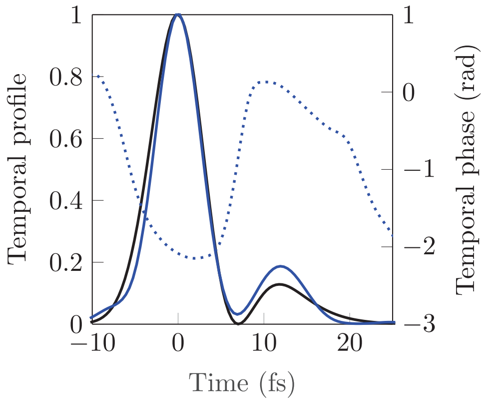

Figure 6. Reconstruction of the temporal profile of the resonant two-photon wavepacket. Temporal intensity (blue solid) and phase (blue dotted) of the EWP retrieved from the experiment. The simulated temporal intensity is shown in black line.

the direct one. As the autoionizing state decays in the continuum, the contribution of both ionization paths become comparable and strong destructive interferences between the two channels lead to a sharp decrease of the temporal intensity around $t = 8$ fs, which is followed by a revival of the EWP. When the intensity profile goes to zero, the temporal phase jumps. The intensity decreases rapidly after 12 fs, much faster than the theoretical lifetime of 17 fs (table 1). This apparently-faster decay of the autoionizing state results from the finite pulse effects and is well reproduced by simulations, indicated by the black line in figure 6 and obtained by Fourier transforming the simulated spectral amplitude [figure 4 (a)] and phase [figure 5(a)]. It occurs because the short IR pulse probes the decay during a limited amount of time (less than $\simeq$ 15 fs). This observation does not reflect a real modification of the decay rate but is only the result of the lack of spectral resolution. A similar temporal evolution was obtained in [25], with some deviation due to the different experimental conditions.

5. Time-frequency representation

5.1. Time-limited Fourier transform

The spectral and temporal domains provide distinct and complementary pictures of the autoionization dynamics. Similarly to what is done in ultrafast optics to characterize optical wave packets, new insights on the ionization process can be gained by representing the evolution of electronic wave packets in the time-frequency space. This can be achieved by using time-frequency representations, e.g. based on inverse Fourier transforms of the complex temporal amplitude of the wave packet with a temporal window. These transforms can be generally written as

$$S(E_\mathrm{f}, t) = \int_{-\infty}^{+\infty} \mathrm{d}\tau\ \tilde{A}_{\mathrm{n}+1}(\tau)\alpha(\tau - t)\exp\left(-i\frac{E_\mathrm{f}\tau}{\hbar}\right), \quad (10)$$

where $\tilde{A}_{\mathrm{n}+1}(\tau)$ is the Fourier transform of $A_{\mathrm{n}+1}(E_\mathrm{f})$ and $\alpha(\tau - t)$ is the window function used to limit the temporal extent of the Fourier transform. This function can be a Heaviside function [$\alpha(t) = \Theta(-t)$], and we refer to equation 10 as a cumulative Fourier transform (CFT) [15] ($S = S_\mathrm{C}$). We also use a Super Gaussian function: $\alpha(t) = \exp[-t^6/(2\Delta t^6)]$, where Δt is the window width (typically 15 fs). In this case, equation 10 is a short-time Fourier transform (STFT) [44] ($S = S_\mathrm{ST}$).

$S_\mathrm{C}(E_\mathrm{f}, t)$ represents the spectral amplitude accumulated until time t and its temporal variation shows how the wave packet builds up in the continuum, as shown in figure 7(a) and (b). $S_\mathrm{ST}(E_\mathrm{f}, t)$ represents the spectral amplitude emitted within the time window and shows the evolution of the instantaneous frequencies emitted in the continuum [figure 7(c) and (d)]. Both representations indicate that during the first 5 fs, a smooth gaussian-like EWP emerges in the continuum. The shape of the wave packet reflects that of the ionizing pulse, revealing that the direct ionization is dominant. Passed this time, the direct and resonant paths start interfering giving rise to destructive interferences at the center of the wave packet (around $E_\mathrm{f} = 58.7$ eV) and constructive interferences on both sides. After 8 fs, the two representations start to differ. The STFT shows that the interferences disappear and a weak, spectrally narrow decay is observed around 58.6 eV. The XUV pulse has then passed the interaction region and the atoms cannot be directly ionized. However, the sp2$^+$ state can still decay in the continuum thus giving rise to this weak decay. In contrast, the CFT barely changes after 8 fs because of the small contribution from the decay to the accumulated spectral amplitude. Finally, figure 7(e) shows a STFT obtained from simulations carried out with a long IR pulse. In this case, a decay corresponding to a 17 fs lifetime can be observed.

5.2. Wigner representation

The Wigner distribution (WD) is an alternative way of representing the time-frequency structure of the wave packet [45, 44]. Contrary to the STFT, the WD does not require gating the Fourier transform with an arbitrarily chosen window function. The WD can be defined both in the time and frequency domains as

$$W(E_\mathrm{f}, t) = \int_{-\infty}^{+\infty} \mathrm{d}\tau\ \tilde{A}_{\mathrm{n}+1}\left(t + \frac{\tau}{2}\right)\tilde{A}^*_{\mathrm{n}+1}\left(t - \frac{\tau}{2}\right)\exp\left(\frac{-iE_\mathrm{f}\tau}{\hbar}\right)$$

$$= \frac{1}{2\pi}\int_{-\infty}^{+\infty} \mathrm{d}\varepsilon\ A_{\mathrm{n}+1}\left(E_\mathrm{f} + \frac{\varepsilon}{2}\right)A^*_{\mathrm{n}+1}\left(E_\mathrm{f} - \frac{\varepsilon}{2}\right)\exp\left(\frac{i\varepsilon t}{\hbar}\right) \quad (11)$$