Supporting Information:

Excited State Dynamics of the Isolated Green Fluorescent Protein Chromophore Anion Following UV Excitation

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Relative contribution of S_3 autodetachment to internal conversion

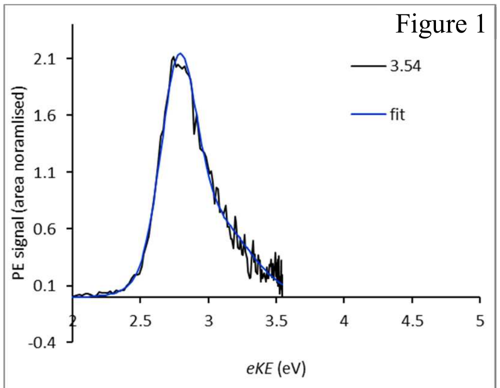


Figure 1

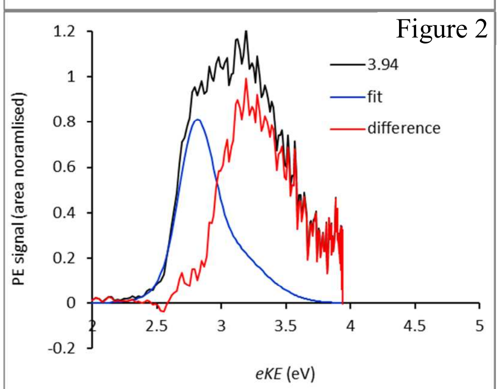


Figure 2

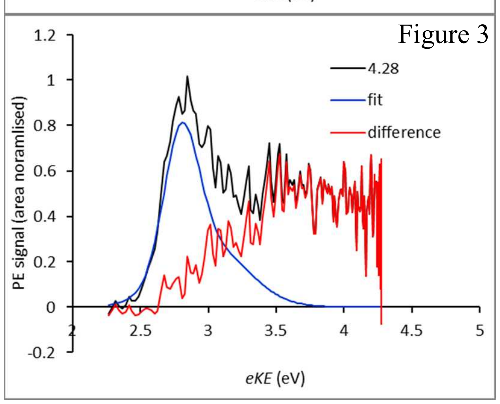


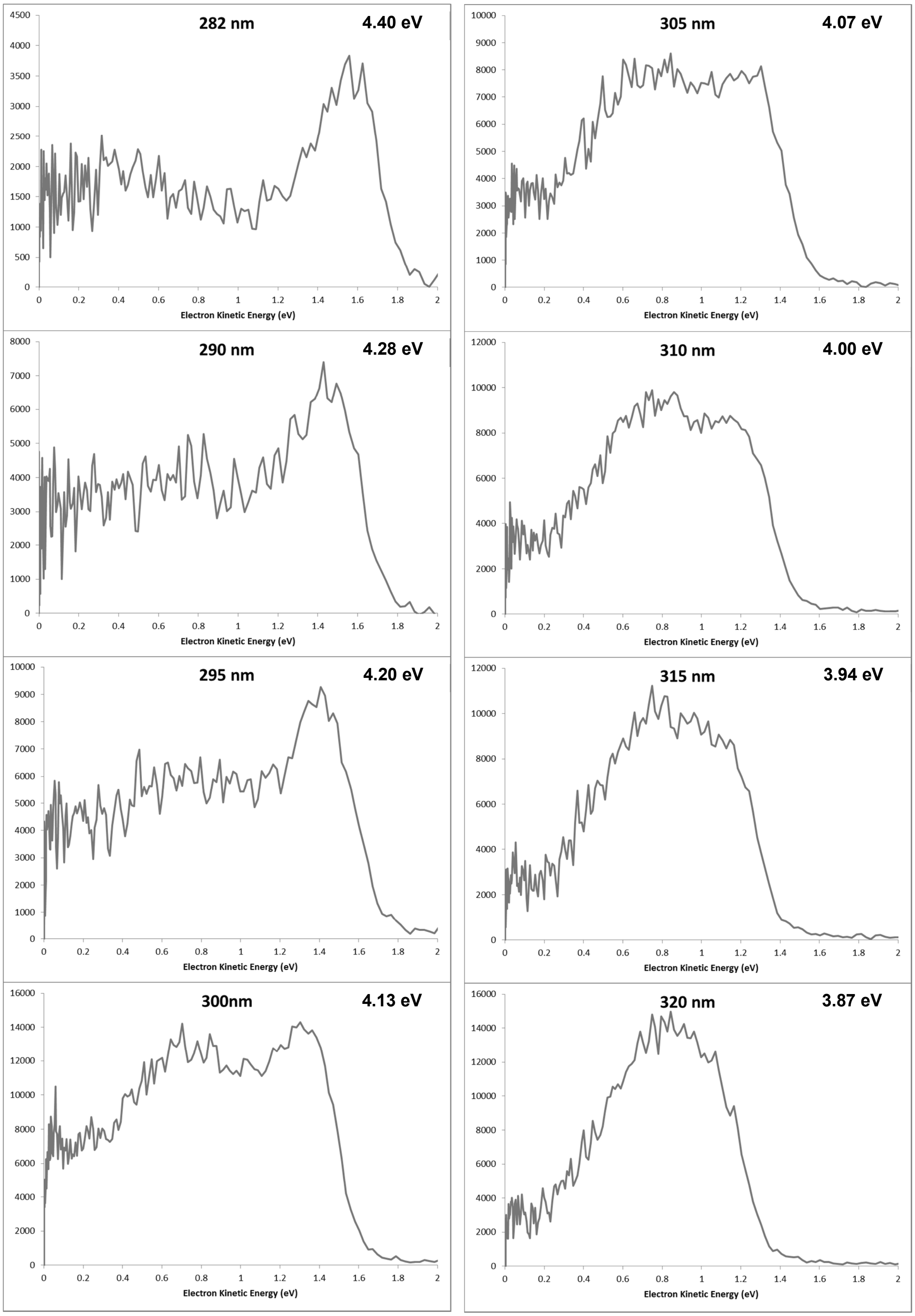
Figure 3

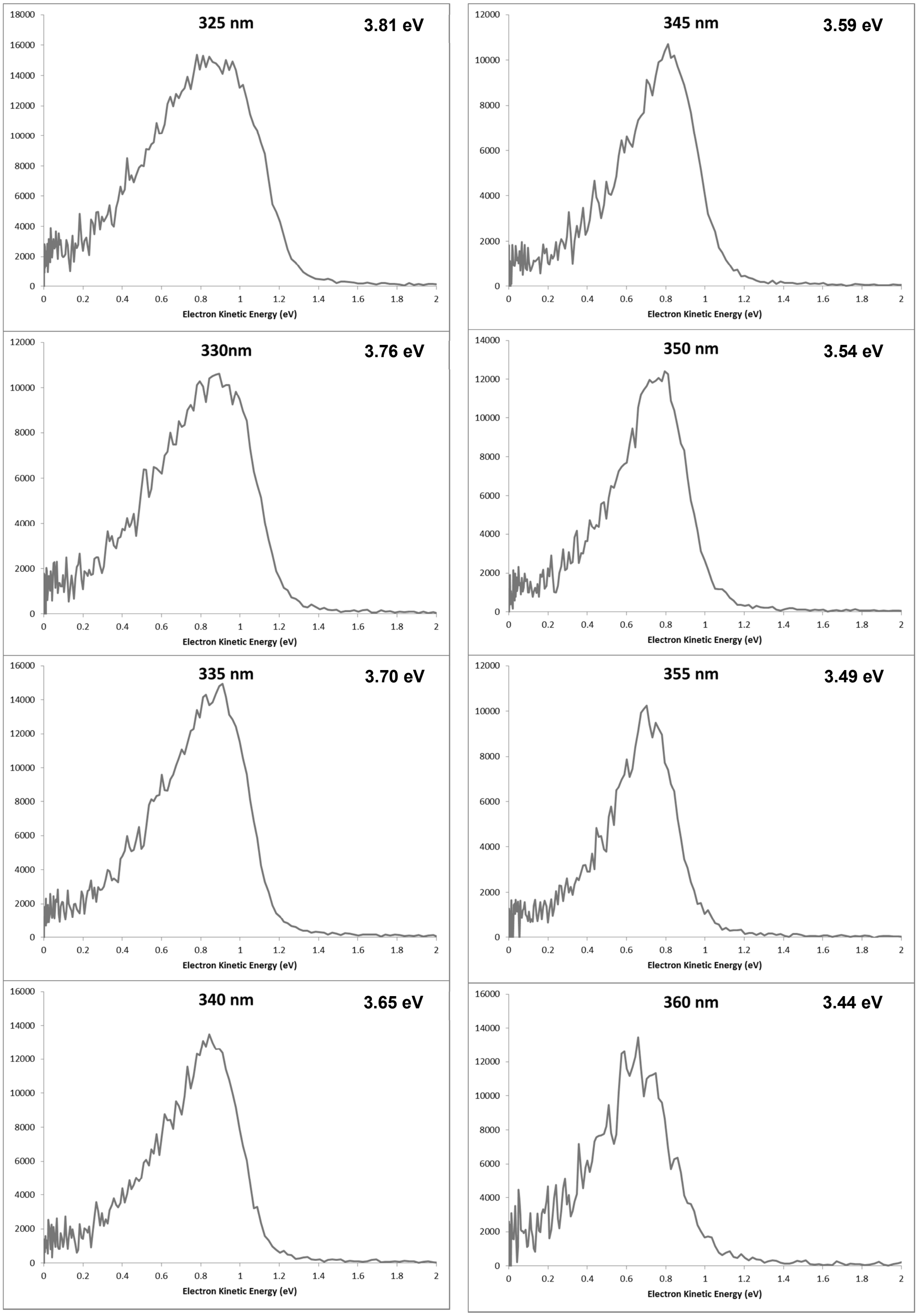
To determine the relative contribution of the $S_3 \rightarrow D_0$ autodetachment channel compared to all other channels (*i.e.* $S_3 \rightarrow S_2$ internal conversion), we have fitted the PE spectrum at $h\nu$ = 3.54 eV to a function (see Figure 1, blue line).

