Linked attosecond phase interferometry for molecular frame measurements

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High-harmonic spectroscopy uses attosecond techniques to measure single-atom or molecule photorecombination cross-sections. Whereas the amplitude of the extreme-ultraviolet light is easily measurable, the phase is more challenging to access. However, the phase contains information necessary for tomographic imaging of the molecular orbital wavefunction with attosecond-ångström resolution. Present techniques cannot simultaneously measure the phase as a function of molecular angle and photon frequency, which is necessary for a full reconstruction of the wavefunction. We overcome this limitation with an all-optical method that does not require any *ad hoc* assumptions about the phase. We apply it to record the full phase map of aligned bromine molecules relative to reference xenon atoms. It allows us to resolve, both spectrally and angularly, the participation of multiple molecular orbitals, and infer a phase of ionization. This method opens a path to time-resolved molecular orbital tomography.

The high-harmonic generation (HHG) process is composed of three steps: ionization, propagation and photorecombination¹. Each step contributes an amplitude and a phase to the emitted field $E_{\text{Mol}}(q, \theta) = |D_{\text{Mol}}(q, \theta)|e^{i\Phi_{\text{Mol}}(q, \theta)}$. Here, q is the harmonic order of the emission, and θ is the molecular alignment angle. HHG forms the basis for high-harmonic spectroscopy^{2–5}. The phase of the HHG emission contains information about the attosecond synchronization of electron recollision dynamics⁶, the instantaneous ionization potential⁷, the photorecombination dipole moment⁸ and the role of a possible ionization phase^{9,10}. Combined with the recently developed coherent detection of chemical reactions¹¹, knowledge of both amplitude and phase in the molecular frame gives access to the attosecond emission from molecules undergoing chemical dynamics. In particular, knowledge of the recombination phase is necessary for tomographic imaging of the molecular orbital wavefunction^{12–15}.

As illustrated in Fig. 1, in molecules, the phase $\Phi_{\text{Mol}}(q, \theta)$ is a function of harmonic order q and molecular alignment angle θ . The phase is measured at present by methods developed in attosecond physics—RABBIT (reconstruction of attosecond beating by interference of two-photon transitions¹⁶) and FROG-CRAB (frequency-resolved optical gating for complete reconstruction of attosecond bursts¹⁷)—by using a synchronized infrared laser field to couple adjacent harmonics in the photoelectron spectrum. These techniques measure the derivative of the spectral phase, and cannot compare the phase between different targets or as a function of molecular angle. A self-referencing spectral interferometry approach¹⁴, where the HHG signal from an imperfectly aligned ensemble of molecules is exploited, determines the angular variation of the phase but leaves the harmonic-order dependence undetermined.

In keeping with the traditions in the field of optical measurement, we call our method by an acronym that is also the name of a small animal. LAPIN (French for rabbit; linked attosecond phase interferometry) is a two-step procedure. A two-source interferometer measures the phase versus molecular angle, $\Phi_{\text{Mol}}(\theta; q)$, and the HHG spectrum of the aligned target molecule mixed

Figure 1 | In aligned molecules, the high-harmonic spectral phase $\Phi_{\text{Mol}}(q, \theta)$ is a function of both harmonic order q and molecular alignment angle θ with respect to the driving laser field polarization axis (linear). Existing techniques can only measure one-dimensional cuts, either the harmonic phase $\Phi_{\text{Mol}}(q; \theta)$ (black line), or the angular phase $\Phi_{\text{Mol}}(\theta; q)$ (white dashed line). Here, we measure the two-dimensional phase $\Phi_{\text{Mol}}(q, \theta)$ relative to that of a reference atom $\Phi_{\text{Ref}}(q)$.

with a reference atom is recorded. Each of these steps has been previously demonstrated^{9,18–20}. The difficulty until now was the lack of coupling between the two coordinates q and θ of the two-dimensional phase $\Phi_{\text{Mol}}(q, \theta)$. We show that by combining

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Figure 2 | Spectral harmonic phase interferometry of aligned Br₂ molecules. **a**, Two XUV sources created in a supersonic gas jet interfere in the far field (XUV detector). We laser-align the molecules in the top source and observe the movement of the interference fringes as a function of alignment angle θ , providing a measurement of the high-harmonic spectral phase $\Phi_{\text{HPI}}(\theta; q)$. **b**, $\Phi_{\text{HPI}}(\theta; q)$ for harmonic orders $q = 13$ – 23 (cutoff). **c**, The measured vertical motion of fringes for $q = 17$ as the molecule is rotated from -100° to 100° . The distance between two bright fringes (dark red) corresponds to 2π in phase (see Supplementary Section SI.B for details).

these two measurements, we can unequivocally determine the two-dimensional molecular phase $\Phi_{\text{Mol}}(q, \theta)$ relative to that of a reference atom $\Phi_{\text{Ref}}(q)$. By making the phase measurement relative to a reference atom, we remove the strong atto-chirp⁶ that is measured by RABBIT (ref. 16), giving a more accurate measure of the molecular phase. On the other hand, the loss of the atto-chirp information means that the attosecond pulse shape cannot be reconstructed. We apply LAPIN to aligned Br₂ molecules and use xenon as reference atoms.

In the first step, we perform two-source harmonic phase interferometry⁹ (HPI). As illustrated in Fig. 2a, we obtain two identical extreme-ultraviolet (XUV) sources by spatially splitting the incoming laser beam using refractive elements placed between the focusing mirror and the gas jet¹⁸ (see Supplementary Section SI for experimental details). Using a thin gas jet allows us to minimize propagation effects and, therefore, to measure the single-molecule response at the XUV detector⁵. The peak intensity of the fundamental pulse in each source is estimated to be $1.5 \times 10^{14} \text{ W cm}^{-2}$, and the two sources are separated vertically by approximately $150 \mu\text{m}$ in the gas jet. We impulsively laser-align²¹ only the molecules in the top source using a non-ionizing and stretched (130 fs, $3 \times 10^{13} \text{ W cm}^{-2}$) laser pulse that arrives 0.5 ps earlier to provide prompt molecular alignment. The molecular alignment angle is varied by rotating the alignment pulse polarization with respect to the two-source probe; all polarizations are linear.

The electromagnetic interference between the emitted fields from the top source with aligned (E_{top}) and the bottom source with randomly aligned (E_{bottom}) molecules creates fringes in the far field at the XUV detector, shown in Fig. 2a. Varying the molecular angle, in the top source alone, causes the fringes to move up or down. The

variation of the fringe position with molecular angle determines the angular phase for each harmonic, $\Phi_{\text{HPI}}(\theta; q)$. See Supplementary Section SI.B for the definition of the sign convention.

For $q = 17$, the fringe displacement and the corresponding phase variation are shown respectively in Fig. 2c,b. The distance between two bright fringes (dark red) is 2π in phase. We arbitrarily choose $\Phi_{\text{HPI}}(\theta = 0^\circ; q) = 0$ because no connection is made between adjacent harmonics in this measurement. Another approach, exploiting the interference between partially aligned molecules, also gives access to the angular phase¹⁴. However, it requires some assumptions about the functional form of the rotational wave packet versus time, and it also needs a phase retrieval algorithm.

