

CHEMICAL PHYSICS

Probing matter with nonlinear spectroscopy

Ultrafast nonlinear spectroscopy can unravel the dynamics of highly excited electronic states

By **Stephen R. Leone**^{1,2,3} and **Daniel M. Neumark**^{1,2}

In the Bohr model of the atom, the nominal orbiting period for a 1s electron in the hydrogen atom is 150 as (1 as = 10^{-18} s). Attosecond light pulses are thus in principle short enough to follow electron dynamics in real time (1). Moreover, with such pulses, the time-resolved measurements can be extended to subfemtosecond lifetimes, probe electronic and vibrational coherences in atoms and molecules, and by means of attosecond photochemistry, follow the earliest dynamics of photoexcited molecules as they dissociate or isomerize. Attosecond light pulses have recently been incorporated into four-wave mixing (FWM) experiments in gases and solids, by combining one attosecond pulse with two visible optical pulses or multiple attosecond pulses themselves. This now allows more accurate determination of quantum pathways in transient electronic states.

Attosecond pulses generally lie in the extreme ultraviolet (XUV; from 15 to 100 eV) and soft x-ray (SXR; from 100 to 2000 eV) regions of the electromagnetic spectrum. XUV light below 30 eV generally excites valence electrons in atoms and molecules into unoccupied orbitals, whereas higher-energy

photons typically excite core electrons into unoccupied valence orbitals. Because core electrons are localized on specific atoms, the energies of core-to-valence transitions are highly element specific and thus allow monitoring of the evolving electronic environment on specific atoms in photoexcited molecules. As an example, one can use attosecond XUV pulses to monitor core-to-valence transitions around 47 eV on the iodine atom in photoexcited iodomethane (CH_3I). This experiment captures the instant of passage through a conical intersection (CI), a multidimensional crossing between electronic states in a polyatomic molecule in which the outcome of a photodissociation event is determined (2). More generally, CIs mitigate photodamage of molecules and regulate many processes in living systems.

To understand the technical challenges involved in generating attosecond light pulses, it must be understood that light with a wavelength λ represents an electromagnetic field with period λ/c , where c is the speed of light, and that the minimum duration of a light pulse is approximately one optical period. For near-infrared (NIR) light at 800 nm, which is the center wavelength of the titanium-sapphire lasers that are most commonly used in ultrafast applications, the optical period is 2.6 fs. This value represents an approximate

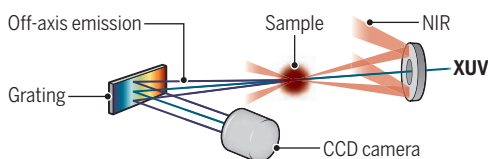
lower bound to the shortest achievable pulse at 800 nm. Therefore, higher photon energies are needed for which the period is correspondingly shorter; for example, at 100 eV (12.5 nm) the optical period is 41 as. Hence, in many of the attosecond experiments performed to date, the attosecond pulses are formed through the process of high harmonic generation (HHG) by using a tabletop laser system; HHG provides a relatively straightforward means of upconverting infrared and visible electromagnetic radiation into XUV and SXR wavelengths.

In HHG (3), an intense femtosecond laser pulse interacts with a nonlinear medium—typically, inert gases at low pressure. The rare gas atoms undergo tunnel or field ionization driven by the oscillating electric field of the laser. As the sign of the oscillating electric field reverses, the electron is driven back toward the ion and recombines, converting the gained kinetic energy into an attosecond burst of XUV or SXR light upon recollision. Methods have been developed that select a single burst from this process, a so-called isolated attosecond pulse. It is now possible to obtain 50 isolated pulses whose photon energies extend well into the SXR region (4). This allows the investigation of core-to-valence transitions in an expanding number of elements because

Nonlinear spectroscopy with extreme-ultraviolet attosecond laser pulses

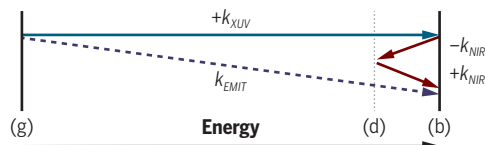
Attosecond four-wave mixing experiment

Extreme ultraviolet (XUV) pulses and two near-infrared (NIR) beams pass through a sample. The off-axis emission is spatially separated from the incident XUV beam and dispersed by a grating onto a charge-coupled device (CCD) camera.