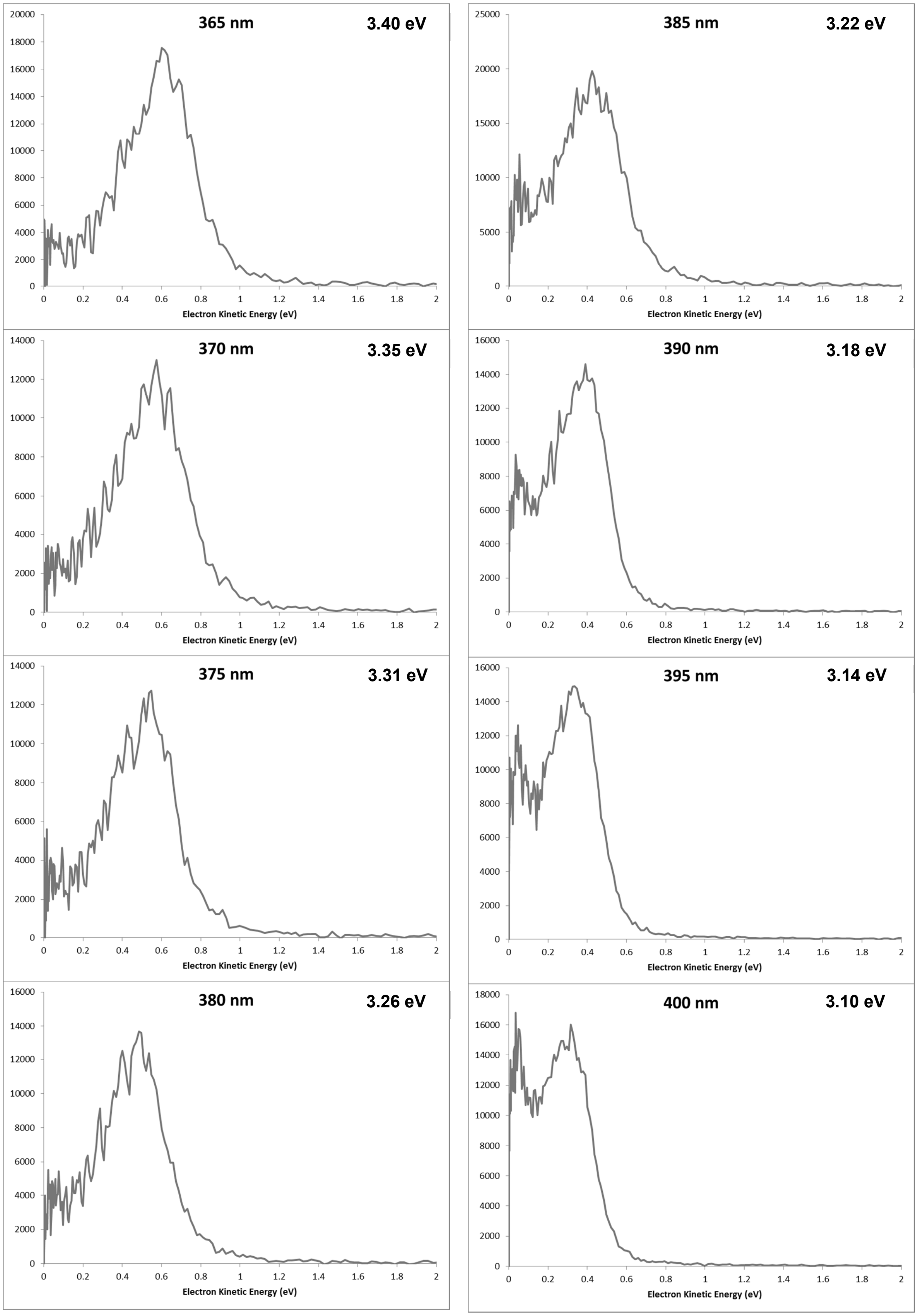
This fit is then used to extract the contribution of the $S_3 \rightarrow D_0$ autodetachment channel. For example, we fit the rising edge of the $h\nu$ = 3.94 eV spectrum to this and retain the difference (see Figure 2, red). We follow the same procedure for other photon energies, and $h\nu$ = 4.28 eV is shown as an example (see Figure 3).