In the second step, we generate XUV radiation in a mixture of Br₂ molecules and xenon reference atoms. We use the latter as a local oscillator to connect the phase of the Br₂ emission between adjacent harmonics, $\Phi_{\text{Mol}}(q; \theta)$. We prepare a gas mixture with a molar ratio $r \approx 0.2:1$ of Xe atoms to Br₂ molecules. In Fig. 3a, we show the measured XUV signal $S_{\text{Mix}}(q, \theta, r)$ from this gas mixture, and in Fig. 3b the signal $S_{\text{Mol}}(q, \theta)$ from Br₂ alone, the density of Br₂ molecules being the same in both cases (see Supplementary Section SI for details). All measured signals are normalized according to $S_{\text{Mol}}(q, \theta = 0^\circ) = 1$. As the signal intensity with the mixed gases is ~ 7 times weaker than for pure Br₂ alone, we infer strong destructive interference between the emission of the two species. This even leads to a reversal of the signal angular modulation as seen for harmonic order $q = 19$.

The bromine molecules are entrained in a helium carrier gas in the pulsed valve gas expansion. Owing to helium's high ionization potential of 24.6 eV, the helium gas by itself provides no HHG signal. We can add $\sim 4\%$ by pressure of xenon to the

Figure 3 | Mixed-gases interferometry results. **a**, Measured HHG signal $S_{\text{Mix}}(q, \theta)$ from a gas mixture of aligned Br_2 molecules and reference Xe atoms (ratio $r \approx 1:0.2$). **b**, $S_{\text{Mol}}(q, \theta)$ from aligned Br_2 molecules alone. All measured signals are normalized choosing $S_{\text{Mol}}(q, \theta = 0^\circ) = 1$. The polarization of the HHG (probe) driving laser field is fixed (linear along $\theta = 0^\circ$) and the molecular alignment angle θ is varied by rotating the polarization (also linear) of the prompt laser-alignment pump beam.

Table 1 | Relative emission amplitude $r\sqrt{S_{\text{Ref}}(q)/S_{\text{Mol}}(q, \theta = 0^\circ)}$ of the reference atom, as determined by the LAPIN procedure.

Harmonic order	13	15	17	19	21	23
Relative amplitude	0.66	0.48	0.72	1.55	1.64	1.37

All measured signals are normalized to $S_{\text{Mol}}(q, \theta = 0^\circ) = 1$.

helium, without affecting the gas expansion. However, we cannot directly measure the HHG spectrum from the reference atom alone $S_{\text{Ref}}(q)$, as done in other experiments^{19,20}, because the pulsed valve operation and thereby the gas expansion are different without Br_2 vapours. Instead, we separately record the HHG spectra of bromine molecules alone [$S_{\text{Mol}}(q, \theta)$] and of the gas mixture [$S_{\text{Mix}}(q, \theta)$]. This removes the difficulty in matching gas expansion conditions with and without Br_2 molecules, and relieves the necessity to know the precise ratio of gas pressures r : our fitting procedure uniquely determines the reference atom contribution. We express the mixed-gases emission as the coherent sum of the emission from each species²⁰:

$$S_{\text{Mix}}(q, \theta, r) = S_{\text{Mol}}(q, \theta) + r^2 S_{\text{Ref}}(q) + 2r\sqrt{S_{\text{Ref}}(q)}\sqrt{S_{\text{Mol}}(q, \theta)}\cos\Delta\Phi_{\text{Mix}}(q, \theta) \quad (1)$$

Here, we define $\Delta\Phi_{\text{Mix}}(q, \theta) = \Phi_{\text{Mol}}(q, \theta) - \Phi_{\text{Ref}}(q)$ as the phase difference between the electromagnetic emission from the aligned molecules $E_{\text{Mol}}(q, \theta)$ and the reference atom $E_{\text{Ref}}(q)$. We know all quantities except for $r^2 S_{\text{Ref}}(q)$ and $\Delta\Phi_{\text{Mix}}(q, \theta)$. For each harmonic order q , we have 21 measurements corresponding to different molecular angles θ . Therefore, there is sufficient information to determine both $r^2 S_{\text{Ref}}(q)$ and $|\Delta\Phi_{\text{Mix}}(q, \theta)|$, provided that we parameterize the phase.

In mixed-gases interferometry, an ambiguity on the phase arises because $\cos\Delta\Phi_{\text{Mix}}(q, \theta)$ is symmetric around $\Delta\Phi_{\text{Mix}}(q, \theta) = 0$. Two solutions, $\pm\Delta\Phi_{\text{Mix}}(q, \theta)$, can satisfy equation (1), thereby accessing only $|\Phi_{\text{Mol}}(q, \theta) - \Phi_{\text{Ref}}(q)|$. Previous work¹⁹ assumed a direction of the phase difference $\Delta\Phi_{\text{Mix}}(q, \theta)$ to extract it. Here, we can use the redundant information provided by the spectral phase interferometry measurement (Fig. 2) to lift the sign ambiguity of the phase. For this purpose, we combine both experimental measurements into a global fitting procedure described in Supplementary Section SII.B.

Figure 4 | Experimentally determined relative phase $\Delta\Phi_{\text{Mix}}(q, \theta)$ between the molecule and reference atom. The mixed-gases (Fig. 3) and harmonic phase interferometry (Fig. 2) measurements are combined in the LAPIN procedure.

The relative signal amplitude from the reference atom $r\sqrt{S_{\text{Ref}}(q)/S_{\text{Mol}}(q, \theta = 0^\circ)}$ and phase $\Delta\Phi_{\text{Mix}}(q, \theta)$, determined by the LAPIN fitting procedure, are respectively shown in Table 1 and Fig. 4. For all harmonic orders q , the variation of $\Delta\Phi_{\text{Mix}}(q, \theta)$ with molecular angle resembles closely the phase measured by harmonic phase interferometry $\Phi_{\text{HPI}}(\theta; q)$ in Fig. 2b. In both cases, the low harmonics ($q = 13, 15$) modulate less, the strongest modulation occurs at $q = 17$ and the cutoff harmonics ($q = 21, 23$) show a double modulation.

We have now demonstrated the LAPIN method, and its ability to measure the full two-dimensional spectral amplitude and phase of attosecond emission from aligned molecules relative to that of reference atoms. This XUV photonics method is important for molecular imaging¹⁵ as it extracts only contributions to HHG that are target-specific (as opposed to laser-specific), such as the photorecombination dipole. We now proceed to interpret the measurement and to compare it with single-molecule quantum chemistry predictions. We will extract both the amplitude and phase of the recombination dipole moment, using the retrieved relative electromagnetic phase $\Delta\Phi_{\text{Mix}}(q, \theta)$ and amplitude $r\sqrt{S_{\text{Ref}}(q)/S_{\text{Mol}}(q, \theta = 0^\circ)}$.

