Supplementary Information to the article “Attosecond imaging of molecular electronic wave-packets”

Experimental setup

Supplementary Figure 1: Schematic of the experimental setup. The laser beam enters at the upper left of the scheme. The part transmitted through the first beam splitter is the beam producing nonadiabatic alignment1 of the molecules in the HHG gas jet. In the lower left part of the figure, the drilled mirror based interferometer for the RABITT measurement is depicted. Here, the large annular beam is the harmonic generating beam, whereas the small central part is the probe beam for RABITT. From the focusing lens on, the setup is placed under vacuum.

The RABITT method

We detect the harmonic emission with photon energies larger than $I_p^{Ne} = 21.6$ eV by photoionizing neon atoms and detecting the released photoelectrons with a magnetic bottle electron spectrometer. Intensity spectra, corrected for the energy-dependent ionization cross-section of neon, readily yield the XUV spectral intensities.

The spectral phase $\varphi(\omega)$ of the harmonics is measured with the RABITT technique2-5. It is based on the analysis of sidebands, created in the photoelectron spectrum by absorption of one harmonic photon and simultaneous absorption or stimulated emission of one infrared (IR) photon from a weak probe beam, which is also present in the detection volume. This probe beam having the same frequency $\omega_L$ as the generating beam, this leads to the interference of two quantum paths “absorption of harmonic $q$ and absorption of 1 IR photon” and “absorption of harmonic $q+2$ and stimulated emission of 1 IR photon” at the same photoelectron energy, $(q+1)\omega_L - I_p^{Ne}$. Varying the phase of the IR probe field by varying its delay $\tau$ relative to the generating beam and thus the harmonic beam leads to a modulation of the sideband intensity $S_{q+1}(\tau)$ as

$$S_{q+1}(\tau) \propto \cos(2\omega_L \tau + \varphi_{q+2} - \varphi_q - \Delta \phi^\mu),$$

(S1)

where $\varphi_{q+2}$ and $\varphi_q$ are the spectral phases of harmonics $q+2$ and $q$, respectively, and $\Delta \phi^\mu$ is a small phase correction, characteristic of the target gas, which can be calculated for rare gas atoms3,4.

Extracting the phase of the oscillating sidebands via a Fourier transform thus yields the relative phase of neighbouring harmonic orders $q$ and $q+2$, and thus the group delay, also called emission time

$$t_e(q+1) = (\partial \varphi / \partial \omega)|_{q+1} \approx (\varphi_{q+2} - \varphi_q)/(2\omega_L).$$

(S2)
The RABITT method can be complemented by using the interference of the probe beam with the generating beam in the HHG medium, that leads to a small modulation of the total harmonic yield \( \propto \cos (\omega_0 t + \alpha_0) \). The phase of this modulation serves as a reference for the sideband phases in our measurements, leading to the determination of a ‘time reference’ for the group delay values, modulo \( \pi/\omega_0 \), on a scale where \( t=0 \) is located at an extremum of the generating IR field.

The experimental observable is thus the derivative of the spectral phase \( \varphi(\omega) \) with respect to frequency and \( \varphi(\omega) \) is obtained by concatenating the measured relative phases. The spectral phase is thus determined up to an integration constant \( \varphi_0 \).

**Details on the phase data analysis**

In a series of RABITT scans where the molecule alignment angle is varied and experimental conditions otherwise remain the same, the ‘time reference’ fluctuates over a narrow range (typically \( \pm 50 \) as), see Supplementary Fig. 2a. For instance, at 30° and 80°, almost all group delays are shifted downwards, indicating a modification of the ‘time reference’. We have never observed a systematic shift of the ‘time reference’ with the angle: in another series of measurements, such shifts occur at different angles. Therefore, the observed shifts are probably a measurement error rather than a real single-molecule effect. Albeit being small, these fluctuations induce rather large errors in the integration performed to obtain the spectral phases. This is the reason why we usually remove them.

To this end, we choose a sideband order where we suppose that the group delay does not vary with the angle – in general the lowest order: sideband 16 – and normalize all curves in the series to the average value for this sideband. The chosen value for the ‘time reference’ is thus not arbitrary but an average over random fluctuations. The result is shown in Supplementary Fig. 2b. These data are then integrated to obtain the spectral phases for each alignment angle. Note that the same integration constant is used for all angles.

For the argon reference scan (shown in the Supplementary Fig. 3), it turns out that the group delay at sideband 16 is almost the same (+2.7 as) as the average value for sideband 16 obtained from the different \( N_2 \) curves. In the integration of the group delay to obtain the spectra phase, the integration constant is set to the same value as in \( N_2 \).

