<http://www.diva-portal.org>

Postprint

This is the accepted version of a paper published in *Journal of Physics B: Atomic, Molecular and Optical Physics*. This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

Citation for the original published paper (version of record):

Larsson, M., Salen, P., van der Meulen, P., Schmidt, H T., Thomas, R D. et al. (2013)
Double core-hole formation in small molecules at the LCLS free electron laser.
Journal of Physics B: Atomic, Molecular and Optical Physics, 46(16 SI): 164030
<http://dx.doi.org/10.1088/0953-4075/46/16/164030>

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-210257>

Double core-hole formation in small molecules at the LCLS free electron laser

M Larsson¹, P Salén¹, P van der Meulen¹, H T Schmidt¹, R D Thomas¹, R Feifel², M N Piancastelli², L. Fang³, B Murphy³, T Osipov³, N Berrah³, E Kukk⁴, K Ueda⁵, J D Bozek⁶, C Bostedt⁶, S Wada^{6,7}, R Richter⁸, V Feyer⁸ and K C Prince^{8,9}

¹Department of Physics, AlbaNova University Center, Stockholm University, 10691 Stockholm, Sweden

²Department of Physics and Astronomy, Uppsala University, 751 20 Uppsala, Sweden

³Physics Department, Western Michigan University, Kalamazoo, Michigan 49008, USA

⁴Department of Physics and Astronomy, University of Turku, 20014 Turku, Finland

⁵IMRAM, Tohoku University, Sendai 980-8577, Japan

⁶SLAC, LCLS, Menlo Park, California 94025, USA

⁷Department of Physical Science, Hiroshima University, Higashi-Hiroshima, 739-8526, Japan

⁸Sincrotrone Trieste, 34149 Basovizza, Trieste, Italy

⁹IOM-CNR, 34149 Basovizza, Trieste, Italy

Abstract

1. Introduction

There is a close connection between physics and analytical chemistry, something which prompted Hercules [1] to give his students the following advice (p. 1752):

“If you want to discover the next major instrumental development for analytical chemistry read the physics literature. Spectroscopic techniques are almost invariably first described by physicists, and chemists develop them for use in chemical analysis”.

Hercules followed his own advice and introduced the, at that time, recently invented technique of electron spectroscopy for chemical analysis [2-4] in his own laboratory. One can debate whether the most important contribution of X-ray photoelectron spectroscopy (XPS) to the chemical community was the chemical shifts or the surface sensitivity the technique offered, but what is not arguable is that K Siegbahn was awarded one half of the 1981 Nobel Prize in Physics “for his contribution to the development of high-resolution electron spectroscopy”.

Standard XPS involves a one-photon-absorption – one-electron-ejection process. Double-electron-excitation/ionization processes induced by a single photon in gas-phase atoms and involving K- and M-shell electrons were observed already a long time ago (see e.g. refs. [5,6]) by means of X-ray absorption spectroscopy. However, these observations had nothing to say about chemical shifts in molecules, and it was not until much later, during the 1980s, that Cederbaum and co-workers theoretically studied chemical shifts resulting from the removal of two 1s electrons from either a single atomic site in the molecule, or from two different atomic sites [7-10]. Their conclusion from theoretical studies of the hydrocarbon molecules CH₄, C₂H_x (x = 2,4,6) and C₆H₆ was that the chemical shifts are enhanced due to formation of two-site double

core-hole states. This work received limited attention because of the experimental difficulties in creating and observing double core-hole states.

One can conceive of two different processes that can produce double core-holes. The absorption of a single photon can, in principle, create two core-holes through electron-electron correlation; however, the cross section for correlation effects giving rise to core-holes on two different sites is extremely small. The other possibility is that the molecule absorbs two photons sequentially within a time duration which is shorter than a typical Auger lifetime of about 5 fs. Single photon formation of one-site double core-hole states was difficult to observe due to the weak nature of the process, but by combining third generation synchrotron light sources with efficient electron detection, the process was finally observed [11, 12].

Sequential absorption of two photons by the core electrons in a molecule requires very intense X-ray pulses of short duration. This became possible when the Linear Coherent Light Source (LCLS) free electron laser at the SLAC National Accelerator Laboratory delivered the world's first X-ray laser beam with sufficient photon energies to ionize the core electrons in second row elements [13-15]. In the first experiments at the atomic, molecular and optical science (AMO) instrument with N₂ as target molecule for the LCLS beam, single-site double core vacancies were observed [16, 17]. In the next generation of experiments, two-site double core-hole states were observed in a molecule (CO) for the first time [18], and used to explore the chemical sensitivity of these states in CO₂, N₂O and N₂ [19]. The realization of the LCLS has inspired theoretical work [21-23] along the lines initiated by Cederbaum and co-workers 25 years ago [7,8].

In this paper we will describe in some more detail the first generation LCLS experiments on molecular double core-hole states.

