in figure 1(a), leading to the appearance of sidebands in between the harmonic peaks (SB38, SB40, SB42) [30, 31]. The energy scale is the total photon energy absorbed in the process (this will be used throughout the article). As shown in figure 1(c), when the delay τ of the IR field relative to the XUV is varied, the intensity of the sidebands oscillates at twice the fundamental frequency according to:

$$I_{n+1}(E_f,\tau) = |A_{n+2-1}(E_f)|^2 + |A_{n+1}(E_f)|^2 + 2|A_{n+2-1}(E_f)||A_{n+1}(E_f)| \times \cos[2\omega_0\tau - \Delta\phi_{XUV}(E_f) - \Delta\varphi_A(E_f)], \quad (3)$$

where E_f is the total energy absorbed, A_{n+1} (A_{n+2-1}) is the complex two-photon transition amplitude corresponding to the absorption of harmonic H_n (H_{n+2}) and the absorption (emission) of one IR photon, respectively, $\Delta\phi_{XUV}$ is the phase difference between two consecutive harmonics, and $\Delta\varphi_A$ is the phase difference between the two-photon transition dipole matrix elements.

The usual implementation of the RABBIT technique consists in integrating $I_{n+1}(E_f,\tau)$ over energy inside each sideband $n+1$ and extract the phase of the $2\omega_0$ oscillations, giving direct access to $\Delta\phi_{XUV}+\Delta\varphi_A$ [19]. Due to the generation mechanism of the high-order harmonics, the XUV pulse train carries an intrinsic quadratic phase, the attochirp, which leads to the approximately linear increasing phase difference $\Delta\phi_{XUV} = \phi_{n+2} - \phi_n$ between consecutive harmonics [31]. The aluminum foil used to filter out the IR after the gas cell partly compensates for this effect [32]. The phase $\Delta\varphi_A$ arises from the two-photon ionization process. In the case of non-resonant ionization, this phase is smoothly varying [33]. In contrast, when one of the paths goes through a bound or quasibound intermediate state [34, 35], $\Delta\varphi_A$ strongly varies with the detuning from the resonance. For instance, when H39 is resonant with $sp2^+$ (see figure 1), $\Delta\varphi_A$ for SB38 and SB40 is affected, while $\Delta\phi_{XUV}$ remains the same. By scanning H39 across the resonance and recording the corresponding RABBIT traces, the spectral variation of $\Delta\varphi_A$ can be recovered. Note, however, that the integration over the sidebands results in a mean value of $\Delta\varphi_A$ over the harmonic bandwidth. In our conditions, the spectral bandwidth of the generated harmonics, equal to 180 meV, is much larger than the $sp2^+$ resonance width (table 1), which results in a strong smoothing of the spectral evolution of $\Delta\varphi_A$ (see supplementary material of [25]).

2.3. Rainbow RABBIT

The high spectral resolution of our spectrometer allows us to use the Rainbow RABBIT technique [25] to directly retrieve the phase variation across the resonance, i.e. $\Delta\varphi_A(E_f)$, by analyzing the $2\omega_0$ oscillations at each energy E_f inside the sidebands (see white lines in figure 1(c)). A single RABBIT trace in resonant conditions may then give access to the full phase information around the resonance.

We compared two different techniques to extract the phase of the sidebands. The first one relies on the fitting of the oscillations of the sidebands based on equation 3 for each energy. The second one is based on the extraction of the phase of the Fourier-transformed oscillations. Both methods give almost identical results. All the phase measurements presented in this article were obtained using the fitting technique.

To extract the amplitude of the resonant two-photon EWP, we Fourier transform the sideband intensity $I_{n+1}(E_f,\tau)$ and extract the signal oscillating at frequency $2\omega_0$ [$\Delta I_{n+1}(E_f)$]. This allows us to eliminate the first two terms in equation (3) which are delay-independent, and contribute to noise. $\Delta I_{n+1}(E_f)$ is the product of the amplitude of the resonant transition with the amplitude of the non resonant transition. For example, for sideband 38, $\Delta I_{38}(E_f) = 2|A_{37+1}(E_f)||A_{39-1}(E_f)|$ where A_{39-1} is the amplitude of the resonant two-photon transition and A_{37+1} is the amplitude of the non resonant transition which is used as reference. To isolate only the resonant amplitude, i.e. $|A_{39-1}(E_f)|$, the same procedure is performed with a non resonant sideband, SB44 (not visible in figure 1), where both paths are non resonant. Assuming that all the non resonant amplitudes are similar, $A_{37+1} \approx A_{43+1} \approx A_{45-1}$, the amplitude of the resonant EWP can be extracted according to [25]:

$$|A_{39-1}| = \frac{\Delta I_{38}}{\sqrt{2\Delta I_{44}}}. \quad (4)$$

2.4. Theoretical description

We use an analytical model introduced in [36], whose validity has been checked against fully correlated *ab-initio* calculations [37]. The interaction between the IR and XUV pulses and the atom is treated within the framework of second-order time-dependent perturbation theory. The spectral amplitudes of the light fields are given by

$$\mathcal{E}_{IR}(\omega,\tau) = \mathcal{E}^0_{IR} e^{i\omega_0\tau} \exp\left[-\frac{(\omega-\omega_0)^2}{2\sigma^2_{IR}}\right]$$
$$\mathcal{E}_{XUV}(\Omega) = \mathcal{E}^0_{XUV} \exp\left[-\frac{(\Omega-\Omega_0)^2}{2\sigma^2_{XUV}}\right], \quad (5)$$

where σ_{IR}, σ_{XUV} are the bandwidths of the IR and XUV fields respectively. ω, Ω denote the IR and XUV photon frequencies, while ω_0, Ω_0 are the respective central frequencies. $\mathcal{E}^0_{IR}$ and $\mathcal{E}^0_{XUV}$ are constant amplitudes. The two-photon transition amplitude