

Electronic Supplementary Information (ESI) for 'On the formation of anions: Frequency-, angle-, and time- resolved photoelectron imaging of the menadione radical anion'

Electronic structure calculations

Menadione X²A'' CASSCF geometry

ATOM	CHARGE	X	Y	Z
C	6.0	1.7361542005	2.5046150142	0.0000000000
C	6.0	0.3987207857	2.1536165314	0.0000000000
C	6.0	-0.0025898260	0.7908050780	0.0000000000
C	6.0	0.9905488703	-0.2125033071	0.0000000000
C	6.0	2.3586600963	0.1649254610	0.0000000000
C	6.0	2.7310191841	1.4965963127	0.0000000000
H	1.0	2.0238987606	3.5486928278	0.0000000000
H	1.0	-0.3728159808	2.9078339194	0.0000000000
H	1.0	3.0991685260	-0.6202612349	0.0000000000
H	1.0	3.7789768593	1.7695618999	0.0000000000
C	6.0	0.6241515892	-1.6372529160	0.0000000000
C	6.0	-1.4371597365	0.4610268762	0.0000000000
C	6.0	-1.7677755813	-0.9398589198	0.0000000000
C	6.0	-0.7803839891	-1.9122553597	0.0000000000
O	8.0	1.4921674998	-2.5300291298	0.0000000000
O	8.0	-2.2965046001	1.3658258979	0.0000000000
C	6.0	-3.2253689743	-1.3450516735	0.0000000000
H	1.0	-3.8657998996	-0.4667005675	0.0000000000
H	1.0	-3.4693538393	-1.9474711311	-0.8809290063
H	1.0	-3.4693538393	-1.9474711311	0.8809290063
H	1.0	-1.0610071054	-2.9596394479	0.0000000000

Menadione X¹A' CASSCF geometry

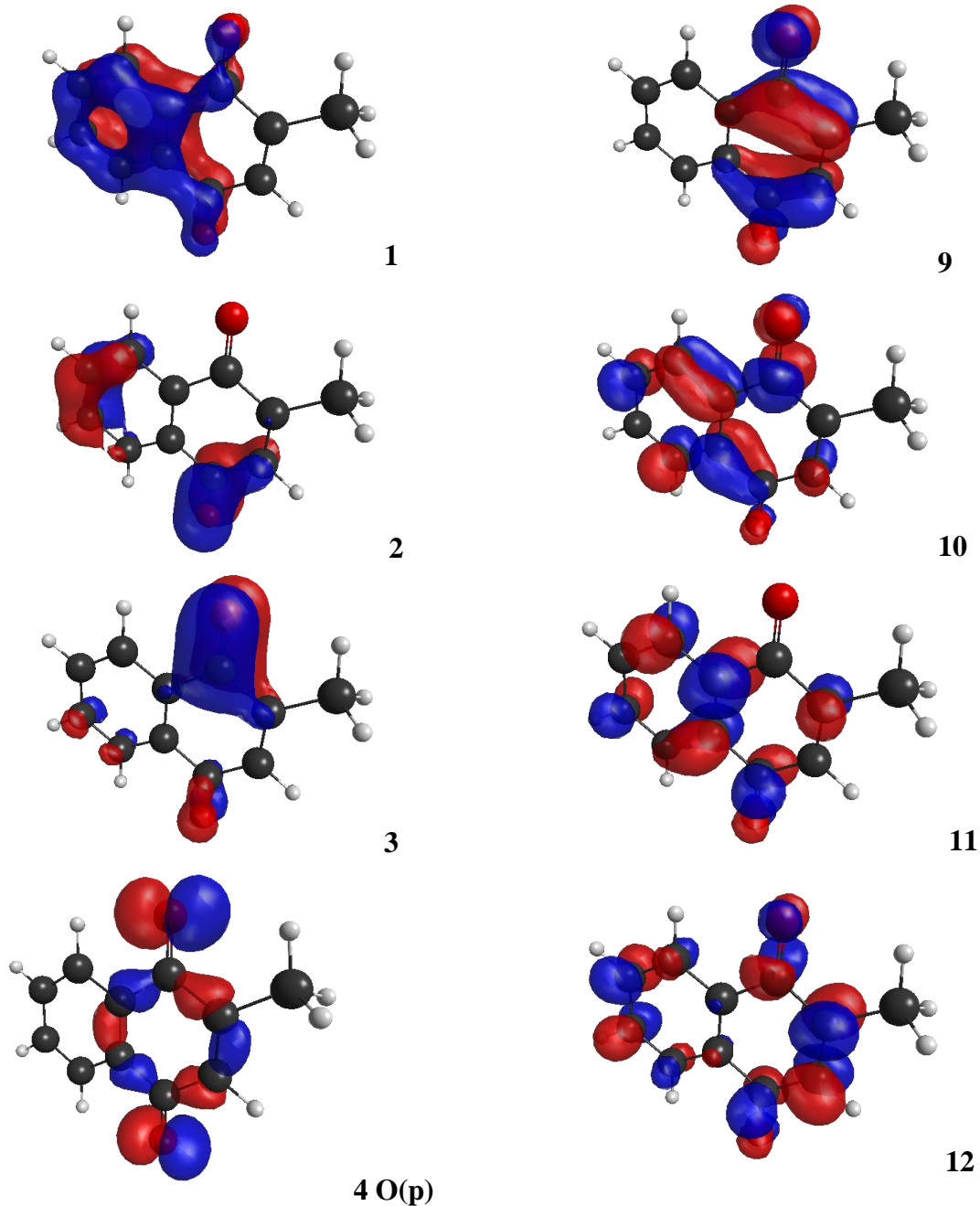
ATOM	CHARGE	X	Y	Z
C	6.0	1.7563512673	2.5142934310	0.0000000000
C	6.0	0.4080898147	2.1653182901	0.0000000000
C	6.0	0.0323800228	0.8123362338	0.0000000000
C	6.0	1.0201090211	-0.1834285956	0.0000000000
C	6.0	2.3773256922	0.1733611149	0.0000000000
C	6.0	2.7429954719	1.5169931940	0.0000000000
H	1.0	2.0416387961	3.5564721346	0.0000000000
H	1.0	-0.3590472714	2.9228678213	0.0000000000
H	1.0	3.1233543412	-0.6054052528	0.0000000000
H	1.0	3.7882286092	1.7907856257	0.0000000000
C	6.0	0.6226174764	-1.6181271304	0.0000000000
C	6.0	-1.4168988939	0.4503463960	0.0000000000
C	6.0	-1.7930071489	-0.9953271452	0.0000000000
C	6.0	-0.8206178388	-1.9351252759	0.0000000000
O	8.0	1.4452085372	-2.5097704538	0.0000000000

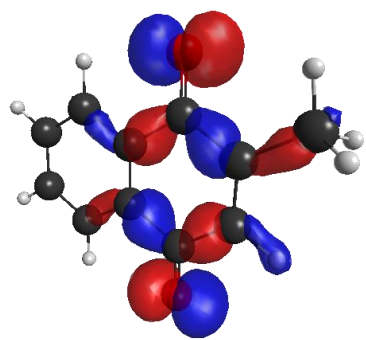
O	8.0	-2.2697912909	1.3117203919	0.0000000000
C	6.0	-3.2598214600	-1.3587826277	0.0000000000
H	1.0	-3.8818906331	-0.4695736983	0.0000000000
H	1.0	-3.5058506604	-1.9520395542	-0.8815797763
H	1.0	-3.5058506604	-1.9520395542	0.8815797763
H	1.0	-1.0601701921	-2.9898703453	0.0000000000