2. Experiment

The AMO instrument [14] at the LCLS was used in the experiment. This instrument consists of 5 e-Time-of-Flight (eTOF) spectrometers and a Wiley-McLaren integrating ion spectrometer (iTOF). The e-TOFs and their orientation with respect to the light beam are similar in design to those in ref. [24], which was developed for third generation synchrotron light sources. Three of the e-TOFs are positioned in the y - z (dipole) plane perpendicular to the X-ray FEL beam, whereas the remaining two are positioned at 54.7° out of the y - z plane. The e-TOFs are supplied with electron lens systems, which can be used to slow the electrons down and hence increase the energy resolution. The angular acceptance is a compromise between signal and energy resolution. The acceptance angle is about 1/1800 of the full 4π solid angle. The iTOF has a much higher acceptance angle than the eTOFs, and almost 100% of the ions created in the interaction volume are collected.

One third of the 3 km SLAC linac is used to inject electron bunches into a 100 m long undulator at a repetition rate of 60-120 Hz, which generates X-ray pulses containing 10^{12} photons and with pulse duration of about 10 fs when operated in 40 pC charge mode. A set of four mirrors are used to create two soft-X-ray branches, of which one goes to the AMO end station and the other branch goes to the soft X-ray Material Science (SXR) instrument, as shown in Figure 1. The mirrors provide a sharp cut-off at 2000 eV. In addition to these two soft X-ray end stations, the Near Experimental Hall also contains the hard X-ray pump-probe (XPP) instrument. Three additional hard X-ray instruments are located in the Far Experimental Hall.

Two plane-ellipse mirrors in a Kirkpatrick-Baez (KB) configuration focus the X-ray beam on the interaction region in the AMO end station to an elliptical profile with full-width half

maximum (FWHM) lengths of the major and minor axes of 2.2 μm and 1.2 μm [25]. The curvature of the KB mirrors can be changed so that the focus position is moved 20 mm from optimum. This was an important part of the present experiment, since it provided a linear, “synchrotron-like” background.

The eTOFs are each supplied with a multichannel plate (MCP) detector. Electrons ejected from the molecules as a direct or indirect (Auger) result of the interaction with the X-ray FEL beam travel in the TOF beam tubes and strike the MCPs, which causes an electron cascade across the plates resulting in a 10^6 gain. In the experiments, the LCLS photon beam produced a signal rate of more than one electron arriving at each detector per pulse. A fast digitizing board was used to measure the amplitude of the signal as a function of its arrival time. The MCP at the iTOF is biased with a negative voltage instead of positive; otherwise the iTOF is operated in the same way as the eTOFS.

The data stream from the instruments operates at the repetition rate of LCLS, i.e. 60-120 Hz, and the data are acquired and processed in real time. The data acquisition software infrastructure is set up so that the data are displayed in real time to the users. This is an important aspect, since it allows the users to assess whether the experimental conditions are suitable and to modify the experimental parameters if they are not. Data from each individual photon pulse and each spectrometer are stored together with all software controlled and measured parameters (pulse energy, photon energy, etc.). The data are uniquely retrievable for the off-line data processing.

3. Data reduction

The raw data from the eTOF were analyzed with a C++ program in order to extract the flight times of the electrons. For an accurate determination of these flight times, the oscillatory component of the digitalized detector signal traces (probably due to an impedance mismatch) was removed by a FFT (Fast Fourier Transform) based deconvolution technique. The principal of this deconvolution technique is to divide the signal trace corresponding to each laser shot by the response function of an electron detection in the frequency domain. The response function for each eTOF is extracted from signal traces where only one electron is registered, in order to avoid distortions from close lying detections, and an average is formed. Figure 1(a) shows the, in such a way, constructed response function after smoothening. For every signal trace the Fast Fourier Transform (FFT) of the eTOF trace is divided by the FFT of the response function. Division by the response function leads to large amplitude noise at high frequencies, which needs to be filtered out. Since a step function introduces large oscillations in the signal when transformed back to the time domain, a smooth filtering function is used. The smooth filtering in the frequency domain is performed by multiplying the FFTd trace with $F = (\sin(f/w)/(f/w))^2$, where f is the frequency. When F reaches zero the higher frequencies are put to zero. The width (w) of F affects the resolution of the spectra because the multiplication of a $(\sin(f/w)/(f/w))^2$ function in the frequency domain corresponds to a convolution with a triangle in the time domain, which is narrower for larger w . The width has to be balanced in a way such that it is small enough to filter the high frequencies, but large enough to achieve good temporal resolution. We used a parameter w of approximately 1.0×10^8 Hz. Finally the inverse FFT is applied to get back to the time domain.

Figure 1. (a) Response function of an electron detection on the MCP. (b) Example of a photoelectron signal trace (blue) generated from one X-ray pulse. The red line represents the trace after the deconvolution, which was performed in order to remove the dip and oscillatory component following the main peak of each detection. The correction of the peak position by the deconvolution can be observed in peak C.

