Observing the ultrafast buildup of a Fano resonance in the time domain

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Although the time-dependent buildup of asymmetric Fano line shapes in absorption spectra has been of great theoretical interest in the past decade, experimental verification of the predictions has been elusive. Here, we report the experimental observation of the emergence of a Fano resonance in the prototype system of helium by interrupting the autoionization process of a correlated two-electron excited state with a strong laser field. The tunable temporal gate between excitation and termination of the resonance allows us to follow the formation of a Fano line shape in time. The agreement with ab initio calculations validates our experimental time-gating technique for addressing an even broader range of topics, such as the emergence of electron correlation, the onset of electron-internuclear coupling, and quasi-particle formation.

Fano resonances generally occur in the course of excitation of discrete quantum states embedded in and coupled to a continuum (1, 2). As such, they play a fundamental role in nuclear, atomic, molecular, and condensed-matter physics as well as photonics (3–12). In the prominent example of helium, the discrete doubly excited states are located within different sets of continua, where the prominent 2s2p state is coupled only to the continuum of singly ionized ground-state helium He+ (1s). Coulomb interaction among the two electrons leads to autoionization, thus coupling the discrete state and the 1s continuum and giving rise to the famous asymmetric Fano line profiles. Following the early scientific work on attosecond dynamics in laser-driven field ionization (SFI) by use of an intense near-infrared (NIR) laser pulse. The key idea is that the NIR pulse acts as a temporal gate of the Fano resonance decay. By varying the time delay between the XUV and the NIR pulse with subfemtosecond precision, we tracked the evolution of the Fano line shape in real time (Fig. 1).

Upon excitation, the XUV pulse triggers the formation of the line shape (28), that show that the energy distribution of the electrons ejected within one third of the state lifetime (corresponding to 6 fs in the case of the 2s2p state in helium) after the initial excitation is governed by the frequency range of the excitation pulse. Now, by increasing the time delay τ between excitation and ionization, the doubly excited state has time to decay, and the interference with the direct contributions builds up; the oscillating dipole is granted more and more time to emit the optical response. This gives rise to a narrower


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SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/354/6313/734/suppl/DC1
Supplementary Text
Figs. S1 to S7
Movie S1
References (31–43)

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**Fig. 1.** Time-dependent formation of a Fano profile. The top (spectral domain) and the bottom (time domain) planes schematically show the connection between the measured absorption line shape and the temporal evolution of the dipole response (purple) for five time delays \( \tau_1 \) to \( \tau_5 \). After excitation of the autoionizing state by the XUV pulse (blue), the dipole decays exponentially, until the decay is terminated by autoionization (green). By experimentally controlling the time delay between excitation (start) and autoionization (stop), the buildup of the asymmetric Fano resonance is resolved in time.

**Fig. 2.** Experimental observation of the Fano line formation in doubly excited helium. Transient absorption spectrum in terms of the optical density (OD) of the helium target (vertical axis) as a function of the XUV photon energy \( E \) and time delay \( \tau \geq 0 \) between XUV excitation and subsequent NIR ionization of the 2s2p state. For better readability, the OD values are color-coded. The reference function of the XUV photon energy profile formation of a Fano line is shown in the inset. The transient absorption spectrum in terms of the optical density (OD) of the helium target (vertical axis) as a function of the XUV photon energy \( E \) and time delay \( \tau \geq 0 \) between XUV excitation and subsequent NIR ionization of the 2s2p state. The experimental data were averaged over one optical cycle in order to suppress the fast oscillation of the 2s2p state absorbance due to two-photon coupling to the \( s_{23}^+ \) state (28, 29) and to increase the signal-to-noise ratio.

Near-complete depletion to well below 1% is first reached around \( \tau \approx 5 \) fs, which is in good agreement with the experimental observation. With a fall time (10 to 90% depletion) of \( \approx 4 \) fs, the efficiency of the gate closure by the NIR pulse on time scales short as compared with the lifetime is confirmed. Moreover, as can be expected for a strong-field ionization process, the depletion of the excited state depends exponentially on the applied field strength (Fig. 3, inset).

We next compared both experiment and ab initio calculation to the analytic description of an isolated Fano resonance that is excited and depleted impulsively. The existing analytical predictions describe the photoelectron spectrum in different scenarios: either the time-dependent buildup of the continuum component of the Fano resonance (16, 18, 24), or the final distribution of photoelectrons after a sudden removal of the bound population (20). The four resulting photoelectron spectra are identical in the case of an isolated Fano resonance and an infinitely short gate. In order to be directly comparable with our experiment, we derived (supplementary text) an analytic expression of the transient absorption spectrum based on the description by Chu and Lin (18)

\[
\sigma(\epsilon, \tau) \approx \Re \left\{ 1 + \frac{(q - i\Delta)^2}{1 - i\Delta} \left[ 1 - e^{-\left( \Gamma (1 - \epsilon) \right)^{2}} \right] \right\} \tag{1}
\]

Here, \( q \) and \( \Gamma \) are the Fano \( q \)-parameter and the resonance width, respectively, and \( \epsilon \) is the spectral line, with the details of the autoionization process encoded in it. After approximately one lifetime, at \( \tau \approx 15 \) fs, the Fano spectral signature is already more pronounced and continuously narrows down as the time delay is increased. For time delays substantially longer than the lifetime, the original Fano absorption profile is recovered. At the end of the delay range presented in Fig. 2, the measured line shape already closely resembles the Fano line. However, this comparison is affected by the finite experimental resolution (50 meV FWHM), which has a noticeable effect on the narrow unperturbed line. According to analytic theory (16, 18, 20), it takes roughly 100 fs for the 2s2p Fano line to develop an amplitude of 95%, and 140 fs to develop an amplitude of 99%, regarding the peak amplitude in the limit \( \tau \to \infty \).