Optimized MCSCF orbitals in the menadione CASSCF active space

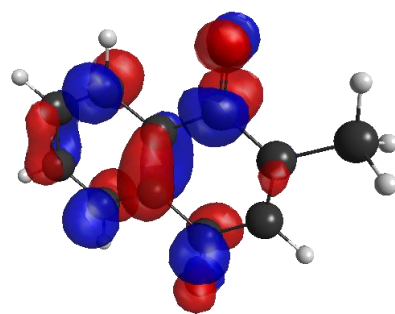
π and O(p) orbitals

π^* orbitals

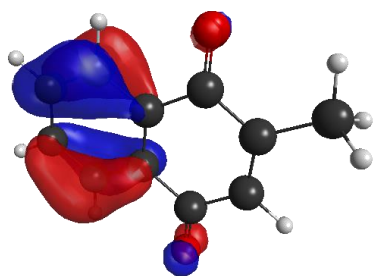




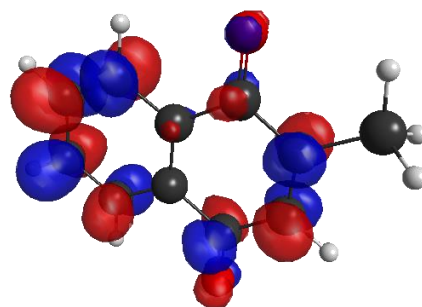
5 O(p)