Figure 1(b) demonstrates the effect of the deconvolution on a single trace. The peaks of the raw trace (blue) displays the dip and oscillatory tail of the signal, which accompanies each detection of an electron. This is effectively removed in the deconvoluted trace (red). One can see that the used, averaged, response function in figure 1(a) roughly corresponds to the response functions in the signal trace, although, as there is a slight variation in its form between different detections, they are not identical. The blue and red traces in figure 1(b) consist of one isolated and two close lying detections. It is clear from the response function that, in the absence of deconvolution, the tail of peak B will interfere with peak C. Hence, the shape of peak C will be distorted and its position shifted. Looking at figure 1(b) one may see that, for peak A and B, the position of the blue and red peaks are matching, while there is a shift for peak C. This is mainly an effect from the dip of peak B which distorts the shape of peak C and leads to a shift, but which is corrected for by the deconvolution. Hence, the deconvolution allows one to analyze data from measurements which were run at a high count rate, where the probability of close lying peaks is high.

The output from the C++ program was a matrix which contained the flight times, extracted from the deconvoluted traces, of up to 10 electrons for a certain laser shot and eTOF. In a Matlab® routine the flight times were converted into kinetic energy according to a formula given from SIMION® simulations for the eTOFs. Time zero for the flight times was set such that the conversion to energy results in a spectrum which is calibrated to the positions of known Auger peaks. The Matlab routine sorted the hits into the 5 different eTOFs and into chosen sizes of energy bins. Because the size of the time bins increases with respect to the fixed size of energy bin, there are always time bins that are distributed over more than one energy bin. This has been taken into account in the analysis.

The photon energy of the laser beam has a jitter from pulse to pulse, which leads to a broadening of the photoelectron peaks of approximately 1.5 eV. However, from the recorded photon energy of every laser pulse, a jitter correction could be applied in the Matlab routine.

4. Preparatory simulations

When deciding the photon energy for a photoelectron experiment one seeks to avoid overlapping Auger and photoelectron spectral peaks. Only the kinetic energy of the photoelectrons depends on the photon energy, while the Auger electrons are fixed at one kinetic energy region. Thus, overlap could be avoided by selecting a sufficiently high, or low, photon energy, which generates photoelectrons with kinetic energies above, or below, the Auger bands. However, access to a large photoionization cross section also requires the photon energy to be as close to the relevant absorption edge as possible, which is the reason a very high photon energy might be a bad choice. On the other hand it has to be sufficiently high to ionize all states of interest. Therefore it may be necessary to select the photon energy so that the photoelectron lines fit in between the Auger bands.

In order to choose the photon energy it is useful to plot a graph of the kinetic energy of the Auger- and photoelectrons as a function of photon energy. This allows us to find an optimal photon energy where all peaks are isolated. Figure 2 shows such a graph for the CO₂ molecule. The single core-hole (SCH) and double core-hole (DCH) binding energies were taken from reference [23] and the Auger energies from reference [24]. The energies for the 1st and 2nd Auger electron generated from the single-site double core-hole (ssDCH) state were derived from calculations of the binding energies for the CC, CVV and VVVV (C=core, V=valence) states of CO₂ [23,27]. Similar calculations for the corresponding Auger electrons for the two-site double core-hole (tsDCH) states predict that they should be located within the energy regions of the normal Auger bands. For this experiment we decided to use a photon energy of 705 eV in the case of CO₂, where all the spectral features are separated and we have access to SCH and DCH peaks from both O and C. A similar analysis was performed for the other molecules.

Figure 2. Energy diagram of the kinetic energy of Auger and core ionized photoelectrons as a function of photon energy for CO₂.

It is also useful to estimate the intensities of the peaks associated with the nonlinear states in the spectrum. Therefore, as an aid for interpretation of the experimental results we performed simulations of the spectra, which allowed us to see the effect of pulse energy, pulse length and spot size at the sample. The simulations are based on an atomic model by Rohringer and Santra [28], which is used to set up coupled rate equations for the occupation probabilities of molecular states. Starting from the ground state with an occupation probability equal to one, the coupled rate equations generate occupation probabilities for different states as a function of time. The input parameters are the photoionization cross sections, Auger decay rates and the parameters

which define the intensity profile of the laser pulse. The latter parameters: pulse length, beam diameter and number of photons in the pulse, are chosen so that they match the experimental values. We assume a Gaussian temporal shape of the pulse and a cylindrical spatial intensity profile which is constant as a function of distance from the center of the beam and drops to zero above the beam radius. The total probability for a certain process is determined by calculating the integrated probability for the final transition over the whole laser pulse. For example, the probability for a two-photon ionization, where the first photon ionizes the molecule to a SCH state with occupation probability $P_p(t)$ at time t , would be:

$$P_{pp} = \sigma \int_{-\infty}^{\infty} j(t) P_p(t) dt, \quad (1)$$

where σ is the cross section for the transition to the final state and $j(t)$ is the photon flux. By calculating the probability for the relevant processes in this way, the relative integrated intensities of their associated spectral peaks can be simulated.

