Direct Measurement of Core-Level Relaxation Dynamics on a Surface-Adsorbate System

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The coupling between electronic states in a surface-adsorbate system is fundamental to the understanding of many surface interactions. In this Letter, we present the first direct time-resolved observations of the lifetime of core-excited states of an atom adsorbed onto a surface. By comparing laser-assisted photoemission from a substrate with a delayed Auger decay process from an adsorbate, we measure the lifetime of the $4d^{-1}$ core level of xenon on Pt(111) to be 7.1 ± 1.1 fs. This result opens up time-domain measurements of surface dynamics where energy-resolved measurements may provide incomplete information.

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Charge-transfer processes between substrates and adsorbates are of great importance in many areas of surface science [1]. Various approaches have been used to obtain information about charge-transfer time scales, including line-shape analysis [2], core-hole clock spectroscopy [3,4], and direct time-domain pump-probe experiments [5,6]. Line-shape analysis has been successfully applied to the study of core-hole lifetimes in isolated molecules and atoms, where spectral line shapes are mainly homogeneously broadened. Thus, the spectral linewidth is unambiguously related to the dynamics of simple decay processes, because no further energy and momentum dissipation processes exist.

However, in the case of adsorbates on solid surfaces, inhomogeneous contributions due to the substrate (distortions, dislocations, and impurities) and due to adsorbate-substrate vibrations can increase the linewidth. Charge-transfer processes between the adsorbate and substrate can increase the homogeneous linewidth. For adsorbate states, in general, a clear separation between homogeneous and inhomogeneous broadening is not always possible. Time-domain measurements promise to directly observe dynamics unaltered by additional inhomogeneous contributions. However, these experiments require a time resolution comparable to typical electronic charge-transfer time scales, which are often in the range of a few femtoseconds and in some cases can even be subfemtosecond [7].

Core-hole clock spectroscopy is a method that seeks to overcome the limitations of pure energy- or time-domain methods, by using a sequence of energy-resolved measurements in conjunction with an adsorbate core level as an internal "reference clock" for investigating fast electron relaxation dynamics [3,4]. However, this technique requires accurate knowledge of core-hole lifetimes in adsorbate-substrate systems, which may differ from the core-hole lifetime of the same atom or molecule in the gas phase.

The first time-resolved studies of electronic and charge-transfer dynamics at surfaces investigated valence band resonances of chemisorbed and physisorbed atoms and molecules on metallic surfaces [8,9]. These experiments used time-resolved two-photon photoemission, driven by a combination of ultraviolet and infrared (UV + IR) photons with energies up to a few eV. Therefore, these studies explored adsorbate states in the valence and conduction bands just below the vacuum level. To date however, investigations of core energy levels have been performed only in the energy domain [10].

In this Letter, we present the first time-domain measurement of Auger decay from a complex materials system—an adsorbate on a surface [Xe/Pt(111)]. By comparing laser-assisted photoemission from a Pt substrate with the delayed laser-assisted Auger decay from Xe, we measure the core-hole lifetime for the $4d$ vacancy in atomic Xe absorbed on a Pt(111) surface to be 7 ± 1 fs. This measurement is possible despite the many complexities that result from the metallic substrate, such as above-threshold photoemission, hot electrons, and space-charge effects. The extracted lifetime for the Xe/Pt $4d$ core hole is consistent with high-resolution linewidth measurements of Xe in the gas phase, clearly validating our approach. Furthermore, our results demonstrate that time-resolved measurements are possible that can definitively identify the nature of any spectral broadening in more tightly bound systems, such as chemisorbed systems.

In a laser-assisted process, an atom is irradiated simultaneously by an ultrafast soft x ray (SXR) and a laser beam. Characteristic sidebands appear surrounding the SXR photoemission peaks, corresponding to simultaneous absorption and emission of laser photons. The magnitude and shape of these sidebands change as the time delay between the SXR and laser beams is changed, encoding information about the underlying electron dynamics. Laser-assisted Auger decay (LAAD) and laser-assisted photoelectric effect (LAPE) were first used to characterize ultrashort x-ray pulses [11,12], and later used to measure atomic core-hole lifetimes in free atoms [13]. Laser-assisted photoemission from a surface, which is the laser-assisted version of the original photoelectric effect, has only recently been observed [14,15].