We recall that all three HHG steps contribute to the phase: ionization (I), propagation (P) and photorecombination (R). As the same laser field is used to simultaneously generate harmonics in Br_2 and Xe in mixed-gases interferometry, the phase difference ($\Delta\Phi_p(q)$) associated with the acceleration of the electron in the continuum essentially cancels out. However, a contribution associated with the difference in ionization potential ($\Delta I_p = -1.58$ eV) between Br_2 ($I_{p, \text{HOMO}} = 10.55$ eV) and Xe ($I_p = 12.13$ eV) remains: $\Delta\Phi_p(q) = -\Delta I_p \tau_q$ (refs 13, 22, 23), with τ_q being the calculated classical electron excursion time associated with the short trajectory harmonic order q . As a result, we can extract a relative phase $\Delta\Phi_{\text{Mol-Ref}}(q, \theta)$ between the molecule (The highest occupied molecular orbital, HOMO, is the molecular reference point) and the reference atom that includes contributions from both the photorecombination (R) and possibly the ionization (I) steps^{9,10}:

$$\begin{aligned} \Delta\Phi_{\text{Mol-Ref}}(q, \theta) &= \Delta\Phi_{\text{Mix}}(q, \theta) - \Delta\Phi_p(q) \\ &= \Delta\Phi_R(q, \theta) + \Delta\Phi_I(q, \theta) \end{aligned} \quad (2)$$

At this point we could also remove the recombination phase of the reference xenon atom, which we calculated and show

Figure 5 | Experimentally determined molecular frame amplitude and phase compared with model calculations. **a,b**, LAPIN-retrieved relative amplitude $\sqrt{S_{\text{Mol}}(q, \theta)/S_{\text{Ref}}(q)}$ (**a**) and phase $\Delta\Phi_{\text{Mol-Ref}}(q, \theta)$ (**b**) between the emission from Br₂ molecules and reference Xe atoms. **c,d**, Calculated relative amplitude (**c**) and phase contribution (**d**) from multiple orbitals altogether (HOMO + HOMO-1 + HOMO-2). **e**, We progressively add the coherent contributions from each orbital to the total amplitude and phase. The theoretical calculations (**c**)–(**e**) are relative to the same calculations for xenon atoms, and hence can be directly compared to the experiment. For clarity, all amplitudes are normalized to the values at $\theta = 90^\circ$ ((**a**), (**c**)) for each harmonic order (see Supplementary Section SIII for unnormalized plots). All amplitudes and phases are, respectively, shown using common colour scales.

in Supplementary Section SII.A. Instead, we will leave out the experimentally determined amplitude and phase of bromine relative to xenon (see Fig. 5a,b), and include the calculated xenon recombination amplitude and phase in the theoretical model, which we shall describe next.

At the laser intensity $I_{\text{probe}} = 1.5 \times 10^{14} \text{ W cm}^{-2}$ used in the experiment, multiple molecular orbitals of Br₂ (HOMO, HOMO-1 and HOMO-2) can significantly contribute to HHG (refs 9,24,25). Indeed, a strong-field approximation calculation²⁶ on atoms with $I_{\text{p,HOMO}} = 10.55 \text{ eV}$, $I_{\text{p,HOMO-1}} = 13.09 \text{ eV}$ and $I_{\text{p,HOMO-2}} = 14.62 \text{ eV}$ shows that, although HOMO emits the strongest for $q \leq 15$, the contributions from HOMO-1 and HOMO-2 become dominant for $q \geq 17$ (see Supplementary Fig. S7b). To simulate the experiment, we coherently add the contributions from HOMO, HOMO-1 and HOMO-2 along the lines of refs 9,25, using molecular photorecombination dipoles obtained by quantum scattering calculations^{27,28} (see Supplementary Section SIII for details on the theoretical model). To be consistent with our definition of $\Delta\Phi_{\text{Mol-Ref}}(q, \theta)$ retrieved experimentally (see equation (2)), we also take HOMO as the molecular reference point and include the ionization potential differences relative to HOMO when calculating the expected photorecombination dipole relative phase $\Delta\Phi_{\text{R}}(q, \theta) = \Phi_{\text{Mol,R}}(q, \theta) - \Phi_{\text{Ref,R}}(q)$ (see Supplementary Equations S10–S12). In Fig. 5c–e, we show the progressive contribution of each orbital to the total relative amplitude (Fig. 5c) and phase (Fig. 5d).

The calculated amplitude and phase in Fig. 5c,d are in good agreement with the LAPIN experimental results in Fig. 5a,b. Our calculations reveal that HOMO-1 is responsible for the amplitude and phase mainly peaking at $\theta = 90^\circ$ (see Fig. 5e lower panel). An amplitude minimum in the vicinity of $q = 21$ and $\theta = 0^\circ$,

accompanied by a rapid local phase variation with increasing q , is observed experimentally. The position of this minimum ($q = 21$) is consistent with the two-centre interference model²⁹; a similar feature around $q = 23$ was also observed in the recombination dipole of aligned CO₂ measured by the RABBIT technique⁸, and around $q = 33$ (50 eV) measured by the generalized orbital tomography approach¹⁴, Br₂ and CO₂ having the same ordering of valence molecular orbitals. However, the dependence of that spectral feature on laser intensity⁹ and wavelength²⁵ in CO₂ instead supports the participation of multiple orbitals²⁴. Here, our calculations in Fig. 5c–e qualitatively reproduce the spectral minimum and rapid phase variation observed experimentally in Fig. 5a,b: they would also originate from the interplay of multiple orbitals. Less good agreement between experiment and theory is visible at lower harmonic orders, suggesting that our model based on the strong-field approximation may overestimate the relative contribution from the HOMO.

For quantitative agreement between experiment and theory phases (Fig. 5b,d), we need to add an overall constant $\Gamma \approx -0.9\pi$ to the calculated recombination phase $\Phi_{\text{Mol,R}}(q, \theta) - \Phi_{\text{Ref,R}}(q)$. On the basis of equation (2), this suggests an additional constant phase difference between the emission from HOMO and xenon, $\Gamma \approx -0.9\pi$. Although the concept of an ionization phase is not yet fully understood^{9,10}, $\Delta\Phi_{\text{I}} \approx -0.9\pi$ would explain the overall shift between the experiment and the model. As a result, comparing LAPIN measurements to our model allows us to report an additional, previously unaccounted for, phase difference between the emission of two species in mixed-gases experiments^{19,20,23}. This needs to be further investigated by more detailed modelling, which could include multielectron attosecond dynamics and sub-cycle laser-driven population evolution of the electron–hole first created

by ionization^{9,10}. Our results on Br₂ support previous results in CO₂ where no ionization phase is observed between the XUV emission from different molecular orbitals⁹.

We have combined two all-optical techniques, namely two-source harmonic phase and mixed-gases interferometries, allowing us to first solve for the full two-dimensional (q, θ) molecular high-harmonic photorecombination dipole amplitude and phase relative to those of a reference atom. Accessing these full quantities is especially important for the development of single-molecule tomographic imaging by HHG (ref. 12–15). Although we demonstrated the LAPIN technique using 30-fs laser pulses, unlike RABBIT (ref. 16), it will work for few-cycle pulses where individual harmonics are not resolved. Moreover, it is *in situ*: it uses a single gas jet and an XUV spectrometer, whereas present techniques require a second gas jet and a photoelectron spectrometer^{16,17}. LAPIN is applicable to any molecular systems that can be expanded in the gaseous phase; these include: aligned²¹, three-dimensionally aligned³⁰ and oriented³¹ polyatomic molecules. As its retrieval procedure directly measures the full phase map relative to the reference atom, LAPIN offers the opportunity to benchmark new theoretical models² and extend them to larger molecules. The combination of LAPIN and time-resolved homodyne high-harmonic spectroscopy¹¹ now provides all necessary information for dynamical tomographic imaging of chemical reactions. This procedure will surely bring new insights into single-molecule electronic dynamics underlying photochemical processes such as photosynthesis^{32,33}.