The cross section for photoionization of a second electron from a 1s orbital, from an atom that already has a core-hole, was calculated from a hydrogen based model [29] applied with the appropriate atomic number of the atom. The Auger rate for the ssDCH state was estimated as three times that of a SCH state [30]. The energy positions of the DCH-peaks were taken from reference [23] and the intensity and positions of the satellite peaks from reference [31]. Ionization of valence electrons was neglected because of its comparatively low cross-section. Furthermore shake-off processes, double-Auger decays and molecular effects, such as the influence of the atoms on each other or dissociation, were not considered in the simulation.

Figure 3 displays such a simulated spectrum of CO₂ at 5 eV resolution and using an X-ray pulse of 705 eV photon energy, 10 fs duration and $6 \cdot 10^{15}$ W/cm² peak intensity. These pulse parameters reflect those used at the experiment and were derived from comparison of the simulations and experimental spectra subsequent to the experiment, as described in section 5.1. The positions of the SCH and DCH states are given from reference 23 and those of the PAP (Photoelectron-Auger-Photoelectron) peaks are estimated based on calculations of the CVV-state [27] and experimental values of the double valence electron binding energy [32]. In the simulated spectrum the relative intensities of the various linear and nonlinear signals are revealed. Note that the O SCH peak has been reduced by a factor of 5. The simulation illustrates the difficulties in resolving some of the nonlinear signals from the spectrum itself, due to their overlap with the shake-up satellite contributions. This demonstrates the need for the measuring strategy employed in these experiments using a focused and unfocused beam in the interaction region and subtracting the unfocused from the focused spectra in order to emphasize the nonlinear signals. Further simulation results and comparison with the experimental spectra are presented in the next section.

Figure 3. Simulated photoelectron spectrum for CO₂ using a photon energy of 705 eV. The O SCH peak has been reduced by a factor 5.

5. Results and discussion

5.1. Experimental results

In the previous section we described the motivation for separating the nonlinear from the linear photoelectron signals, based on simulations. This was achieved experimentally by subtracting a measurement performed with an unfocused X-ray beam in the interaction region from that performed with a focused beam. In figure 4 and 5 the photoelectron spectra for the molecules CO₂, N₂O and N₂ are presented. The measurements with a focused and unfocused beam are displayed in blue and green, respectively, while the difference spectra are displayed in magenta. As a guidance to help identifying the peaks associated with the nonlinear states we used theoretical predictions of both their position [12,23,27,32] and integrated intensity. The simulated peaks based on these predictions are shown as grey solid lines in figure 4 and 5 for the DCH states as well as for the structures associated with the PAP process. This latter contribution is expected to be significant when the pulse duration is longer than the Auger lifetime. Their locations can be calculated from the relevant doubly and triply ionized states of the molecule [12,27,32]. The yellow vertical lines indicate the calculated, and the black vertical lines the experimental positions of the peaks (the estimated error is represented by the horizontal line).

Figure 4. Photoelectron spectra of N_2 (a) and N_2O (b) with a photon energy of 596 eV and 517 eV, respectively. Blue curve: focused X-rays; green curve unfocused; spectra are normalized at the SCH peak. Magenta curve: difference spectra. Black vertical lines: experimental energies of the SCH, DCH and PAP features; horizontal lines: estimated errors; lines yellow vertical lines: theoretical energies [23], grey lines: simulated peaks.

Figure 5. Photoelectron spectra of CO_2 near the O SCH line (a) and C SCH line (b), photon energy 705 eV. Blue curve: focused X-rays; green curve: unfocused X-rays; spectra are normalized at the SCH peak. Magenta curve: difference spectrum. Black vertical lines: experimental energies of the SCH, DCH and PAP features; horizontal lines: estimated errors; yellow vertical lines: theoretical energies [23], grey lines: simulated peaks.

The simulated intensities were normalized to the ssDCH peak, which is usually the most isolated and pronounced structure, by adjusting the pulse energy so that the relative intensity of the simulated SCH and ssDCH peaks matched the experimental values. For N_2O , where the ssDCH structure is missing, the tsDCH was used for normalization. The pulse duration was set to 10 fs, estimated from the electron bunch length, and the beam diameter was fixed at 3.4 μm [25] for all simulations. The widths of the simulated peaks match the experimental resolution which was given from the width of the SCH peaks. The resolution is approximately 5 eV in all cases

except for the spectrum in figure 5(b), where it is ~ 8 eV because of the higher kinetic energy of the electrons in the eTOF tube. Since the PAP structures may be broadened by the fact that they consist of several peaks originating from ionization of states associated with distinct Auger decays, their simulated widths were roughly estimated from the experimental PAP structures. A summary of the simulated integrated intensities for the DCH and PAP peaks is presented in Table 1.