A schematic overview of the experiment is shown in Fig. 1. A temperature-controlled Pt(111) sample was mounted on a translation and rotation stage inside an ultrahigh vacuum chamber (2×10^{-10} mbar). The SXR and IR beams were generated using an amplified Ti:sapphire laser system producing 2 mJ of energy per pulse, at a wavelength of 780 nm, with a repetition rate of 2 kHz and a pulse duration of 25 fs. Approximately 10% of the laser energy was used for the IR beam, while the remainder of the output was used to generate high harmonics in a helium-filled hollow waveguide. Flat and curved Si:Mo SXR multilayer mirrors were used to spectrally select the 57th harmonic (at a wavelength of 13.7 nm, or energy 90.8 eV) and to focus the resultant SXR beam onto the Pt surface to a ~0.1 mm spot diameter. A 200 nm-thick Zr filter blocked the copropagating IR light in the SXR beam line. The IR beam was directed through a variable optical-delay line and focusing lens before overlapping with the soft-x-ray beam on the sample at a small angle of 1°. The kinetic energy of the photoemitted electrons was analyzed using a time-of-flight detector oriented at 90° with respect to the SXR beam. Before dosing the surface with xenon, the Pt surface was cleaned via three cycles of oxygen annealing at 450 °C and flashing to 1000 °C.

After dosing the Pt(111) surface with a monolayer of Xe at a temperature of 84 K, three distinct features can be distinguished in the photoelectron spectrum. Around the Fermi edge, corresponding to photoelectron kinetic energies of ~85 eV, we observe the *d* band of Pt [Fig. 2(a)]. At photoelectron kinetic energies between 22 and 26 eV, we detect the Xe 4*d* core levels [Fig. 2(c)], while at energies between 35 and 42 eV, we observe the Xe *NOO* Auger electrons [Fig. 2(b)]. In the presence of an intense laser field, sidebands appear in the Xe/Pt(111) photoemission spectrum [see, for example, Fig. 2(a)] over the entire energy range.

Viewed in a perturbative two-step model, electrons photoemitted by the SXR beam can absorb or emit photons from the IR beam, leading to sidebands in the photoelec-

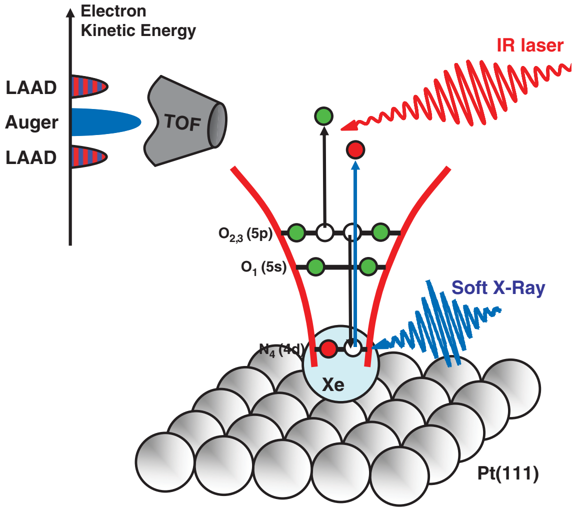

FIG. 1 (color). Schematic of the experiment. Ultrafast SXR and IR pulses are focused onto a Xe/Pt(111) surface, where the kinetic energy of the photoemitted electrons is measured by a time-of-flight detector. An electron from the Xe N_4 (4*d*) shell is ejected by the SXR, followed by filling of the core hole by an $O_{2,3}$ (5*p*) shell electron and ejection of a secondary (Auger) electron from the $O_{2,3}$ shell. In the presence of the IR beam, sidebands appear in the photoelectron spectrum of both Xe and Pt. By comparing the sideband amplitude vs time delay for the Pt and Xe, we can extract the lifetime of the Xe 4*d* core hole.

