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ИНДУЦИРОВАННОЕ РЕНТГЕНОВСКИМ ЛАЗЕРОМ НА СВОБОДНЫХ ЭЛЕКТРОНАХ ФОРМИРОВАНИЕ ПАР КОР-ДЫРКА В МНОГОАТОМНЫХ МОЛЕКУЛАХ

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X-RAY FEL-INDUCED DOUBLE CORE-HOLE FORMATION IN POLYATOMIC MOLECULES

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Для исследования образования молекулярных двойных кор-дырочных состояний при последовательном двухфотонном поглощении рентгеновских лучей используются очень интенсивные, сверхкороткие мягкие рентгеновские импульсы LCLS-рентгеновского лазера на свободных электронах. Влияние критических параметров LCLS – таких, как число фотонов в импульсе, длительность импульса и размер фокусного пятна – на фотоэлектронный и оже-спектры моделируется в деталях, и результаты этого моделирования используются как вспомогательные в интерпретации экспериментально полученных спектров. Представлен обзор результатов двухфотонных экспериментов на LCLS.

***Ключевые слова**: лазер на свободных электронах, рентгеновский лазер, многоатомная молекула, двойное состояние кор-дырка.*

We use extremely intense, ultrashort soft X-Ray pulses generated by the LCLS X-Ray Free Electron Laser to investigate the production of molecular double core-hole states by sequential two-photon X-Ray absorption. The effect of critical LCLS parameters such as the number of photons per pulse, the pulse duration, and the focal spot size on the photoelectron and Auger spectra is modeled in detail and the results of these simulations are used as an aid in the interpretation of the experimental spectra obtained. We review here the results from the two-photon experiments at LCLS.

***Keywords**: free electron laser, X-ray laser, polyatomic molecule, double core-hole state.*

Introduction

The discovery of chemical shifts in photoelectron spectroscopy [1], [2] was an important consequence of the development of this technique, and for which Kai Siegbahn was awarded the 1981 Nobel Prize in physics. Chemical analysis by means of electron spectroscopy is well established for many years, and there are commercially available

instruments. The basic principle is the absorption of one photon by a molecule, and the ejection of one electron, which is energy analyzed. If the photon energy is sufficient to ionize a K-shell electron, the exact energy of the electron provides information about the local chemical environment. The ionization energy depends on where in a molecule an atom is located.

Cederbaum et al. [3] realized that two-site Double Core Hole States (tsDCHs) could be a more sensitive probe of the local chemical environment than are the usual single core-hole states. However, in 1986 it was not known how to produce K-shell vacancies on two different atoms in a molecule. The cross section for creating holes in the K-shell at two different atomic sites by the absorption of one photon is vanishingly small, and the photon flow from synchrotron radiation sources is too low to allow the absorption of a second photon while the first core-hole still exists. The reason is that the first core-hole is extremely short-lived owing to the Auger effect, which fills the core vacancy within less than 10 fs. This puts huge demands on the light source, demands that a synchrotron light source cannot fulfil.

The advent of free electron lasers in the X-ray regime has changed the situation. Free electron lasers, so far only the Linac Coherent Light Source (LCLS) at the SLAC National Accelerator Laboratory, operated by Stanford University, can deliver so many X-ray photons (10^{12}) during such time duration (10 fs) so that a molecule can absorb two photons during one photo pulse. The second photon can be absorbed before the first vacancy is filled, thus creating a molecule with a tsDCH state. Theoretical predictions showing that this should be possible was presented [4], and it was first verified experimentally shortly after [5].

Experiment

Figure 1 shows the electron accelerator at the SLAC National Accelerator Laboratory, the undulator which produces the X-rays, the AMO (Atomic, Molecular, Optical) hutch, and the electron and ion time-of-flights that are used to record and energy analyze the photoelectrons and photoions [6].

The free-electron laser was running with compressed 40 pC electron bunches at a repetition rate of 60 Hz to generate laser pulses of ~10 fs duration with a pulse energy of approximately 0.2 mJ, a photon energy of between 520 and 705 (±15) eV, and a pulse energy width of about 0.5%. The laser pulse length is difficult to measure directly for short X-ray pulses and was estimated from the peak electron current of the electron bunch. The photon energy is determined indirectly from the electron bunch kinetic energy. The pulse energy is given from detectors located upstream of the beamline optics which overestimate the pulse energy at the experiment by about 85% due to losses downstream.

