

## Femtosecond X-Ray Fluorescence

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Using few-cycle-driven coherent laser harmonics,  $K$ -shell vacancies have been created in light elements, such as boron ( $E_B = 188$  eV) and carbon ( $E_B = 284$  eV), on a time scale of a few femtoseconds for the first time. The capability of detecting x-ray fluorescence excited by few-femtosecond radiation with an accuracy of the order of 1 eV paves the way for probing the evolution of the microscopic environment of selected atoms in chemical and biochemical reactions on previously inaccessible time scales ( $<100$  fs) by tracing the temporal evolution of the “chemical shift” of peaks associated with inner-shell electronic transitions in time-resolved x-ray fluorescence and photoelectron spectra.

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The creation of inner-shell vacancies in atoms is followed by the emission of photoelectrons and fluorescence photons, the energy of which not only identifies the atom itself but, if measured with sufficient precision, also serves as a “fingerprint” of its local chemical and electronic environment [1]. In light elements with an atomic number  $Z < 10$  (B, C, N, O, F), which are important constituents of a vast number of molecular systems and have  $K$ -shell binding energies in the range of 0.1–1 keV, chemical shifts of the energy of  $K$ -shell photoelectrons or  $K_\alpha$  photons are of the order of 1–10 eV.

Thus far, chemical analysis by means of x-ray spectroscopies has been primarily performed on *static* samples. Dynamical chemical shifts could be measured only in a few experiments using x-ray absorption spectroscopy or x-ray photoelectron spectroscopy [2] on microsecond or longer time scales. However, the formation and breaking of chemical bonds often takes place on the femtosecond time scale. Ultrafast molecular and surface dynamics have so far been studied primarily by *optical* pump-probe spectroscopy [3]. Whereas reactions can be precisely triggered and, to some extent, even steered by shaped ultrashort laser pulses [4], probing the valence electronic optical properties by a delayed probe pulse in the visible or nearby spectral regions provides satisfactory insight into the transition states of the evolving reaction only for the simplest molecules. Recently, time-resolved x-ray absorption [5] and diffraction [6] was shown to permit direct observation of atomic-scale motion with a time resolution of  $\approx 1$  ps or slightly better by using sub-ps x-ray pulses emitted by fs-laser-driven nonthermal plasmas [7]. The work presented here constitutes the first step towards time-resolved x-ray spectroscopy of solid-state and molecular dynamics on a sub-100-fs time scale.

The feasibility of femtosecond ( $<10^{-13}$  s) x-ray spectroscopy depends on the availability of sufficiently short and energetic x-ray pulses. Up to now, only high-order harmonics of femtosecond laser pulses [8] could be demonstrated to yield sub-100-fs XUV (extreme ultraviolet) pulses. High harmonic generation has re-

cently been extended well into the soft x-ray regime ( $E_{ph} > 100$  eV) by using very short ( $<25$  fs) driver pulses [9,10]. In this Letter, we report the observation of  $K$ -shell vacancies in light elements by means of x-ray fluorescence using few-cycle-driven laser harmonics as the excitation source. The peak of the fs x-ray fluorescence spectrum can already be determined, in spite of the extremely low ( $\approx 10^{-3}$ ) fluorescence yield of low- $Z$  atoms, with a precision of the order of 1 eV with a present-day sub-10-fs high harmonic source. The presented results indicate that x-ray probing of molecular dynamics with a few fs resolution may become feasible *up to photon energies in the water window* by means of time-resolved x-ray fluorescence, x-ray absorption, or x-ray photoelectron spectroscopy.

