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Attosecond dynamics through a Fano resonance: Monitoring the birth of a photoelectron

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The dynamics of quantum systems are encoded in the amplitude and phase of wave packets. However, the rapidity of electron dynamics on the attosecond scale has precluded the complete characterization of electron wave packets in the time domain. Using spectrally resolved electron interferometry, we were able to measure the amplitude and phase of a photoelectron wave packet created through a Fano autoionizing resonance in helium. In our setup, replicas obtained by two-photon transitions interfere with reference wave packets that are formed through smooth continua, allowing the full temporal reconstruction, purely from experimental data, of the resonant wave packet released in the continuum. In turn, this resolves the buildup of the autoionizing resonance on an attosecond time scale. Our results, in excellent agreement with ab initio time-dependent calculations, raise prospects for detailed investigations of ultrafast photoemission dynamics governed by electron correlation, as well as coherent control over structured electron wave packets.

Tracking electronic dynamics on the attosecond time scale and angstrom length scale is a key to understanding and controlling the quantum mechanical underpinnings of physical and chemical transformations (*1*). One of the most fundamental electronic processes in this context is photoionization, the dynamics of which are fully encoded in the released electron wave packet (EWP) and the final ionic state. The development of broadband coherent sources of attosecond pulses has opened the possibility of investigating these processes with attosecond resolution. On such a short time scale, few techniques (*2*–*5*) are able to provide access to both spectral amplitude and phase. The spectral derivative of the phase, the group delay, is a practical quantity for describing general wave packet properties reflecting the ionization dynamics. Recently, photoemission delays have been measured in a variety of systems: noble gas atoms (*6*–*8*), molecules (*9*), and solids (*10*). In the gas phase, these attosecond delays give insight into the scattering of the electron in the ionic potential; in the solid state, they provide information on the transport dynamics toward the surface. However, the physical relevance of group delays is restricted to fairly unstructured wave packets.

The necessity to go beyond simple delays arises for more complex ionization dynamics when the broadband excitation encompasses continuum structures associated with, for example, autoionizing states, shape resonances, and Cooper minima (*11*–*13*). These structures induce strong spectral variations of the amplitude and phase of the EWP corresponding to different time scales, ranging from the attosecond to the femtosecond domains. In general, the long-term evolution of the EWP amplitude [e.g., the lifetime of Fano autoionizing resonances (*14*)] can be characterized directly in the time domain (*15*), or in the spectral domain with the use of conventional spectroscopic techniques (*16*). However, the EWP phase is required for reconstruction of the full ionization dynamics. In particular, the short-term response associated with broadband excitation remains unexplored (*17*). It is mainly determined by the spectral phase variation over the resonance bandwidth, which has so far not been measured. An additional difficulty is that the characterization techniques often involve strong infrared probe fields that (i) strongly perturb the resonant structures (*18*–*20*) so that the field-free intrinsic dynamics cannot be accessed, and (ii) require elaborate theoretical input for decoding the electron spectrograms (*21*).

Here, we extend attosecond photoionization spectroscopy to the full reconstruction of the time-dependent EWPs produced by coherent broadband excitation through resonant structures. To this end, we have developed a perturbative interferometric scheme enabling the direct measurement of the spectral amplitude and phase of the unperturbed resonant EWP. Interferences between the latter and a reference nonresonant EWP are achieved through two-photon replicas obtained by photoionizing the target with an extreme ultraviolet (XUV) harmonic comb combined with the mid-infrared (MIR) fundamental field. This spectrally resolved technique is easy to implement and offers straightforward access to the EWP characteristics without complex analysis or theoretical input. We apply it to the investigation of the test case of the doubly excited 2s2p autoionizing resonance of helium, for which ab initio time-dependent calculations can be performed (*22*, *23*), thereby providing a benchmark for our experimental study.

Autoionization occurs when a system is excited in structured spectral regions where resonant states are embedded into a continuum. The system can then either directly ionize or transiently remain in the resonant bound state before ionizing. Coupling between the resonant state and continuum states of the same energy through configuration interaction leads to the well-known Fano spectral line shapes (*14*). Of particular interest is the autoionization decay from doubly excited states (*16*) that is a direct consequence of the electron-electron repulsion. Using our spectrally resolved technique, we directly access the complete ionization dynamics (including interferences at birth time) and monitor the resonance buildup on a subfemtosecond time scale—an endeavor of attosecond science (*17*, *24*).

The concept of the method is shown in Fig. 1A. We photoionize helium with a comb of mutually coherent odd harmonics derived from an optical parametric amplifier (OPA) MIR source. The harmonic of order 63 (H_{63}) is driven into the 2s2p resonance, at 60.15 eV from the ground state, by tuning the OPA central wavelength λ_{OPA} to 1295 nm. Because the harmonic width (400 meV) is much larger than the resonance width (Γ = 37 meV), a broad resonant EWP with complex spectral amplitude $A_R(E)$ is produced. Simultaneously, nonresonant EWPs are created by the neighboring harmonics H_{61} and H_{65} in smooth regions of the continuum; each of these can serve as a reference, denoted $A_{NR}(E)$, to probe the resonant EWP.

To induce interference, we use two-photon transitions to create replicas that spectrally overlap with each other. A weak fraction of the fundamental MIR pulse, of angular frequency $\omega_0 = 2\pi c/\lambda_{OPA}$, is superimposed on the harmonic comb with a delay τ. Its intensity (~2×10^{11} W/cm^2) is sufficiently high to induce perturbative two-photon XUV-MIR transitions but is low enough to avoid transitions involving more than one MIR photon [e.g., depletion of the doubly excited state by multiphoton ionization (*15*), or distortion of the resonance line shape (*19*)]. Most important, the MIR spectral width (26 meV) is smaller than both the harmonic and resonance widths, ensuring that each EWP produced in the two-photon process is a faithful, spectrally shifted, replica of the unperturbed EWP produced in

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