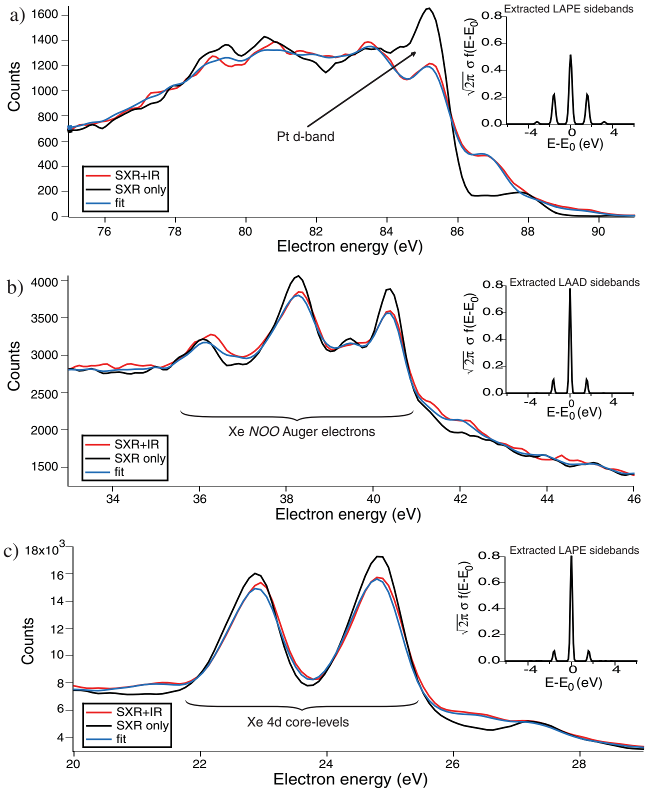

FIG. 2 (color). Extraction of the LAPE/LAAD sideband amplitudes for Xe/Pt(111) at zero time delay between the IR and SXR beams. (a) Photoelectron spectra of the Pt *d* band; (b) of the Xe Auger *NOO* bands; and (c) of the Xe 4*d* peaks. Red (black) lines represent the spectra with (without) the IR pulse present. The blue lines show the fit to the SXR + IR curve when the LAPE response function from Eq. (1) is convolved with the SXR-only spectrum. The insets show the extracted LAPE/LAAD response function associated with the fit.

tron spectrum. To quantitatively predict the sideband intensities, we model the absorption and emission of up to two IR photons by a laser-assisted photoemission response function given by

$$f(E-E_0)=\frac{1-2A_1-2A_2}{\sqrt{2\pi\sigma^2}}e^{(E-E_0)^2/2\sigma^2}+\sum_{\pm}\left(\frac{A_1}{\sqrt{2\pi\sigma^2}}e^{(E-E_0\pm\hbar\omega)^2/2\sigma^2}+\frac{A_2}{\sqrt{2\pi\sigma^2}}e^{(E-E_0\pm 2\hbar\omega)^2/2\sigma^2}\right), \quad (1)$$

where A_1 and A_2 represent the first- and second-order sideband intensities, σ the width, and $\hbar\omega$ the peak separation. For low IR intensities, careful comparison of theory and experiment have shown that the sideband height can be modeled by the square of a Bessel function $A_1 = J_1^2(x)$ [16], with the argument given by $x=\sqrt{\frac{16\pi\alpha}{m_e\hbar}\frac{IE_{\mathrm{kin}}}{\omega_{\mathrm{IR}}^4}}$.

For small intensities, A_1 approaches the asymptote $A_1^* = x^2/4$, and becomes linear in the IR laser intensity I:

$$A_1^* \approx \frac{IE_{\mathrm{kin}}}{\omega_{\mathrm{IR}}^4}. \quad (2)$$

Here, E_{kin} represents the kinetic energy of the photoemitted electron, and ω_{IR} the IR photon energy. In this linear regime, A_1 directly provides a suitable observable to follow the electron dynamics. At higher intensities, however, A_1 levels off and shows a sublinear behavior. To obtain a signal linear in I throughout the entire intensity range, we project the sideband heights onto the asymptote by replacing all measured A_1 by the corresponding values A_1^* [17].

