate as well as laser-seeded or self-seeded photon facilities.

Key words: Free electron laser, multiphoton ionization, chemical analysis, double core-hole, single site-double core-hole, two-site double core-hole.

Introduction

The advent of short pulse, intense, free-electron lasers (FELs) [1-5] has already allowed the exploration of novel states of atoms [6-13], molecules [14-26] and clusters [27, 29], as well as time-resolved studies of molecule-photon interaction dynamics [30-31]. These novel light sources target core electrons, which are highly localized around the nucleus with a Z^2 scaling of core binding energies, and provide atom specific spectroscopic information. The FEL-based research in gas phase systems impacts applications ranging from single-pulse imaging of biomolecules to high energy-density materials [11,14, 26, 27, 29, 32, 33]. Imaging at a resolution of atomic level requires very short and intense x-ray pulses delivered effectively by FELs [34] to record diffraction pattern from biological molecules before they explode due to massive Coulomb explosion [35-39]. Biomolecular imaging has been demonstrated with resolution of tens of nanometers [40], but imaging at atomic resolution demands the understanding of ultrafast multiphoton inner-shell ionization dynamics which is ubiquitous in matter interactions with intense x-ray light and has been very well studied by spectroscopic methodologies [6, 14, 15,18, 26].

FEL sources have the ability to produce atoms and molecules with multiple electron vacancies in core orbitals through the sequential absorption of multiple photons on a time scale comparable to or shorter than Auger lifetime. In other words, FEL pulses efficiently empty the innermost electronic shells, creating a transient hollow state of matter. Specifically, this requires high fluence and short x-ray pulse duration to produce double core-hole (DCH) states via the sequential absorption of two x-ray photons in a time scale on the order of the Auger lifetime, which is about 4-8 fs for atoms [41]. In 2009, The Linac Coherent Light Source (LCLS) at SLAC National Laboratory was the only facility that could allow such experiments. New facilities in Asia and Europe [1-5] enable however similar experiments.

Twenty-eight years ago, it was suggested that DCHs could provide the basis for richer, sensitive, spectroscopies than conventional inner-shell photoelectron spectroscopies [42]. In a molecule, two configurations of DCHs are possible due to the availability of more than one atomic site where the core holes can be created. For example, DCHs can be produced with both vacancies on a single site (ssDCH) and DCHs with single vacancies on two different sites (tsDCH) as shown in Fig. 1 for the case of CO. It has been shown that the presence of the first core hole increases the binding energy of the remaining core

electrons and the relative location of the second core-hole to the first one significantly affects the degree of the energy increase. With different states' energies and configurations, the decay pathways and the resultant molecular fragmentation patterns are different for ssDCH and tsDCH states [42]. The magnitude of the binding energy shifts of the second core-electron leads to unique spectral signatures that provide new information on the chemical environment of the first core hole site [42-45]. These predictions present the potential of DCH spectroscopy to identify molecules with nearly equivalent atomic constituents. This possibility was the compelling motivation for our collaboration [21, 23, 25] to carry out DCH experiments using the LCLS which is key to the success of our measurements as explained above. In particular, the strong incentive to experimentally investigate tsDCH states was their predicted [42-45] much higher sensitivity to the chemical environment of the core-hole site compared to single core-hole (SCH) or ssDCH. This was demonstrated with the calculations of single ionization potentials (IP) and double core-hole ionization potentials (DIP) for a series of molecules [42-45]. The increased sensitivity originates from the fact that the DIP of tsDCH states is directly coupled to changes induced in the valence charge distribution of the two different atomic sites. In fact, the predicted high sensitivity of the tsDCHs to the chemical environment is related to the flow of electron density in the creation of the tsDCH states as well as the change of bond length [42-45].

Fig. 1. Cartoon design of (a) the electronic structure of the CO molecule, (b) the SCH ionization at the C K-edge (labeled SCH_C) and the SCH ionization at the O K-edge (labeled SCH_O), and (c) the ssDCH ionization at the C K-edge (labeled DCHSS_C), the ssDCH ionization of the O K-edge (labeled DCHSS_O) and the tsDCH (labeled DCHTS) ionization [23].

