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Abstract
We report the first measurement of the near oxygen K-edge auger spectrum of the glycine molecule. Our work employed an x-ray free electron laser as the photon source operated with input photon energies tunable between 527 and 547 eV. Complete electron spectra were recorded at each photon energy in the tuning range, revealing resonant and non-resonant auger structures. Finally ab initio theoretical predictions are compared with the measured above the edge auger spectrum and an assignment of auger decay channels is performed.
1. Introduction

Auger decay following core ionization is a well-known example of a process driven by electron correlations that may occur in atoms, molecules or condensed phase matter. The process of auger decay involves first the removal, or excitation, of an energetically deeply bound electron typically from within an atomic inner shell state. This leads to ultrafast electronic rearrangement in the atom or molecule resulting in the emission of a second electron in addition to the primary electron ionization/excitation. There is intrinsic interest in understanding the auger electron signature of a molecule to confirm theoretical calculations of the valence and inner valence states of the molecule and the molecular ion. Moreover, since the core electrons are energetically and spatially well localized the auger process in a molecule can be selectively initiated by choice of photon energy close to the absorption edge of a particular atomic species within the molecule. In this way a well defined location within the molecule, determined by the position of that specific atom, can be probed by the initiation of an auger process. Therefore it appears there is a potential path to measure charge dynamics in molecules by using auger initiation or auger probing.

In recent years x-ray free electron lasers have been extensively developed. This development opened the access to both high brightness and few femtosecond pulses [1–3]. The latter property permits the consideration of auger electron signal as a route to recover charge dynamics in molecules [4, 5]. In order to do so, one has first to determine the response of molecules to excitation in the soft x-ray range and disentangle the different electron emission channels (i.e.: direct valence photoemission and auger electron emission). The high brightness and the photon energy tunability of the x-ray FEL permit to obtain an energy dependent measurement of the molecules response in a short time. Therefore, such a characterization can be done prior to a time dependent measurement in similar experimental conditions.

The processes occurring in organic molecules are of particular interest for obvious biological reasons. Therefore glycine was chosen as it is the simplest biological molecule. Several near edge absorption fine structure (NEXAFS) spectroscopy measurements have been realized in glycine with synchrotron radiation sources in both solid [6, 7] (thin layer deposition) and gas phase [8, 9]. To date, however, no measured auger spectra are reported for this system in the literature. In this article we present an auger electron study on the glycine molecule over a range of photon energies spanning 20 eV around the oxygen K-edge. Thus we can compare the result of excitation processes below the oxygen core ionization energy that lead to resonant auger electrons and the result of core ionization giving birth to normal auger electrons. In the latter case we can also compute the auger spectrum relying on ab initio algebraic diagrammatic construction (ADC) approach and compare the predictions to our measurements. The calculation gives us also access to the molecular orbitals contributions in the final above the edge auger spectrum.

2. Experimental methods

The experiment was conducted on an x-ray free electron laser beamline (LCLS [10], AMO end station [11]) providing tuneable x-ray femtosecond pulses in self-amplified spontaneous emission (SASE) mode around $E_{\text{photon}} = 537 \text{ eV}$ at 120 Hz repetition rate with a pulse energy of 50–550 µJ. The photon energy was tuned by a fine scan of the electron beam energy. The range of electron bunch energy offset spanned from $-25$ to $+25$ MeV which corresponds to a maximum offset of $\pm 10$ eV in photon energy. The electron beam energy was measured on a shot-by-shot basis by means of a beam position monitor in the final dispersive region to account for energy jitter coming from fluctuations of the electron accelerator radio frequency field. This electron bunch energy was calibrated to obtain the photon energy measuring the absorption at the $\pi^*$ resonance and the oxygen K-edge of a mylar filter [12]. In SASE mode a photon bandwidth of around 0.5% is expected and corresponds to an absolute bandwidth of $\sim 2.5$ eV in our experiment. X-ray pulse energy was monitored shot-by-shot using fluorescence from N$_2$ in a gas detector and tuned with a gas attenuator.

