## LETTERS

## Following a chemical reaction using high-harmonic interferometry

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The study of chemical reactions on the molecular (femtosecond) timescale typically uses pump laser pulses to excite molecules and subsequent probe pulses to interrogate them. The ultrashort pump pulse can excite only a small fraction of molecules, and the probe wavelength must be carefully chosen to discriminate between excited and unexcited molecules. The past decade has seen the emergence of new methods that are also aimed at imaging chemical reactions as they occur, based on X-ray diffraction<sup>1</sup>, electron diffraction<sup>2</sup> or laser-induced recollision<sup>3,4</sup>—with spectral selection not available for any of these new methods. Here we show that in the case of high-harmonic spectroscopy based on recollision, this apparent limitation becomes a major advantage owing to the coherent nature of the attosecond high-harmonic pulse generation. The coherence allows the unexcited molecules to act as local oscillators against which the dynamics are observed, so a transient grating technique<sup>5,6</sup> can be used to reconstruct the amplitude and phase of emission from the excited molecules. We then extract structural information from the amplitude, which encodes the internuclear separation, by quantum interference at short times and by scattering of the recollision electron at longer times. The phase records the attosecond dynamics of the electrons, giving access to the evolving ionization potentials and the electronic structure of the transient molecule. In our experiment, we are able to document a temporal shift of the high-harmonic field of less than an attosecond  $(1 \text{ as} = 10^{-18} \text{ s})$  between the stretched and compressed geometry of weakly vibrationally excited Br<sub>2</sub> in the electronic ground state. The ability to probe structural and electronic features, combined with high time resolution, make high-harmonic spectroscopy ideally suited to measuring coupled electronic and nuclear dynamics occurring in photochemical reactions and to characterizing the electronic structure of transition states.

To image a molecule with an intense femtosecond laser field  $(\sim 10^{14} \text{ W cm}^{-2})$ , we extract an electron wave packet from one of the valence orbitals and drive it back to interfere with the remaining bound electronic state. If the electron recombines, it emits extremeultraviolet (XUV) radiation in a train of attosecond pulses, a process known as high-harmonic generation (HHG). All molecules in the sample radiate coherently in a phase-matched process. HHG can image a molecular orbital<sup>3</sup> and probe rotational<sup>7,8</sup> and vibrational dynamics<sup>9,10</sup> in the electronic ground state. We demonstrate how HHG can also be applied to observe a chemical reaction in real time<sup>11</sup>.

Molecular bromine (Br<sub>2</sub>) serves as our exemplary molecule. Excitation at 400 nm transfers population from the X  ${}^{1}\Sigma_{g}{}^{+}$  ground state to the repulsive C  ${}^{1}\Pi_{1u}$  state in which it dissociates (Fig. 1a). Dissociation is essentially adiabatic, resulting in two bromine atoms in the  ${}^{2}P_{3/2}$ ,  $|m_{J}| = 1/2$  state<sup>12</sup>. High-harmonic generation from a coherent superposition of two electronic states can proceed by ionizing from and recombining to the same or the other electronic state

(Supplementary Information section 1). All emitted fields are phaselocked to the generating field and interfere with each other, as illustrated in Fig. 1b. Once the overlap of the excited and ground-state



Figure 1 | High-harmonic interferometry of dissociating Br<sub>2</sub>. a, Potential energy curves of the ground and excited (C  ${}^{1}\Pi_{1u}$ ) state of Br<sub>2</sub> (black and blue lines, respectively) and the lowest electronic states of Br<sub>2</sub><sup>+</sup> (red lines) as a function of the internuclear separation, *R*. Also shown (thicker lines) are the ground-state nuclear wavefunction (black) and the calculated excited-state wave packet (blue) at selected delays  $\Delta t$  following a 40-fs excitation pulse centred at 400 nm. **b**, Starting from the electronic ground state of Br<sub>2</sub>, a small fraction of the sample is excited and undergoes dissociation. An intense 30-fs 800-nm pulse (red) probes the dissociation dynamics at variable delays after excitation. The two electronic states, represented by their most weakly bound orbital, emit high harmonics (turquoise) that differ in amplitude and in phase ( $\Delta \phi$ ).

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vibrational wave packets is lost, however, the coherent superposition can no longer be distinguished from a mixed sample of distinct ground-state and excited-state molecules. Only harmonics created by ionizing and recombining to the same state are possible.

