which takes into account the extended bandwidths of both IR and XUV pulses, can be approximated, in the case of IR photon absorption, as

$$A_{n+1}(E_f) = -i\hbar \int_0^\infty d\Omega\, \mathcal{E}_{IR}(\Omega_{fg}-\Omega,\tau)\mathcal{E}_{XUV}(\Omega)M_{fg}(\Omega), \quad (6)$$

where $\Omega_{fg} = (E_f - E_g)/\hbar$. The index $n+1$ indicates that we consider absorption of the nth harmonic plus one IR photon (see equation 3). The two-photon transition matrix element M_{fg} can be written as:

$$M_{fg}(\Omega) \propto \sum\!\!\!\!\!\!\int dE \frac{\langle\psi_{E_f}|T|\Psi_E\rangle\langle\Psi_E|T|g\rangle}{E_g + \hbar\Omega - E + i0^+}, \quad (7)$$

where $|g\rangle$ is the ground state $1s^2$, $|\Psi_E\rangle$ is the intermediate state and $|\psi_{E_f}\rangle$ is the final state. These states are respectively at the energies E_g, E and E_f and are coupled by the dipole transition operator T. The calculation of the two-photon transition matrix element requires to sum over all the intermediate discrete or continuum states.

Our theoretical derivation follows the well-known formalism developed by U. Fano [5] to account for the interaction between the continuum channels and the quasi-bound states and generalizes it to include the influence of a weak IR field, in the perturbative limit. Fano's theoretical approach consists in calculating the eigenstates of $H = H_0 + V$, where V couples the bound state $|\varphi\rangle$ and the nonresonant continuum states $|\psi_E\rangle$ of the unperturbed Hamiltonian H_0. Following Fano's formalism, one can easily relate the eigenstates of H, $|\Phi\rangle$ (with energy E_Φ) and $|\Psi_E\rangle$ with those of H_0, $|\varphi\rangle$ and $|\psi_E\rangle$ [5]. The asymmetry parameter q introduced in equation (1) is equal to

$$q = \frac{\langle\Phi|T|g\rangle}{\pi V_E^*\langle\psi_E|T|g\rangle}, \quad (8)$$

where $V_E = \langle\psi_E|V|\varphi\rangle$. The autoionizing state bandwidth Γ is equal to $2\pi|V_E|^2$.

As shown in [36], the effect of an autoionizing resonance in the intermediate state of a two-photon absorption process can be taken into account by multiplying the nonresonant two-photon matrix element M_{fg} calculated using unperturbed wavefunctions $|\psi_E\rangle$ by $R(\epsilon, q_{eff})$, which includes the effect of the resonance. The effective parameter q_{eff} is complex and equal to $q(1-\gamma) + i\gamma$, where γ is a real parameter that depends on the relative strength of the direct transition from the intermediate bound state to the final continuum versus the nonradiative coupling of the bound state to the intermediate continuum state followed by the dipole coupling to the final continuum. Both ϵ and q are calculated at the energy $E_g + \hbar\Omega$. In the absence of a resonance in the final continuum state, γ is usually small [36]. In the present work, we used $\gamma_{sp2^+} = -0.025$, $\gamma_{sp3^+,\epsilon s} = -0.117$, $\gamma_{sp3^+,\epsilon d} = -0.390$.

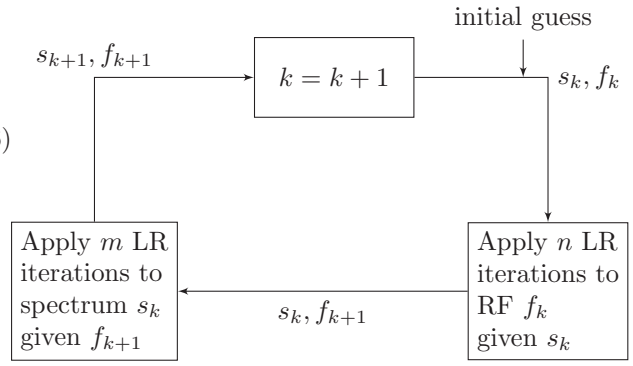

Figure 2. Principle of the deconvolution algorithm.

3. Experimental limitations

In this section, we discuss limitations which are inherent to the measurement process.

3.1. Spectrometer resolution

For each delay, the measured time of flight spectrum is a convolution of the photoelectron spectrum with the electron spectrometer response function (RF), which limits our spectral resolution. In this work, we implement a deconvolution algorithm to retrieve the real photoelectron spectrum. We assume an energy independent spectrometer response within the range of study and apply a two-dimensional iterative blind deconvolution algorithm based on the maximum likelihood Lucy-Richardson (LR) method [38, 39]. Given a measured (convoluted) spectrum S, a blind algorithm attempts to find the real photoelectron spectrum s and the RF f such that $S = f \otimes s + n$, where n is noise contamination and $\otimes$ is the convolution operator. The algorithm starts from an initial estimate of s and f. For each cycle, multiple Lucy-Richardson iterations are performed (see figure 2),

$$f_{k+1} = \frac{1}{\sum s_k} f_k s_k \star \left(\frac{S}{f_k \otimes s_k}\right)$$
$$s_{k+1} = \frac{1}{\sum f_{k+1}} s_k f_{k+1} \star \left(\frac{S}{f_{k+1} \otimes s_k}\right) \quad (9)$$

where $\star$ is the correlation operator and the symbol $\sum$ denotes the spectral integral. We impose the constraint that the RF should be Gaussian. For each cycle, the likelihood that the retrieved quantities reproduce the measured spectrum by a convolution increases. For a detailed description of the algorithm, see [40]. The RFs retrieved for the different spectra were similar, with a spectral width of 89±5 meV at full width half maximum, close to the estimated experimental resolution. This shows the stability of the deconvolution algorithm.