The radiation pulses interacted with a jet of neutral glycine (NH$_2$CH$_2$COOH) molecules produced in gas phase by an oven [13] at $\sim 400$ K from a 99% pure glycine sample obtained from Sigma Aldrich. With this sublimation source, we reached a target density of $\sim 10^{11}$ molecules cm$^{-3}$ in the interaction region.

Electrons created in the interaction region were collected by a 2 m long magnetic bottle time-of-flight spectrometer (dubbed free electron laser correlations) that was previously used for multi-particle correlation experiments at the LCLS [14]. This spectrometer is equipped with an MCP detector from which the signals were sent to a digitiser. The calibration of this spectrometer was obtained by measuring the O$_2$ auger lines. A retardation potential of 450 V was applied to the drift tube to optimize the resolution for electron kinetic energies between 460 and 540 eV. Although this retardation potential was mainly used to measure the auger spectrum of glycine near the oxygen K-edge, a set of different retardation potentials (200, 300 and 380 V) were also investigated. All the data was recorded on a shot-to-shot basis and was sorted with respect to the photon energy and normalized against pulse energy.

3. Theoretical methods

For ab initio calculations of the auger decay spectra the ionization energies were obtained using the extended second-
order algebraic diagrammatic construction [ADC(2)x] method for the singly [15] and doubly [16] ionized states. The total and partial decay widths of the core-ionized states were calculated using the Fano-ADC method [17]. Briefly, this $L^2$ method rests on evaluation of the generalized Fano expression [18, 19] for the decay width, $\Gamma$, through the matrix element of the full many-electron Hamiltonian $\mathcal{H}$ between the bound-like $|\Phi\rangle$ and the continuum-like $|\chi_{\alpha,c}\rangle$ components of the wave function at the energy of the decaying state $E_\alpha$:

$$\Gamma = 2\pi \sum_{\alpha=1}^{N_c} \left| \left\langle \Phi | \mathcal{H} - E_\alpha | \chi_{\alpha,c} \right\rangle \right|^2.$$ (1)

The summation runs over $N_c$ decay channels, $\epsilon_{\alpha}$ is the kinetic energy of the emitted electron for the $\alpha$'s decay channel. The many-electron wave functions $|\Phi\rangle$ and $|\chi_{\alpha,c}\rangle$ are obtained using the ADC(2)x scheme for single ionization [15].

In the center of the Fano-ADC computational procedure is the configuration selection scheme that sorts out the many-electron ADC basis states into those contributing to the expansion of the initial (bound-like) state and to the final (continuum-like) states. In the present study, we employ the energy-based configuration selection scheme [17]. As part of the Fano-ADC procedure, Stieltjes imaging [20–22] was applied to series of increasing order block-Lanczos pseudospectra of the final state Hamiltonian until convergence with respect to the block-Lanczos iterations was reached [23, 24]. The calculations have been performed by using the MOLCAS quantum chemistry package [25] for Hartree–Fock self-consistent field calculations and our own implementations of the ADC methods. For the energy calculations, aug-pCVDZ basis sets [26–28] were used on all atomic centers. Converged auger decay widths were obtained in aug-pCVQZ basis [26–28] without $g$ functions, uncontracted on the atomic centres with the initial core vacancy.

4. Results and discussion

For each photon energy the emitted electrons were recorded for kinetic energies down to $E_k \approx 460$ eV with the 450 V retardation potential. The spectrum comprises valence photoelectrons as well as auger electrons triggered by vacancies created in oxygen core orbitals. Figure 1 presents a 2D map of the recorded electron signal where the horizontal axis corresponds to electron kinetic energy and the vertical axis corresponds to photon energy $E_{\text{photon}}$.

The low intensity valence photoelectron signal is visible in the map as it drifts linearly with the photon energy. The rest of the signal corresponds to electrons emitted through auger decay.