Table 1. Simulated integrated intensities [Rohr , Santra] of DCH and PAP states relative to a suitable SCH line for N_2 , N_2O and CO_2 . The intensities have been calculated using the experimental parameters: beam diameter = 3.4 μm FWHM; pulse length = 10 fs FWHM; photon energy N_2 = 596 eV, N_2O = 517 eV, CO_2 = 705 eV; number of photons per pulse: N_2 = 6.9 μJ , N_2O = 3.9 μJ , CO_2 = 5.9 μJ . These values correspond to a peak intensity of roughly 7×10^{15} W/cm². The peak intensity was chosen so that the ratio between the integrated area of the SCH and single-site (ss) DCH peaks corresponded to that of the experiment. Note that the PAP structures may be broadened by the fact that they consist of several peaks originating from ionization of states associated with distinct Auger decays. For the two PAP intensities of N_2O it is assumed that the first core-hole is formed in the N atom indicated by the first column.

Molecule	Integrated intensities relative to the SCH line (X^{-1})				
N_2	$N^{-1}=1$	$N^{-2}=0.032$	$N^{-1}N^{-1}=0.052$		PAP=0.049
N_2O (N_t)	$N_t^{-1}=1$	$N_t^{-2}=0.044$	$N_c^{-1}N_t^{-1}=0.047$		PAP=0.081
N_2O (N_c)	$N_c^{-1}=1$	$N_c^{-2}=0.044$	$N_t^{-1}N_c^{-1}=0.047$		PAP=0.081
CO_2 ($O1s$)	$O^{-1}=1$	$O^{-2}=0.019$	$O^{-1}O^{-1}=0.032$	$C^{-1}O^{-1}=0.018$	PAP=0.105
CO_2 ($C1s$)	$O^{-1}=1$	$C^{-2}=0.002$		$O^{-1}C^{-1}=0.012$	PAP=0.021

Figure 4(a) shows the photoelectron spectra of N_2 at kinetic energies below the N SCH peak at 186 eV using a photon energy of 596 eV. The measurement recorded with the unfocused beam is essentially free from nonlinear contributions and is therefore comparable to a synchrotron spectrum. It is dominated by the large SCH peak and smaller structures on the lower kinetic energy side, where one anticipates shake-up and shake-off satellites. The most intense shake-up satellites are predicted between kinetic energies of about 155-175 eV [33,34] and can be observed in both the focused and unfocused spectra. At lower electron kinetic energies one expects to find shake-off and smaller satellites.

The difference spectrum of figure 4(a) reveals three clear peaks at kinetic energies of ~ 102 , ~ 155 and ~ 169 eV, which matches both the predicted positions and intensities reasonably well. Hence, they may be assigned to ssDCH, PAP and tsDCH states, respectively. A continuous background is also visible in the difference spectrum, as for the other molecules studied. The source of this signal is not entirely clear but may partly originate from core ionization of atomic

ions produced by rapid fragmentation [Berrah ?????], satellites to the PAP and DCH peaks, or may be related to secondary electrons that are not completely eliminated in the subtraction procedure due to the different source volumes in the focused and unfocused measurements.

Figure 4(b) shows the corresponding photoelectron spectra for N₂O. The photon energy here was 517 eV, chosen below the ionization edge of oxygen in order to generate N related DCH states exclusively. This facilitates easier comparison between the N⁻¹N⁻¹ tsDCH in N₂ and N₂O. The kinetic-energy region of interest is smaller for N₂O than N₂, due to the reduced photon energy, but for ease of comparison the same kinetic energy-scale as in figure 4(a) is used.

The asymmetry of N₂O, with one central (N_c) and one terminal (N_t) N atom, manifests itself in a splitting of the N SCH peak of about 4.0 eV. This splitting appears to be just resolved in the focused and unfocused spectrum. The tsDCH structure in the difference spectrum consists of contributions from the N_c⁻¹N_t⁻¹ (N_c followed by N_t core-ionization) and N_t⁻¹N_c⁻¹ (N_t followed by N_c core-ionization) state, where the same splitting is expected and also seems to be just resolved.

The photoelectron spectra of CO₂ were obtained with a photon energy of 705 eV and are displayed in figure 5. Figure 5(a) and 5(b) originate from the same measurement but zoom in on the distinct kinetic energy regions below the O and C SCH peak, respectively. The assignments of the peaks are marked in the figures. Overall the experimental and simulated peaks, which are all normalized to the O ssDCH peak, fit quite well. For the peak at ~152 eV in figure 5(a), theory predicts contributions from two close lying tsDCH states separated by ~2 eV [23]. One arises when a 1s electron is ejected from each O atom (O⁻¹O⁻¹) and the other when the first electron originates from the C atom and the second from one of the O atoms (C⁻¹O⁻¹). However, the energy resolution here is ~5 eV, and we do not resolve these contributions. The simulated peaks indicate that the combined C⁻¹O⁻¹ tsDCH peak in the experimental spectrum is of approximately the right intensity with respect to the O ssDCH peak. This is also true for the O⁻¹C⁻¹ tsDCH peak in figure 5(b). The PAP peaks are also observed here, but the carbon (1s)⁻² ssDCH peak cannot be positively identified. This is in full agreement with our simulations which indicate a much reduced intensity for this particular feature.

