1 Supplementary Information

In order to determine decay rates and their associated amplitudes, the time-resolved photoelectron spectra were fitted to eq. (2) of the paper by constructing and minimising the chi-squared function using MINUIT minimisation libraries as part of ROOT scientific software.[1] The MIGRAD fitting strategy (Davidon-Fletcher-Powell variable-metric algorithm) was employed from within the MINUIT package. The errors of the parameters were derived for the 95% confidence interval.

Integrated photoelectron counts and fits across discernible portions of the time-resolved photoelectron spectra, following excitation at 269, 250, 240 and 238 nm, are presented in Fig. S1 and S2 below.

References

1 R. Brun and F. Rademakers, *Nucl. Instrum. Meth. A*, 1997, **389**, 81–86.

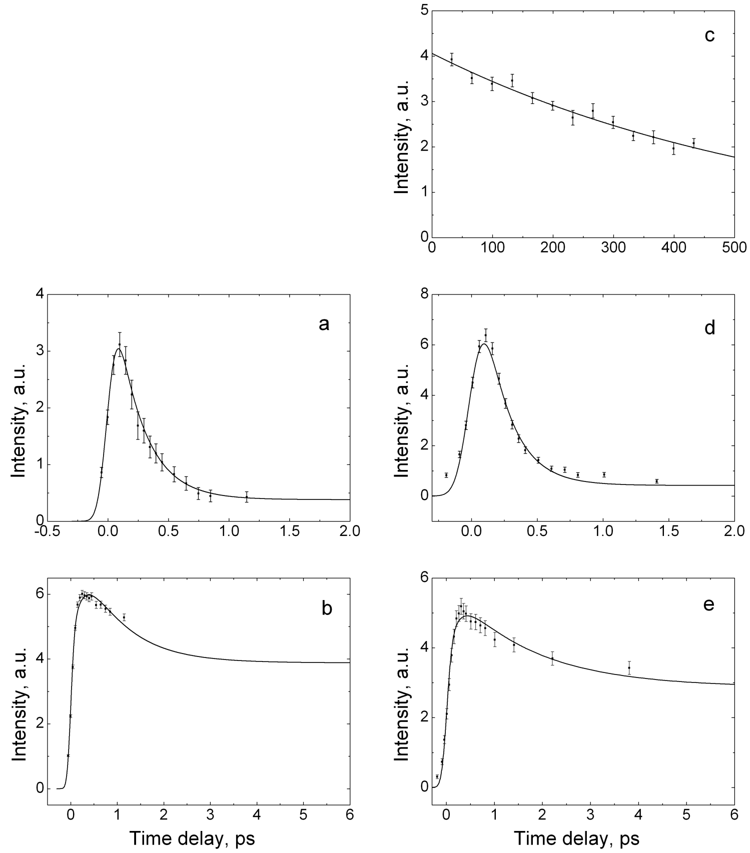

Fig. S1 Integrated photoelectron counts as a function of pump-probe delay following excitation at 269 nm (left column) and 250 nm (right column): experimental data (points with error bars representing one standard deviation) and fits (solid lines). (c) Total photoelectron signal as a function of pump-probe delay. (a) and (d) Photoelectron signal integrated over the sharp peak in the photoelectron spectrum (0.9 eV to 1.1 eV). (b) and (e) Photoelectron signal integrated over the low energy part of the photoelectron spectrum (0.48 eV to 0.72 eV).

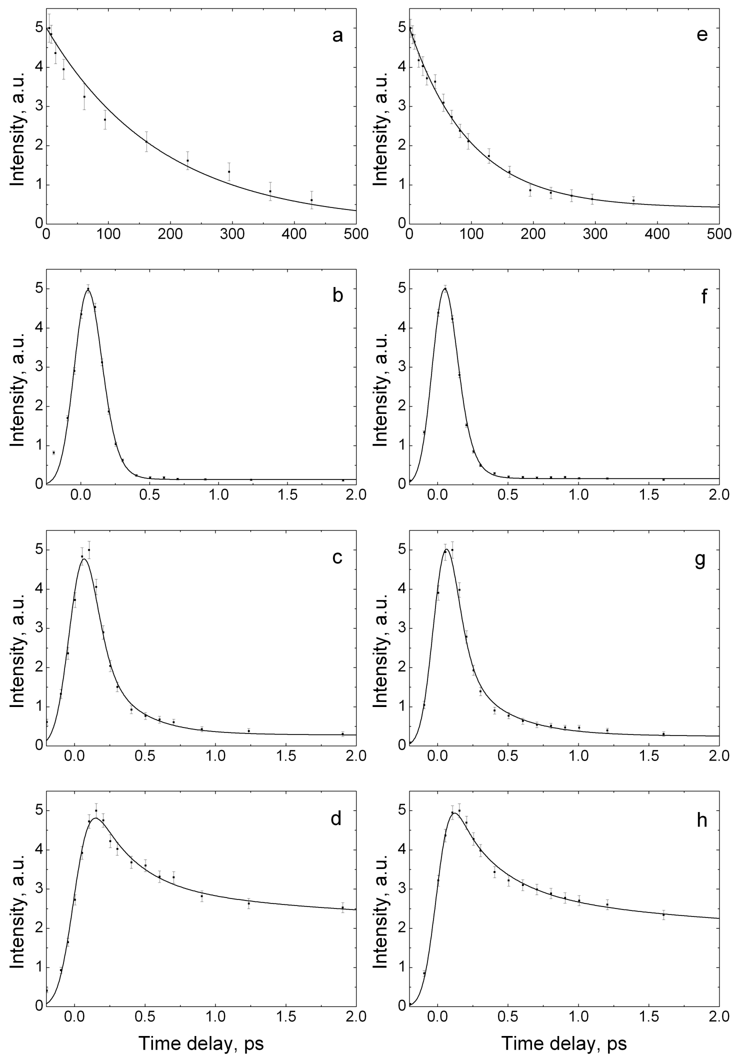

Fig. S2 Integrated photoelectron counts as a function of pump-probe delay following excitation at 240 nm (left column) and 238 nm (right column): experimental data (points with error bars representing one standard deviation) and fits (solid lines). (a) and (e) Total photoelectron signal as a function of pump-probe delay. (b) and (f) Photoelectron signal integrated over the high eKE part of the spectra (1.3 - 1.7 eV). (c) and (g) Photoelectron signal integrated over the sharp peak in the photoelectron spectrum (0.9 eV to 1.1 eV). (d) and (h) Photoelectron signal integrated over the low energy part of the photoelectron spectrum (0.48 eV to 0.72 eV).