In the photon energy region spanning from $E_{\text{photon}} = 547$ eV down to $E_{\text{photon}} = 539$ eV we observe normal auger electron signal that corresponds to core ionization followed by auger decay from the cationic to the dicationic state. We recall here that the 1s ionization threshold was previously estimated to be 535 eV [6, 7] in the condensed phase and 538.4 eV (C=O) to 540 eV (C–O–H) in the gas phase [9]. Therefore the observed oxygen 1s ionization potential at 539 eV is consistent with the literature. The auger spectrum in this photon energy region is characterized by a kinetic energy cut-off located around $E_k = 507$ eV. We can extract an estimation of the double ionization potential (DIP) of the glycine to be 32 eV. So far, only a theoretical value of 26.43 eV for the DIP was published [29]. We also note a variation in the signal intensity with photon energy clearly identified for the brightest peak. Indeed the signal at $E_k = 500$ eV reaches a maximum in intensity at $E_{\text{photon}} = 540$ eV then decreases with a local minimum at $E_{\text{photon}} = 543$ eV and then increases again for the highest photon energy. This behaviour is clearly seen in the tail of this strongest feature (around $E_k = 495$ eV). It traduces the existence of excited states corresponding to resonant transitions from the core to $\sigma$ orbitals that lie above the core ionization limit [8] ($\sigma_{C=O-H}^*$ at 540 eV and $\sigma_{C-O}^*$ at 544 eV).

Below $E_{\text{photon}} = 539$ eV, electron kinetic energy cut-off dramatically increases up to $E_k = 525$ eV and slowly decreases as the photon energy decreases. The high kinetic energy cut-offs are particularly visible for the photon energy region $E_{\text{photon}} = 532–538$ eV where resonant excitation processes are possibly populating excited states including the two oxygen $\pi^*$ resonances and the 3p Rydberg resonance [8, 9] although they overlap with the valence photoelectron signal. We observe that the highest kinetic energy extension of the cut-off (around $E_k = 525$ eV) is compatible with that expected for the $\pi_{C=O-H}^*$ and the Rydberg resonances (respectively 525 and 527 eV). The low signal associated with $\pi_{C=O}^*$ ionization made it difficult to establish an accurate cut-off position for this ionization channel. In this configuration, the neutral system decays through auger emission to the cation.

Our results can be compared with previous gas phase studies on glycine by looking at the NEXAFS signal. Figure 2 exposes the total electron yield with respect to the excitation (photon) energy. The spectrum appears a lot less structured than those observed by Gordon et al [8, 9], both obtained with...
synchrotron light source and recorded with a time of flight spectrometer at the so-called ‘magic angle’ of 54.7° with respect to the polarization axis of the radiation. This is to be expected as the bandwidth of the SASE x-ray pulses used in the experiment reported here is large (2.5 eV) in comparison to narrow band synchrotron pulses used by Gordon and Plekan. Nevertheless, the broad feature presents several resonances marked by vertical red lines.

Having identified the near edge structure of glycine, we take a closer look at the auger spectra for both resonant and non-resonant excitation. Figure 3 presents those spectra for every photon energy in 1 eV increment and plotted on top of each other. In the range of $E_{\text{photon}} = 530-539$ eV, where we access near edge absorption structures, the strong signal increase corresponds to resonant auger electrons. The position of the cut-off energy extends to $E_k = 525$ eV as expected from the discussion above. The spectra exhibit three main features with maxima respectively at $E_k = 468, 484$ and 506 eV that are clearly visible up to $E_{\text{photon}} = 536$ eV.

Between $E_{\text{photon}} = 536$ eV and $E_{\text{photon}} = 538$ eV we observe the transition of the electron spectrum from the $\pi^*$ resonant spectrum to the above the edge auger spectrum. In this region near the ionization edge we also expect to see resonant excitation to Rydberg states. The overlap between the $\pi^*$ resonant signal and the above edge signal can lead to the smeared distribution we recorded. Therefore it is difficult to conclude the effect of the Rydberg resonances on the auger electrons. Nevertheless, highly excited states such as Rydberg states must be accompanied by a high kinetic energy signal cut-off. It appears that this cutoff limit is very similar for the $\pi^*_C-O-H$ and the Rydberg resonances but a variation of 1 eV towards higher energy for the Rydberg resonance can be seen.