The LCLS allowed pioneering DCH experiments in atoms [11] and in N₂ [24, 25] validating theoretical predictions [42-45]. One of the first experiments even optically laser aligned N₂ and measured the electron angular distribution which carries information about the shape of valence orbitals [24]. These first attempts to measure DCH enabled other improved work on other systems [6, 21, 23, 45, 46].

Almost simultaneously, the intriguing phenomenon of FEL-based DCH in molecules was being explored using conventional synchrotron x-ray sources, whose brightness is too low to produce observable DCHs through sequential absorption processes. However, DCH states can be produced through single-photon absorption with synchrotron x-ray, as a result of electron correlation. This was previously observed in atoms [47], and more recently has been observed in molecules thanks to coincidence techniques which in fact provide a much cleaner signal [48-60] compared to present FEL-based measurements. The reason for the complexity of the FEL-based data is that since the FEL is so intense, the resulting measured photoelectron spectra contain, in addition to the non-linear signatures, the spectral lines corresponding to SCH ionization of the molecular ion as well as the atomic fragment ions in addition to that of the parent molecules. For example in the case of N₂ [25, 61], we recorded in the photoelectron spectra, the SCH

spectral lines of N_2^+ and N_2^{2+} as well as the photoelectrons from SCH high charge state atomic ionization of N^{m+} . Unfortunately, some of these lines overlap or are very close to the sequential two-photon inner-shell double ionization lines. As mentioned above, electron-electron coincidence experiments however are able to sort the data and isolate and extract only the events of interest such as the DCH lines as realized by impressive work [48-60]. Standard coincidence experiments such as the one conducted at synchrotron facilities that use as a clock the MHz repetition rate [48,49] are hard to conduct at the LCLS presently due to the low repetition rate of 120 Hz.

We highlight in this article recent examples of molecular DCH measurements in N_2 , N_2O , CO and CO_2 carried out at the LCLS with our collaboration [21, 23]. We chose these systems so we could compare the chemical environment of N in N_2 and N_2O as well as that of C in CO and CO_2 .

Experimental method

The experiments were performed at the atomic, molecular, and optical physics end-station [11, 15, 26,62]. The high field physics chamber we used consists of one ion and five electron time-of-flight (TOF) spectrometers. The molecules were introduced into the vacuum system through a 100 μm pulsed nozzle. The electron TOF spectrometers [62] were used to analyze the electrons produced in the interaction of the molecules with the LCLS pulses. The photon energy and pulse durations are specified in each highlighted case described next in this paper [21,23]. Unless otherwise noted, the pulse energies quoted here are nominal values measured upstream from the beam line optics. These values are reduced by 65%–85% in the interaction region due to photon beam transport losses [11, 23, 26]. The photon beam was focused by Kirkpatrick-Baez (KB) mirrors to an area of about 2 μm^2 [62]. It is worth noting that a magnetic bottle was also used for the DCH measurements of atoms [6] and molecules at the LCLS. In this case, a correlation method (similar to electron coincidence) called “partial covariance mapping” was used to provide a complete picture of the ionization processes competing in hollow atom or molecule formation. This methodology was used effectively in the case of Ne [6], providing a map that allowed visualization of hollow atom formation and decay, unfolding overlapped signals of non-linear sequences of photoionization and Auger decay events not previously observed [11] with a simple ion-TOF spectrometer.