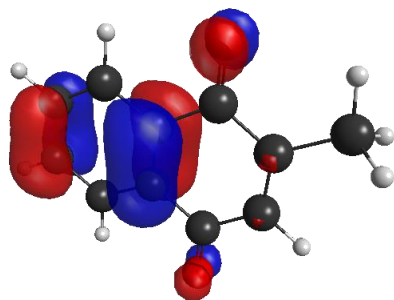
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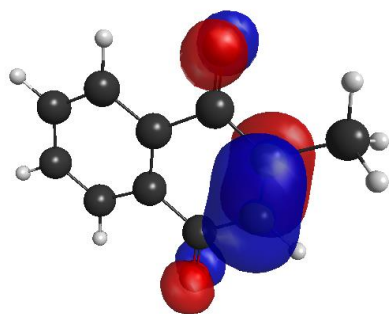
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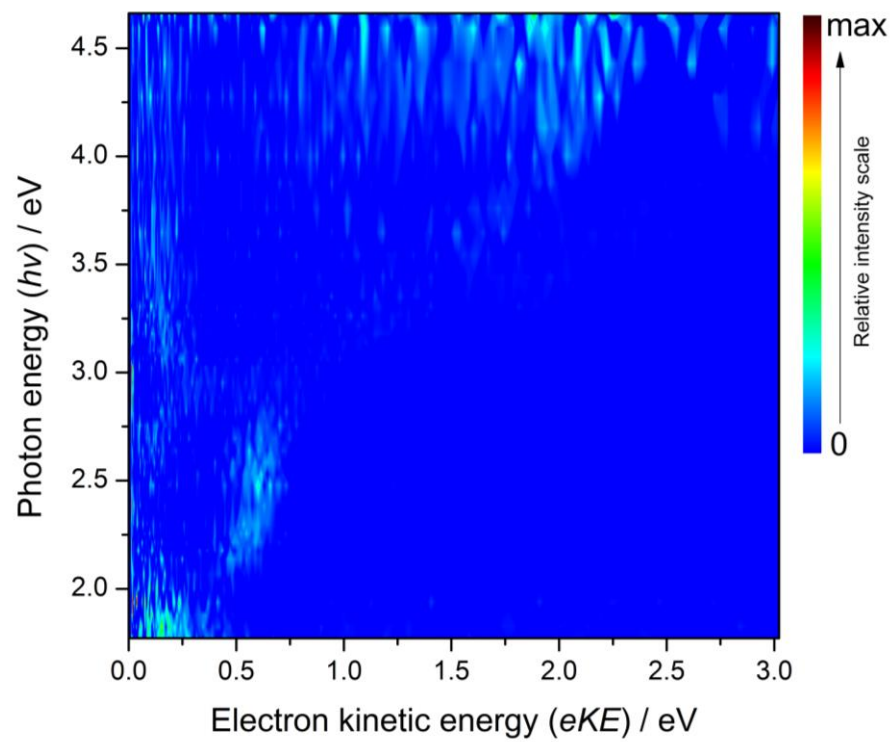
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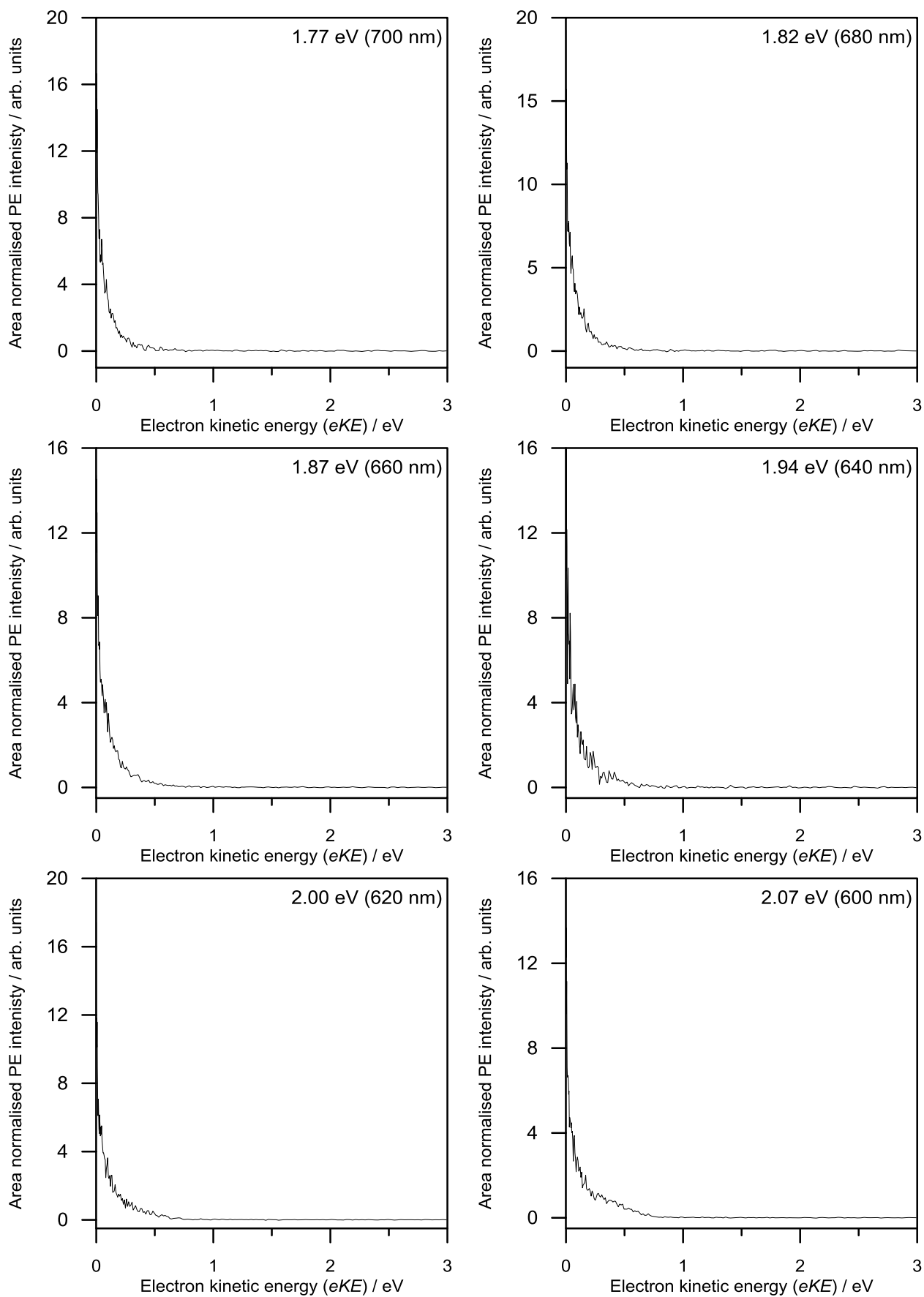
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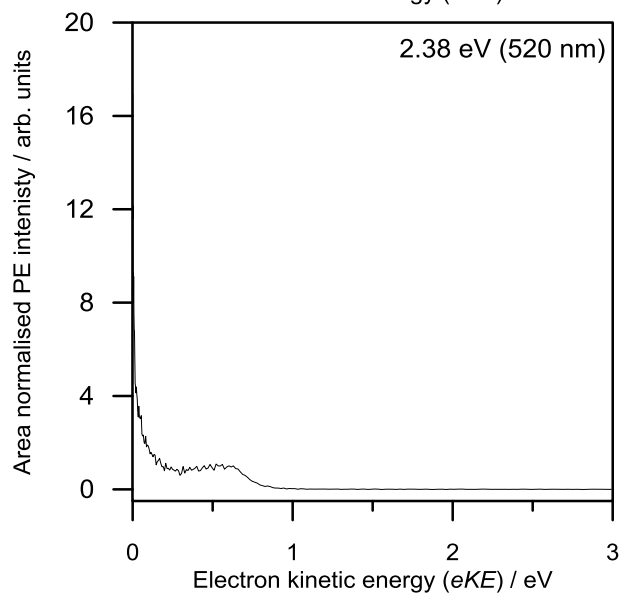
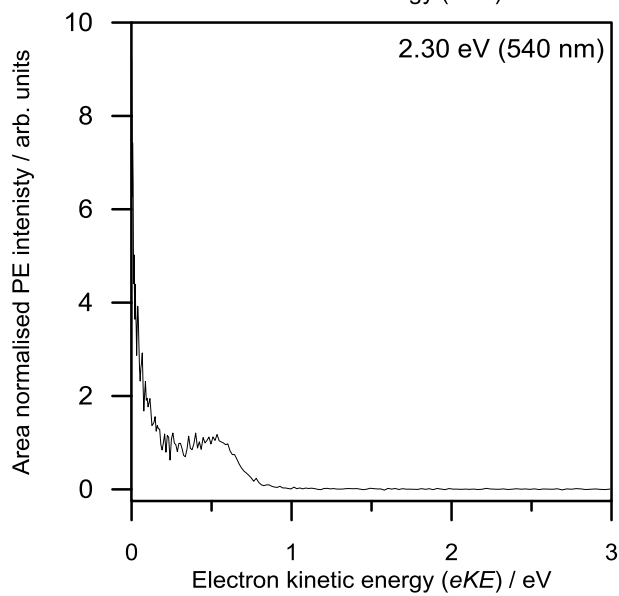
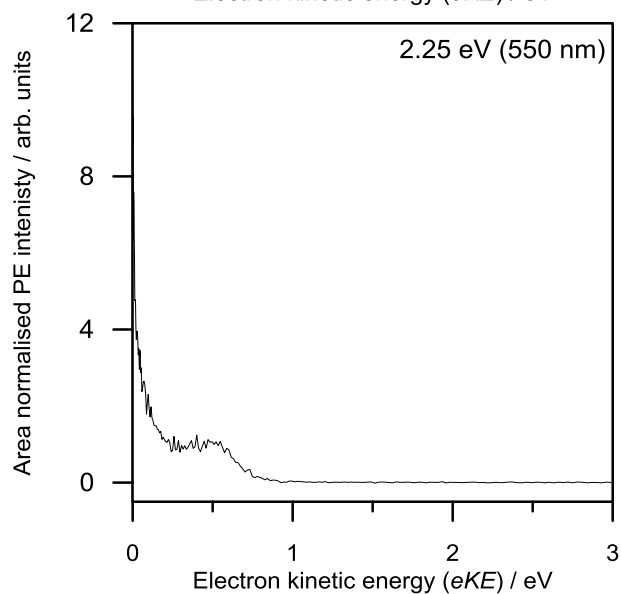
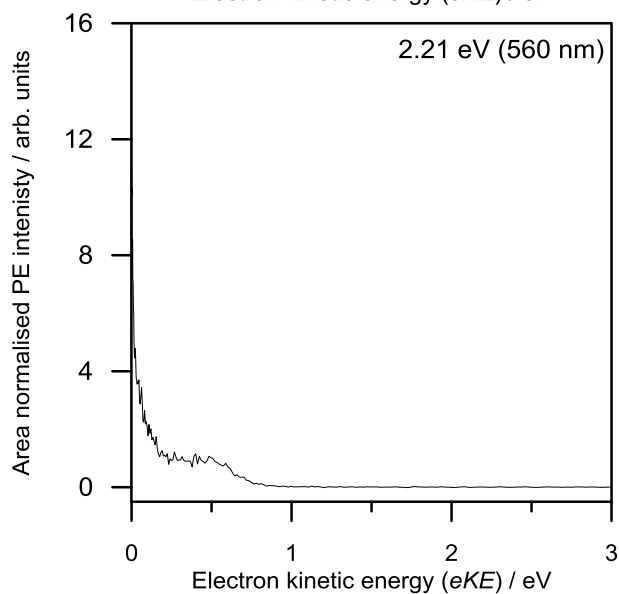
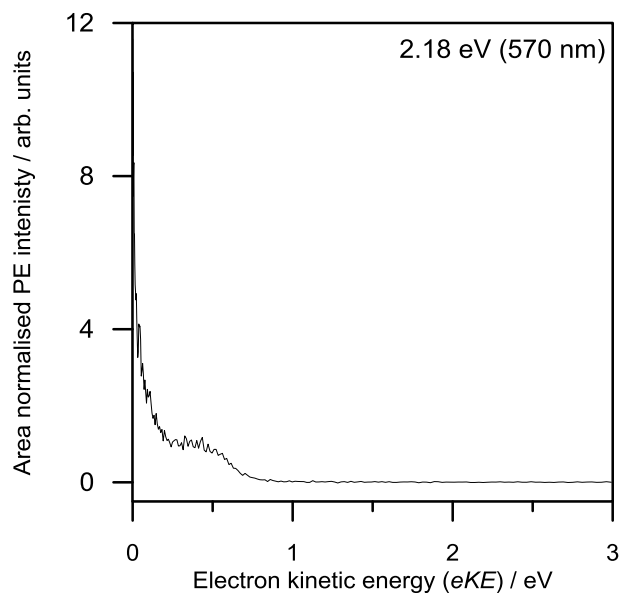
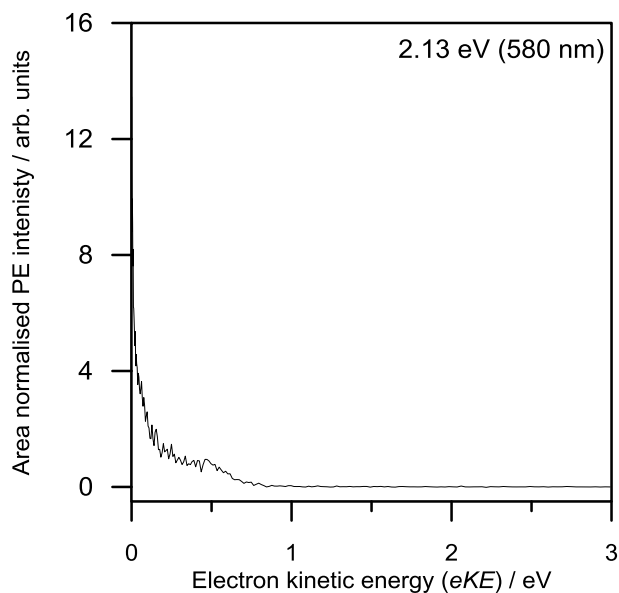
Residuals in the global frequency-resolved photoelectron spectrum fit