Our experiment captures the most substantial changes in the line shape; further extending the time delay is not possible with our current setup.
The stages of the buildup (Fig. 4, darker colors), and peak-to-baseline ratios, especially at later times, are visible in the data. The three theoretical descriptions (analytic, ab initio, and experimental) are compared. The analytic theory shows the expected behavior, while the ab initio calculations capture the details of the transition. The experimental results are consistent with the predictions, confirming the validity of the methods used.

Fig. 4. Comparison between analytic theory, ab initio calculation, and experimental results for the helium 2s2p Fano line formation. (A) Absorption spectra calculated for a series of time delays between XUV and NIR according to the analytic expression of Eq. 1. (B) Numerically simulated absorption spectra for a 7-fs FWHM NIR pulse, with peak intensity of 20 TW/cm². (C) Experimentally recorded spectra. The theoretical spectral amplitudes in (A) and (B) are scaled to match the experimental peak and valley at 32 fs. Because of the finite duration of the NIR pulse in (B) and (C), the effective beginning of the line formation is not at t = 0. Thus, the analytic spectra are shifted by 4.5 fs in time-delay in order to ensure comparability among the three data sets.

REFERENCE AND NOTES
A bioinspired iron catalyst for nitrate and perchlorate reduction

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Nitrate and perchlorate have considerable use in technology, synthetic materials, and agriculture; as a result, they have become pervasive water pollutants. Industrial strategies to chemically reduce these oxyanions often require the use of harsh conditions, but microorganisms can efficiently reduce them enzymatically. We developed an iron catalyst inspired by the active sites of nitrate reductase and (per)chlorate reductase enzymes. The catalyst features a secondary coordination sphere that aids in oxyanion deoxygenation. Upon reduction of the oxyanions, an iron(III)-oxo is formed, which in the presence of protons and electrons regenerates the catalyst and releases water.

The most efficient reduction of nitrogen- and chlorine-containing oxyanions is achieved by the microbial metalloenzymes (per)chlorate reductase and nitrate reductase during anaerobic respiration (1, 2). The active sites of the two metalloenzymes are similar and allow each enzyme to reduce both nitrogen- and chlorine-containing oxyanions (Fig. 1) (1, 2). Both reductases also feature extensive hydrogen-bonding networks, which facilitate the movement of protons and water about the active site and stabilize reactive intermediates (3–5). Disruption of this network in nitrate reductase via mutagenesis results in the complete loss of activity because of the low stability of high-valent Mo=O intermediates (3, 4). Furthermore, positively charged residues near the active site in (per)chlorate reductase aid in the binding of perchlorate to the Mo-center (5). The noncovalent interactions found within the metalloenzymes play an important role in facilitating reactivity (1–5). Incorporating these interactions into transition-metal complexes may aid in oxyanion reactivity because most transition-metal systems are not capable of these reductions (12–17).

The challenge in reducing these oxyanions lies not only in their unfavorable reduction potentials but also in their low binding affinity to transition-metal centers (12). These inorganic oxyanions have long been touted for their weak complexity, poor nucleophilicity, and consequent their kinetic inertness toward oxidation and reduction (12). Therefore, harsh reaction conditions (such as low pH, high temperature, photolysis, and/or long reaction times) are required to facilitate oxyanion reduction in homogenous systems (12–17).

Inspired by the active sites of nitrate and (per)chlorate reductase, we developed a nonheme platform that incorporates the following features:

(i) an earth-abundant redox-active metal center (iron) and (ii) a secondary coordination sphere that facilitates deoxygenation of substrates and high-valent iron-oxo intermediates. Previously, we reported the synthesis and characterization of a family of late, first-row transition-metal complexes [N(afaCy)3MOTf]OTf (M = Mn, Fe, and Co), featuring the dative (azafulvene-amine) coordination mode of the ligand and the presence of the amino-derived secondary coordination sphere (18–22). The ability of the ligand to undergo tautomerization may be a key feature during multi-electron reactions because it can facilitate proton and electron transfer between the substrate and the metal center. Furthermore, the secondary coordination sphere orients substrates binding to the metal center, as demonstrated in our nitrite reduction studies, in which a single hydrogen bond stabilized a key metal-nitrito intermediate (21, 22).

The addition of tetrabutylammonium nitrite ([NBu4][NO2]) to 2 equivalents (eq) of [N(afaCy)3]FeOTf (Fe2O-Tf; OTf, trifluoromethanesulfonate) afforded the iron(III)-oxo complex [N(afaCy)3]FeO2OTf (Fe2O3-O) and NO(g), which was trapped by Fe4-OTf to furnish the iron(II)-nitrosyl species [N(afaCy)3]FeNO2OTf (Fe3+NO (21)). Given the facile one-electron reduction of nitrite by Fe2+OTf, we sought to explore the reduction of...
Editor's Summary

Watching as helium goes topsy-turvy

Theorists have long pondered the underpinnings of the Fano resonance, a spectral feature that resembles adjacent rightside-up and upside-down peaks. An especially well-studied instance of this feature appears in the electronic spectrum of helium as a transient state undergoes delayed ionization. Two studies have now traced the dynamics of this state in real time. Gruson et al. used photoelectron spectroscopy to extract the amplitude and phase of the electron wave packet after inducing its interference with reference wave packets tuned into resonance at variable delays. Kaldun et al. used extreme ultraviolet absorption spectroscopy to probe the transient state while variably forcing ionization with a strong near-infrared field.

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