Results

For the experiments reported below, the LCLS generated x-ray pulses with a FWHM pulse duration of about 10 fs, a photon energy between 517 eV and 705 eV, and a pulse energy of approximately 30 μJ at the interaction region. A tightly focused FEL beam with an intensity of about 3×10^{16} W/cm² in the interaction region enables sequential multiphoton ionization of the molecules. In order to eliminate the signal provided from SCH ionization described above, spectra were taken with an unfocused beam of about 1×10^{14} W/cm² and were subtracted from spectra taken with the focused beam as shown in the main panel of Fig. 2 for the photoionization of N_2 (Fig. 2a) and N_2O (Fig. 2b). The insets show the focused and unfocused spectra as well as the difference spectra. This method of recording the data insured that we could extract the nonlinear contributions of the photoelectron signal and clearly isolate the signal of DCH events. The examination of the spectra difference reveals a number of features that are unambiguously related to the sequential absorption of two FEL photons. The identification of the spectra lines was guided by theory [44]. It was predicted that photoelectrons of ssDCH state should have kinetic energies about 50–100 eV lower than the ordinary $1s^1$ photoline (depending upon the atomic species within the molecule) [44]. This spectral line for ssDCH is shown clearly in Fig. 2a for N_2 at around 100 eV kinetic energy, ~90 eV lower than the SCH line. The identification of the tsDCH states is in general more difficult since they are positioned much closer to the main photoline, and are shifted to lower energy by only about 10–20 eV according to calculations [44]. This line is shown clearly in Fig. 2a for N_2 at around 170 eV kinetic energy, 20eV lower than the SCH line. In order to observe the DCH signature, it is

important to use photons with a pulse duration comparable or less than the Auger decay time of the atoms that compose the molecule, hence, an FEL is necessary for DCH experiments. If the pulse duration exceeds the Auger lifetime significantly, Auger decay can take place before the absorption of a second photon allowing photoionization-Auger-photoionization (PAP), as shown between 150-160 eV in Fig. 2a. We carried out the same type of measurement in the case of N_2O shown in Fig 2b. Since N_2O presents an asymmetry with one central (N_c) and one terminal (N_t) nitrogen atom, we were able to observe the tsDCH for $N_t^{-1}N_c^{-1}$ as well as the tsDCH for $N_c^{-1}N_t^{-1}$.

Fig.2. Photoelectron spectra of N_2 (a) and N_2O (b) with a photon energy of 596 eV and 517 eV, respectively [21]. Blue area: data taken with focused x-ray beam; green area: data taken with unfocused x-ray beam; spectra are normalized at the SCH peak. Magenta area: difference spectra. Black vertical lines: experimental photoelectron kinetic energies for the SCH, DCH, and PAP features; horizontal lines: estimated errors; yellow vertical lines: theoretical values of photoelectron kinetic energies.

Fig. 3. Photoelectron spectra of carbon in CO molecule recorded at 700 eV photon energy, approximately 10 fs pulse duration [23]. Calculated state energies and intensities are marked by vertical thick lines with head markers: tsDCH (dashed line), ssDCH (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 that is marked by the thin dashed line.

We also carried out similar photoelectron measurements in CO, shown in Fig.3, which depicts a sequence of ionization events in the main panel. All of these spectral lines are obtained with absorption of a single x-ray pulse. In the main panel, the calculated position of the tsDCH and ssDCH states labelled as DCHTS and DCHSS_C respectively are indicated with vertical lines, which align well with the experimental

spectral peaks. In fact, the most intense peak in the spectrum is that of tsDCH flagged by the heavy black dashed line.

The measurement of the tsDCH can also be achieved using Auger electron spectroscopy. We demonstrate in Fig.4 a clear signature of the tsDCH in the Auger electron spectra of C and O. The tsDCH peaks shown in the difference spectrum (black curves in the main panel) are the most intense, consistent with the calculation (colored area in the main panel), in addition to the ssDCH for both C and O.

Fig. 4. Auger spectra compared to theoretical DCH Auger spectra [23]. Measurements were 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 spectrum is shown as the black curve. Theoretical Auger spectra are shown in the main panel: overall calculation (yellow shaded area); ssDCH (solid blue curve); tsDCH (solid red curve); ssDCH secondary processes (dashed blue curve); tsDCH secondary processes (dashed red curve).

