

ULTRAFAST SCIENCE

Molecular structure in an instant

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The observation that there is interference between a laser-induced electron wave and a single molecule means that it may be possible to image changes in molecular structure with a sub-femtosecond resolution.

Scientists have long dreamt of being able to instantaneously image molecular structure with a temporal resolution less than a femtosecond (10^{-15} s) — the timescale of fundamental physical and chemical changes. A technique with the potential to do this is reported by Kanai *et al.*¹ on page 470 of this issue. The measurement uses an intense laser field to tear an electron from a molecule (ionization), accelerate it and then drive it back towards the molecule a fraction of an optical cycle later (about 1 femtosecond). The electron recombines with the molecule, giving up the energy it acquired (typically 30–70 eV) as a single, soft X-ray photon in a process known as high-order harmonic generation.

The returning electron can be considered as a superposition of electron waves of different energy and momentum. The de Broglie wavelength of an electron wave is given by $\lambda = h/p$ where h is Planck's constant and p is the momentum of the electron. The intensity of emission at a particular X-ray photon energy is sensitive to the wavelength of the electron wave and the shape of the wavefunction of the electrons in the molecule. It is possible to use this phenomenon to probe structures because the electron wavelength is comparable to the size of the molecular wavefunction.

When the electron wavelength matches the distance between the nuclei of the molecule, the internuclear separation, interference occurs between the emission amplitudes from different parts of the molecule and modulates the total intensity of soft X-ray emission

(Fig. 1). The value of the photon energy at which the modulation is observed indicates the internuclear spacing at that instant. This type of interference in the high-order harmonic process from molecules was first predicted several years ago², but had not yet been seen.

Kanai and co-workers¹ now report that they have observed this phenomenon. Their experiment involved the measurement of high-order harmonic generation from a gas of linear molecules (N_2 , O_2 or CO_2) with their axes aligned in space. An initial, ultrafast laser pulse, which excites a 'rotational wavepacket' (a coherent superposition of states) in the molecules, controls the molecular alignment³. The rotational wavepacket then exhibits strong molecular-axis alignment at regular periods (every 5.4 picoseconds in the case of CO_2). A second, higher-intensity, ultrafast laser pulse (about 2×10^{14} W cm^{-2}) then produces high-harmonic emission from molecules close to the maximum degree of alignment. By precisely varying the delay before the second pulse, the emission intensity for different magnitudes and angles of alignment can be measured.

The set-up and the principle are similar to those employed by Itatani *et al.*⁴, who used a tomographic retrieval technique to image the electronic states of a nitrogen molecule. The advance of Kanai *et al.* is the simultaneous observation of the ionization and the intensity of the soft X-ray emission, allowing the efficiency of the first, ionization step of the process to be separated from the efficiency of

the final step when the electron wave recombines with the molecular electronic state.

The authors found a minimum in the harmonic emission from CO_2 at maximum ionization. In contrast, O_2 and N_2 had maximum harmonic emission at maximum ionization. For CO_2 , the greatly reduced efficiency of the recombination step results from destructive interference. The parts of the molecular electronic state of CO_2 located near the two oxygen atoms make equal but opposite contributions to the X-ray emission, as Kanai *et al.* explain. The suppression of the harmonic emission occurred when the two oxygen atoms in the molecule are separated by exactly one complete wavelength of the electron wave. The soft X-ray emission amplitude from each of the two oxygen atoms is then exactly out of phase, leading to destructive interference in the total emission.

In principle, laser-driven electron-wave interference provides a powerful tool for measuring the distances between atoms in molecules with a resolution of a fraction of a nanometre. The technique directly pinpoints the position of the atomic nuclei and complements tomographic reconstruction⁴, which can retrieve the full electronic wavefunction. The information retrieved through tomographic imaging is more complete. But Kanai and co-workers' technique is much easier to implement as it requires only the measurement of the angular dependence of ion and harmonic signals, and requires no sophisticated processing of the data. By observing the emitted soft X-ray spectrum over a range of photon energies, it is possible to see the interference arising from different bond lengths.

This proof-of-principle experiment has only looked at a very simple, linear triatomic molecule, and it will have to be tested with complex molecules. Nevertheless, it may be possible to use this method to carry out pump-probe studies that follow the internuclear separation as it changes on a timescale of a few femtoseconds.

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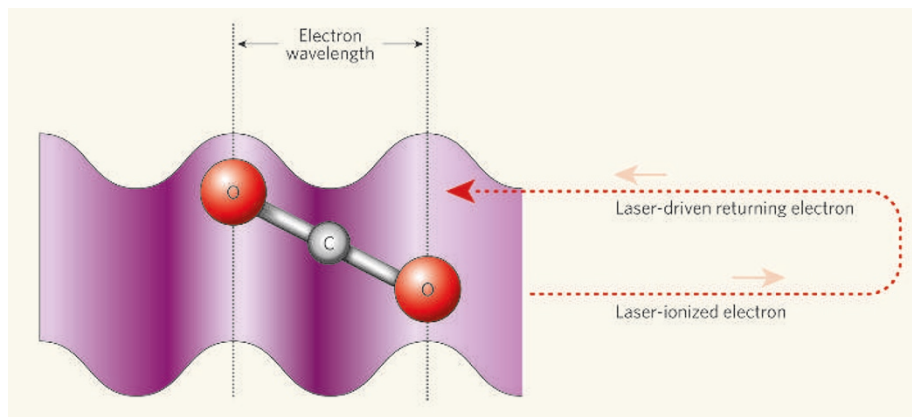


Figure 1 | The electron-wave interference technique. An electron escapes from a CO_2 molecule upon ionization by an intense near-infrared laser field. The laser field then accelerates and returns the emitted electron, producing soft X-ray radiation (not shown) when the electron recombines with the molecule — all within the same optical cycle. The returning electron has a wavelength given by $\lambda = h/p$ (where h is Planck's constant and p is the momentum of the electron). A strong interference modulation of the soft X-ray intensity is observed if λ matches the spacing between the two oxygen atoms (red) in the molecule.

1. Kanai, T., Minemoto, S. & Sakai, H. *Nature* **435**, 470–474 (2005).
2. Lein, M., Hay, N., Velotta, R., Marangos, J. P. & Knight, P. L. *Phys. Rev. A* **66**, 023805 (2002).
3. Rosca-Pruna, F. & Vrakking, M. J. J. *Phys. Rev. Lett.* **87**, 153902 (2001).
4. Itatani, J. *et al.* *Nature* **432**, 867–871 (2004).