Watching electrons in action: Still hard, but getting easier

In the closest thing yet obtained to a movie of a breaking chemical bond, there's a surprise ending.

By Johanna L. Miller

Electrons are the drivers of chemistry. They form the chemical bonds that connect atoms into complex molecules. When they move around, they break bonds, create new bonds, and transform molecules into different ones. When chemists hone their intuition for categorizing and predicting the results of chemical reactions (as described in the 2019 *PT* column "How to succeed in orgo without really trying"), most of what they ask themselves is, Where are the electrons inclined to go?

The chemist's mental picture is merely a heuristic. Experiments have never observed the real-time and real-space flow of electrons during a chemical reaction. But now researchers led by Dao Xiang, of Shanghai Jiao Tong University in China, have taken a step toward filming an electron reaction movie.[1] For their proof-of-principle experiment, they studied the photodissociation of ammonia, illustrated in figure 1: A laser pulse hits an NH_3 molecule and rips off one of its hydrogen atoms. The researchers probe the dissociating molecules with precisely timed blasts of electrons, which scatter off the molecular nuclei and electrons and give information about their whereabouts.

The result is still not a full 3D image of all the moving nuclei and electrons. Rather, as shown in figure 2, it's a measurement of the change in the charge-pair distribution function (CPDF), the electric-charge correlations at a particular distance. The CPDF is sensitive to all 14 particles—4 nuclei and 10 electrons—in the NH_3 molecule, and much of what it measures has nothing to do with electrons. For example, the blue (negative) streak that appears at 1 Å corresponds to the loss of one of the N–H nuclear pairs, which in the starting molecule are that distance apart.

But some of what's seen in the CPDF must be probing electron dynamics. The starting NH_3 molecule is only about 2 Å across, so any negative signals at larger distances than that can't correspond to the loss of nucleus–nucleus or electron–electron pairs. Rather, they must represent the formation of new electron–nucleus charge pairs. The diffuse, transient blue feature between 2 Å and 4 Å, which fades by about 300 fs,

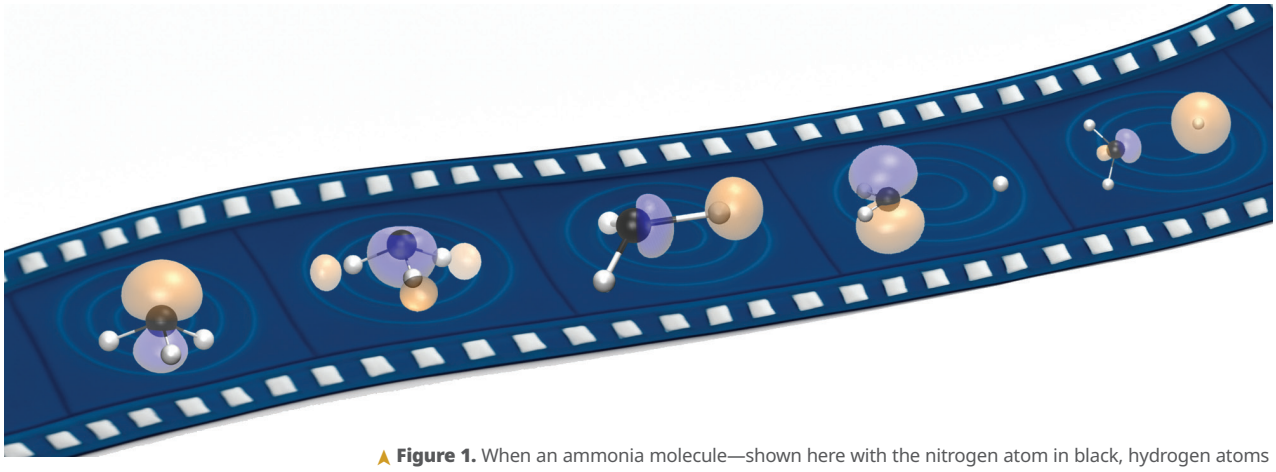

Figure 1. When an ammonia molecule—shown here with the nitrogen atom in black, hydrogen atoms in white, and representative electron orbitals as diffuse clouds—absorbs a UV photon, it loses one of its hydrogen atoms. Or does it? (Illustration courtesy of Hui Jiang/Shanghai Jiao Tong University.)

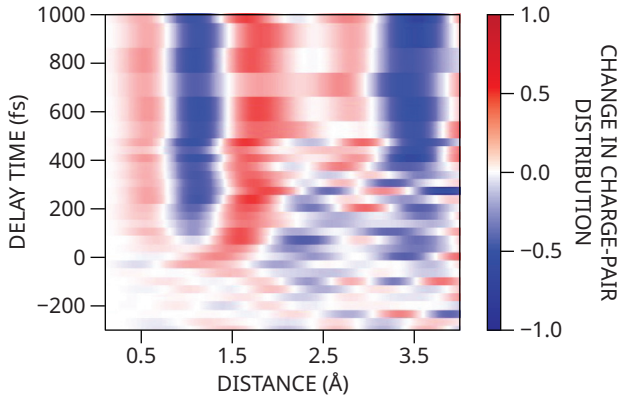

Figure 2. The experimentally obtained charge-pair distribution function shows how charge correlations change in space and time during the ammonia-dissociation reaction. Red (positive) signals can represent either the gain of nucleus–nucleus or electron–electron correlations or the loss of nucleus–electron correlations; blue (negative) signals represent the opposite. (Figure adapted from ref. 1.)

arises from the rearrangement of electrons during the molecular dissociation, and it's roughly in agreement with *ab initio* theory calculations.

The strong, steady blue feature at 3.5 Å—which doesn't appear in the *ab initio* calculations—is another story. It's not the hallmark of a molecule still undergoing a reaction. Rather, it suggests that at least some of the NH_3 molecules are returning to a relatively static structure. The researchers infer from it that many of the molecules use the laser energy not to dissociate but to vibrate: They remain intact, and they stretch their N–H bonds to uncharacteristically long distances. Theory had acknowledged that outcome as a possibility, but only for a much smaller fraction of the molecules. PT

Reference

1. T. Wang et al., "Probing valence electron and hydrogen dynamics using charge-pair imaging with ultrafast electron diffraction," *Phys. Rev. Lett.* **135**, 233002 (2025).

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