The experiment on CO was conducted using the same methodology of measuring spectra with focused and unfocused FEL beam and then subtracting the spectra (shown in the inset in Fig. 4). We also present in Fig. 4 our calculation results [44]. First, the yellow shaded area represents the total calculated contributions by all Auger (filling the SCH or one of the DCHs) and secondary Auger (filling the remaining core hole after one of the DCHs is filled) processes from both ssDCH and tsDCH states. Second, the red solid and dashed curves represent tsDCH Auger and secondary Auger processes, respectively while the blue solid and dashed curves represent ssDCH Auger and secondary Auger. The Auger data from Fig. 4 corroborate the observation in the photoelectron spectra shown in Fig. 3. The comparison between measurements and calculation clearly identify the DCH spectral features but also show a lower calculated intensity of the tsDCH spectral lines. We should note however that because Auger decays of highly charged SCH states and molecular fragments are also present they may contribute to the discrepancy between the experimental and the theoretical intensity yield results.

In order to explore the chemical environment of similar molecules we also investigated the CO₂ molecular case to compare it to the CO case described above. We show in Fig. 5(a,b) the photoelectron spectra of CO₂ for a broad kinetic energy range that covers features near both the SCH for O and C. Fig 5a shows the tsDCH for O⁻¹O⁻¹ and C⁻¹O⁻¹, which are not resolved, as well as the ssDCH for the O⁻² fragment. The unresolved O⁻¹O⁻¹ and C⁻¹O⁻¹ peaks agree with the calculations which predict that these two closely lying structures are separated by about 2 eV [44] which is below our energy resolution of 5 eV [21]. The tsDCH are formed when an O 1s electron is ejected from parent molecular ion with a core hole at a different O site (O⁻¹O⁻¹) or from the parent molecular ion with a core hole at the C site (C⁻¹O⁻¹). Fig. 5(b) focuses on the spectral lines of O⁻¹C⁻¹ tsDCH, i.e., a C 1s electron is ionized from a parent molecular ion with a core hole at one of the O sites, in which case the photoline lies in the kinetic energy region near

the C SCH peak. We note that in the case of a homonuclear diatomic molecule such as N_2 , as shown above in Fig 2a, the photoelectron spectrum is less congested.

Fig. 5 Photoelectron spectra of CO_2 near the O SCH line (a) and C SCH line (b), photon energy 705 eV [21]. Blue area: data taken with focused x-ray beam; green area: data taken with unfocused x-ray beam; spectra are normalized at the SCH peak. Magenta area: difference spectra. Black vertical lines: experimental photoelectron kinetic energies for the SCH, DCH, and PAP features; horizontal lines: estimated errors; yellow vertical lines: theoretical values of photoelectron kinetic energies.

Discussion

The goal of this work was to gauge whether x-ray two-photon photoelectron spectroscopy (also referred to as DCH spectroscopy) using short (comparable or shorter than the Auger lifetime of atoms thus few fs) and intense light sources such as FEL is a viable methodology for chemical analysis. From the data analysis of the data presented above for N_2 , N_2O , CO and CO_2 , we extracted key elements that are relevant to molecular chemical environments. The experimental values are compared to calculation carried out by our and other teams as shown in table 1. Table 1 lists the single ionization potential (IP) and double ionization potentials (DIP) for the DCH and SCH states which are used to determine the chemical shifts ΔE which is defined as $DIP-IP(\text{first site})-IP(\text{second site})$ or $DIP(S_i^{-1}, S_j^{-1}) - IP(S_i^{-1}) - IP(S_j^{-1})$. Experimentally, the chemical shift is measured as the difference between the kinetic energies or binding energies of the second core electron and first core electron. Table 1 compares the experimental and calculated chemical shifts for tsDCH (ΔE_2) and ssDCH (ΔE_1). We explained above how the tsDCH sensitivity to chemical environment is connected to the flow of electron density. The density flow direction is indicated by the interatomic relaxation energy (IRC) which can be retrieved from the chemical shift of tsDCH, i.e. ΔE_2 , as $\Delta E_2 = 1/r - IRC$ where r is the distance between the two core holes [44]. The sign of IRC indicates the electron density dynamics: whether electrons “flow” into or out of the second core hole site upon the creation of the first core hole [21, 44].