The DCH-, and in particular the tsDCH states, have been predicted to be highly sensitive to the chemical environment [7-10,23]. The high sensitivity of the tsDCH is related to the flow of electrons between the core ionized atoms which can be quantified by the generalized interatomic relaxation energy, IRC. Thus it is useful to compare experimental values of the IRC with theoretical predictions as a test of the theory. The separation between the tsDCH and corresponding SCH peak, ΔE_2 , is expressed as $\Delta E_2 = 1/r - \text{IRC}$, where r is the distance between the two core-holes [35]. Thus by extracting ΔE_2 from the spectra, and given that r is known [35], the IRC is obtained.

ΔE_2 also allows you to obtain the double ionization potentials (DIPs) of the tsDCH states from $\Delta E_2 = \text{DIP}(S_i^{-1}, S_j^{-1}) - \text{IP}(S_i^{-1}) - \text{IP}(S_j^{-1})$, where $\text{IP}(S_i^{-1})$ and $\text{IP}(S_j^{-1})$ are the SCH ionization potentials of atom i and j . Hence, by determining ΔE_2 from the spectra of the molecules N₂, N₂O, CO₂ and CO [18], we may test the predicted sensitivity of the tsDCH state to the chemical environment in the following way. By comparing N₂ and N₂O with respect to ΔE_2 of the N⁻¹N⁻¹ tsDCH state, and comparing CO and CO₂ with respect to ΔE_2 of the O⁻¹C⁻¹ tsDCH state, the influence of the additional O atom on ΔE_2 may be investigated in both cases. From ΔE_2 one may then extract the DIP and determine the energy shift between the DIPs of the tsDCH states, induced by the extra O atom.

Precise extracted values of ΔE_2 , DIP and IRC can be found in reference [19]. In summary

we find that the theoretical predictions of IRC are verified by the experiment. For example, the experiment supports the predicted modest difference between the IRC of the $N^{-1}N^{-1}$ tsDCH in N_2 and N_2O . This is manifested experimentally by the relatively small difference of ΔE_2 (3.7 eV) between the two states, which is only slightly larger than the difference in the IPs of N in N_2 and N_2O , respectively (0.9 eV for N_t , and 2.6 eV for N_c). The effect is, however, more pronounced in the case of CO and CO_2 . Here, ΔE_2 for the $O^{-1}C^{-1}$ tsDCH state of CO_2 is 5.1 ± 2.3 eV lower than that of CO, in good agreement with the predicted value of 5.3 eV [23]. The corresponding experimental DIP difference between the $O^{-1}C^{-1}$ tsDCH states is 6.7 eV, which may be compared with the IP difference between C^{-1} SCH states in CO and CO_2 which is only 0.3 eV. The higher sensitivity of tsDCH states to the chemical environment is evident. A similar comparison for N_2 - N_2O is hindered by the non-degeneracy of the N^{-1} SCH states.

The theory for IRC predicts that for diatomic molecules, creation of the core-hole decreases the electron density on the other atom and thus the relaxation is suppressed for the core-hole creation of the second atom, resulting in a negative IRC. For triatomic molecules, in which one of the core-holes is located at the center atom, the extra atom plays the role of an electron donor to the other two atoms with core-holes and enhances the relaxation of the double core-hole at the other two sites, resulting in a positive IRC. We find for the two pairs of molecules that the relaxation is suppressed ($IRC < 0$) for the diatomic CO and N_2 , and enhanced ($IRC > 0$) for the triatomic CO_2 and N_2O , as predicted [23].

5.2. Simulation results

The simulations of the relative intensities of the experimental spectral features are based on coupled rate equations which generate the occupation probabilities for various states as a function of time. In figure 6, N_2 and CO are used as examples to demonstrate the time evolution of the occupation probability normalized to one, P , for different linear and nonlinear states. The black curve in figure 6(a) represents the 10 fs FWHM laser pulse, while the red, green, blue, orange and purple curves represent the occupation probability of the SCH, tsDCH, ssDCH, PA and PAP states respectively. The laser peak intensity is 6.8×10^{15} W/cm², which is an estimate based on the relative experimental intensities of the nonlinear and linear contributions. The figure shows that the P_{SCH} increases with the pulse intensity and, due to the Auger decay time (5.6 fs for N_2), its maximum at about 3-4 fs is delayed with respect to the peak of the laser pulse. At this point the formation rate of the SCH states turns from positive to negative because the Auger decay rate, together with the formation rate of DCH states, become superior. The increasing Auger decay of SCH states leads to a build-up of P_{PA} , and thus of P_{PAP} , which are slightly delayed with respect to that of P_{SCH} . The PAP and DCH occupation probabilities are moderate compared with that of the SCH at this laser peak intensity. One may also note that the P_{ssDCH} is smaller than the P_{tsDCH} , which is due to the two times smaller cross-section for ejecting the second electron, and higher ssDCH Auger rate, in the former case.