The LAPE response function from Eq. (1) can be considered to be independent of the electron kinetic energy. Thus, the photoemission spectrum when both IR and SXR beams are present can be assumed to be a convolution of the SXR-only spectrum with the LAPE response function of Eq. (1). We fit this convolution to the SXR + IR spectrum, allowing the sideband intensities, width, and peak separation to serve as fitting parameters. In Eq. (1), the factor in front of the first Gaussian peak is chosen to normalize the response function to 1. Consequently, the parameters A_1 and A_2 give the fraction of electrons scattered into the first and second sidebands, respectively.

Equation (2) implies that the ratio of the sideband heights of the Pt d band and the Xe $4d$ peaks should be equal to the ratio of their corresponding photoelectron kinetic energies. To verify this experimentally, one can consider the first-order sideband height at the Pt d band ($A_{d\text{-band}}^*$), with a value of 0.26 ± 0.01, for a photoemitted electron kinetic energy of 85.1 eV. For the first-order sidebands surrounding the Xe $4d$ peak (A_{Xe}^*), their height is 0.08 ± 0.01, corresponding to an electron kinetic energy of 24.8 eV. Thus, the sideband height ratio yields 3.43 ± 0.02, while the electron kinetic energy ratio is 3.4. This good agreement of the extracted sideband heights with that predicted by theory, coupled with the excellent agreement of the fit from Eq. (1) and the experimental data over a very broad energy range (blue and red curves of Fig. 2), confirms that LAPE and LAAD processes are responsible for all the large changes in the SXR photoemission spectrum of Xe/Pt in the presence of an intense IR beam.

Figure 3 shows a series of photoelectron spectra at a peak IR laser intensity of 1.3×10^{11} W/cm^2, for relative time delays of -50 to 50 fs between the SXR and IR beams. Negative time delay corresponds to the SXR pump arriving after the IR probe. The IR beam polarization was chosen parallel to the direction of detection in order to maximize the laser-assisted photoemission sidebands. Because of the low intensity of the IR beam used in this experiment, we do not observe above-threshold photoemission effects [18,19] at the kinetic energies of the Xe $4d$ peaks, or space-charge effects [20,21] at the Fermi edge. In Fig. 3, the time evolution of the redistribution of electrons can be observed, both at the Pt d band and in the region of the Xe Auger peaks.

For each time delay, the sideband height at the Pt d band and at the Xe Auger peaks are independently obtained using the same analysis as the one presented in Fig. 2. The results for the projected first-order sideband amplitudes are plotted in Fig. 4. The left and right axes have been scaled with respect to each other in order to match the ratio between the kinetic energies of the Pt d band and the Auger peaks. The time evolution of the sideband height for the Pt d-band electrons ($A_{d\text{-band}}^*$) corresponds to a cross-correlation between the SXR and the IR pulses. A Gaussian fit yields a FWHM value of 36.1 ± 1.5 fs, centered at time zero. Since our IR pulse duration is 35.5 ± 1.2 fs, measured using the frequency resolved optical gat-

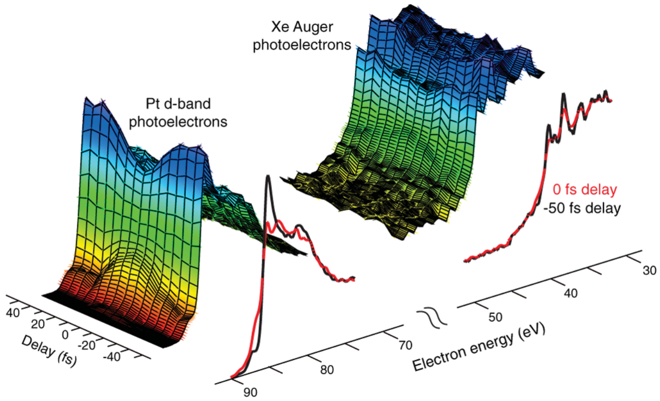

FIG. 3 (color). Photoelectron spectra from Xe/Pt(111) as a function of time delay. Negative time delays denote that the SXR pump pulse arrives after the IR probe pulse. The time evolution of the redistribution of electrons due to the IR dressing at the Pt d band and at the Xe Auger photoelectron peaks can be observed. The spectra shown in the lineouts correspond to the photoelectron spectrum at zero (red) and at -50 (black) fs time delay between the SXR and the IR pulses.