The tsDCH states’s sensitivity to the chemical environment is revealed in ΔE_2 , thus the examination of the ΔE_2 values and comparison of these values for N_2 vs. N_2O and for CO vs. CO_2 , as shown in Table 1. This allows us to distinguish these species with similar atomic composition. Based on Table 1, we learn the following. First, the reasonable agreement between the measurements and the calculations validates the DCH theoretical model. Second, it is noted that the DIP difference between the $O^{-1}C^{-1}$ tsDCH states is 6.7 eV, while the IP difference between C^{-1} SCH states in CO and CO_2 is only 0.3 eV. This proves that DCH spectroscopy is much more sensitive to the chemical environment of the target atomic site which is C in the above example. Finally, comparing ΔE_2 of [N_2 and N_2O] and of [CO and CO_2], we find a decrease of 3.7 eV and 5.1 eV for N_2O and CO_2 with respect to N_2 and CO. This is due to the change in

bond length ($1/r$) and the difference in IRC both related to an extra O atom. However, the contribution to the decrease of ΔE_2 by the increase of the bond length is only approximately 0.4 eV [21]. Hence, the difference in IRC due to the different chemical environment of the N and C atoms is the major reason to the change in ΔE_2 . In fact, the sign of IRC even flips if we compare the case with and without the extra O atom for both pairs of molecules (CO , CO_2). A negative sign, as in the case of diatomic molecule N_2 and CO , indicates that the electron density at the site where the second core hole will be created decreases once the first hole is produced, i.e., the creation of a core hole draws electrons away from the other site. As to the triatomic molecules N_2O and CO_2 , the positive sign indicates an increase of the electron density or a direction of electron flow opposite to that of their diatomic counterparts. It is the extra atom that supplies electrons to the core-hole sites as an electron donor, preventing an electron density drop at the site of the second core-hole.

Table 1. Experimental [21] and theoretical [44] ionization potentials as well as ΔE_1 , ΔE_2 and the generalized interatomic relaxation energy, IRC, for states of N_2 , N_2O , CO_2 and CO . $\text{IP}(\text{S}^{-1})$: SCH ionization potential, $\text{DIP}(\text{S}^{-2})$: ssDCH double ionization potential, $\text{DIP}(\text{S}_i^{-1}, \text{S}_j^{-1})$: tsDCH double ionization potential. Experimental DIPs are calculated as the sum of the experimental $\text{IP}(\text{S}^{-1})$, calibrated to known values, and the relevant IP of the ion, determined in our experiments. The experimental value of the IP for CO ($\text{O } 1s$) = 542.5 eV was taken from reference 65. Errors are calculated as the root mean square of the estimated errors for the positions of the spectral peaks.