In our experiments coherent x-ray harmonic radiation [11] is generated by focusing 0.7-mJ linearly polarized  $\approx 790$ -nm laser pulses of 5–7 fs in duration at a 1 kHz repetition rate [12] into a quasistatic He gas cell [9]. The He atoms are exposed to peak electric fields of  $\approx 6 \times 10^{15}$  W/cm<sup>2</sup> over an effective interaction length of  $\approx 0.3$  mm and emit coherent soft x-ray harmonic radiation up to photon energies exceeding 500 eV [9]. Maximum yield at high ( $>200$  eV) photon energies is achieved at backing pressures of 4–6 bars. The emission time at these photon energies is estimated to be less than 5 fs. The soft x-ray photons are delivered in a well-collimated beam (divergence  $\approx 1$  mrad) and hit the sample at a position of  $\approx 0.6$  m from the He source. Infrared laser light is blocked and XUV harmonics at  $E_{ph} < 100$  eV are suppressed by a 200-nm silver filter.

Emission from the irradiated sample is detected with an energy-dispersive x-ray (EDX) spectrometer equipped with a liquid-nitrogen-cooled Si(Li) detector. The detector is placed with its entrance window close to the illuminated spot on the sample ( $\approx 10$  mm) to maximize the solid angle for fluorescence detection. It is several millimeters behind the window and has an area of 10 mm<sup>2</sup>. The detector window (Norvar) transmitting x rays down to energies of  $\approx 120$  eV is covered with an aperture of 4 mm

in diameter and a 200-nm-thick titanium foil to prevent laser light and lower-order harmonics reaching the detector and to keep the average count rate below 0.01 count/laser pulse for safe pileup rejection. Because of the low fluorescence yield for light elements, e.g., 0.17% in boron, the characteristic radiation flux is small and superimposed on a large background originating from coherent scattering in the soft-ray regime [13]. This can be suppressed by using a  $p$ -polarized (electric field vector parallel to the plane of incidence) collimated x-ray beam impinging at an angle of  $\approx 45^\circ$  ( $\approx$  Brewster angle) on the sample and by setting the axis of detection perpendicular to the direction of the excitation beam [14]. If a volume target with ideally smooth surface (zero roughness) is irradiated by a collimated (spatially coherent) x-ray beam in this geometry, coherent scattering results in a collimated, spatially coherent output beam with a relative intensity that is several orders of magnitude lower for  $p$  than for  $s$  polarization (electric field vector perpendicular to the plane of incidence). In practice, finite surface roughness increases the cone of scattered radiation, and, in case of a large detection solid angle, substantially reduces this extinction ratio.

Polished thick volume samples of boron nitride (BN) and carbon (C) have been irradiated in the above described geometry because theory predicts high-order harmonic radiation to be polarized parallel to the electric field vector of the driving laser field. Figure 1 depicts the energy spectrum of the radiation scattered and emitted from the BN sample irradiated by  $1.5 \times 10^6$  x-ray harmonic pulses driven by a vertical (open circles) or horizontal (full circles) laser electric field under (otherwise) identical experimental conditions.  $K$ -shell fluorescence from boron, the spectrum of which should peak at about 183 eV, is completely buried in scattered radiation in the former case. By contrast, for

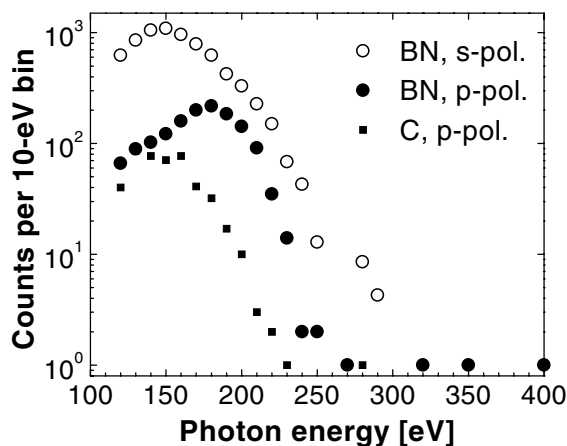


FIG. 1. Energy spectrum of x rays from a BN sample irradiated with laser harmonics. The spectrum has been produced by  $1.5 \times 10^6$  laser shots with vertical (open circles) and horizontal (full circles) laser polarization (detector filter: 200 nm Ti). Full squares: scattered radiation from carbon illuminated by  $p$ -polarized radiation for comparison.