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Author contributions

J.B.B., H.J.W., P.S., D.M.V. and P.B.C. conceived the experiment and helped prepare the manuscript. J.B.B. and H.J.W. performed all experiments. J.B.B. and D.M.V. developed the LAPIN algorithm. J.B.B. did all data analysis and calculations, prepared all figures and led the writing of the manuscript.

Additional information

Supplementary information is available in the [online version of the paper](#). Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to D.M.V.

Competing financial interests

The authors declare no competing financial interests.

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Figure S1. (a) The high harmonics experimental setup composed of a source chamber and an XUV spectrometer. Bromine (Br_2) vapors are injected in a supersonic gas jet using a carrier gas (helium + xenon) that flows through liquid Br_2 . High-harmonic spectra from a gas mixture of (b) xenon ($\approx 4\%$) + helium and (c) unaligned Br_2 ($\approx 20\%$) + helium. The pulsed valve operation is different in these two cases due to the presence or not of bromine vapors. We solve this problem by using gas mixtures always containing Br_2 , see section II.B for more details. No harmonics are generated from helium alone.

I. EXPERIMENTAL SETUP

A. General

To perform the experiment, we use the output of a Ti:Sapphire multi-pass laser system (32 fs, 800 nm, 50 Hz, 12 mJ per pulse). An optical setup that both splits and recombines laser pulses for pump-probe experiments precedes the high-harmonic vacuum chamber. As seen in Fig. S1, we generate the high-harmonic radiation in a source chamber (pulsed valve, $250\ \mu\text{m}$ orifice, total backing pressure is $P_{\text{back}} = 2\ \text{atm.}$) and measure spectra using an XUV spectrometer (a grazing incidence XUV grating, a microchannel plate detector backed by a phosphor screen, and a camera readout).

Bromine (Br_2) is a liquid at room temperature. In order to inject the bromine molecules through the pulsed valve (Parker Hannifin) into the chamber, a carrier gas (helium) was bubbled through the liquid Br_2 . Due to helium's high ionization potential of 24.6 eV, no high harmonic generation signal from helium is observed at the probe intensity $I_{\text{probe}} = 1.5 \times 10^{14}\ \text{W/cm}^2$ employed in the experiment. In the second part of the experiment, mixed gas interferometry, we prepare a mixture of helium + xenon which provides a vapor pressure ratio of $\text{Xe}:\text{Br}_2$ of $0.2:1.0 \pm 10\%$ at the gas jet. The error on r is attributed to measuring gas pressures in the preparation of the $\text{Xe}+\text{He}$ carrier gas. The partial vapor pressure of Br_2 at $T=22^\circ\ \text{Celsius}$ is $\sim 29\ \text{kPa}$ ($\sim 0.3\ \text{atm.}$) [1]. In these conditions, high-harmonic signal is obtained from both Br_2 and xenon, providing an homodyne interference between the emission of each species [2, 3], see Fig. 3 of the main paper.

B. Sign convention and harmonic phase interferometry

In order that others are able to use and reproduce the present results, it is necessary that we establish our conventions regarding phases. In particular, since we are often measuring phase *differences*, the ordering of the contributions

is important. Whenever we use a phase difference such as $\Delta\phi$, we use the order of molecule minus atom, e.g. $\Delta\phi = \phi_{mol} - \phi_{ref}$.

We use the time-dependent Schrodinger equation to establish the sign of the time propagator,

$$\psi(t) = e^{-iHt}\psi(0) = e^{-iEt}\psi(0). \quad (S1)$$

Here H is the Hamiltonian and E is the eigenenergy for a time-independent Hamiltonian. This also defines the sign of the Fourier transform kernel to be $e^{i\omega t}$ [4].

We now define our sign convention for the Strong Field Approximation (SFA) [5] as follows, where we explicitly include the energy of the neutral and the ion [6].

$$\begin{aligned} d(t) = & -i \int d\mathbf{k} \int_0^t dt_1 \left\langle \psi_N \left| e^{iE_N t} \mathbf{r} e^{-iE^+(t-t_1)} e^{-iS_v(t,t_1)} \right| \mathbf{k} + \mathbf{A}(t), \psi^+ \right\rangle \\ & \times \left\langle \mathbf{k} + \mathbf{A}(t_1), \psi^+ \left| \hat{V}_L(t_1) e^{-iE_N t_1} \right| \psi_N \right\rangle \end{aligned} \quad (S2)$$

Here, $\psi_N(1\dots n)$ is the n -electron ground state of the neutral atom, E_N is the total energy of the neutral, $\psi^+(1\dots n-1)$ is the $(n-1)$ -electron wave function of the ion following ionization, E^+ is the total energy of the ion, $V_L = xE_L(t_1)$ is the interaction Hamiltonian due to the laser field, and $S_v(t, t_1) = \int_{t_1}^t (\mathbf{k} + \mathbf{A}(t''))^2 dt''/2$ is the Volkov phase of the electron in the continuum. If we substitute the ionization potential $I_p = E^+ - E_N$, the phase terms become

$$\phi = -S_v(t, t_1) - I_p(t - t_1). \quad (S3)$$

Both S_v and I_p are positive, so this overall term will be negative.

We now define our sign convention for the harmonic phase $\Phi_{Mol}(q, \theta)$. The high harmonic generation process is composed of three steps: ionization, acceleration, and photorecombination [7]. Each step contributes to the total spectral amplitude $|D_{Mol}(q, \theta)|$ and phase $\Phi_{Mol}(q, \theta)$ of the emitted single-molecule real-valued high-harmonic dipolar XUV field E_{Mol} , where θ is the molecular alignment angle and q is the harmonic order at frequency $\Omega = q\omega_0$ with ω_0 being the central frequency of the driving laser field. Following the convention introduced in refs. [8, 9], in the spectral domain, we define the emitted field as:

$$E_{Mol}(q, \theta) = |D_{Mol}(q, \theta)| e^{i\Phi_{Mol}(q, \theta)}. \quad (S4)$$

Using a thin gas jet in the experiment allows us to minimize propagation effects [10] and, therefore, to measure at the XUV detector a signal $S_{Mol}(q, \theta)$ proportional to the single-molecule intensity $|E_{Mol}|^2$. Since we are interested in the relative change of the signal with θ or q , we drop the proportionality sign and directly use the equality:

$$S_{Mol}(q, \theta) = |E_{Mol}(q, \theta)|^2. \quad (S5)$$

The amplitude $|D_{Mol}|$ can be computed directly from the measured HHG spectrum: $|D_{Mol}(q, \theta)| = \sqrt{S_{Mol}(q, \theta)}$. The two-dimensional spectral phase $\Phi_{Mol}(q, \theta)$ of the XUV emission, however, is not readily accessible. We must specify that, for a given alignment angle θ , we refer here to $\Phi_{Mol}(q, \theta)$ as the spectral phase linking adjacent harmonics as can be measured by RABBIT [11–13] or FROG-CRAB [14]. This spectral phase is responsible for the temporal profile of the XUV emission on the attosecond timescale. On the other hand, the detailed variation of the phase over the bandwidth of a given harmonic order q will give access to the femtosecond temporal profile of the XUV emission, see ref. [4] for a detailed description. This finer structure in the harmonic phase can be measured via femtosecond optical techniques adapted to the XUV domain (high-harmonic SPIDER [15] and FROG-CRAB [14]). Next, we shall describe how harmonic phase interferometry allows us to measure $\Phi_{Mol}(\theta; q)$, the variation of the harmonic phase with molecular alignment angle.

