

LETTERS

Direct observation of electron dynamics in the attosecond domain

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Dynamical processes are commonly investigated using laser pump-probe experiments, with a pump pulse exciting the system of interest and a second probe pulse tracking its temporal evolution as a function of the delay between the pulses¹⁻⁶. Because the time resolution attainable in such experiments depends on the temporal definition of the laser pulses, pulse compression to 200 attoseconds (1 as = 10⁻¹⁸ s) is a promising recent development. These ultrafast pulses have been fully characterized⁷, and used to directly measure light waves⁸ and electronic relaxation in free atoms⁹⁻¹¹. But attosecond pulses can only be realized in the extreme ultraviolet and X-ray regime; in contrast, the optical laser pulses typically used for experiments on complex systems last several femtoseconds (1 fs = 10⁻¹⁵ s)^{1,5,6}. Here we monitor the dynamics of ultrafast electron transfer—a process important in photo- and electrochemistry and used in solid-state solar cells, molecular electronics and single-electron devices—on attosecond timescales using core-hole spectroscopy. We push the method, which uses the lifetime of a core electron hole as an internal reference clock for following dynamic processes⁹⁻¹⁹, into the attosecond regime by focusing on short-lived holes with initial and final states in the same electronic shell. This allows us to show that electron transfer from an adsorbed sulphur atom to a ruthenium surface proceeds in about 320 as.

When studying electron transfer processes in complex systems, it is of equal importance to address the temporal evolution of the electron wave packet and the question of which atomic centre an electron is localized at before charge transfer to the substrate occurs. This atom specific information cannot be provided in pump-probe experiments in the spectral regime of optical transitions. By adapting an element specific synchrotron based soft X-ray spectroscopy method, namely core-hole clock spectroscopy, we can effectively determine on an attosecond timescale electron transfer dynamics originating from an atomically localized state by making use of extremely fast Coster-Kronig decay processes of core-excited states.

The principle of core-hole clock spectroscopy is to take the core-hole lifetime τ as an internal reference clock for the temporal evolution of a dynamic process under investigation⁹⁻¹⁹. To study charge transfer on the timescale of τ , the dynamics of an electron resonantly excited into an unoccupied state from an atomically localized adsorbate core level (Fig. 1a) is monitored through the autoionization process that accompanies the core-hole decay (Fig. 1b and c). If the initially excited core electron remains in an atomically localized resonance, a linear relation between the energies of the incoming photon and of the outgoing electron in the autoionization is observed (Fig. 1b). This is the so-called Raman autoionization channel at constant binding energy (I). In contrast, if the initial

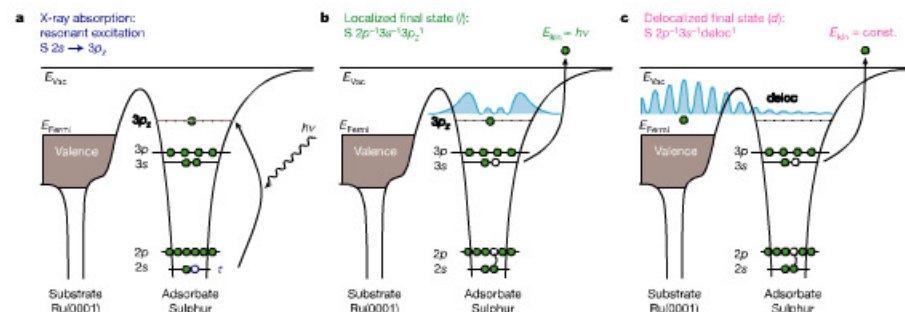


Figure 1 Core-hole clock spectroscopy—schematic overview. **a**, Initially, a core electron is promoted by resonant excitation from the S 2s level into a bound resonance localized at an adsorbed sulphur atom ($S 2s^{-1}3p^1$) on ruthenium ($c(4 \times 2)S/Ru(0001)$) with a core-hole lifetime $\tau = 0.5$ fs. In the autoionization decay processes, Coster-Kronig decay of the S 2s core hole takes place in the presence of this electron, the so-called 'spectator' electron,

leading to two different final states. **b**, Localized final state $S 2p^{-1}3s^{-1}3p^2$: state I . The initially excited electron is still localized at the sulphur atom. **c**, Delocalized final state $S 2p^{-1}3s^{-1}deloc^1$: state d . The initially excited electron has already left the localized resonance. E_{Fermi} , Fermi energy; E_{kin} , kinetic energy.