horizontal polarization the number of counts is substantially reduced and their distribution clearly peaks near 183 eV, indicating that the observed signal is dominated by boron  $K$ -shell fluorescence emission from the irradiated sample. In order to determine the contribution of scattering to this signal, the BN sample is replaced by the C sample (full squares in Fig. 1), which has a refractive index close to that of BN between 100 and 200 eV and hence a nearly identical intrinsic scattering behavior. The extrinsic modification of coherent scattering due to surface roughness is also nearly identical for the C and BN samples, as evidenced by comparable signal levels at  $E_{ph} < 150$  eV.

The boron fluorescence emission spectrum can therefore be obtained to a good accuracy by subtracting the carbon signal (full squares) from the BN signal (full circles) in Fig. 1, yielding the data shown in Fig. 2. The linewidth is limited by detector resolution, resulting in a Gaussian signal shape [15]. A least-squares fit to the measured fluorescence data yields the solid line in Fig. 2 with a peak and a full width at half maximum evaluated as  $E_p = (183.4 \pm 0.8)$  eV and  $\Delta E = (48 \pm 2)$  eV, respectively. The observed fluorescence peak is found to be close to the  $K_\alpha$ -transition in boron (183.3 eV), in spite of the presence of N. This accuracy was reproduced in repeated measurements [16]. Comparison of the signals obtained from the BN sample at  $E_{ph} < 150$  eV and  $E_{ph} > 230$  eV with vertical and horizontal laser polarization provides conclusive evidence for soft-x-ray laser harmonics being well polarized along the laser electric field vector.

The full squares in Fig. 3 represent the measured spectrum of x rays originating from the C sample excited by  $p$ -polarized radiation ( $5 \times 10^6$  laser shots). The spectrum reveals a prominent feature at the  $K_\alpha$  transition in carbon. In order to evaluate the contribution of characteristic emission to the measured signal, intrinsic coherent scattering from the C sample has been calculated, fitted to the

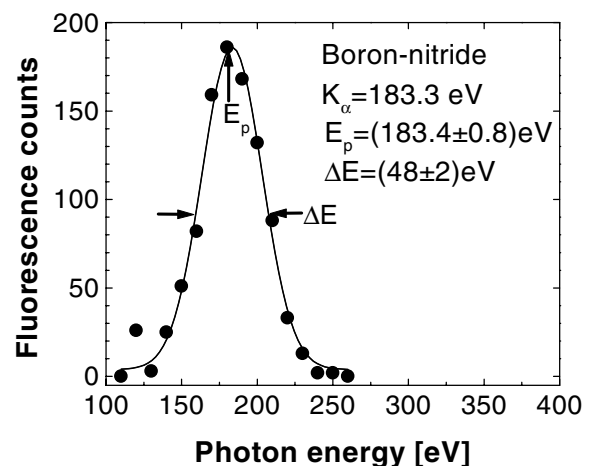


FIG. 2. Laser-harmonic-excited x-ray characteristic emission from boron at 183 eV ( $1.5 \times 10^6$  laser shots), as evaluated from Fig. 1. Solid line: Gaussian fit. The linewidth is instrument limited.

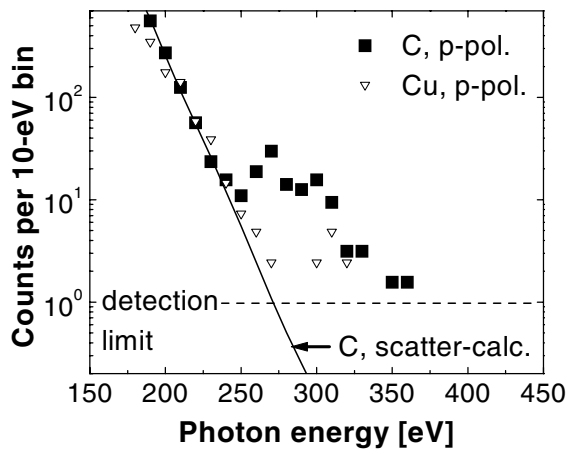


FIG. 3. Energy spectrum of x rays originating from a carbon (full squares) and a copper (open triangles) sample, both irradiated by  $5 \times 10^6$   $p$ -polarized harmonic pulses (detector filter: 200 nm Ag). Solid line: scattered signal from carbon calculated as described in the text.