We form a sinusoidal grating of excited molecules using two pump beams that cross in the medium, as shown in Fig. 2a. Horizontal planes of excited molecules alternate with planes of unexcited molecules. We generate high harmonics from this grating with a delayed 800-nm laser pulse (probe). The experiment is described in Methods. Figure 2b and c shows the yields of harmonics 13 to 21 in both the zero-order (Fig. 2b) and the first-order diffraction (Fig. 2c). The intensity of the zero-order diffraction decreases in all harmonic orders following excitation and subsequently increases to a level that depends on the harmonic order. By contrast, the first-order diffraction signal (not present at negative times) increases, reaching its asymptotic value about 300 fs after the excitation pulse. The zero time-delay and a cross-correlation time of 50 fs is monitored through the appearance of even-order harmonics (Supplementary Information section 6).

From zero- and first-order diffraction, we uniquely extract the harmonic amplitude  $d_e/d_g$  and phase  $|\varphi_e - \varphi_g|$  of the excited state

relative to the ground state. (Here  $d_{e,g}$  and  $\varphi_{e,g}$  are respectively the harmonic amplitudes and phases of the ground (g) and excited (e) states, see Supplementary Information section 2). We show the experimentally determined values in Fig. 3, for pump and probe polarizations parallel (Fig. 3a) or perpendicular (Fig. 3b).

The different time evolution of the amplitude and the phase is striking. Whereas the phase reaches its asymptotic value after  $\sim$ 150 fs, the amplitude takes more than 300 fs. It is also notable that the temporal variation of the amplitude changes with the relative polarization of the excitation and harmonic generation pulses (Fig. 3a and b). In contrast, although the time-dependent phase is different for the different polarizations, it reaches the same asymptotic value at the same time delay. We will first concentrate on the phase, then discuss the amplitude.

There are two main contributions to the phase of high-harmonic radiation (Supplementary Information, section 3). First, the electron and the ion accumulate a relative phase between the time of ionization and the time of recombination. The phase shift between the same harmonic order q being emitted by two electronic states differing in ionization potential by  $\Delta I_p$  can be expressed as  $\Delta \varphi_q \approx \Delta I_p \bar{\tau}_q$  (ref 13), where  $\bar{\tau}_q$  is the average transit time of the electron in the continuum.



**Figure 2** | **High-harmonic transient grating spectroscopy. a**, Two synchronized excitation pulses (400 nm) set up a transient grating of excitation in the molecular beam. A delayed 800-nm pulse generates high harmonics from the excited sample. The periodic modulation of the high-harmonic amplitude and phase in the near field (in the laser focus) results, in the far field (at the detector), in additional first-order diffraction (m = 1) signal. **b**, **c**, Evolution of the normalized intensities of harmonis 13 to 21 for parallel pump and probe polarizations in the zeroth order (**b**) and the first-order diffraction side band (**c**) with pump–probe delay. All signals have been normalized to the signal in the zeroth order at negative time delays, corresponding to molecules in the ground electronic state only.



**Figure 3** | **Reconstruction of high-harmonic phases and amplitudes. a**, **b**, Reconstructed amplitudes (middle) and phases (right) of the excited state relative to the ground state for parallel (**a**) and perpendicular (**b**) polarizations of the 400-nm excitation pulse relative to the 800-nm generating pulse. As the C  $\leftarrow$  X transition in Br<sub>2</sub> is perpendicular, the tunnelionized electron wave packet will follow a recolliding trajectory mostly perpendicular to the disk of excited molecules in **a** and parallel to it in **b**, as shown in the left column. In the insets of **a** and **b** (middle), the curves have been shifted vertically to show that the minimum occurs at different delays for different harmonic orders. **c**, Measured internuclear separation (*R*) as determined by the two-centre interference condition (illustrated on the left) of the dissociating molecule for each harmonic order *q* (error bars, s.d.).  $\lambda_q$  represents the de Broglie wavelength of the electron.

Second, when the electron recombines, the dipolar transition matrix element imposes an amplitude and a phase on the radiation<sup>14,15</sup>. The first contribution depends on the electron trajectory (determined by the laser parameters) and the ionization potential. The second contribution characterizes the electronic structure of the molecule. It depends on the emitted photon energy and the angle of recombination in the molecular frame<sup>3</sup>.