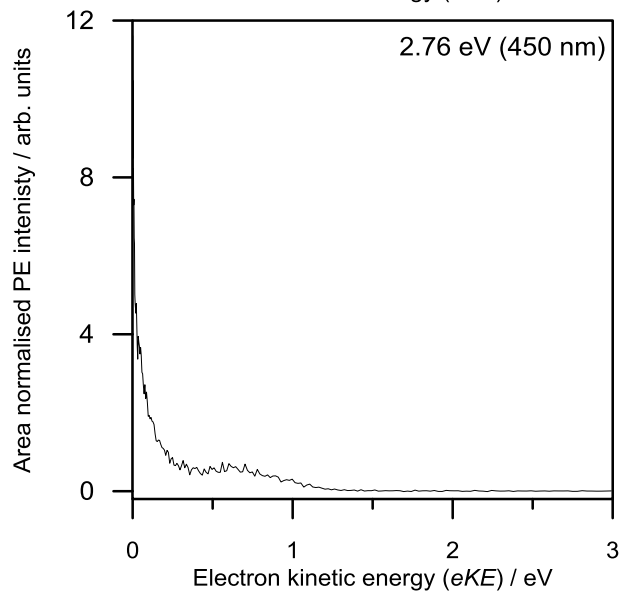
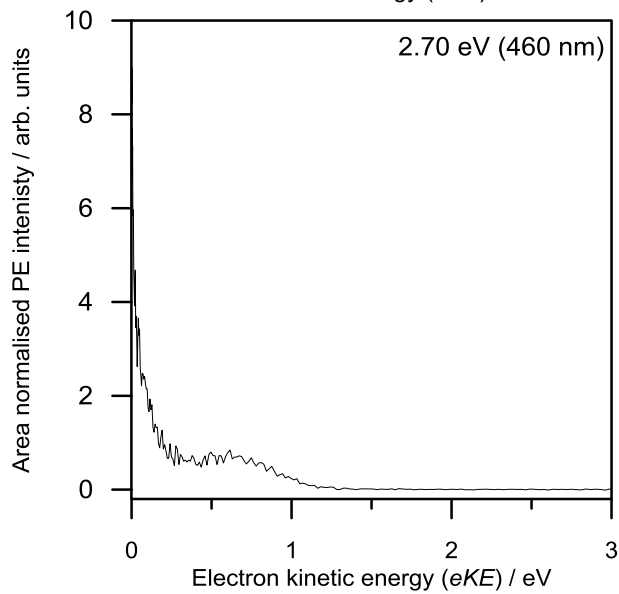
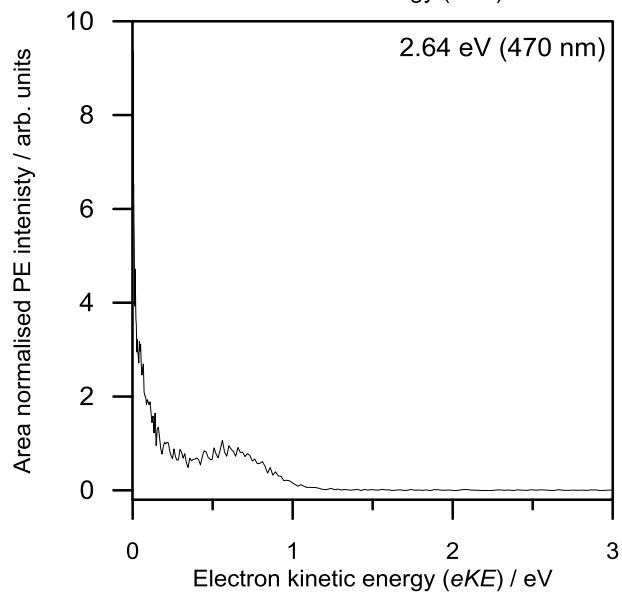
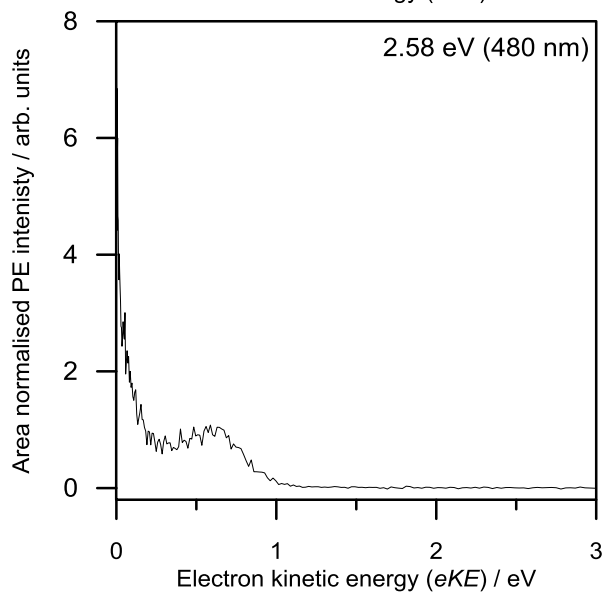
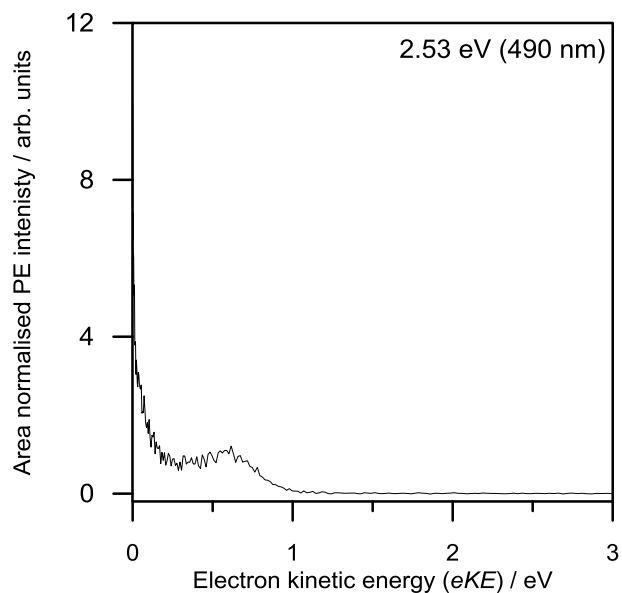
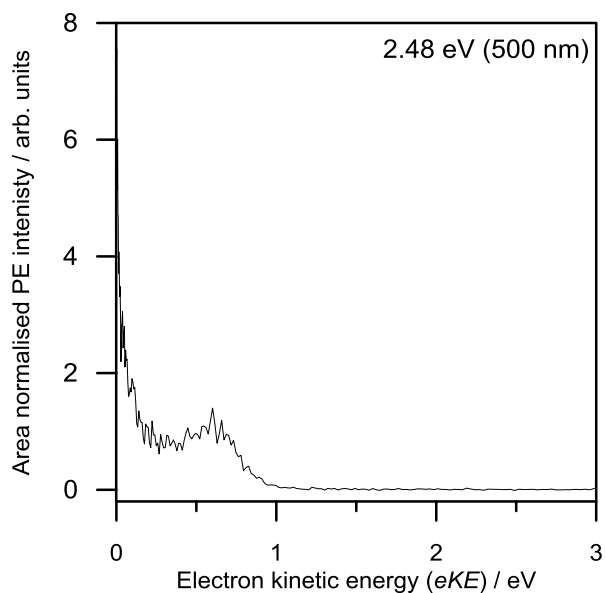
Residual is plotted on the same intensity scale as the simulated signal. The small residuals are proportional to the noise in each reconstructed photoelectron spectrum.