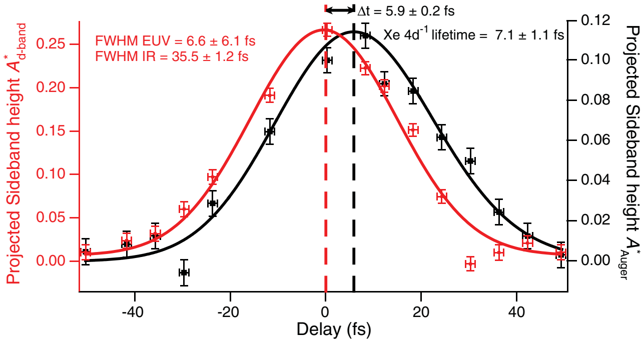

FIG. 4 (color). Sideband height vs time delay for the Pt *d*-band and Xe Auger photoelectrons. The sideband height for the Pt *d* band (red curve) corresponds to a cross correlation between the SXR and the IR pulses. In contrast, the Auger sideband height (black curve) is clearly shifted by 5.9 ± 0.2 fs with respect to time zero, and is also broadened with respect to the Pt *d*-band curve. The shift and broadening are due to the inherent lifetime of the Xe 4*d* core hole. From these curves we extract a Xe 4*d* core-hole lifetime of 7.1 ± 1.1 fs.

ing technique [22], we obtain a SXR pulse duration of 6.6 ± 6.1 fs from the cross-correlation signal.

In contrast to the sideband signal extracted from the Pt *d* band, the sideband signal corresponding to the Xe Auger electrons (A^*_{Auger}) is clearly shifted by ~6 fs with respect to time zero. Moreover, a Gaussian fit yields a broadened FWHM of 40.1 ± 2.1 fs. The observed time shift and broadening are the result of the inherent lifetime of the Xe 4*d* core hole. By fitting the Auger sideband curve with the convolution of a decaying exponential and the direct photoelectron cross correlation obtained from the Pt *d*-band data, we obtain a Xe 4*d* core-hole lifetime of 7.1 ± 1.1 fs. Thus, by comparing laser-assisted photoemission and Auger decay, the characteristic delay of the Auger emission can be precisely measured, making it possible to obtain quite good resolution even using a relatively long 35 fs probe pulse.

As mentioned before, our measured Xe 4*d* core-hole lifetime is consistent with a recent gas-phase energy-domain measurement, that measured a width of 111 ± 3 meV (6.3 ± 0.2 fs) for Xe 4*d* states [23]. The close correspondence between our measurements and previous energy-domain measurements demonstrates that this technique can extract core-hole lifetimes in the time domain, thereby identifying the nature of any spectral broadening in more tightly bound systems, such as chemisorbed systems.

This result also demonstrates the potential of using laser-assisted photoemission from surfaces in the few-optical-cycle regime, where the emission of the electrons occurs over several optical cycles. This few-optical-cycle regime has advantages over the sub-optical-cycle regime [24,25]. This is because in the sub-optical-cycle regime intensities of approximately 2×10^{12} W/cm^2 are required to follow dynamics, which would very likely lead to desorption of the adsorbate from the surface. Here we successfully observe extremely fast dynamics with excellent time resolution and with laser intensity low enough to avoid desorption.

In conclusion, we report the first time-domain measurement of a core-hole lifetime of a complex system—in this case an adsorbate on a substrate. Future experiments can investigate more tightly bonded chemisorbed systems, such as Cs/Pt(111) [26] or CO/Pt(111) [27]. In these systems, the stronger chemical bond (and hence enhanced charge transfer) between substrate and adsorbate is known to influence the linewidth broadening compared with the isolated atom case. As well as uncovering the mechanisms that influence charge transfer at surfaces, these experiments will also provide an exact surface core-hole lifetime as a reference for other charge-transfer techniques such as core-hole clock spectroscopy.

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