The time evolution of the reconstructed phase in Fig. 3 can be split into two regions: the first 150 fs, where the phase varies rapidly, and the subsequent flat region where the phase is independent of the relative polarizations. The rapidly varying phase reflects the fast variation of the ionization potentials with delay. The strong dependence of the phase on the relative polarizations (Fig. 3a versus Fig. 3b) shows that the phase also traces the evolution of the electronic structure of the molecule as it dissociates. This variation occurs because the electronic structure of the bound state to which the electron recombines changes significantly. At asymptotic delays we measure Br atoms relative to ground state molecules. The phase shift is independent of the direction of recombination, because Br<sub>2</sub> dissociates into atoms in the  $|m_I| = 1/2$  magnetic sub-level<sup>12</sup>. The phase shift is 1.8 rad for the thirteenth harmonic (H13). Using the relation  $\Delta \varphi_{\rm q} \approx \Delta I_{\rm p} \bar{\tau}_q$ , with  $\bar{\tau}_q$  from a classical trajectory calculation<sup>16</sup>, we obtain  $\Delta I_{\rm p} = 1.3 \,\mathrm{eV}$ , in good agreement with the known ionization potentials of Br<sub>2</sub> and Br.

We now turn to the temporal evolution of the amplitudes. All harmonics go through a deep minimum at an early time (Fig. 3a and b, insets). The minimum, occurring between  $51 \pm 5$  fs (H21) and  $78 \pm 5$  fs (H13), measures the stretching of the orbital as the molecule dissociates. We obtain almost identical results in both polarizations because at early delays the ionization step selects molecules lying parallel to the laser field. When the electron recombines to the initial state, its de Broglie wavelength  $\lambda_q$  can destructively interfere with the initial state wavefunction (Fig. 3c). When the molecular orbital is an in-phase combination of two atomic orbitals, destructive interference occurs for internuclear separations  $R = [(2n+1)/2]\lambda_q$ (where *n* is an integer; ref. 17). Using n = 1 and the relation  $\Omega = k^2/2$ between the photon energy  $\Omega$  and the electron momentum k, we translate the minimum of H21 to a bond length of 3.3 Å and that in H13 to 3.9 Å (Fig. 3c)-in good agreement with wave-packet calculations (Supplementary Information section 4). Thus, we trace the bond length as a function of time using quantum interference.

As the molecule dissociates, one might expect additional minima corresponding to destructive interference with n > 1. Instead, we observe a slow rise of the amplitudes. At delays larger than 150 fs, the four valence molecular orbitals of Br<sub>2</sub> formed from the 4p atomic orbitals of Br become nearly degenerate, masking quantum interference in ionization or recombination. Consequently, it is only the propagation of the electron in the laser field that is affected by the second atom. For perpendicularly polarized pump and probe beams, the interaction of the ionized electron with the neighbouring atom is maximized, because the electron trajectory between tunnelling and recollision lies in the plane of the disk of dissociating atoms. As we show in Supplementary Fig. 5, the slower recovery of the amplitude in Fig. 3b reflects this fact. This property of high-harmonic spectroscopy is analogous to XAFS (extended X-ray absorption fine structure), and may be useful to probe the chemical environment of a low-I<sub>p</sub> species (for example, a molecule in a helium droplet).

Time-resolved photoelectron measurements of the dissociation of  $Br_2$  have demonstrated how the binding energies shift as the atoms move apart. In refs 18, 19 and 20, the time delay for the appearance of an atomic-like photoelectron spectrum is in the range 40–85 fs. In high-harmonic spectroscopy, recollision is sensitive to the electronic structure of the molecule rather than to the binding energy of individual orbitals. The minima between 50 and 80 fs show that the electron recombines with a two-centre molecular wavefunction. The absence of such minima between 100 and 150 fs suggests that at longer delays the recombination occurs to a single centre. An

analogous transition between two- and one-centre signatures has recently been observed in core-shell photoionization of a static molecule<sup>21</sup>. However, the recovery of the amplitudes in Fig. 3a shows that the atomic character of the electronic wavefunction is only fully established after 300 fs, significantly later than the photoelectron measurements suggest.