measured signal below 230 eV, and extrapolated into the range of fluorescence emission (solid line in Fig. 3). For comparison, we also show the measured spectrum of scattered x rays from copper, the intrinsic scattering of which exhibits, at a somewhat higher rate, a similar spectral dependence. The fact that our superpolished carbon sample has a much lower surface roughness ( $<1$  nm) as compared to the copper sample justifies the neglect of the influence of extrinsic effects on the energy dependence of the scattered signal. The contribution of coherent scattering determined in the above manner (solid line in Fig. 3) has been subtracted from the overall signal (full squares in Fig. 3) for the determination of the carbon  $K$ -shell fluorescence signal induced by sub-10-fs water-window harmonic radiation. The full squares in Fig. 4 show the result of this analysis. In spite of the low signal level a Gaussian fit (solid line in Fig. 4) allows determination of the  $K_{\alpha}$  transition in carbon with good accuracy ( $\pm 1\%$ ).

The experimental results can be analyzed by using the relationship

$$J_K = \int_{E_{\text{abs}}}^{E_{\text{max}}} dE \int_0^d dx J_{\text{in}}(E) e^{-\tilde{\mu}(E)\rho x} \tau_K(E) \times \rho \eta_K G \eta_{\text{det}}(E_K), \quad (1)$$

which connects the count rate  $J_K$  (dimension:  $\text{s}^{-1}$ ) with the spectral distribution of the incident photon flux  $J_{\text{in}}$  ( $\text{s}^{-1} \text{eV}^{-1}$ ), the effective mass absorption coefficient  $\tilde{\mu}(E)$  ( $\text{cm}^2 \text{g}^{-1}$ ) accounting for absorption of the incident as well as emitted radiation and the increased path lengths as compared to the distance  $x$  of the excited infinitesimal volume from the surface (for excitation under oblique incidence), the  $K$ -shell photoabsorption mass coefficient  $\tau_K$  ( $\text{cm}^2 \text{g}^{-1}$ ), the mass density  $\rho$ , the fluorescence yield  $\eta_K$ , and the geometry factor  $G$ , which depends on the detection solid angle and  $\eta_{\text{det}}(E_K)$ , the detection efficiency at the characteristic emission. The

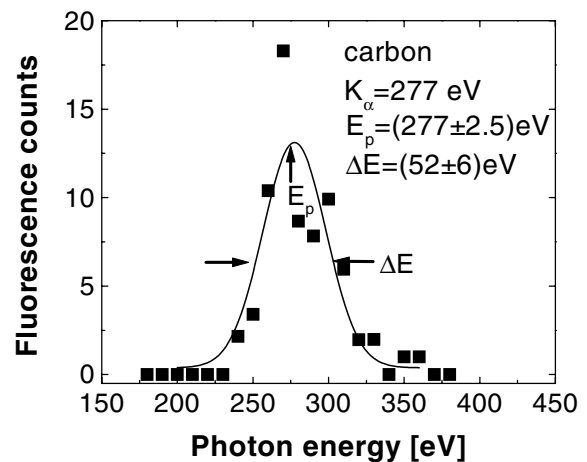


FIG. 4. Full squares, laser-harmonic-excited x-ray characteristic emission from carbon at 277 eV ( $5 \times 10^6$  laser shots), as evaluated from Fig. 3. Solid line: Gaussian fit. The linewidth is instrument limited. Its theoretical value is 7.7 eV, yielding a fluorescence decay time of  $\approx 0.5$  fs.

integration is to be performed from the  $K$  absorption edge  $E_{\text{abs}}$  to the maximum photon energy delivered by the excitation source and from the front to the back surface of the sample, respectively.  $J_{\text{in}} \eta_{\text{det}}(E > E_{\text{abs}})$  can be estimated by measuring the photon energy distribution of the strongly attenuated harmonic beam with the EDX spectrometer.