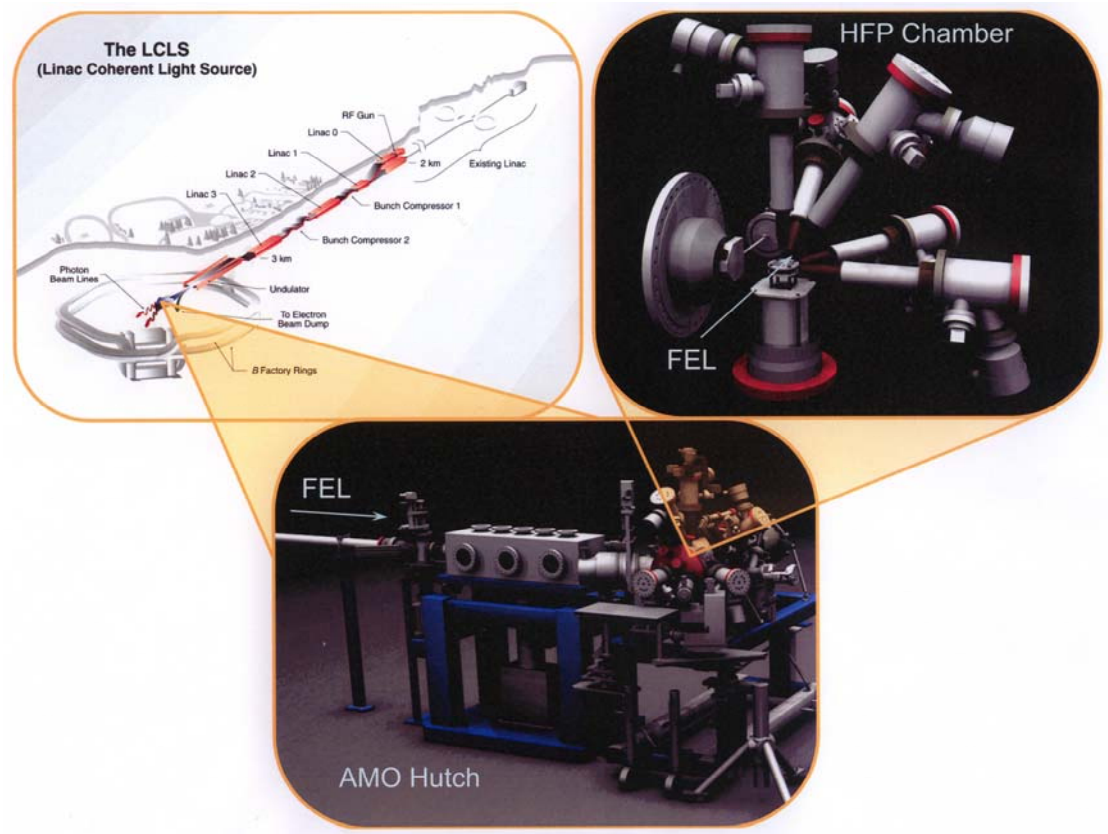

Figure 1 – LCLS at SLAC and the AMO instrument

Each laser pulse intersects a synchronized stream of sample gas with a diameter of about 4 mm, originating from a skimmed, supersonic beam source. The measurements were performed both with a focused and unfocused laser beam in the interaction region. The unfocused data are then subtracted from the focused in order to extract the pure non-linear contributions. Focusing is achieved with Kirkpatrick-Baez (KB) mirrors to an elliptical spot size with a major and minor semi axis of 2.2 μm and 1.2 μm FWHM respectively which corresponds to a beam intensity of roughly 10^{18} W/cm^2 at the focal spot. For the unfocused measurements the stage of the KB mirrors were shifted 20 mm with respect to the position of the optimal focus. This results in a beam spot with major and minor semi axis of 37.5 μm and 20.6 μm FWHM respectively and an intensity of around $3x10^{15}$ W/cm^2.

The ions and electrons produced by the interaction are analyzed with the Atomic, Molecular and Optical (AMO) instrument [7], [8]. It consists of an ion time-of-flight spectrometer (iTOF) to determine charge states and kinetic energies of generated ions, and five eTOFs for measuring the electron kinetic energies at various angles. In these experiments we used two eTOFs oriented at 0^o and 54.7^o (magic angle) with respect to the polarization of the laser beam. Generally the latter detector provided more non-linear signals, probably because of a better alignment to the laser focal spot but also more noise. Except for CO_2, all presented results originate from the experiments performed with the eTOF oriented at magic angle. The CO_2-data were however taken from measurements with the detector oriented at 0^o, due to excessive noise with the other detector. In order to align the iTOF and eTOFs to the interaction region, neon gas was used and the spectrometers were oriented so that a maximum signal from a neon Auger peak was achieved. The electron spectrometers are equipped with multi-element electrostatic lenses and a retardation voltage may be applied in order to increase the energy resolution.

Conclusions

We were successful in the experiment on CO, which was recently performed at LCLS [9]. In this paper the observation of two-site DCH states in CO was demonstrated. This is an important first step towards observations of tsDCH in molecules with atoms having the same atomic number but located at different sites in the molecule, which would allow measurements of chemical shifts that are more sensitive to the chemical environment.

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