Before concluding, we show that spectral interferometry with high harmonics is a general technique. In every photochemistry experiment creating atomic fragments, there is a second static reference naturally present at long time delays. In our case, for time delays greater than  $\sim$ 300 fs, the medium consists of alternating planes of ground-state molecules and atomic fragments. Increasing the pump intensity to the level where the ground state depletion becomes significant, a vibrational wave-packet motion is clearly seen in the phase (Fig. 4)—but not in the amplitude (not shown)—of the highest harmonics (H19 and H21). The minimal observed modulation depth of the relative phase amounts to 0.02 rad for H19. Using the equation  $\Delta \varphi_q \approx \Delta I_p \bar{\tau}_q$ , we measure  $\Delta I_p$  as varying by 0.01 eV between the inner and outer turning points of the vibrational motion. We note that the measured phase shift corresponds to a temporal shift of the harmonic field of 450 zeptoseconds  $(1 \text{ zs}=10^{-21} \text{ s})$ . The sinusoidal variation of the phase with time indicates an essentially linear variation of  $\Delta I_{\rm p}$ with R, which shows that the potential curves of the neutral and the ion are shifted with respect to each other<sup>22</sup>.

Clearly, there is a close connection between high-harmonic and photoelectron spectroscopy. Photoelectron spectroscopy identifies excited-state dynamics by changes in the photoelectron energy<sup>18,20</sup> or angular distribution<sup>23,24</sup>, whereas high-harmonic spectroscopy makes the identification through the interference of the emitted radiation. This interference gives high-harmonic spectroscopy access to both the amplitude and the phase of the recombination dipole. The phase of an outgoing photoelectron wave packet, in contrast, is very difficult to measure<sup>25,26</sup>. Measuring high-harmonic phase will allow us to investigate attosecond dynamics induced by the laser field, electronic wave packets launched through ionization<sup>15</sup>, and non-adiabatic electronic dynamics<sup>27,28</sup>.

Looking forward, measuring the amplitude and phase of the transition moment relative to a fully characterized ground-state reference<sup>3</sup> will allow dynamic imaging of orbitals in a chemical reaction. Other applications in femtochemistry are possible, ranging from simple dissociation dynamics, to proton transfer, to non-adiabatic reaction



**Figure 4** | **Vibration-induced modulation of the high-harmonic phase.** Reconstructed relative phases of harmonics 13 to 21 in an experiment similar to that shown in Fig. 3a but at higher intensity of the 400-nm excitation pulses. The fast transient in the first 200 fs measures the dissociation of the excited state. The subsequent modulation with a period of 100 fs measures the variation of the phase of the vibrating ground-state molecules relative to that of the atoms generated in the photo-dissociation process.

## **METHODS SUMMARY**

The experiment uses a chirped-pulse amplified titanium-sapphire femtosecond laser, a high-harmonic source chamber equipped with a pulsed valve and a XUV spectrometer. The laser beam, comprising 8-mJ pulses of 32-fs duration (fullwidth at half-maximum, FWHM) at 800 nm, is split into two parts of variable intensities using a half-wave plate and a polarizer. The major part is sent through a computer-controlled delay stage towards the high-harmonic chamber, while the minor part is sent through a type I BBO crystal of 100-µm thickness to generate 400-nm pulses. A 50:50 beamsplitter generates two equally intense 400-nm beams that are recombined on a dichroic mirror with the 800-nm beam. The two 400-nm beams and the 800-nm beam are all parallel to each other with a vertical offset of  $\pm 0.75$  cm, and focused into the chamber using an f = 50 cm spherical mirror. The focus of the 800-nm beam is placed 1 mm before the molecular jet to favour the short trajectories. Typical pulse energies amount to 1 mJ (800 nm) and  $3 \mu J$  (400 nm), resulting in respective intensities of  $10^{14}$  W cm<sup>-2</sup> (800 nm) and  $10^{12}$  W cm<sup>-2</sup> in the bright zones of the grating. High-order harmonics are generated in a supersonic expansion of Br<sub>2</sub> seeded in 2 bar of helium. The high harmonics generated by the 800-nm field are spectrally resolved using an aberration-corrected XUV grating and imaged by a micro-channel plate detector backed with a phosphorescent screen using a charge-coupled device camera. The images are transferred to a computer for analysis. The harmonic intensities are extracted by integrating the images spatially and spectrally. We have verified that the reconstructed phases and amplitudes shown in Fig. 3a and b are insensitive to the chirp of the 800-nm laser pulse.

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 $\label{eq:supplementary Information} \ensuremath{\text{Supplementary Information}} \ensuremath{\text{ is linked to the online version of the paper at www.nature.com/nature.}}$ 

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