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Mass Spectrometers for Residual Gas Analysis

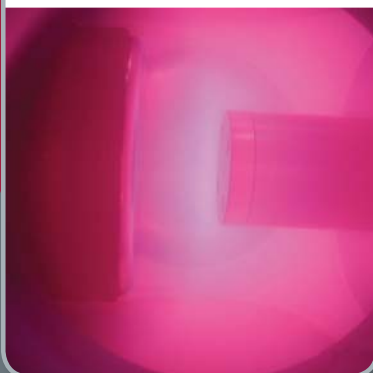
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An attosecond view of electron–nuclear coupling

Even as a hydrogen molecule breaks apart, the dissociating protons hold sway over an escaping electron.

Fundamental to physicists' thinking about molecules is the Born–Oppenheimer approximation: the idea that because electrons and atomic nuclei differ so much in inertia, their dynamics can be mathematically separated. The electrons zip around in a Coulomb potential defined by the nuclear positions alone; the nuclear velocities are assumed to have no effect. It's because of that simplification that we can talk about the rotational, vibrational, and electronic quantum states of a molecule as if they're separate things.

But the approximation doesn't always hold. Sometimes nuclei move too fast for the electrons to readjust. That's especially true in molecules that include hydrogen, the lightest and most easily accelerated nucleus.

Now ETH Zürich's Laura Cattaneo, her adviser Ursula Keller, and their colleagues have gotten the first direct look

at how electronic and nuclear dynamics are entangled in an attosecond experiment.¹ The system under study was the dissociative ionization of molecular hydrogen. Photoexciting H₂ at an energy of 25–40 eV quickly expels an electron and leaves the H₂⁺ ion with enough residual energy to break into H and H⁺ fragments, as shown in figure 1. The Born–Oppenheimer approximation posits that the electron escape and the molecular dissociation happen on completely different time scales, but the researchers found that that's not the case.

Extreme ionization

To get a complete view of the process, the researchers combined two experimental techniques, each of which is challenging in its own right. With cold-target recoil-ion momentum spectroscopy, or COLTRIMS (see PHYSICS TODAY, August 2003, page 19), they measured the mo-

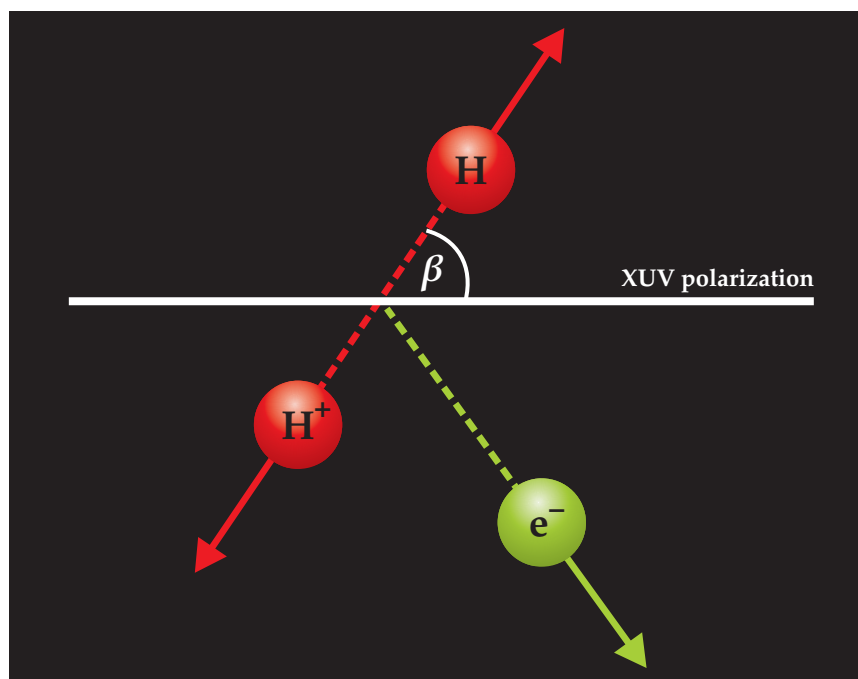
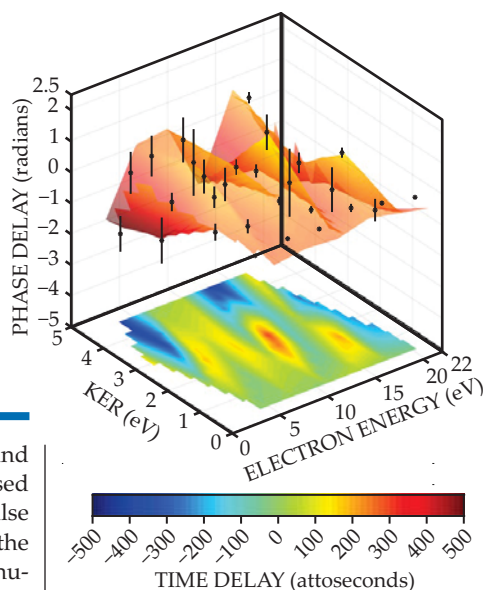