In harmonic phase interferometry (HPI), the interference between the emitted fields from the top source aligned (E_{top}) and bottom source randomly aligned (E_{bottom}) molecules creates an interference in the far field at the XUV detector, see Fig. S2. Both sources are waves traveling to the right with, in addition, the top source also carrying information about the angular-dependent harmonic phase which we denote here as $\Phi_{HPI}(\theta; q)$. Following the phase sign convention in eq. S4 to describe the macroscopic high-harmonic field, the emissions from the top and bottom sources are written:

$$E_{top}(\theta; q) \propto e^{i(kr_1 - \Omega t)} e^{i\Phi_{HPI}(\theta; q)}, \quad E_{bottom}(\theta; q) \propto e^{i(kr_2 - \Omega t) + i\Phi_q}, \quad (S6)$$

where we have introduced an arbitrary constant spectral phase Φ_q for the bottom source which acts as a local oscillator here. By varying the molecular alignment angle from $\theta = 0^\circ$ to 90° in the top source only, we observe the fringes moving along the vertical direction on the XUV detector. The phase difference determines the position of the fringes.

Harmonic Phase Interferometry

Figure S2. Spectral harmonic phase interferometry (HPI) of aligned Br_2 molecules. (a) Two XUV sources created in a supersonic gas jet interfere in the far field. We laser-align the molecules in the top source only and observe the interference fringes moving as a function of alignment angle θ , providing a measurement of the high-harmonic spectral phase $\Phi_{HPI}(\theta; q)$, see text for details. (b) We image the laser foci of both 2-source probe and alignment pulses using an imaging system and a ccd camera, confirming that we align the molecules in the top source only. (c) A typical high-harmonic spectrum (averaged over 50 laser shots) as seen on the detector.

Let us consider the central fringe ($r_1 = r_2$) at $\theta = 0^\circ$. If it moves up when increasing θ , this means that, since the phase difference remains the same: $\Phi_{HPI}(\theta) - \Phi_q + k(r_1 - r_2) = \Phi_{HPI}(\theta = 0^\circ) - \Phi_q$. Since $(r_1 - r_2) < 0$, this straightforwardly means $\Phi_{HPI}(\theta) - \Phi_{HPI}(\theta = 0^\circ) > 0$. In other words, when the fringes move in the upper direction at the detector, the phase $\Phi_{HPI}(\theta; q)$ increases.

We understand from this analysis that, having aligned the molecules in the bottom source instead, the fringes would have moved in the opposite direction. We carefully imaged the laser foci of both the two-source probe and alignment pulses, as seen in Fig. S2(b), to confirm that we were indeed aligning the top source. We also had to carefully examine the entire XUV spectrometer imaging system in order to determine the sense of motion of the fringes.

Since the macroscopic response restricts the emission from randomly aligned molecules (bottom source) to be polarized parallel to the driving field, the motion of the fringes provides a measurement of the phase of the parallel (to the driving laser field) component of the electromagnetic field E_{top} emitted from aligned Br_2 molecules. We have performed polarimetry measurements (not presented here) which indicate that the perpendicular component from aligned Br_2 is small ($\leq 10\%$ in intensity). In other cases, stronger perpendicular emission could affect the measurement in part by changing the fringes' visibility [16].

The position of the fringes in the vertical direction (at the XUV detector, see Fig. 2(c)) is averaged over 1000 laser shots at each molecular angle θ . Molecular alignment (in the top source only) is obtained by the nonadiabatic interaction of a non-ionizing and stretched ($\sim 130\text{ fs}$, $I_{align} = 3 \times 10^{13}\text{ W/cm}^2$) laser pulse with the gas-phase molecules [17]. This pulse comes 0.5 ps earlier to provide prompt molecular alignment. For each given harmonic q -order, the position of the fringes is obtained by first integrating horizontally (over the spectral width of a given harmonic) the averaged signal on the detector and then, by spatially Fourier transforming the profile along the vertical direction [18]. The extracted phase, which we denote as $\Phi_{HPI}(\theta; q)$, is the phase of this transform, where 2π corresponds to the distance between two bright (or dark) fringes. We plot the results for each measured harmonic order $q=13$ to

Figure S3. The amplitude squared ($S_{Ref,R}(q)$, top panel) and phase ($\Phi_{Ref,R}(q)$, lower panel) of the photorecombination (R) differential cross section as calculated by ePolyScat [19, 20] for (a) argon (Ar) and (b) xenon (Xe).

23 (~ 20 -35 eV) in Fig. 2(b) of the main paper. Since we record only the shift of the fringes for each harmonic order versus molecular angle, we cannot relate the phase between harmonic orders. Therefore, we are free to shift each curve in Fig. 2(b) up or down arbitrarily. We arbitrarily choose $\Phi_{HPI}(\theta=0; q)=0$.

II. MIXED GASES INTERFEROMETRY

A. Xenon as reference Atom

In the second step of the LAPIN procedure, mixed gases interferometry, xenon acts as a θ -independent homodyne local oscillator against which we measure the molecular harmonic phase $\Phi_{Mol}(q, \theta)$ of the Br_2 molecules. We choose xenon as a reference because it has a polarizability and an ionization potential ($I_p=12.13$ eV) similar to Br_2 ($I_{p,HOMO}=10.55$ eV, $I_{p,HOMO-1}=13.09$ eV and $I_{p,HOMO-2}=14.62$ eV) [21], offering similar ionization dynamics. Having a reference atom with a much smaller ionization potential ($I_{p,Ref}$) than the molecule's ($I_{p,Mol}$) could engender macroscopic phase mismatch effect due to the large amount of free electrons created by ionization. At the opposite extreme, if $I_{p,Ref}$ is much larger than $I_{p,Mol}$, the reference atom emission will be too small for accurate interferometry. We selected the molar ratio $r \approx 0.20$ in order to approximately balance the intensity of HHG emission from xenon and bromine.

Ideally, to make the molecular amplitude and phase retrieval the most straightforward, one would use a reference atom with flat high-harmonic photorecombination (R) amplitude $\sqrt{S_{Ref,R}(q)}$ and phase $\Phi_{Ref,R}(q)$ in the spectral range of interest, $q=13$ to 23 (~ 20 -35 eV). It is not quite the case for xenon as shown in Fig. S3(b). Later, we will use this calculated differential photorecombination cross section (we take the complex conjugate of the output from ePolyScat [19, 20]) to compute the theoretical relative amplitude $\sqrt{S_{Mol}(q)/S_{Ref}(q)}$ and relative phase $\Phi_{Mol,R}(q, \theta) - \Phi_{Ref,R}(q)$. We will compare those to the experimentally retrieved values by LAPIN, see Fig. 5(a) and (b) of the main paper. In Fig. S3(a), we display the calculated signal $S_{Ref,R}(q)$ (top panel) and phase $\Phi_{Ref,R}(q)$ (lower panel) of argon. We verified the reliability of the calculation by reproducing the argon Cooper minimum in the vicinity of ~ 55 eV [22].