Similar observations can be made for CO. Here one may also observe the delay of the maximum of the P_{SCH} of C compared with that of O, which is due to the longer Auger life time in the former case. This is also reflected in their respective P_{ssDCH} curves. In this case a 10 fs pulse with a laser peak intensity of 3×10^{16} W/cm² was used.

Figure 6. Time evolution of the occupation probabilities for single and double core-hole states in (a) N_2 and (b) CO . The black curve represents the 10 fs X-ray pulse. The beam diameter was $3.4 \mu m$ and the pulse energy was $6.9 \mu J$ in (a) and $30 \mu J$ [18] in (b). The SCH and PA curves have been reduced by a factor (see figure) in order to resolve all curves.

One useful application of the simulations is that it is possible to estimate the X-ray pulse duration by comparing the simulated relative integrated intensities of certain nonlinear peaks, with the corresponding experimental ratios. The dependence of the relative intensities of peaks on the pulse length can be understood by studying the type of plots shown in figure 6. For example the ratio between the PAP and DCH intensities could be expected to be sensitive to the pulse duration for the following reason. The transition probability depends on the overlap between the curves of the pulse and the occupation probability of the state from which the transition is made, see Equation (1). The rise of the PA curve has to wait-in the Auger decay from the SCH states. Thus, for a very short pulse, compared to the Auger lifetime, the PA curve will not yet have increased significantly before the pulse is over. The longer the pulse is, the more insignificant becomes the delay of this rise, which increases the overlap between the pulse and the PA curves. For the DCH states the pulse duration works in the opposite direction. For a short pulse the Auger decay will not have time to decrease the SCH states to a large extent before the pulse is over, while for a long pulse they will be continuously decreased, thus reducing the integral of Equation (1).

The sensitivity of the relative intensities of the different nonlinear states to the pulse length is illustrated in figure 7. It displays the simulated signal intensity for various nonlinear states as a function of the pulse duration for CO . The pulse energy was kept constant at $30 \mu J$. As the included processes are all two-photon processes, these curves are just weakly dependent on the pulse energy, which is why an approximation of this parameter is sufficient. To illustrate this, the stretched black line shows the effect on the PAP O state when doubling the pulse energy. All intensities are normalized to the ssDCH C state. Figure 7 reveals the strong sensitivity of the PAP states with respect to the other states. One may also observe that the relative intensity of the processes which initially eject a C or O core electron is sensitive to the duration of the pulse, due to the different Auger lifetimes of the two atoms.

Figure 7. Demonstration of the sensitivity of various nonlinear states to the pulse duration for CO. All curves are normalized to the ssDCH C state. The stretched curve illustrates the effect on the PAP O state when doubling the pulse energy in order to show the relatively small dependence on the pulse energy.

Ideally one would include as many states as possible in order to estimate the pulse duration from a comparison of the simulations with the experiment. However, the quality of the experimental spectra only permits accurate determination of the integrated intensity for a qualitative analysis of the nonlinear peaks of N_2 . Hence, we will focus on this molecule.

Figure 8 shows how the spectrum of N_2 is affected by the pulse length. The simulated PAP and tsDCH peaks at different pulse durations have been normalized to the intensity of the ssDCH peak at a pulse length of 10 fs. The relative area of the peaks corresponds to the calculated relative probability for generating the states. The peak widths are set to 5 eV FWHM for the ss- and tsDCH peaks and 7 eV FWHM for the PAP peak, estimated from the experimental spectrum. The pulse energy was set to 6.9 μJ and the beam diameter was 3.4 μm . Again in this case one may observe the strong dependence of the PAP/DCH ratio to the pulse duration. A quantitative analysis by comparison of the experimental with the calculated PAP/ssDCH and PAP/tsDCH ratio of the integrated intensities reveals a pulse duration of 10 ± 5 fs. This value fits well with the estimate provided by the LCLS electron bunch-length diagnostics.

Figure 8. Pulse length dependence of the intensity of the PAP peak and tsDCH peak normalized to the ssDCH peak for N_2 .

6. Conclusions

We have investigated molecular DCH formation of the molecules N_2 , N_2O and CO_2 using X-ray photoelectron spectroscopy. The experiments were performed at the LCLS X-ray FEL which produces laser pulses with sufficient peak intensity to enable the creation of DCH states by sequential ionization. The generated photoelectron spectra revealed three main sequential nonlinear contributions: ssDCH states, tsDCH states and structures associated with the PAP process. These assignments were based on the comparison of the experimental spectra with theoretical calculations of the position [12,23,27,32] and intensity of the peaks.