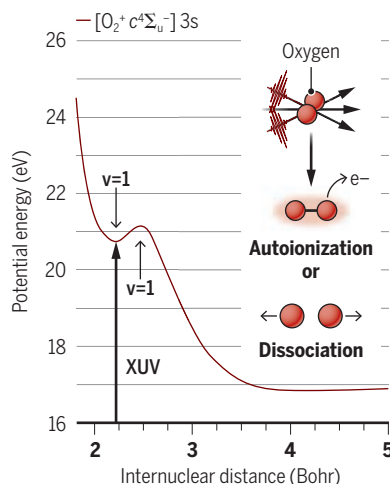
Quantum pathway

This reveals a possible quantum pathway involving one XUV ($+k_{\text{XUV}}$) and two NIR photons ($-k_{\text{NIR}}$ and $+k_{\text{NIR}}$) that leads to off-axis emission (k_{EMIT}).



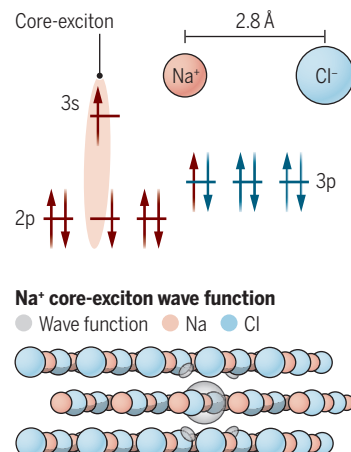
Rydberg series

XUV excitation of the 3s Rydberg state of O_2 at 22 eV decays by autoionization or dissociation.



Core-exciton wave function

XUV excitation of a core-exciton in solid NaCl at 20 to 45 eV excites a 2p core electron on the Na ion to a vacant 3s



the energies of these transitions generally increase with atomic number (5). Isolated attosecond pulses can also be generated with free-electron lasers (FELs) (6). These accelerator-based light sources are much more expensive and complex than tabletop systems, but the reported attosecond pulse intensities and photon energies are considerably higher.

One of the most powerful experimental methods in attosecond science is attosecond transient absorption (ATAS) (7). This approach explores ultrafast dynamics in both gas-phase and solid targets. In its most straightforward implementation, a NIR, visible, or UV pulse photoexcites the sample, and the resulting dynamics are probed with a time-delayed, broadband attosecond pulse that passes through the sample and is then spectrally dispersed by a grating onto an x-ray camera. An appealing feature of this method is that even though the attosecond pulse has a large range of possible energies (10 to 40 eV), the spectral resolution is determined by the grating-camera combination and is typically 0.02 to 0.2 eV.

A distinctive example of ATAS is its application to the electronic nonadiabatic (state-switching) dynamics that occur upon ionization of ethylene (C_2H_4) (8). Gas-phase C_2H_4 is ionized through its interaction with a 10-fs pulse at a wavelength of 1.6 μm . The dynamics of the resulting $C_2H_4^+$ cation are followed by transient absorption of a broadband attosecond pulse spanning 250 to 450 eV (28 to 50 nm). The probe pulse covers the region of carbon core-to-valence transitions around 280 to 290 eV in which a C(1s) electron is excited to an unoccupied valence orbital. The energies of these transitions depend sensitively on the electronic state of the cation. In this work (8), the cation is formed initially in its first excited state (the D_1 state) but then undergoes a nonadiabatic transition to its ground state (the D_0 state) in 6.8 fs. The high time resolution in this experiment thus shows that electronic state switching—of which passage through a CI—occurs almost immediately after photoexcitation.

These experiments can also be carried out in the reverse order, in which the attosecond pulse interacts with the sample first, creating a coherent superposition of highly excited electronic and vibrational states. In this case, transmission of the attosecond pulse is affected by the subsequent NIR pulse, provided that the second pulse arrives before the highly excited states decay (9). In this way, lifetimes can be obtained for the excited

states created by the attosecond pulse with respect to, for example, processes such as autoionization, dissociation, and Auger-Meitner decay (in which one electron fills a vacancy and a different electron is ejected).

However, because multiple quantum pathways contribute to transient absorption in this configuration, the resulting signals can be challenging to interpret. To address this challenge, nonlinear spectroscopic techniques are being developed, one of which is attosecond FWM (see the figure). These experiments are based on ideas developed in infrared and visible FWM experiments, in which a third-order polarization created by three light fields interacting with a sample yields an emission signal at a new angle that is determined by phase matching considerations dictated by momentum conservation of the light field (10).

In tabletop experiments, an attosecond XUV or SXR beam is incident on a target and crossed by two NIR beams at a slight angle. The two NIR pulses can be independently delayed. However, the experiments are often run in either a “bright-state” mode, in which the two NIR pulses are coincident and their time delay relative to the XUV pulse is varied, or a “dark-state” mode, in which the XUV and one NIR pulse are coincident and the delay between those two pulses and the second NIR pulse is varied. In a bright-state scan, the FWM persists only over the lifetime of the bright state, yielding the lifetime of this state. Similarly, a dark-state scan probes states that are accessible only by a two-photon (XUV+NIR) transition. The noncollinear geometry of the beams provides angular phase-matching separation to distinguish the various photon interaction pathways.