B. The Amplitude and Phase Retrieval Procedure

The signal from the gas mixture is a coherent sum of the emission from both molecular and atomic reference species [3]:

$$S_{Mix}(q, \theta, r) = S_{Mol}(q, \theta) + r^2 S_{Ref}(q) + 2r \sqrt{S_{Mol}(q, \theta)} \sqrt{S_{Ref}(q)} \cos \Delta \Phi_{Mix}(q, \theta) \quad (S7)$$

where $r \approx 0.20$ is the Xe/Br₂ molar fraction in the gas jet. We directly measure $S_{Mol}(q, \theta)$ (the HHG spectrum for the bromine molecules alone as a function of molecular alignment angle θ) and $S_{Mix}(q, \theta)$ (the HHG spectrum for the mixture of the bromine molecules and the reference xenon atoms as a function of molecular alignment angle).

The bromine molecules are entrained in a helium carrier gas in the pulsed valve gas expansion. We only add about $\approx 4\%$ by pressure of xenon to the helium, which has negligible effect on the gas expansion. However, we cannot directly measure the HHG spectrum from the reference atom alone $S_{Ref}(q)$ as in other experiments [3, 23], because the pulsed valve operation is different without the presence of Br₂ vapors. Instead, we separately record the HHG spectra of the bromine molecules alone ($S_{Mol}(q, \theta)$) and of the gas mixture ($S_{Mix}(q, \theta)$). This not only removes the difficulty in matching gas expansion conditions with and without Br₂ molecules, but also means that we do not need to know the precise ratio of gas pressures r : our fitting procedure uniquely determines $r^2 S_{Ref}(q)$.

We normalize eq. (S7) by the XUV signal from Br₂ molecules alone $S_{Mol}(q, \theta)$ [see Fig. 3(b) of the main paper, both $S_{Mol}(q, \theta)$ and $S_{Mix}(q, \theta)$ are the respective raw signals normalized by the raw signal from aligned molecules at $\theta = 0^\circ$, i.e, we choose $S_{Mol}(q, \theta = 0^\circ) = 1$]. In Fig. 3, the frequency spectrum in the radial direction does not show individual harmonics. The area under each spectral peak was integrated from the CCD camera image to give a single value for each odd harmonic. The values were then tabulated as a function of angle (21 angles in 10 degrees step) and harmonic order (6 odd orders in 2 orders step). This matrix of values defines a two-dimensional surface. A two-dimensional linear interpolation (function "interp2" in MATLAB) was performed (in 1 degrees and 0.2 orders step) on the surface. Also, the polar coordinates plotting routine employed color interpolation (option "shading interp" in MATLAB) to deliver the plots shown. We obtain the ratio $R_{Mix}(q, \theta, r)$:

$$R_{Mix}(q, \theta, r) = 1 + r^2 \frac{S_{Ref}(q)}{S_{Mol}(q, \theta)} + 2r \sqrt{\frac{S_{Ref}(q)}{S_{Mol}(q, \theta)}} \cos \Delta\Phi_{Mix}(q, \theta) \quad (S8)$$

Here $\Delta\Phi_{Mix}(q, \theta) = \Phi_{Mol}(q, \theta) - \Phi_{Ref}(q)$ is defined as the phase difference between the emission from the aligned molecules $E_{Mol}(q, \theta)$ and that of the reference atom $E_{Ref}(q)$.

We separately record the HHG spectra of the bromine molecules alone ($S_{Mol}(q, \theta)$) and of the gas mixture ($S_{Mix}(q, \theta)$). In eq. S8 we know all quantities except for $r^2 S_{Ref}(q)$ and $\Delta\Phi_{Mix}(q, \theta)$. Therefore we seek to solve for these two unknowns. For each harmonic order q , we have 21 measurements at different molecular angles θ . Therefore there is sufficient information to determine both $r^2 S_{Ref}(q)$ and $\Delta\Phi_{Mix}(q, \theta)$, provided that we parameterize the phase. However the mixed gas measurement alone is not able to determine the sign of the phase due to the cosine function.

In mixed gases interferometry, an ambiguity on the phase arises because $\cos \Delta\Phi_{Mix}(q, \theta)$ is symmetric around $\Delta\Phi_{Mix}(q, \theta) = 0$ [23]. Two solutions, $\pm \Delta\Phi_{Mix}(q, \theta)$, can satisfy eq. S8, thereby accessing only $|\Phi_{Mol}(q, \theta) - \Phi_{Ref}(q)|$ and leaving the *directionality* of $\Phi_{Mol}(q, \theta)$ undetermined. McFarland et al. [23] had to make assumptions about the direction of the phase difference in order to extract the molecular phase. However, we recall that in the first interferometry step (HPI) we measured the *directionality* (up or down) of $\Phi_{HPI}(\theta; q)$, corresponding also to a measurement of the *directionality* of $\Phi_{Mol}(q, \theta)$ based on our definition of E_{Mol} above, see eq. (S4). Therefore we can use the redundant information provided by the HPI measurement to lift the sign ambiguity of the phase. For this purpose, we combine both experimental measurements, $\Phi_{HPI}(\theta; q)$ and $R_{Mix}(q, \theta)$, into a global fitting procedure. This procedure of combining two phase measurements has been given the acronym LAPIN: Linked Attosecond Phase Interferometry.

We parameterize the phase difference using even (0-6) Legendre polynomials P_{2i} ,

$$\Delta\Phi_{Mix}(q, \theta) = \left| \sum_{i=0}^3 a_{2i} P_{2i}(\theta) \right|$$

This parameterization fulfills the symmetry requirements at parallel ($\theta=0^\circ$) and perpendicular ($\theta=90^\circ$) alignments. Using 4 Legendre polynomials is sufficient to match the HPI measurements, but in principle higher orders can be included if necessary. For each harmonic order q , we then need to extract 4 angular parameters a_{2i} and the single value of $r^2 S_{Ref}(q)$. Since there are 21 angular measurements made at each harmonic order q , the system is overdetermined. We include both the mixed gas measurement and the HPI measurement into the error function L_q which is defined as the sum of the residuals,

$$L_q = \sum_{\theta} f_q(\theta)$$

with,

$$f_q(\theta) = [w_1 |R_{Calc}(q, \theta) - R_{Mix}(q, \theta)| + w_2 |\Delta\Phi_{Mix}(q, \theta) - \Delta\Phi_{Mix}(q, \theta = 0^\circ) - \Phi_{HPI}(\theta; q)|] \quad (S9)$$

Figure S4. (a) Flow chart for the LAPIN procedure, see eqs. (S8)-(S9) and the surrounding text for details.

and where $R_{Calc}(q, \theta)$ is the calculated ratio using eq. (S8) and the 5 fitting parameters, and Σ_θ denotes summation over the 21 angular measurements. We apply a nonlinear least-squares fitting procedure (function "lsqcurvefit" in MATLAB) to extract the parameters. This procedure seeks to minimize the error function between the fit and the measurement, i.e., we solve for $L_q = 0$ in eq. (S9). w_1 and w_2 are weighting factors chosen to, respectively, give more importance to the mixed gases or the harmonic phase interferometry measurements. We use $w_1 = w_2 = 1$ to equally take into consideration both interferometry steps. Below, we will discuss the effect of changing w_1 and w_2 . We summarize the LAPIN procedure in the flow chart shown in Fig. S4.