The predicted sensitivity of the tsDCH states to the chemical environment was verified by extraction of relevant parameters from the photoelectron spectra. One such parameter is the IRC, which is central to the theory of the tsDCH states, and in particular to their chemical sensitivity. Our experimentally determined values of IRC follow the trends, and support, this theory. Further, the chemical sensitivity of the tsDCH was exemplified by the large spectral shift of the $O^{-1}C^{-1}$ tsDCH state of CO_2 with respect to that of CO [18], which is induced by the extra O atom.

Simulations of the integrated intensities of the spectral structures associated with the ssDCH, tsDCH and PAP processes were used to study their dependence on the X-ray pulse duration. We found that a comparison of the simulated and experimental relative intensities of, in particular, the PAP and DCH peaks, can be a powerful tool for determining the pulse length of ultra-short X-ray pulses.

References

- [1] Hercules, DM 2004 *J. Chem. Educ.* **81** 1751
- [2] Hagström, S, Nordling, C and Siegbahn, K 1964 *Z. Physik* **178** 439
- [3] Hagström S, Nordling, C and Siegbahn, K 1964 *Phys. Lett.* **9** 235
- [4] Hagström, S 2007 *Physics Today* **60**(11) 74
- [5] Schnopper, HW 1963 *Phys. Rev.* **131** 2558
- [6] Madden, RP and Codling, K 1963 *Phys. Rev. Lett.* **10** 516
- [7] Cederbaum, LS, Tarantelli, F, Sgamelotti, A and Schirmer, J 1986 *J. Chem. Phys.* **85** 6513
- [8] Cederbaum, LS, Tarantelli, F, Sgamelotti, A and Schirmer, J 1987 *J. Chem. Phys.* **86** 2168
- [9] Cederbaum, LS 1987 *Phys. Rev. A* **35** 622
- [10] Ohrendorf, E.M.-L, Cederbaum, LS and Tarantelli, F 1991 *Phys. Rev. A* **44** 205
- [11] Eland, JHD, Tashiro, M, Linusson, P, Ehara, M, Ueda, K and Feifel, R 2010 *Phys. Rev. Lett.* **105** 213005
- [12] Lablanquie, P *et al.* 2011 *Phys. Rev. Lett.* **106** 063003
- [13] Feldhaus, J, Arthur J and Hastings, JB 2005 *J. Phys. B* **38** S799
- [14] Bozek, JD 2009 *Eur. Phys. J. Special Topics* **169** 129
- [15] Young *et al.* 2010 *Nature* **466** 56
- [16] Cryan, JP *et al.* 2010 *Phys. Rev. Lett.* **105** 083004
- [17] Fang, L *et al.* 2010 *Phys. Rev. Lett.* **105** 083005
- [18] Berrah, N *et al.* 2011 *PNAS* **108** 16912
- [19] Salén, P *et al* 2012 *Phys. Rev. Lett.* **108** 153003
- [20] Santra, R, Kryzhevoi, NV and Cederbaum, LS 2009 *Phys. Rev. Lett.* **103** 013002
- [21] Kryzhevoi, NV, Santra, R and Cederbaum, LS 2011 *J. Chem. Phys.* **135** 084302
- [22] Tashiro, M, Ehara, M, Fukuzawa, H, Ueda, K, Buth, C, Kryzhevoi, NV and Cederbaum, LS 2010 *J. Chem. Phys.* **132** 184302
- [24] Hemmers, O, Whitfield, SB, Glans, P, Wang, H, Lindle, DW, Wehlitz R and Sellin IA 1998 *Rev. Sci. Instr.* **69**, 3809
- [25] Chalupsky, J *et al.* 2011 *Nucl. Instr. Meth. Phys. Res. A* **631** 130
- [26] Moddeman, WE, Carlson, TA, Krause, MO, Pullen, BP, Bull, WE and Schweitzer, GK 1971 *J. Chem. Phys.* **55** (5) 2317
- [27] Tashiro, M, Ueda, K and Ehara, M (to be published).
- [28] Rohringer, N and Santra, R 2007 *Phys. Rev A* **76** 033416
- [29] Band, IM, Trzhaskovskaya, MB, Verner, DA and Yakovlev, DG 1990 *Astron. Astrophys.* **237** 267
- [30] ????????????????
- [31] Maier, K, Kivimäki, A, Kempgens, B, Hergenbahn, U, Neeb, M, Rüdél, A, Piancastelli, MN and Bradshaw, AM 1998 *Phys. Rev. A* **58** (5) 3654
- [32] Eland, JHD 2003 *Chem. Phys.* **294** 171
- [33] Svensson, S, Naves de Brito, A, Keane, MP, Correia, N, Karlsson, L, Liegener, C-M and Ågren, H 1992 *J. Phys. B* **25** 135
- [34] EKempgens, B, Kivimäki, A, Neeb, M, Köppe, HM, Bradshaw, AM and Feldhaus, J 1996 *J. Phys. B* **29** 5389
- [35] Bondlengths can be found at: <http://cccbdb.nist.gov/>