**Supplementary Figure 2: Fluctuation of the ‘time reference’ for the group delays.** In both panels, dashed lines mark the group delays measured for the argon reference, with the line colors corresponding to the sideband order. (a) ‘Raw’ group delays extracted for each sideband in a series of RABITT scans for \( N_2 \) for alignment angles from 0° to 90°. Clearly, the dominating variation of the group delay with angle is irregular and reproduced by every sideband. It is due to fluctuations of the ‘time reference’. (b) Group delays after the values for each individual angle were shifted such that the group delay at sideband 16 is the same and equal to the average value of the fluctuating data. Integrating these data (i.e. concatenating the group delays of subsequent sidebands for each individual alignment angle) yields the spectral phases for nitrogen at the individual alignment angles and for the argon reference. The difference between the two is then the sought-for dipole phase, shown in Fig. 2b of the main paper.
In summary: (i) the recombination dipole phase, obtained as the difference between the spectral phases for the molecule and the reference atom, is set to zero at harmonic 15 for all angles (by always using the same integration constant). (ii) The recombination dipole phase is also set to zero at harmonic 17 for all alignment angles (by setting the same group delay at sideband 16 for all scans).

Point (i) concerns two issues. First, it contains the ‘absolute’ phase difference between the H15 emissions from N2 and argon as a function of alignment angle. In our experiments, we do not measure it but it could be accessed through the gas mixing method\textsuperscript{7-9}. We assume an angle-independent H15 phase, which is supported by recent interferometric experiments\textsuperscript{10} demonstrating a very weak angular dependence of the phase of low harmonics in N$_2$. Second, it also implicitly includes any constant phase such as the theoretical correction $-\delta$\textsubscript{r}, which removes the scattering phase shift and allows a plane-wave tomographic reconstruction. Since the latter correction is not known, the H15 phase difference is an adjustable parameter which is chosen in order to get the most consistent tomographic reconstructions.

Obviously, a global phase shift transfers amplitude from the real to the imaginary part and vice versa, i.e. if it has the ‘wrong’ value, the separation into HOMO and HOMO-1 is lost.

In point (ii), we decide to dismiss the ‘angle-dependent time reference’ information that can in principle be extracted from RABITTT measurements, because we are convinced that in our data, this information is dominated by noise. Note that the group delay variation is obtained from the interference of two-photon transitions in the detection gas, visible on the sidebands (see paragraph ‘The RABITTT method’), whereas the ‘time reference’ is obtained from the interference of the IR generating and probe beams in the HHG medium – so the two pieces of information really stem from different processes occuring at different parts of the setup. Setting the same ‘time reference’ for all angles due to the limited precision of its measurement simply means that we neglect a possible (small) angle-dependent linear component of the dipole phase.

The phases resulting from the above procedure are shown in Fig. 2b) and used for the reconstructions presented in Fig. 4.

**Intensity calibration**

The effective harmonic generation intensity for the measurements reported here is determined via both the experimentally observed cut-off position and the ‘attochirp’, i.e. the slope of the measured group delay vs. harmonic order. For rare gas atoms, it has been shown that the harmonic group delay, also called emission time, agrees with recombination instants calculated with the SFA model\textsuperscript{3}. The slope of the calculated recombination times is inversely proportional to the generating laser intensity.

![Supplementary Figure 3: Determination of the effective experimental intensity.](image)

Supplementary Figure 3: Determination of the effective experimental intensity. The red and blue lines show recombination times for argon ($I_p=15.76$ eV), calculated by solving the saddle-point equations of the SFA model for an intensity of $1.2\times10^{14}$ W cm$^{-2}$ and $1.0\times10^{14}$ W cm$^{-2}$, respectively. Only the points for the short trajectory contribution are shown. They have been shifted by -240 as in order to facilitate direct comparison with the experimental group delay of the argon reference measurement (squares), used for the study presented in this paper.
Comparing to the measured emission times thus allows determining the effective generation intensity in the experiment. Supplementary Figure 3 shows such a comparison with the argon reference measurement used in the study reported here. The spectral position where the emission time saturates marks the cut-off position and agrees best with a calculation for $1.2 \times 10^{14}$ W cm$^{-2}$. The mean slope of the experimental emission time falls between the simulations for $1.2 \times 10^{14}$ W cm$^{-2}$ and $1.0 \times 10^{14}$ W cm$^{-2}$. Had we used the smaller intensity for the calculations discussed in this paper, the conclusions would have been the same. Notably, the harmonic order where the continuum-phase difference $\Delta \phi_c$ takes the value of $-\pi$ (cf. Fig. 3a of the main paper), would only shift from 25 to 23 in this case. A calculation analogous to that shown in Fig. 1b of the main paper would give a shift of -50 as of the attosecond pulse peak when varying the HOMO-1:HOMO ratio of the contributions to HHG from 0:1 to 2:1.