Attosecond FWM has been used to probe the decay dynamics of very short-lived electronic states in both gas-phase and solid samples. As an example, attosecond FWM was applied to the 3s Rydberg state of oxygen (O_2) that lies at 21 eV (11). This state is a member of a Rydberg series that converges to the $c^4S^-_u$ state of O_2^+ . It comprises a very shallow well that supports two vibrational levels. These vibrational states can decay through predissociation to form two O atoms, or through autoionization to $O_2^+ + e^-$. Bright-state scans were carried out on the valence ($v = 0$ and $v = 1$ levels supported by the potential energy curve, yielding lifetimes of 5.8 and 4.5 fs, respectively. Analysis of these results shows that autoionization is the dominant decay channel for both vibrational states. Moreover, although the $v = 1$ level predissociates more rapidly than the $v = 0$ level, its autoionization rate is higher too, and both channels need to be accounted for to interpret the results. This

experiment (11) provides an exquisite probe of the competition between these two channels, which is of fundamental interest in understanding the decay dynamics of highly excited molecular electronic states.

Attosecond FWM can also be applied to solid samples, such as the dynamics of core excitons in solid sodium chloride (NaCl) (12). NaCl exhibits strong absorption bands around 33.5 eV that are attributed to excitation of Na(2p) core electrons into localized electronic states of unoccupied Na(3s) orbitals, essentially creating a localized hydrogenic-like Rydberg state within the solid. A combination of bright- and dark-state scans shows evidence for at least five distinct states underlying this absorption band, all of which exhibit decoherence lifetimes of less than 10 fs. These short lifetimes are attributed mainly to electronic effects, including configuration interactions from electron-electron correlation that couple the multiple electronic states that compose the excitonic bands in this energy range.

These attosecond FWM experiments pave the way for more ambitious nonlinear attosecond and x-ray spectroscopy experiments, some of which are already being carried out at FELs (13). Moreover, such experiments provide the foundation for nonlinear spectroscopy experiments with multiple attosecond XUV and/or SXR light pulses (14). Current tabletop laser systems do not provide sufficient flux at high photon energies to conduct such multiple-attosecond-pulse experiments, but it will be possible to perform them at FELs in the future. For example, one proposed experiment that combines x-ray diffraction and stimulated x-ray Raman spectroscopy has the capability to directly probe the changes in electron density associated with passage through a CI (15). ■

REFERENCES AND NOTES

1. M. Drescher *et al.*, *Science* **291**, 1923 (2001).
2. K. F. Chang *et al.*, *J. Chem. Phys.* **154**, 234301 (2021).
3. P. B. Corkum, *Phys. Rev. Lett.* **71**, 1994 (1993).
4. J. Li *et al.*, *Nat. Commun.* **8**, 186 (2017).
5. T. Popmintchev *et al.*, *Science* **336**, 1287 (2012).
6. J. Duris *et al.*, *Nat. Photonics* **14**, 30 (2020).
7. E. Goulielmakis *et al.*, *Nature* **466**, 739 (2010).
8. K. S. Zinchenko *et al.*, *Science* **371**, 489 (2021).
9. H. Wang *et al.*, *Phys. Rev. Lett.* **105**, 143002 (2010).
10. P. Hamm, M. Zanni, *Concepts and Methods of 2D Infrared Spectroscopy* (Cambridge Univ. Press, 2011).
11. Y.-C. Lin *et al.*, *Faraday Discuss.* **228**, 537 (2021).
12. J. D. Gaynor *et al.*, *Phys. Rev. B* **103**, 245140 (2021).
13. F. Bencivenga *et al.*, *Nature* **520**, 205 (2015).
14. M. Kowaleski *et al.*, *Chem. Rev.* **117**, 12165 (2017).
15. Y. Nam *et al.*, *J. Phys. Chem. Lett.* **12**, 12300 (2021).

ACKNOWLEDGMENTS

The authors are primarily supported by the director, Office of Basic Energy Science, Chemical Sciences Division of the US Department of Energy, under contract DE-AC02-05CH11231. Additional support was provided by the Air Force Office of Scientific Research under grant FA9550-20-1-0334 (to S.R.L.).

¹Department of Chemistry, University of California, Berkeley, CA, USA. ²Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA. ³Department of Physics, University of California, Berkeley, CA, USA. Email: dneumark@berkeley.edu; srl@berkeley.edu