In Fig. S5(a)-(c), we show the results of the fitting procedure for the case of $q=13, 17$ and 23 . We obtain $R_{Mix}(q, \theta, r = 0.2)$ (triangles pointing down) from dividing the signal from the mix $S_{Mix}(q, \theta)$ (diamonds) by the one from molecules alone $S_{Mol}(q, \theta)$ (open circles). Every point is averaged over 1000 laser shots and the $\pm$ error bars on raw measurements are obtained by calculating the standard deviation at each point. From the LAPIN fitting procedure ($L_q = 0$), we obtain both the reference atom signal $r^2 S_{Ref}(q)$ (see table in Fig. 4(a) of the main paper) and the relative angular phase $\Delta\Phi_{Mix}(q, \theta)$ (crosses).

The robustness of LAPIN is measured by the goodness of the fits shown in Fig. S5(a)-(c). As shown in eq. (S9), the LAPIN procedure seeks to fulfill two criteria for each harmonic order: (i) consistency between the angular variation of the retrieved phase $\Delta\Phi_{Mix}(q, \theta)$ (crosses) and the independently measured phase in the first step $\Phi_{HPI}(\theta; q)$ (dashed line), and (ii) good overlap between R_{Calc} (solid line) and R_{Mix} (triangles pointing down). We observe similarly good robustness across all harmonic orders (maybe less for $q = 23$) as measured by the squared norm of the residuals $\chi^2(q = 17 - 23) = \Sigma_\theta f_q(\theta)^2 = [0.11, 0.17, 0.03, 0.06, 0.04, 0.62]$. From the total solution ($r^2 S_{Ref}(q)$ and $\Delta\Phi_{Mix}(q, \theta)$) and using eq. (S8), we compute the value of $\cos \Delta\Phi_{Mix}(q, \theta)$, which is shown in Fig. S5(d). The result confirms that the interference between aligned Br_2 molecules and xenon is strongly destructive, consistent with the raw mixed gases measurements presented in Fig. (3) of the main paper.

We have also solved for $\Delta\Phi_{Mix}(q, \theta)$ based solely on (A) mixed gas interferometry ($w_1=1, w_2=0$). In that case, we manually used the HPI measurement to lift the ambiguity of the sign of $\Delta\Phi_{Mix}(q, \theta)$, see Fig. S6(a)-(c). For example, in Fig. S6(d), we select the solution where the phase increases with increasing (starting at $\theta=0^\circ$) molecular angle (circles), the other solution being symmetric with $\Delta\Phi_{Mix}(q, \theta)=0$ or π (not shown). The LAPIN ($w_1=1, w_2=1$) solution is also shown (crosses). We also explored the (B) procedure where we would take $\Delta\Phi_{Mix}(q, \theta) = \Phi_{HPI}(\theta; q = 17) + C(q)$, that is, shifting vertically by a constant phase $C(q)$ determined from mixed gas interferometry. This would usually give a solution (black solid line) close to the LAPIN ($w_1 = w_2=1$) solution (crosses). As expected, decreasing the weight ($w_1=1, w_2=0.1$) given to the first interferometry step (HPI), pulls the solution (squares) back towards the mixed gases only (circles).

Overlap between the R_{Calc} solution and R_{Mix} is always observed: all different solutions for $\Delta\Phi_{Mix}(q, \theta)$, see Fig.

Figure S5. (a) Fitting procedure for q =(a)13, (b) 17 and (c) 23, see text for details. (d) The retrieved value for $\cos \Delta\Phi_{Mix}(q, \theta)$, refer to eq. (S8), showing that the interference between Br₂ and xenon is destructive over the full (q, θ) range covered in the experiment.

Figure S6. (a) One can extract $\Delta\Phi_{Mix}(q, \theta)$ by mixed gas interferometry only. (b) However, two solutions for $\Delta\Phi_{Mix}(q, \theta)$ are possible since $\cos \Delta\Phi_{Mix}(q, \theta)$ is symmetric around $\Delta\Phi_{Mix} = 0$. (c) The harmonic phase interferometry step allows to unequivocally determine the curvature (case 1 or 2) of $\Delta\Phi_{Mix}(q, \theta) = \Phi_{Mol}(q, \theta) - \Phi_{Ref}(q)$. (d) Effect of changing the relative weights in the global LAPIN fitting procedure for $q=17$.

S6(d), are accompanied by different retrieved amplitudes $r\sqrt{S_{Ref}}$ which all lie inside the range $\pm 50\%$ of the LAPIN solution. The case of $q=17$ in Fig. S6(d) presents the strongest difference between the two extrema solutions (A) and (B) discussed above. We attribute the discrepancies between the (A) and (B) extrema solutions to various possible reasons: a small orthogonal component of E_{Mol} provides an extra term not accounted for in eqs. (S7) and (S8), and the different generation conditions between the HPI and mixed gases steps (1 source vs 2 sources) probe molecules from slightly different locations in the gas jet expansion (e.g. different degrees of alignment).

In general, for all harmonic orders q , we observe that the LAPIN solution ($w_1=1, w_2=1$) falls between the (A)

Figure S7. (a) The highest occupied molecular orbitals of Br₂ have similar ionization potentials. Throughout this work, both experimentally and theoretically, we always measure the amplitude and phase of the XUV emission from aligned Br₂ molecules (above) relative to a reference Xenon atom (below). (b) Calculated high-harmonic spectra from atomic-like species of ionization potentials of the Br₂ HOMOs, where we used a gaussian pulse of full width at half maximum of 30fs (centered on 800nm) and peak intensity $I_{probe} = 1.5 \times 10^{14} \text{ W/cm}^2$.

and (B) extrema and that all solutions are similar (modulation depth and location on the vertical phase axis). First, this confirms the consistency between the measurements from individual interferometry steps and second, most importantly, justifies using the LAPIN procedure for finding a unique solution that simultaneously takes both measurements into account.

III. THEORY: PARTICIPATION OF MULTIPLE MOLECULAR ORBITALS

At the laser intensity $I_{probe} = 1.5 \times 10^{14} \text{ W/cm}^2$ used in the experiment, multiple highest occupied molecular orbitals (HOMO) can significantly participate to the high harmonic generation process [18, 24]. In Br₂, HOMO, HOMO-1 and HOMO-2, have similar vertical ionization potentials ($I_{p,HOMO}=10.55 \text{ eV}$, $I_{p,HOMO-1}=13.09 \text{ eV}$ and $I_{p,HOMO-2}=14.62 \text{ eV}$), see Fig. S7(a). In order to estimate the contribution from each orbital, we use the Strong Field Approximation (SFA) along the lines of ref. [25], where we use the Yudin-Ivanov model [26] for the instantaneous ionization rate, and treat each molecular orbital as an atomic emitter [27] with a flat photorecombination cross section ($=1$). We observe that although HOMO emits the strongest for $q \leq 15$, the contribution from HOMO-1 and HOMO-2 becomes dominant at $q \geq 17$, see Fig. S7(b).