**Error estimation for the attosecond pulse timing**

The error bar for individual group delay measurements is given by the standard deviation of the phase within the FWHM of the $2\omega_0$ peak in the RABITT trace Fourier transform. This error amounts to typically ±30 as (see, e.g., Supplementary Figure 3). This value gives an upper limit for the fluctuations of the attosecond pulse peak position due to experimental uncertainties. Another way of testing the reliability of the temporal shift shown in Fig. 1a of the main paper is to perform a statistical study of the pulse peak positions obtained with several measurements under same conditions. The result is shown in Supplementary Figure 4. In panel a, we show the pulse peak positions obtained in two series of RABITT scans for alignment angles $\theta$ from 0° to 90° in steps of 10° under same experimental conditions (i.e. gas pressure, pulse energies and focusing conditions), but independent from another on different days. For each point, the group delay for H17 was normalized to the same value. The two series show the same trend, as confirmed by the linear fits, which are almost parallel. The smooth, almost monotonic shift is thus reproduced in a second data acquisition run. The data used in the main paper is the one represented by the diamonds in Supplementary Figure 4a. The small offset between the two series may be due to a small difference of the effective HHG driving laser intensity.

To improve statistics somewhat, we average in Supplementary Figure 4b the pulse peak positions from these two series and several other measurements done for $\theta = 0°$ and $\theta = 90°$. All these data have been obtained under equal experimental conditions (i.e. gas pressure, pulse energies and focusing conditions), but independent from each other on different days. The error bars attributed to the averaged pulse peak positions indicate the range over which the averaged values fluctuate. Including more measurements in the analysis, the value of the temporal shift between $\theta = 0°$ and $\theta = 90°$ remains -50 as, with error bars of ±20 as on each point. For the intermediate angles, the error is essentially given by the offset between the two series shown in panel a.

Supplementary Figure 4: Error estimation for the attosecond pulse peak position. (a) Two independent series of RABITT scans with 10° steps in $\theta$ show the same trend, confirmed by the linear fits that are almost parallel. (b) Averaging these two series as well as other scans for $\theta = 0°$ and $\theta = 90°$ obtained under same conditions confirms the shift between the attosecond emission for $\theta = 0°$ and $\theta = 90°$, and its significance compared to the timing fluctuations due to experimental uncertainties.
Influence of the Cooper minimum on the argon reference

Using argon as a reference in order to calibrate the re-colliding wavepacket complex amplitude becomes questionable in the region of the Cooper-minimum\textsuperscript{11,12}. In HHG, this leads to a minimum of the spectral intensity at a photon energy of 51 eV as well as a (theoretically predicted) phase variation of 2.6 rad over a width of 20 eV around this position\textsuperscript{13}. For a 795 nm laser, this leads to the spectral minimum appearing at H33 and the phase variation would spread from H27 to H39. This corresponds to an average variation of 0.4 rad between two odd harmonic orders, and thus a group delay shift of 0.4 rad / 2\omega_c = 90 as.

In our argon reference scan, the last group delay value, measured for SB30, is indeed \approx 80 as lower than the previous point instead of saturating as expected from the SFA result (see Supplementary Figure 2). This variation is reproduced in other measurements done with argon on the same day, i.e. under (as close as possible) equal conditions, without, however appearing systematically. We thus consider it as a variation linked to the precise experimental conditions rather than due to a phase jump linked to the Cooper minimum. Data taken with the same laser and a similar setup as used for our experiments show that no significant deviation of the group delay measured for argon from the SFA calculation is observed up to\textsuperscript{14} SB32.

If there is a signature of the Cooper minimum in our argon reference data, then it only appears on the very last harmonic order, H31. It may thus amplify the increase of the amplitude ratio (Fig. 2a of the main paper) as well as the increase of the phase difference (Fig. 2b of the main paper). However, it cannot explain the qualitative features discussed in our paper.

Phase difference, $\Delta \phi_c$, accumulated during the continuum excursion

The quantum paths contributing to HHG are associated with an accumulated phase given by the action along the path\textsuperscript{1}

$$S([t_i, t_r, \vec{p}]) = \hbar \omega L \left[ \int_{t_i}^{t_r} \frac{1}{2} \left( \frac{\vec{p} + A(t')}{m} \right)^2 - e \right] dt', \quad (S3)$$

where $t_i$ and $t_r$ are the instants of ionization and recombination, respectively, $\vec{p}$ is the electron drift momentum, $A(t')$ is the vector potential of the driving laser field and $e$ is the bound state energy (e.g. for the HOMO, $e = -I_p$).