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excitation involves an electronic state delocalized over many atomic centres (that is, the excited atomic resonance is coupled to a continuum), we obtain independently of the incident photon energy autoionization at constant kinetic electron energy (Fig. 1c). This is the charge transfer channel of autoionization (*d*). Owing to this different dispersive behaviour, the Raman (*l*) and charge transfer (*d*) channels of autoionization can be spectroscopically separated (Fig. 2a), and the ratio of Raman to charge transfer intensity is related to the degree of atomic localization in the excited state on the timescale τ of the core-hole decay. This can be translated into a dynamic picture of an electron residence time, or alternatively as the charge transfer time, τ_{CT} , of electron hopping to the substrate. As spectral intensities are compared, the \sqrt{N} uncertainty (where N is the number of events) allows a statistically significant analysis only as long as the intensities of the spectroscopic channels are less than one order of magnitude apart. Thus a temporal range of charge transfer times between $0.1\tau \leq \tau_{CT} \leq 10\tau$ becomes accessible. The typical core-hole lifetimes of inner shell vacancies lie at oxygen KLL ($\tau = 4$ fs; ref. 20), nitrogen KLL ($\tau = 5$ fs; ref. 20), carbon KLL ($\tau = 6$ fs; ref. 20), and argon $L_{2,3}M_{4,5}M_{4,5}$ ($\tau = 6$ fs; refs 13, 18). We note that the core-hole lifetimes depend only weakly on the chemical environment. In a comparison between atomic and molecular systems, variations of the order of roughly 20% have been observed¹⁹.

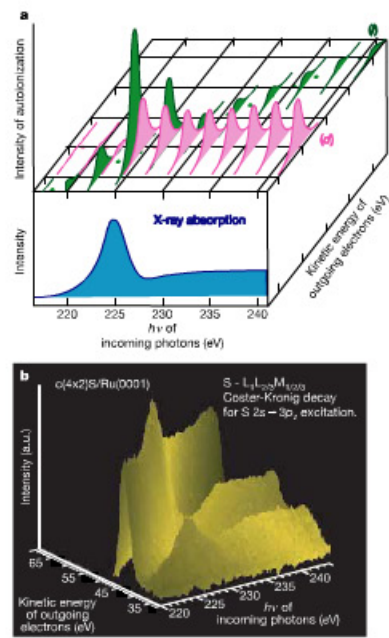


Figure 2 | Core-hole clock spectroscopy—the spectroscopic signatures. **a**, Diagram of the spectroscopic autoionization signatures leading to a localized final state (*l*) with linear dispersion and a delocalized final state (*d*) at constant kinetic energy, and their relation to resonant excitation by X-ray absorption. **b**, Experimental sulphur $L_{1,2,3}M_{4,5}$ Coster-Kronig autoionization spectra of $c(4 \times 2)/S/Ru(0001)$ as a function of incident photon energy.

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To access dynamic processes in the attosecond range reliably, shorter core-hole lifetimes are required. Our approach is to perform attosecond charge transfer core-hole clock spectroscopy in the soft X-ray region by monitoring Coster-Kronig autoionization channels

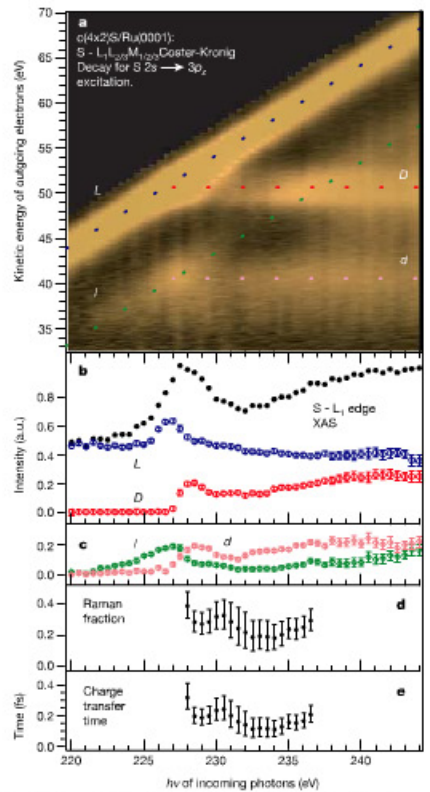


Figure 3 | Quantitative charge transfer analysis of sulphur $L_{1,2,3}M_{4,5}$ Coster-Kronig autoionization spectra of $c(4 \times 2)/S/Ru(0001)$ as a function of photon energy. **a**, Experimental intensities as a function of incoming photon energy and kinetic energy of the outgoing electrons. Lighter colours correspond to higher autoionization intensity. Shown are Raman channels with linear dispersion for localized final states *l* ($2p^{-1}3p^{-1}3p^1$) at 170.7 eV binding energy and *l* ($2p^{-1}3s^{-1}3p^1$) at 181.7 eV binding energy, and charge transfer channels with delocalized final states *D* ($2p^{-1}3p^{-1}deloc^1$) at 50.8 eV kinetic energy and *d* ($2p^{-1}3s^{-1}deloc^1$) at 40.6 eV kinetic energy. **b**, Sum of spectral intensities representing the S- $L_{1,2}$ edge X-ray absorption spectrum. Also shown are separate intensities of the spectral channels (*l*, *D*) from curve fitting with Lorentzians of 3.3 eV FWHM. Error bars show the standard deviation of each fit. **c**, Separate intensities of the spectral channels (*l*, *d*) from curve fitting with Lorentzians of 3.3 eV FWHM. Error bars show the standard deviation of each fit. **d**, Raman fraction $f = l/(l + d)$ as a function of photon energy. Error bars are derived from the standard deviation of the fits (see **c**). **e**, Charge transfer time obtained from the Raman fraction as $\tau_{CT} = \tau f/(1 - f)$ and the S 2s core-hole lifetime $\tau = 0.5$ fs. Error bars are derived from the standard deviation of the fits (see **c**).