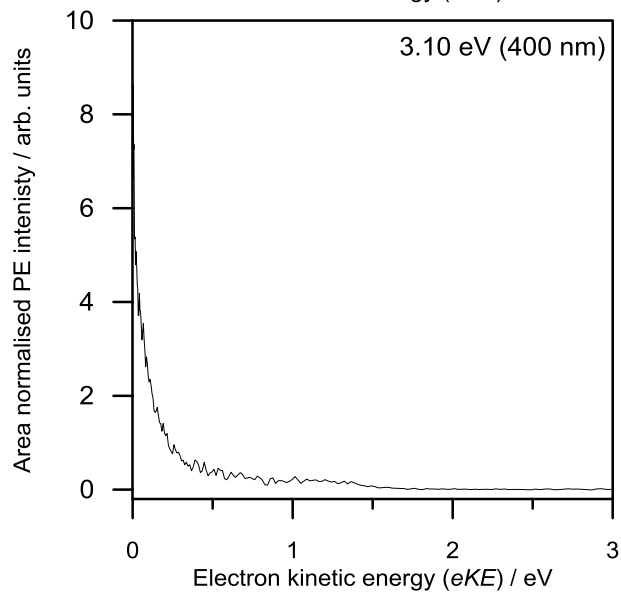
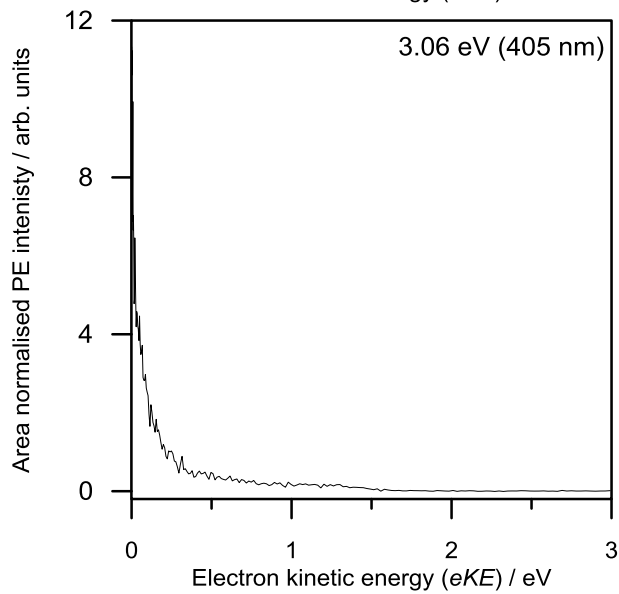
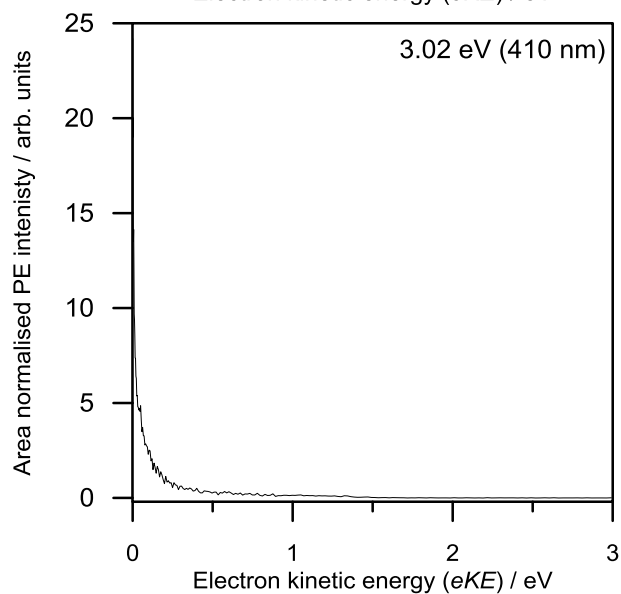
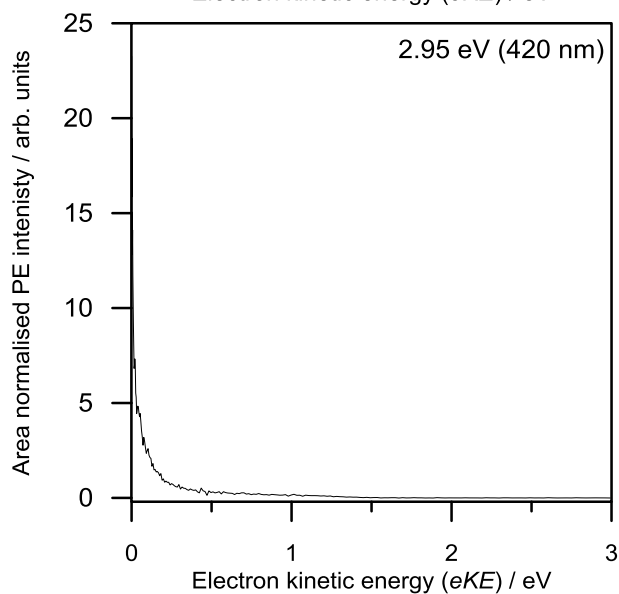
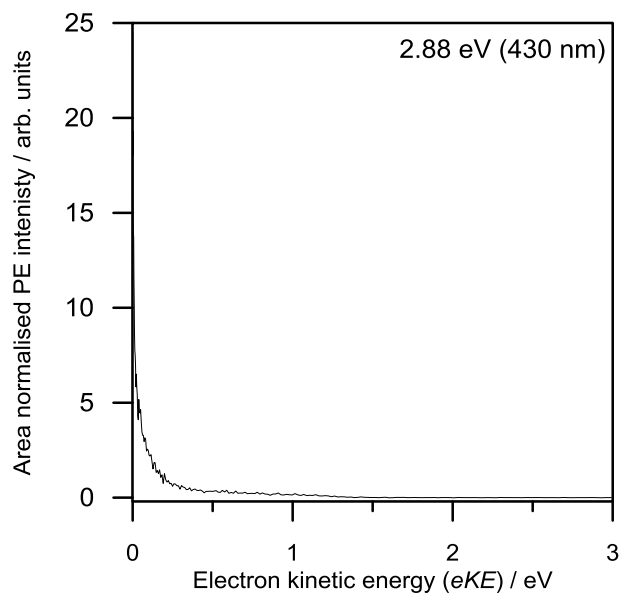
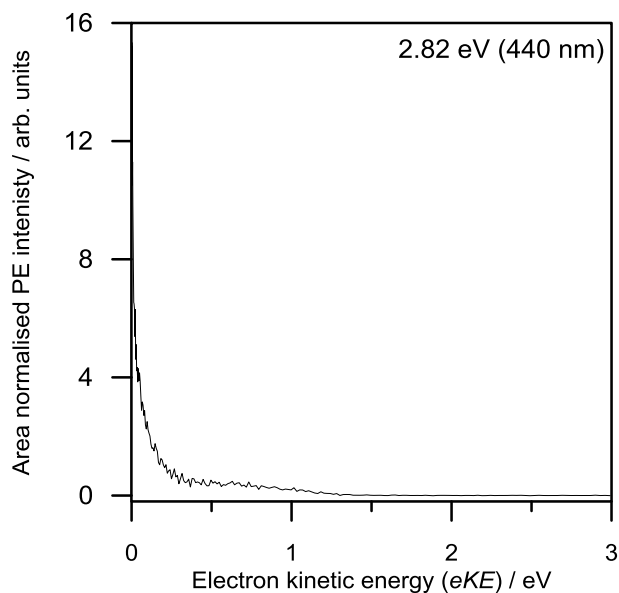