FIGURE 1. DISSOCIATIVE PHOTOIONIZATION of molecular hydrogen. Measurable degrees of freedom include the electron kinetic energy, the kinetic energy released in the H₂⁺ dissociation, the angle β between the H momentum and the ionizing extreme UV (XUV) polarization, and the time delay between XUV absorption and electron emission.

FIGURE 2. PHOTOIONIZATION DELAY

as a function of electron kinetic energy and KER, the kinetic energy released in the H_2 dissociation. The 3D plot shows the measured RABBIT phase, and the 2D projection shows the same information converted into a time in attoseconds. Because there's no way to tell what phase corresponds to an absolute time delay of zero, all measurements are relative to an arbitrary origin. (Adapted from ref. 1.)



menta of the electron and the H^+ ion and calculated the kinetic energy released (KER) in each H_2^+ breakup. To avoid false coincidences—mistakenly matching the electron from one molecule with the nuclei of another—they collected data at a glacial pace, with no more than one molecule ionized per laser shot.

The attosecond temporal precision was provided by RABBIT (reconstruction of attosecond beating by interference of two-photon transitions; see *PHYSICS TODAY*, January 2018, page 18). The technique combines an incident IR wave with a train of subfemtosecond extreme UV (XUV) pulses made up of odd-numbered high harmonics of the IR frequency. Of particular interest are two-photon processes, induced by a combination of one XUV photon and one IR photon, which excite the molecules at the energies of the even-numbered harmonics. Adjusting the relative timing of the XUV and IR waveforms modulates the intensity of the two-photon ionization signal. The phase of the modulation is a measure of how long it takes the ionization to occur.

The XUV pulse train is a superposition of photons of several different energies, and which one of them excites a particular molecule can't be chosen in advance; it must be deduced after the fact by adding up KER, the electron kinetic energy, and the H_2 dissociation energy. Because a large number of events are required before the modulation phase can be seen, it might be tempting to group together ionization events with different KERs, as long as their excitation energies are the same.

But the Zürich researchers didn't do that. Instead, they sorted their detected ionizations by KER, electron kinetic energy, and the angle β between the XUV polarization and the H atom momentum, and they determined the photoionization delay for each group separately. Figure 2 shows their results for β near

90° , expressed as both the RABBIT phase and the relative time delay.

According to the Born–Oppenheimer approximation, the photoionization delay and KER should have nothing to do with each other: The electron should be long gone by the time the H_2^+ ion finally dissociates, so neither should have any effect on the other. Except for a small region where the excitation is resonant with other H_2 states, the two-dimensional plot in figure 2 should be a uniform green. But it's not.

Cattaneo and her colleagues interpret their results to mean that the electron isn't moving so much faster than the nuclei after all: As the electron is making its escape, but before it's fled the Coulomb potential of the H_2^+ ion, the nuclei are already starting to separate. Because the nuclear trajectories depend on KER, so does the net force exerted on the electron. The lingering Coulomb interaction between the ion and the escaping electron changes the electron's velocity enough to alter the measured photoionization delay by hundreds of attoseconds.

Attosecond measurements are meant to capture the motions of electrons alone. But as the Zürich researchers showed, H nuclei, at least, can move around enough on an attosecond time scale to influence the outcome of an experiment. That could prove to be an important caveat as attosecond methods are applied to larger and more complicated molecules. Virtually every organic or biological molecule, after all, contains some hydrogen.

Johanna Miller

Reference

1. L. Cattaneo et al., *Nat. Phys.*, in press, doi:10.1038/s41567-018-0103-2.

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Mass Spectrometers for Surface Analysis

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