At higher photon energies, the auger structure shifts to lower kinetic energy: above $E_{\text{photon}} = 539$ eV, the spectrum structure does not change with photon energy and is therefore assumed to reflect the normal auger spectrum. It exhibits three main features all shifted down by 10 eV of kinetic energy with respect to the near edge photon energy case. It is close to the expected energy shift between the decay from the neutral to the cation and decay from the cation to the dication system (for the neutral system: $\text{IP} = 10$ eV, $\text{DIP} = 32$ eV). Comparing the spectra at $E_{\text{photon}} = 543$ eV and $E_{\text{photon}} = 535$ eV, we note that the high photon energy spectrum exhibits more resolved structure. The apparent smearing of the resonant auger spectra is the result of a large photon energy bandwidth for a given central frequency which, as a consequence, mixes the resonant contributions as it has already been seen in the photoabsorption spectrum in figure 2.

In addition to the extensive study of the auger spectrum near the oxygen K-edge, we recorded above the carbon and nitrogen K-edges auger spectra by using lower retardation potentials on the magnetic bottle time-of-flight spectrometer for $E_{\text{photon}} = 560$ eV. The retardation potentials used were respectively 200 and 300 V. The figures 4(a) and (b) present a comparison of those results with ab initio calculations. Although the experimental resolution is low due to high electron kinetic energy, there is a qualitative agreement of the auger electron structure between the measured data and the theoretical ones.
The theoretical spectrum is decomposed into the different electronic configurations contributing to the auger decay channels (figure 4(d)): outer valence to core orbital recombination accompanied by outer valence electron emission (ov–ov), inner valence to core recombination with outer valence electron emission (iv–ov) and inner valence to core recombination with inner valence electron emission (iv–iv). The distinction between inner valence molecular orbitals (6a' to 10a') and outer valence orbitals (11a' to 20a') is done considering their underlying 2s or 2p atomic character. Nevertheless, all those orbitals are delocalized over the entire molecule. We observe that the highest kinetic energy feature around 495 eV is mainly composed by electrons emitted through channels (ov–ov) and (iv–ov). The second structure (E_k = 475 eV) is essentially the result of inner valence to core recombination with two main emission configurations: (iv–ov) and (ov–ov). Interestingly, the third band (E_k = 455 eV) is composed by the three possible configurations in relatively equal proportions. The presence of the (ov–ov) configuration at this low energy stresses the extremely mixed character of corresponding dicaticon states and is the illustration of the breakdown of the molecular orbital picture of double ionisation for this auger decay channel.

5. Conclusion

In this article, we performed the first measurement of auger spectrum in glycine. We have demonstrated the use of x-ray FEL pulses for the investigation of auger processes occurring near the oxygen K-edge of a small organic molecule (glycine) in the gas phase. We recorded auger spectra as a function of photon energy, following their evolution through resonant and non resonant processes. Thus we obtained a full picture on the evolution of the auger spectra. In our experiment we scanned the SASE FEL photon energy by FEL pulses for the investigation of auger processes occurring near the oxygen K-edge of a small organic molecule (glycine) in the gas phase. We recorded auger spectra as a function of photon energy, following their evolution through resonant and non resonant processes. Thus we obtained a full picture on the evolution of the auger spectra. In our experiment we scanned the SASE FEL photon energy by scanning the electron energy which was found to have a number of advantages. The high photon flux allows the electron spectrum to be rapidly accumulated despite the relatively low sample density allowing the total scan time in these measurements to be within 10 min. This paves the way for future time resolved experiments in the pump–probe mode where the time for accumulation of data at each value of photon energy and time delay should be short to allow complete measurements to be acquired in a few hours. Further measurements with narrow band sources, however, would be desirable to fully resolve the near edge structures and the details of the resonant auger spectra in the glycine molecule.

Finally the above the edge auger spectrum has been compared with ab initio calculation, revealing a good agreement between experiment and theory for the glycine I isomer. The theory also allowed to determine the dominant configuration in the decay channels constituting the above oxygen K-edge auger spectrum of glycine.
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