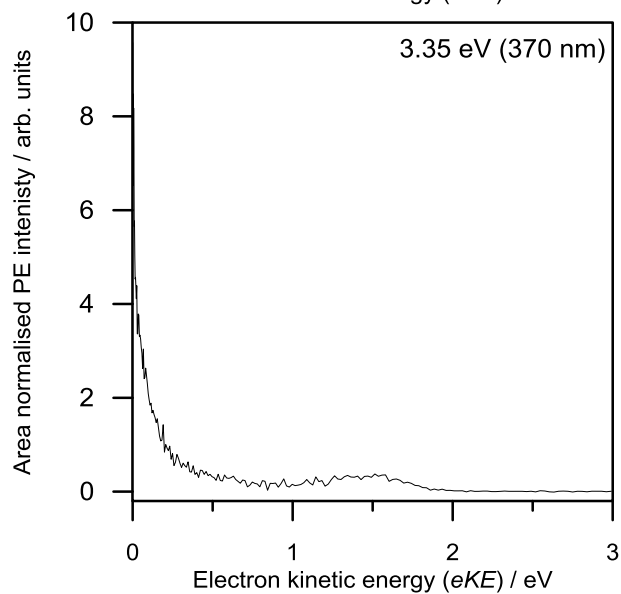
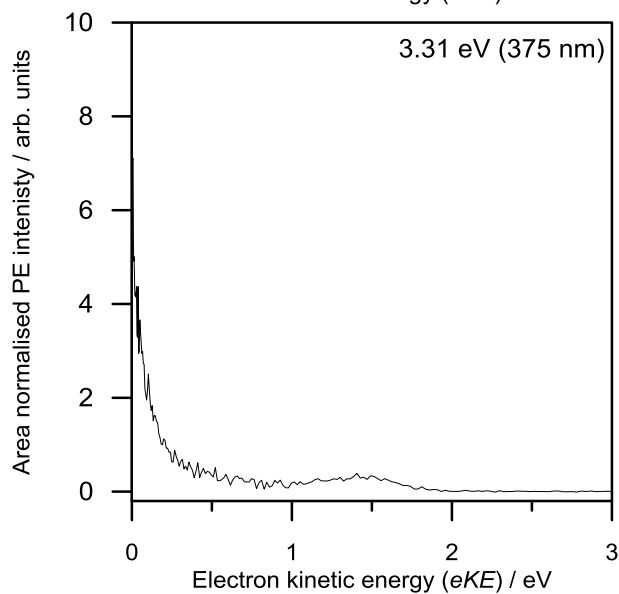
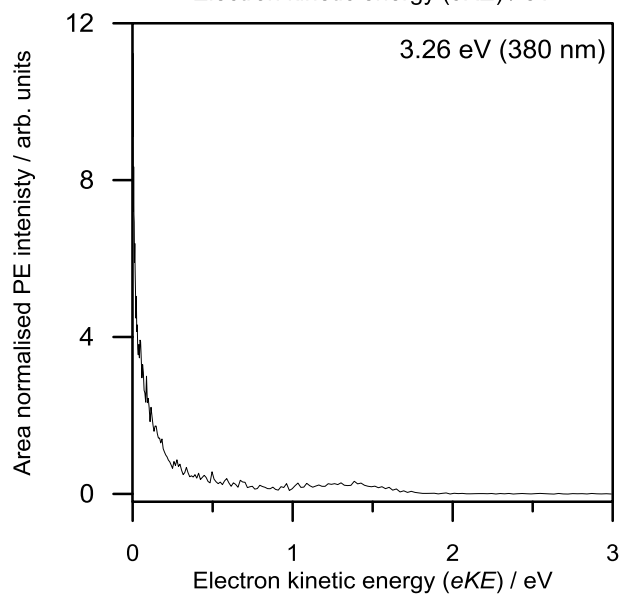
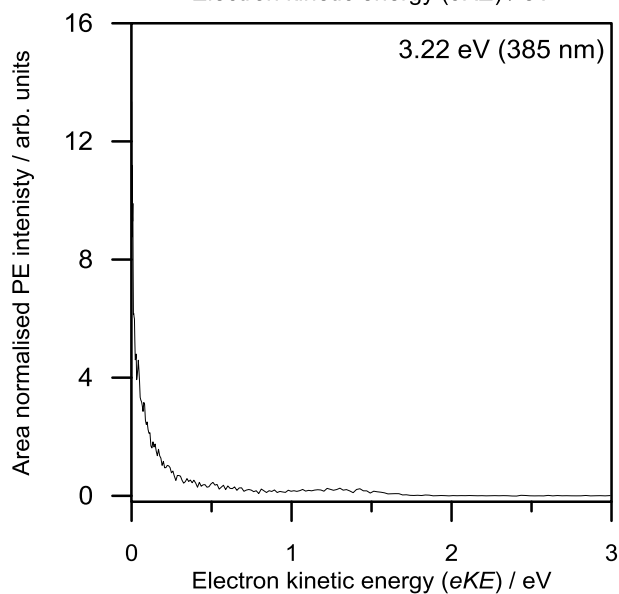
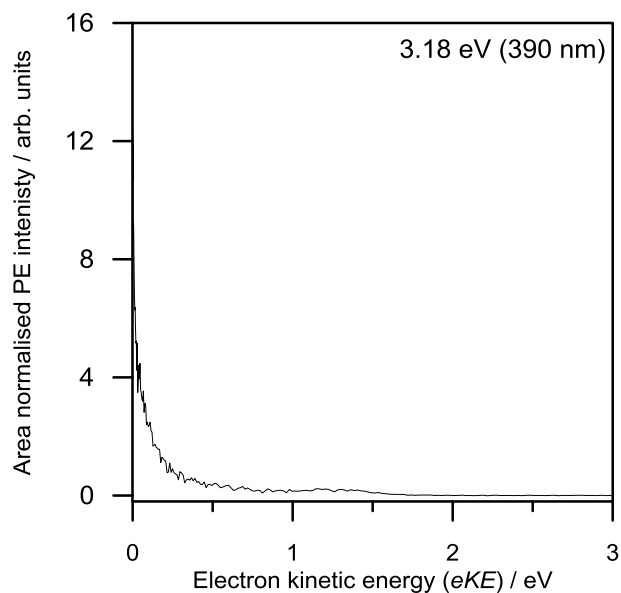
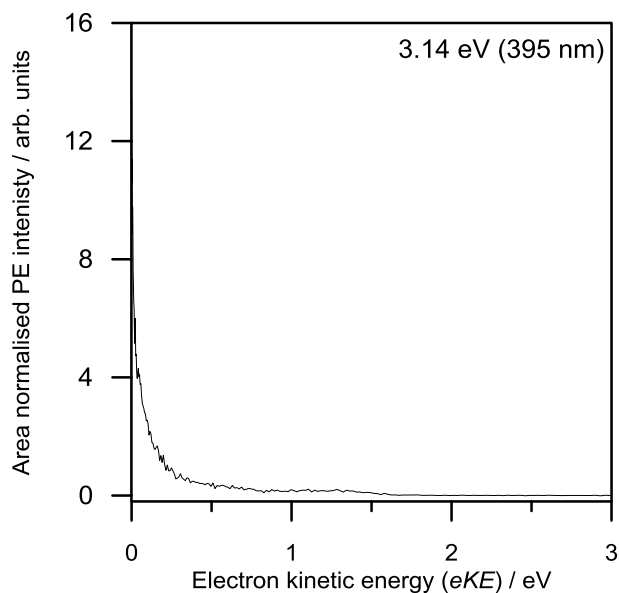
All photoelectron spectra included in the frequency-resolved plot