Molecule	$\text{IP}(\text{S}^{-1})$ (eV)	$\text{DIP}(\text{S}^{-2})$ (eV)	$\text{DIP}(\text{S}_i^{-1}, \text{S}_j^{-1})$ (eV)	$\square_1(\text{S}^{-2})$ (eV)	$\square_2(\text{S}_i^{-1}, \text{S}_j^{-1})$ (eV)	IRC (eV)
<u>N_2</u> Exp. Theory [44]	(N^{-1}) 409.9±0.3 [63] 411.0	(N^{-2}) 903.2±1.1 901.2	($\text{N}^{-1}\text{N}^{-1}$) 836.2±1.6 836.4	(N^{-2}) 83.4±1.1 79.2	($\text{N}^{-1}\text{N}^{-1}$) 16.4±1.6 14.3	($\text{N}^{-1}\text{N}^{-1}$) -3.29±1.6 -0.65
<u>$\text{N}_2\text{O} (\text{N}_t)$</u> Exp. Theory [44]	(N_t^{-1}) 409.0±0.5 408.6	(N_t^{-2}) 893.9	($\text{N}_c^{-1}\text{N}_t^{-1}$) 834.2±2.1 833.2	(N_t^{-2}) 76.7	($\text{N}_c^{-1}\text{N}_t^{-1}$) 12.7±2.1 12.1	($\text{N}_c^{-1}\text{N}_t^{-1}$) 0.09±2.1 1.11
<u>$\text{N}_2\text{O} (\text{N}_c)$</u> Exp. Theory [44]	(N_c^{-1}) 412.5±0.5 [63] 412.5	(N_c^{-2}) 902.3	($\text{N}_t^{-1}\text{N}_c^{-1}$) 834.2±1.6 833.2	(N_c^{-2}) 77.3	($\text{N}_t^{-1}\text{N}_c^{-1}$) 12.7±1.6 12.1	($\text{N}_t^{-1}\text{N}_c^{-1}$) 0.09±1.6 1.11
<u>$\text{CO}_2 (\text{O } 1s)$</u> Exp. Theory [44]	(O^{-1}) 540.6±0.5 [64] 542.9	(O^{-2}) 1173.2±1. 6 1171.9		(O^{-2}) 92.0±1.5 86.2	($\text{O}^{-1}\text{O}^{-1}+\text{C}^{-1}\text{O}^{-1}$) 12.8±1.6 9.1	
<u>$\text{CO}_2 (\text{C } 1s)$</u> Exp. Theory [44]	(C^{-1}) 296.8±0.5 [64] 297.6	(C^{-2}) 664.6	($\text{O}^{-1}\text{C}^{-1}$) 848.6±1.6 851.2	(C^{-2}) 69.3	($\text{O}^{-1}\text{C}^{-1}$) 11.2±1.6 10.6	($\text{O}^{-1}\text{C}^{-1}$) 1.21±1.6 1.79
<u>$\text{CO} (\text{C } 1s)$</u> Exp. [8] Theory [44]	(C^{-1}) 296.5±0.5 296.4	(C^{-2}) 667.9±3.6 664.4	($\text{O}^{-1}\text{C}^{-1}$) 855.3±1.2 855.2	(C^{-2}) 74.9±4.0 71.7	($\text{O}^{-1}\text{C}^{-1}$) 16.3±1.2 15.9	($\text{O}^{-1}\text{C}^{-1}$) -3.53±1.2 -2.8

Conclusions

The future is bright with all light sources since they are complementary, allowing different experimental approaches to be used, enabling verification of results extracted from various methodologies. Contribution to electron spectroscopy for chemical analysis (ESCA) has certainly been achieved with FEL light sources to complement synchrotron light sources ESCA. It is possible in the future that high harmonic generation (HHG) lasers could perhaps also enable DCH measurements in the cases where the laser fluence is high enough to allow double photon absorption.

Future FEL facilities which are under construction such as the XFEL in Germany and the LCLS II in the US as well as other FEL facilities around the world will make the new chemical analysis method suitable to larger systems including biomolecules. These facilities are taking advantage of advances in focusing capabilities [66] and peak brightness to promise an even robust regime of multiphoton absorption per atom. In addition, these new FEL facilities will provide high repetition rates which will allow coincidence measurements [67]. Furthermore, the pulse duration is planned to be even shorter [68], and the bandwidth narrower thanks to laser-seeding or self-seeding [69] allowing the experiments to beat the Auger clock by mostly producing hollow exotic systems; i.e., minimizing the PAP lines since the pulse will be over before Auger cascade. One can also imagine that time-resolved studies with sub-fs, intense laser sources will be possible using x-ray split and delay devices [70, 71] to carry out x-ray pump –x-ray probe experiments. This will make possible measurement of the electron dynamics in real time to extract the timing information of various physical and chemical processes.

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