In order to simulate the experiment, we need to coherently add the contributions from HOMO, HOMO-1 and HOMO-2 which we denote respectively with the indices $j = 0 - 2$. Using the SFA framework, we write the total complex molecular frame dipole along the lines of refs. [18, 28]:

$$D_{Mult}(q, \alpha) = \sqrt{c_0(q)^2 I_0(\alpha)} R_0(q, \alpha) e^{i\phi_0(q)} + \sqrt{c_1(q)^2 I_1(\alpha)} R_1(q, \alpha) e^{i\phi_1(q)} + \sqrt{c_2(q)^2 I_2(\alpha)} R_2(q, \alpha) e^{i\phi_2(q)} \quad (\text{S10})$$

where the normalized spectral weights $c_j(q)^2$ (see Fig. S8(a)) are obtained by normalizing the atomic XUV spectra by the one of xenon in Fig. S7(b), and the R_j are the complex recombination dipoles. α denotes the angle between the molecular axis and the laser polarization in the molecular frame (throughout the paper, we have chosen θ as the angle between the alignment distribution axis and the laser polarization in the laboratory frame, not to confuse with the opposite notation in ref. [29]). The angular ionization profiles $I_j(\alpha)$ are chosen to contain the signature of the corresponding molecular orbitals [18] (see Fig. S8(b)).

The phases $\phi_j(q) = -\Delta I_{p,j} \tau_q$ (see Fig. S8(c)) carry the effect of the different ionization potentials associated to each orbitals with respect to HOMO [2, 5, 30], τ_q being the classical electron excursion time associated with the short trajectory harmonic order q for HOMO. Recent experiments [31] show that the electron birth time can differ from

Figure S8. (a) High-harmonic spectral contribution from each orbitals from an SFA calculation with atomic species (b) The corresponding molecular frame ionization profiles taken from ref. [18] and (c) the additional phase due to the difference in ionization potential of each orbitals with respect to HOMO ($\Delta I_{p,0}=0$).

the classical birth time by up to 100 asec, and that different orbitals in CO_2 have birth times varying by up to 40 asec. These corrections can amount to up to 10% for the transit time, and would change the value of $\Delta I_{p,j}\tau_q$ by 0.4 radians. This could be a significant correction, although it is much less than the $\Gamma \approx 3$ radians difference that we see between the experiment and the model, see main paper. Since Shafrir *et al.* show that the correction to the birth time depends on the species, it is not clear what correction should be applied to the present case of Br_2 . We use $\Delta I_{p,0}=0$ to be consistent with our definition of the retrieved phase in the main paper, where HOMO is the molecular reference point when compared to the reference atom, see Fig. S7(a).

The complex molecular frame differential photorecombination dipoles $R_i(q, \alpha)$ are obtained by ePolyScat calculations [19, 20]. We calculate Hartree-Fock orbitals using GAMESS [32] using a cc-pVTZ basis set for bromine. Each ionization channel is treated separately [18], composed of a neutral ground state and a final ionic state. This effectively describes three Dyson orbitals corresponding approximately to ionization from different orbitals of the neutral molecule. These quantum chemistry calculations are then used as input to ePolyScat to calculate the transition moments from bound states to continuum states of various kinetic energies, for each ionization channel separately. We include only the parallel (to the driving field) polarization component and take the complex conjugate of the ePolyScat (photoionization) output.

We obtain the calculated laboratory frame relative XUV amplitude $\sqrt{S_{Mol}(q, \theta)}/\sqrt{S_{Ref}(q)}$ (see Fig. S9(c)) by performing a coherent convolution of the molecular frame emission D_{Mult} with the alignment distribution $A(\theta', \phi')$ [33]:

$$\sqrt{S_{Mol}(q, \theta)}/\sqrt{S_{Ref}(q)} = \left| \int_{\theta'=0}^{\theta'=\pi} \int_{\phi'=0}^{\phi'=2\pi} D_{Mult}(q, \alpha(\theta', \phi', \theta)) A(\theta', \phi') \sin \theta' d\phi' d\theta' \right| / \sqrt{S_{Ref,R}(q)}. \quad (\text{S11})$$

α is the angle between the laser polarization (linear) and the molecular axis, θ is the angle between the main axis of the prolate alignment distribution $A(\theta', \phi')$ and the laser polarization, and (θ', ϕ') are, respectively, the angles with respect to the distribution axis and in a plane perpendicular to that axis. The angles are related via a frame transformation [29]: $\cos \alpha = \cos \theta \cos \theta' - \sin \theta \sin \theta' \sin \phi'$. We use an alignment distribution $A(\theta', \phi')$ of degree of alignment $\langle \cos^2 \theta' \rangle = 0.55$, based on our experimental conditions ($P_{back}=2$ atm., $T_{rot}=30\text{-}40\text{K}$, $I_{align}=3 \times 10^{13}$ W/cm²) and supported by a time-dependent Schrödinger equation calculation of prompt alignment in these conditions for Br_2 [34]. The corresponding alignment distribution $A(\theta')$ has an analytical form [29] and the dependence on ϕ' is lost by cylindrical symmetry. The missing Ω^2 prefactor in eq. (S11) [33] is implicitly included via the calculated spectral (purely real) amplitudes $c_j(q)$ in eq. (S10) and cancels out since eq. (S11) is a ratio. In this manner, we express the reference atom amplitude $\sqrt{S_{Ref}(q)}$ as a product of the contribution from the ionization step, included implicitly via the normalized coefficients $c_j(q)$ described earlier, and the photorecombination step via $\sqrt{S_{Ref,R}(q)}$ shown in Fig. S3(b) (top panel).

The calculated laboratory frame photorecombination (R) phase difference between the molecule and the reference

Figure S9. LAPIN experimental results: relative (a) amplitude and (b) phase. The corresponding results from our theoretical model based on the strong-field approximation including the contributions from HOMO, HOMO-1 and HOMO-2 are shown in (c) and (d). (e) The calculated laboratory frame relative amplitudes (left) and phases (right) from individual orbitals, notice the varying color scales. We use eqs. (S10-S12) and show the contribution from each orbital separately: HOMO ($j=0$, top), HOMO-1 ($j=1$, middle) and HOMO-2 ($j=2$, bottom).

atom (see Fig. S9(d)) is then obtained in the following way:

$$\Phi_{Mol,R}(q, \theta) - \Phi_{Ref,R}(q) = \arg \left[\int_{\theta'=0}^{\theta'=\pi} \int_{\phi'=0}^{\phi'=2\pi} D_{Mult}(q, \alpha(\theta', \phi', \theta)) A(\theta', \phi') \sin \theta' d\phi' d\theta' \right] - \Phi_{Ref,R}(q) \quad (S12)$$

$\Phi_{Ref,R}(q)$ is shown in Fig. S3(b).

In Fig. S9(e), we show the individual contribution of each molecular orbital ($j = 0-2$ in eq.(S10)) to the total relative amplitude (eq.(S11)) and phase (eq.(S12)) to which we add the constant $\Gamma \approx -0.9\pi$. We note that Br_2 and CO_2 have the same sequence of valence molecular orbitals. Our calculated amplitudes and phases in Fig. S9(e) compare qualitatively well with other calculations made in CO_2 using a different approach for calculating the photorecombination dipole moments [18].

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