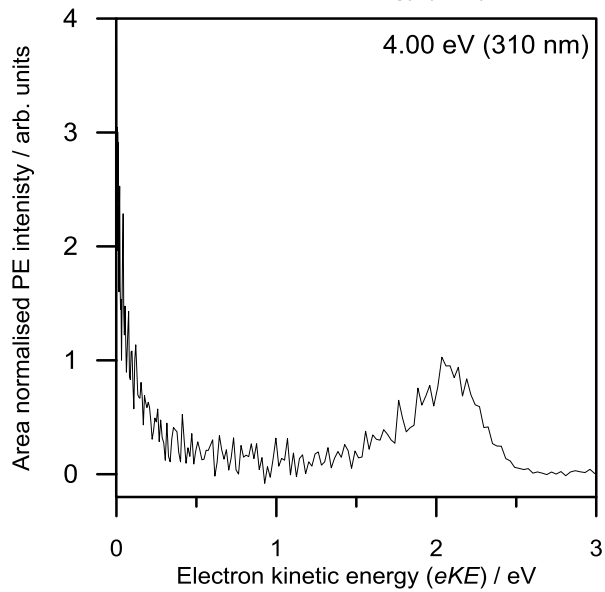
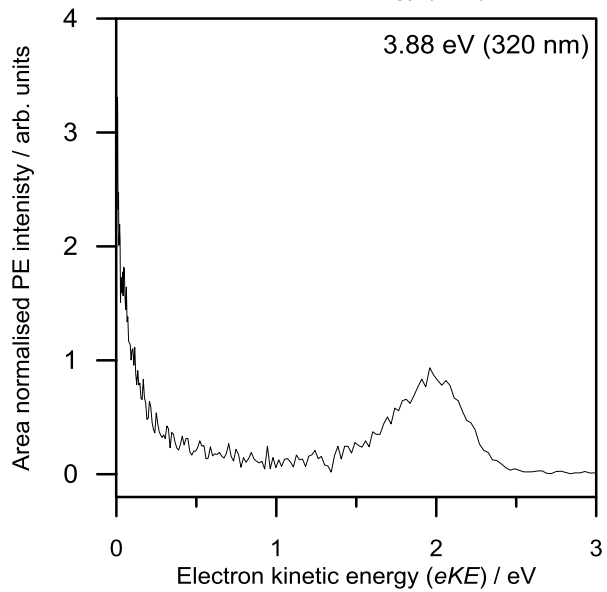
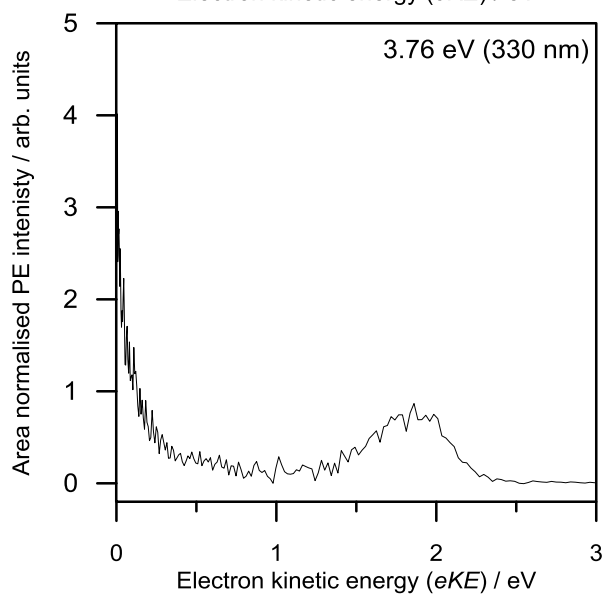
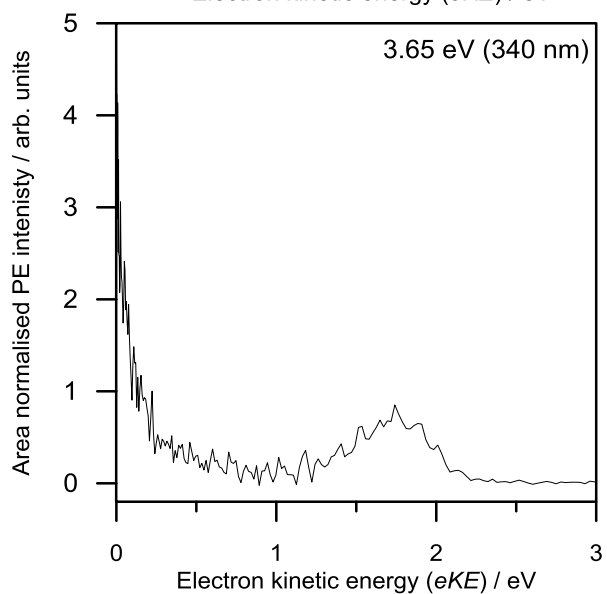
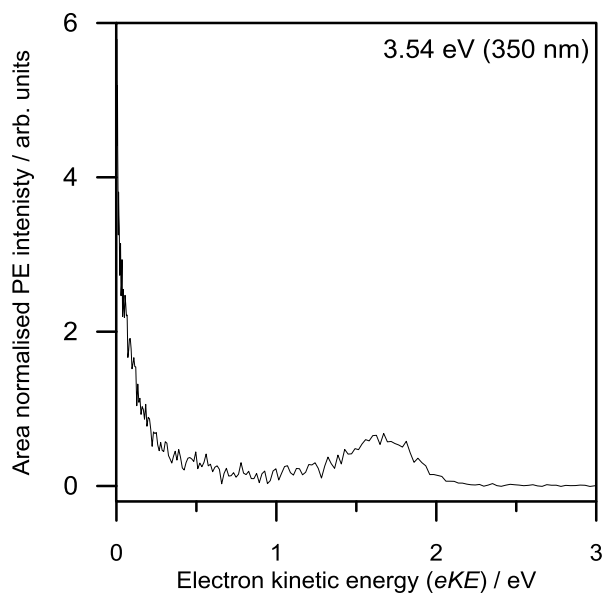
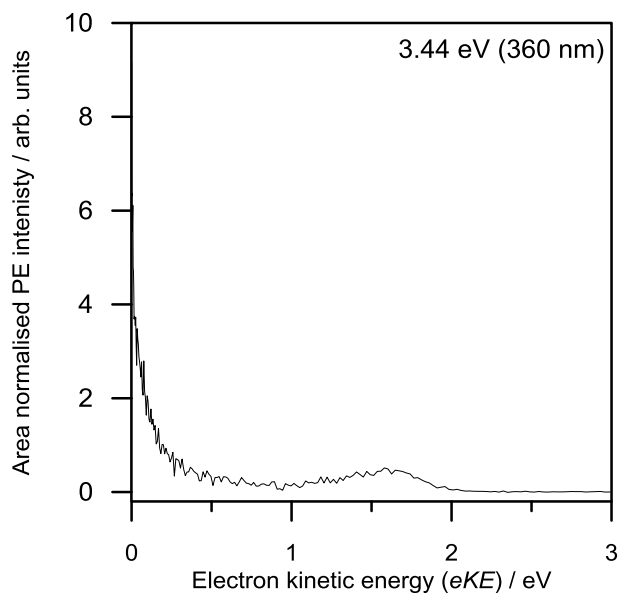


