effects, ranging from a smoothing of the amplitude and phase of the two-photon EWP to a modification of the oscillation frequency of the sidebands. For nonresonant transitions, such that M_{fg} does not depend on the frequency over the pulse bandwidth, equation 6 is a convolution of the one-photon wave packet with the IR pulse. On the contrary, in the case of ionization through an autoionizing state, due to the strong frequency dependence of $M_{\mathrm{fg}}(\Omega)$, the two-photon wave packet cannot be approximated as the convolution of the one-photon wave packet with the IR pulse. This leads to a smoothing of both amplitude and phase which cannot be corrected by the deconvolution algorithm. In our experimental conditions, the large bandwidth of the IR pulse (135 meV) prevents us from approximating the measured amplitude and phase to those of the one-photon wave packet as evidenced in figure 4(b).

3.3. Harmonic blueshift

As described in section 2.1, the high-order harmonics are produced by focusing (part of) the laser beam in a gas cell. The laser intensity is high enough so that the front of the pulse can partially ionize the medium, thus creating a low density plasma in which the pulse propagates. The interaction of the IR pulse with the plasma leads to a blue shift of the laser central frequency that results in harmonics separated in frequency by $2(\omega_0 + \delta_\omega)$ [41]. Since the probe IR pulse does not propagate through the gas cell and is thus not blue-shifted, the contributions from the lower and higher harmonics to the sideband do not perfectly overlap in frequency. In the absence of blue shift, the quadratic phase variation *inside* the harmonic lines (due to the harmonic chirp, not to be confused with the atto-chirp [42, 43]) does not influence our measurement. Indeed, the variations of $\phi_{\mathrm{n}+2}$ and ϕ_{n} are similar over the pulse bandwidth so that $\Delta\phi_{XUV}$ only contributes to a constant phase in equation 3. In the presence of a blue shift, $\Delta\phi_{XUV}$ varies linearly with frequency, with a coefficient equal to $-8\delta_\omega\phi''_{\mathrm{n}}$, where ϕ''_{n} is the harmonic group delay dispersion. In the experimental results, a linear phase variation was indeed observed for the nonresonant sidebands. This linear phase is removed in all the results presented below.

4. Results

4.1. Spectral domain

The $\mathrm{sp2}^+$ and $\mathrm{sp3}^+$ resonances are independently excited by tuning respectively harmonics 39 and 41 to the autoionizing states. When harmonic 39 is resonant with the $\mathrm{sp2}^+$ resonance, a clear amplitude modulation of the two-photon wave packet extracted from SB38 is observed [figure 4(a)]. In particular, due to the broad harmonic profile, the amplitude exhibits a double structure which results from the ionization via both resonant and non-resonant continua. The first peak, centered at $E_{\mathrm{f}} = 58.6$ eV, and the dip at $E_{\mathrm{f}} = 58.7$ eV result from ionization via the $\mathrm{sp2}^+$ resonance (green dashed line) and present the typical constructive and destructive interferences characteristic of the Fano profile. The second peak, centered at $E_{\mathrm{f}} = 58.8$ eV, originates from the ionization via a non resonant continuum which is probed by the high energy part of the harmonic. When harmonic 41 is resonant with the $\mathrm{sp3}^+$ state, the amplitude of the sideband oscillations is very smooth and no clear signature of the resonance is observed in the reconstructed amplitude of the resonant EWP (not shown). The width of the $\mathrm{sp3}^+$ resonance (8 meV) is extremely small compared to that of the harmonics (180 meV) and IR pulse (135 meV), and the strong broadening of the resonance profile by the finite pulse effects leads to a smooth EWP amplitude.

Figure 5 displays the phases measured for sidebands 38, 40 and 42 when harmonic 39 is resonant with the $\mathrm{sp2}^+$ state (upper row) and when harmonic 41 is resonant with the $\mathrm{sp3}^+$ state (lower row). As in figure 4(b), we only show the frequency interval such that the phase can be extracted with good accuracy. For both resonances, we can measure a clear phase variation induced by the resonance while the third non resonant sideband, shown for comparison (either SB42 in the first row or SB38 in the second row), exhibits a flat phase, since the two-photon ionization occurs through a smooth continuum. As expected, the phase variations observed for the sidebands where the resonance is one IR photon above or below are similar, except for an opposite sign. For the $\mathrm{sp2}^+$resonance, a fast phase variation of 1.2 rad is observed across the resonant part of the sideband. For the $\mathrm{sp3}^+$ resonance, despite the smooth amplitude of the resonant wave packet, a phase variation of 0.3 rad is measured, indicating that the EWP is strongly affected by the $\mathrm{sp3}^+$ state. However, despite their similar q values, the phase jump measured for the $\mathrm{sp3}^+$ is smaller than the one measured for the $\mathrm{sp2}^+$ state. The difference between the phases measured for the two autoionizing states originates from the fact that the width of the $\mathrm{sp3}^+$ resonance is almost four times narrower than that of the $\mathrm{sp2}^+$ state and is consequently much more sensitive to the finite pulse effects. In general, phase measurements are more sensitive to the presence of a resonance than amplitude measurements. In the absence of a resonance, the phase is flat, while the amplitude reflects that of the excitation pulse. Phase measurements are thus "background-free", while