An infinite number of quantum paths contribute to the emission of each harmonic order. However, in the strong field regime\textsuperscript{15}, only a few closed quantum paths with stationary phase dominate, meaning that they satisfy $\delta S([t_i, t_r, \vec{p}]) = 0$. We only consider the quantum paths with the shortest electron excursion times $\tau = (t_r - t_i)$ (i.e. the ‘short’ trajectories dominating our experimental signal), thus associating each harmonic frequency $q\omega_L$ with a single quantum path. Varying $e$, the phase for this quantum path changes by (for $\Delta e$ small against $p^2/2$):

$$\Delta \phi_c(\omega) = \frac{dS}{de} \bigg|_{e=\text{const.}}$$

$$\Delta e = \left[ (t_r - t_i) + \frac{\partial S}{\partial t_r} \frac{\partial t_r}{\partial e} + \frac{\partial S}{\partial t_i} \frac{\partial t_i}{\partial e} + \frac{\partial S}{\partial p} \frac{\partial p}{\partial e} \right] \Delta \omega = \Delta e \tau. \quad (S4)$$

Gauge dependence of orbital tomography

The recombination dipole, for a single orbital $\psi$ of energy $e$, reads in the length and velocity form respectively:

$$\vec{d}_{len}(\vec{k}) = \int [\psi(\vec{r})]^* \vec{r} e^{i\vec{k} \cdot \vec{r}} d\vec{r} \quad (S5)$$

$$\vec{d}_{vel}(\vec{k}) = \frac{i\vec{k}}{2\epsilon} - e \int [\psi(\vec{r})]^* e^{i\vec{k} \cdot \vec{r}} d\vec{r} \quad (S6)$$

Expressions (1) and (2) in the main text make use of the former. Both forms would be rigorously equal if plane waves were molecular scattering eigenstates. This is however not the case, which makes the tomographic procedure gauge dependent. When confronting the experimental and simulated
reconstructions for the HOMO in the length gauge (Fig 4a,c) on the one hand, and in the velocity gauge (Supplementary Fig 5a,b) on the other hand, it is noticeable that the length gauge is more suited to our study, confirming previous predictions\textsuperscript{16}.

**Imaginary part of the experimental reconstructions**

Imposing a $\sigma_g$ (respectively $\pi_u$) symmetry to both real and imaginary parts of the experimental dipole transfers the inappropriate HOMO-1 (respectively HOMO) contribution into the imaginary part of the reconstructed orbital. We show in Supplementary Figure 6a the imaginary part associated with the experimental real-valued HOMO reconstruction (Fig. 4a in the main text). It has to be compared to the imaginary-valued simulated reconstruction obtained by computing the HOMO-1 dipole from $0^\circ$ to $90^\circ$ and extrapolating it up to $360^\circ$ enforcing the HOMO symmetry (Supplementary Figure 6b). Despite being \textit{a priori} unphysical, these reconstructions, when compared to each other, confirm the analysis and interpretation of our experimental data.

**Supplementary Figure 5: Tomography in the velocity gauge.** (a) Experimental and (b) simulated reconstructions of the HOMO in the velocity gauge. The agreement is less satisfactory than in the length gauge (Fig. 4a,c).

**Supplementary Figure 6: Spurious contributions to the reconstructions.** (a) Imaginary part of the experimental reconstruction in the HOMO symmetry and (b) imaginary-valued simulated reconstruction from the HOMO-1 dipole with the HOMO symmetry enforced, see text. Both were performed in the length gauge. The difference in sign, also seen in Fig. 4b,d is consistent with the $-\pi$ phase accumulated by the HOMO-1 contribution in the HHG process (see main text). The agreement between experiment and simulation supports the main conclusions of our work.
Importance of the phase in the reconstructions

In order to emphasize the major role of the dipole phases in obtaining correct reconstructions, we have applied the tomographic procedure to the experimental dipole with enforced constant phases, which has the consequence to merge the HOMO and HOMO-1 contributions, and to smooth out all structural phase jumps. Supplementary Figure 7 displays the result obtained when enforcing the HOMO symmetry: the signatures characterizing the HOMO, that are present in the correct experimental reconstruction (Fig. 4a in the main text), have now disappeared in favour of the dominating HOMO-1 contribution (displayed alone in Supplementary Figure 6a with the same symmetry).

Supplementary Figure 7: Experimental reconstruction without the phase. Reconstruction from the experimental dipole with the HOMO symmetry, when enforcing a constant phase over the whole span. The results now contains both HOMO and HOMO-1 contributions, and is dominated by the latter (relative weights can be seen in the color-scales of Fig. 4a,b)

References