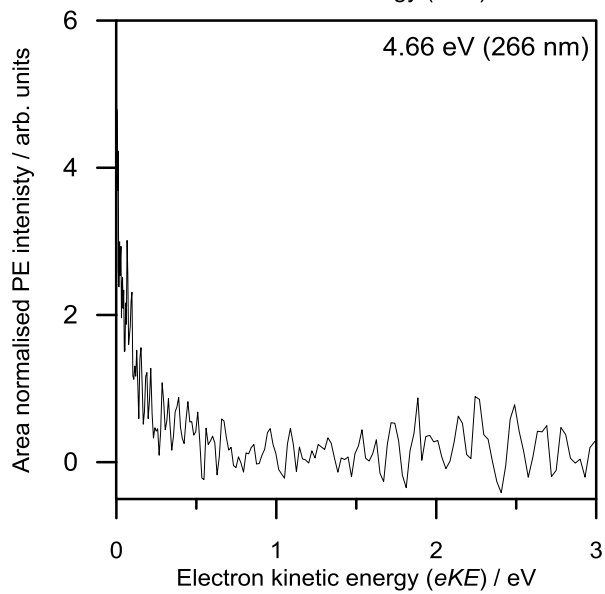
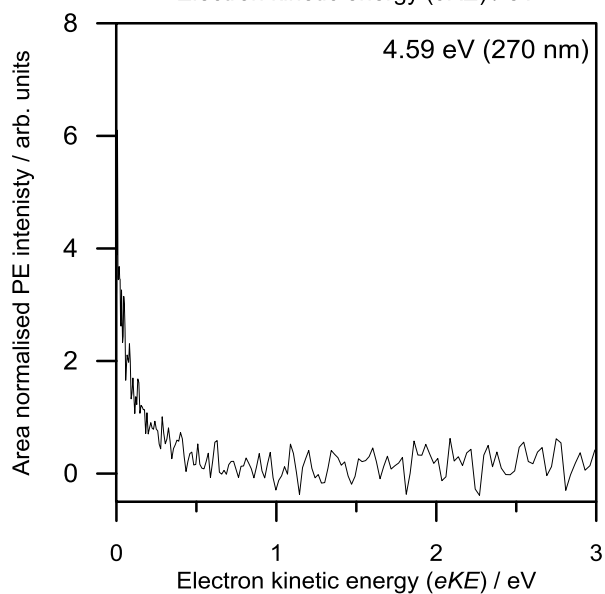
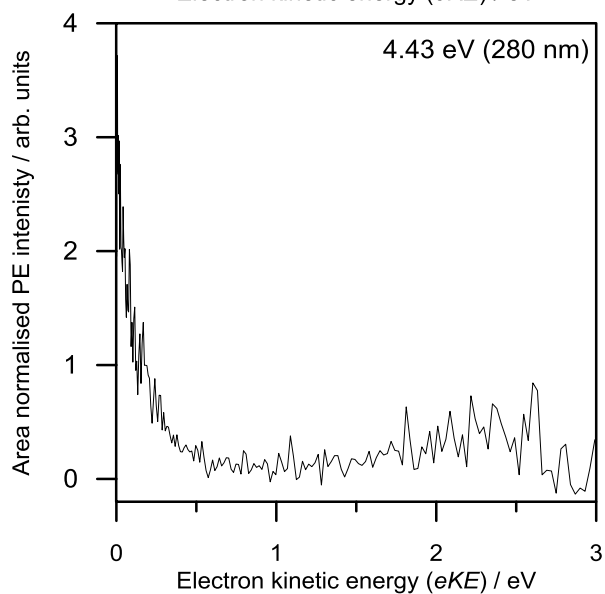
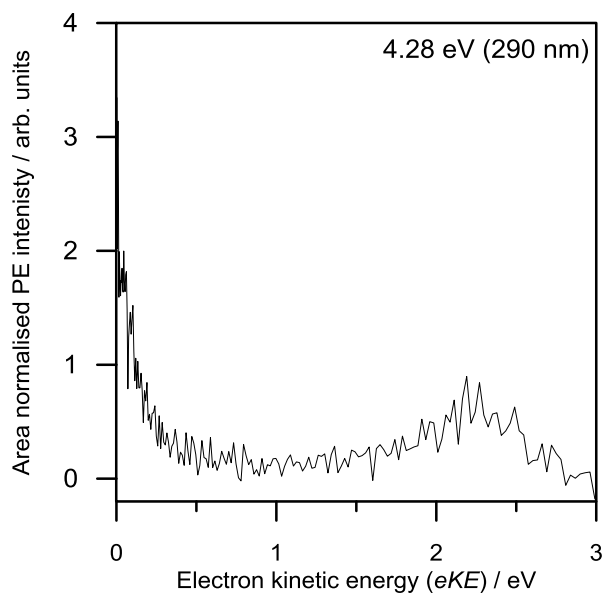
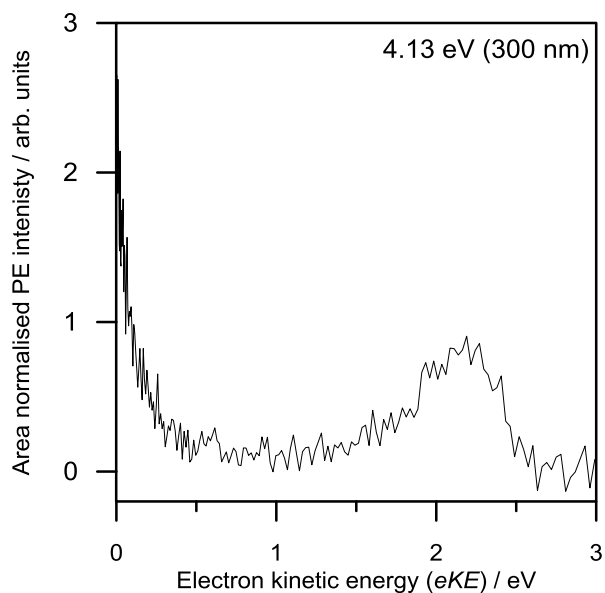












Example time-resolved photoelectron spectra for the 3.10 eV + 1.55 eV (400 nm + 800 nm) pump-probe scheme illustrating the A3 and A2* components

