Attosecond dynamics of autoionizing states in electronic molecular wave packets

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Abstract: By combining an isolated attosecond pulse and a few-cycle infrared field, we resolve in time the autoionization dynamics of two series of Fano resonances in nitrogen.

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1.   Introduction

Electronic correlation plays a fundamental role in the temporal evolution of multi-electron wave-packets in atoms and molecules [1]. The dynamics of electronic wave-packets can evolve on timescales that can be as fast as few tens of attoseconds. In particular, the autoionization of bound states embedded in the continuum is a fundamental process for the investigation of ultrafast phenomena driven by electronic-correlation. In molecules the observation and manipulation of the electronic motion in real time using field-controlled few-cycle pulses open new perspectives towards the demonstration of chemical reactivity driven by the electronic motion [2].

In this work, we observe the temporal dynamics of a complex multi-electron wave-packet in nitrogen composed by autoionizing states (Fano resonances) and excited states of the neutral molecule. The electronic wave-packet is excited by a broadband(energy range 15-21 eV) isolated attosecond pulse and probed by a synchronized few-cycle carrier-envelope-phase stable infrared (IR) pulse. The extreme ultraviolet (XUV) spectra transmitted through a 3-mm-thick cell filled with nitrogen are acquired as a function of the relative delay between the XUV and the IR pulses.

2.   Experimental results and interpretation

The states populated by the absorption of an XUV photon are identified by their signature in the photo-absorption cross-section, as shown on the right-hand side of Fig. 1a, which reports the cross-section without IR field in the energy range 16.7-18.6 eV. The absorption and (apparent) emission features correspond to the two Hopfield series [3], which have been identified as the two series of Fano resonances $nd\sigma_g$ $^1\Sigma_u^+$ and $nd\pi_g$ $^1\Pi_u$, respectively. These states autoionize to the ground $X^2\Sigma_g^+(I_p = 15.58$ eV$)$ and first excited $A^2\Pi_u(E = 16.94$ eV$)$ ionic states [4–6]. Due to the broadband attosecond pulse, excited states of the neutral molecules below the ionization threshold are populated at the same time (not shown). Figure 1a shows the evolution of the absorption cross section as a function of the relative delay between the XUV and IR pulses. When the IR field arrives after the XUV pulse (t<0), the cross-section is characterized by fast oscillations with a period of $T = 1.3$ fs corresponding to half-optical cycle and by an overall decrease (increase) of the signal for the $nd\sigma_g$ $^1\Sigma_u^+$ ($nd\pi_g$ $^1\Pi_u$) Fano resonances. The signals recover to the original value (t>0) after few-tens of femtoseconds.

The dynamics after the initial excitation is characterized by the quantum beating between the Fano resonances and the wave-packet components below the ionization threshold, and by the autoionization process, leading to the emission of an electron. The interaction with the IR pulse allows one to disentangle and to time-resolve these two mechanisms. After the initial excitation, the action of the IR field modifies the coherent evolution of the superposition of states by modifying the complex amplitudes of the components of the wave-packet on a sub-cycle timescale. Groups of states that present an energy difference of about 3.1 eV (corresponding to two IR photons), can be coupled by a two-IR-photon mechanism leading to oscillations of the absorption cross-section. The process can be regarded as the result of an interference mechanism in the absorption of XUV radiation at a fixed energy between a direct and an indirect path: in the first one, Fano resonances are populated by absorption of a single XUV photon ($\hbar\omega_{XUV}$), while in the latter one Fano resonances are populated by the two-IR photon excitation ($2\hbar\omega_{IR}$) of a bound excited state initially

populated by single XUV photon absorption ($\hbar\omega_{XUV} - 2\hbar\omega_{IR}$). The attosecond pulse duration ensure that the groups of states are populated coherently, i.e. on a sub-IR-cycle timescale. The modulation of the absorption cross-section, therefore, is a direct evidence of the coherent attosecond evolution of the electronic wave-packet. A theoretical model based on the time-dependent perturbation theory was developed in order to simulate all possible transitions between the components of the electronic wave-packet excited by the XUV field and probed by the IR pulse. We will present simulations based on this model, which turn out to be in good agreement with the experimental results.

The autoionization dynamics of the Fano resonances can be probed observing that the interaction with the IR pulse can lead to emission of an electron, if the state has not decayed yet, thus determining a reduction of the effective lifetime and a broadening of the absorption feature [7]. The broadening and the corresponding signal reduction (increase) can be observed in Fig. 1b, for all Fano resonances. The relevant autoionization times can be estimated by fitting the signal integrated around the resonance as a function of the relative delay between the XUV and IR pulses, as shown in Fig. 1b, which reports the signals for the two Fano resonances ($n = 3$) $nd\sigma_g \ ^1\Sigma_u^+$ (black) and $nd\pi_g \ ^1\Pi_u$ (red) at energies E = 17.15 eV and 17.3 eV, respectively. From the exponential fits (dashed lines), autoionization times of $\tau = 20.0$ fs and 27.6 fs can be estimated, respectively.
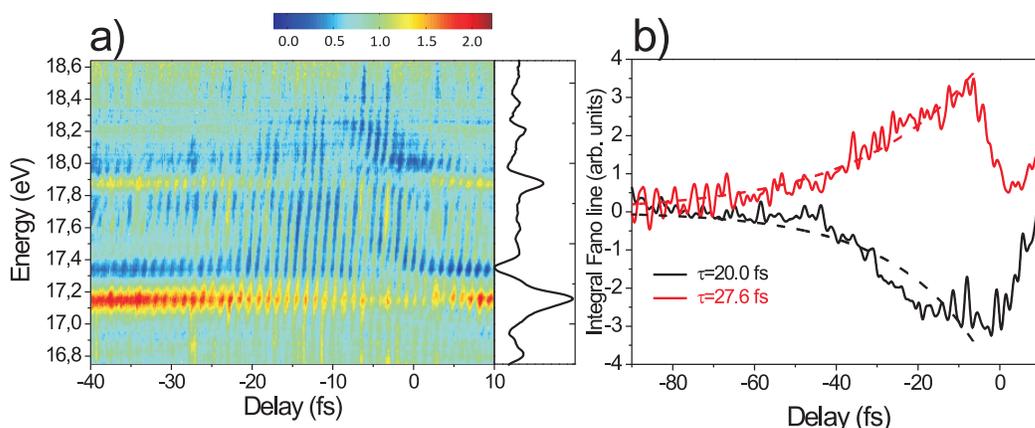

Fig. 1. a) Absorption cross-section as a function of the relative delay between the isolated attosecond pulse and the few-cycle IR field. The nitrogen cross-section without IR field is shown on the right-hand side for reference. b)Delay-dependence of the integrated cross-section signal (solid line) around the Fano resonances n = 3 of the series $nd\sigma_g \ ^1\Sigma_u^+$ (black) and $nd\pi_g \ ^1\Pi_u$ (red). The values indicate the decay constants τ of the two exponential fits (dashed lines).

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