Because of a limited selection of metal filters available for our experiments, the x-ray harmonic photon yields at optimum helium pressure could, under conditions of safe pileup rejection, be determined only with several different sets of filters in subsequent measurements to cover the entire spectral range of interest (150–400 eV). A single measurement yielded access to this range at a strongly reduced pressure only (Fig. 5). By using these measurements and estimating  $\eta_{\text{det}}(E_K)/\eta_{\text{det}}(E > E_{\text{abs}})$  (which can be assessed without knowledge of the absolute detection efficiency), Eq. (1) allows the prediction of the detector count rates associated with characteristic emission. This prediction agrees within an order of magnitude with the measured count rates. However, the absolute photon flux evaluated from the EDX spectrometry of the source, upon assuming an intrinsic detector quantum efficiency of 100%, appears to be several orders of magnitude lower than previous estimates obtained from measurements using wavelength-dispersive spectrometry [17]. This suggests the presence of significant attenuation in our experiments, the origins of which (e.g., surface contaminations, oxid layers, dead layer in detector, beam clipping by apertures, etc.) are not yet identified in detail.

In our experiments,  $K$ -shell vacancies are created within less than 5 fs owing to the ultrashort duration of the excitation pulse from the few-cycle-driven harmonic source [9] and disappear virtually instantaneously due to ultrafast Auger relaxation, giving rise to *fluorescence emission*

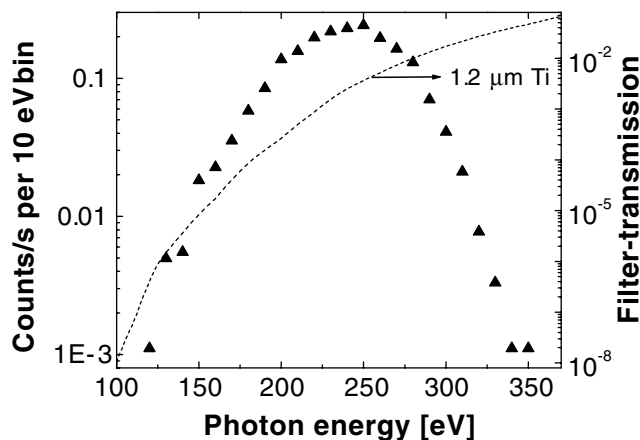


FIG. 5. X-ray photon energy spectrum of the few-cycle-driven He harmonic source at a reduced pressure of  $\approx 50$  mbar (triangles) as transmitted through  $1.2\text{-}\mu\text{m}$  titanium (dashed curve) and detected by the EDX spectrometer.

lasting merely a few femtoseconds. Even though it takes comparatively long measurement times to acquire the signals shown in Figs. 2 and 4, each individual x-ray photon contributing to these signals is emitted as a few-fs burst that can be reproducibly brought in coincidence with a few-fs precision with any stage of molecular dynamics triggered by sub-10-fs light. This opens the way to taking ultra-short snapshots of characteristic  $K_\alpha$  radiation (or related x-ray absorption or photoelectron spectra), subject to dynamical chemical shifts, from selected (light) constituent atoms of molecular systems during their evolution. Ongoing source development [18] holds promise for developing a versatile tool for direct and, owing to the broad harmonic spectrum, simultaneous observation of the evolution of the microscopic environment of low- $Z$  atoms in a wide range of physical, chemical, and biological processes with the capability of resolving dynamics down to the sub-10-fs time scale.

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