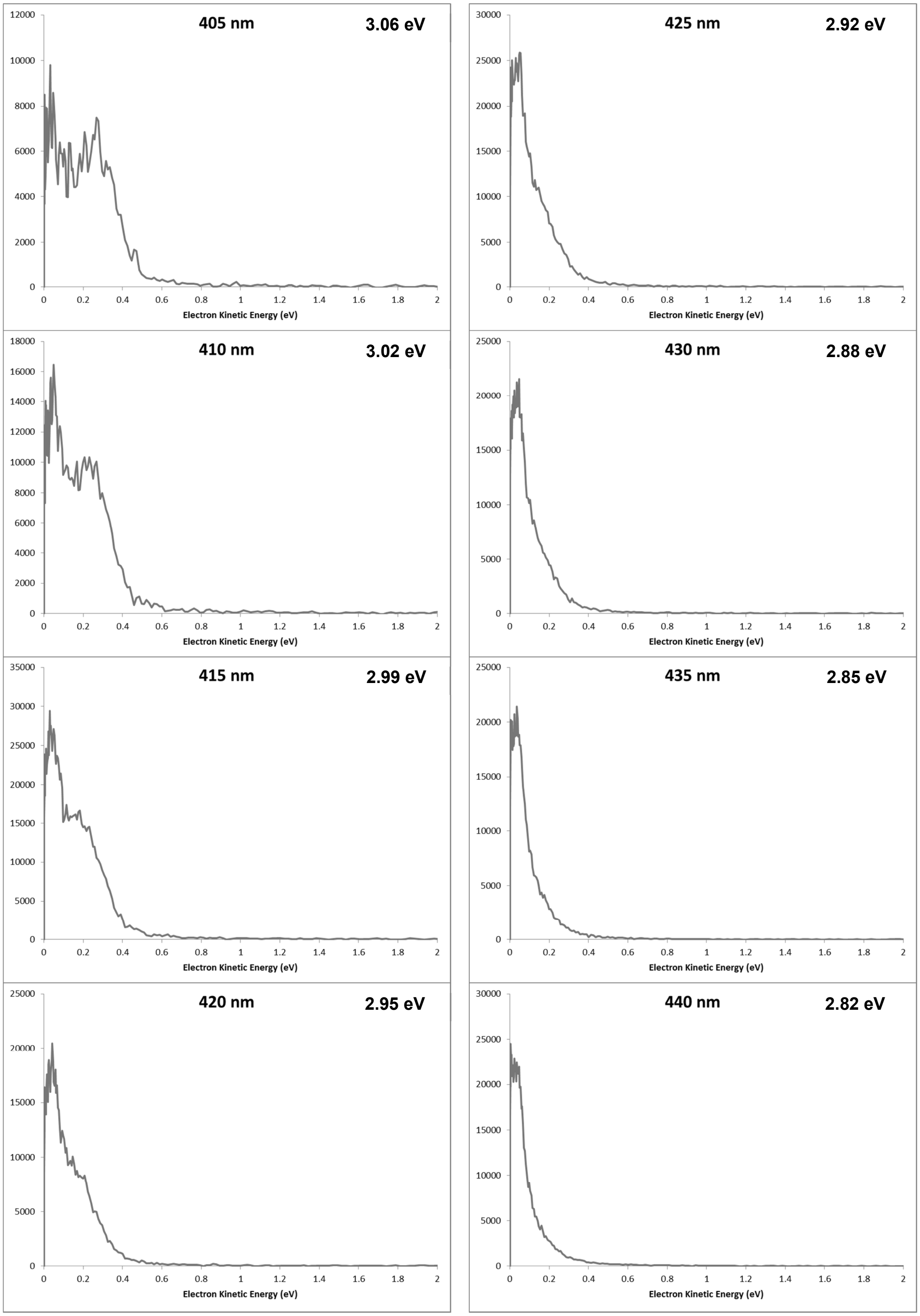
Note that the PE spectra are normalized to the total PE signal in each spectrum. To attain the best fits, we require the $S_3 \rightarrow D_0$ autodetachment channel to be the same across the range, as shown. The ratio $S_3 \rightarrow D_0$: $S_3 \rightarrow S_2$ is found to be 0.7:1 and 0.6:1 for $h\nu$ = 3.94 and 4.28 eV, respectively. Hence, the channel leading to $S_3 \rightarrow S_2$ internal conversion has a slightly higher yield that the $S_3 \rightarrow D_0$ autodetachment and therefore a slightly shorter lifetime. The observed lifetime is $(\tau_{obs})^{-1} = (\tau_{IC})^{-1} + (\tau_{AD})^{-1} < 40$ fs, where τ_{IC} and τ_{AD} are the internal conversion and autodetachment lifetimes. The lifetimes are related to the relative yields by $\tau_{IC}/\tau_{AD} = 0.7$ or 0.6 for $h\nu$ = 3.94 and 4.28 eV, respectively. Thus, $\tau_{IC} < 65$ fs and $\tau_{AD} < 100$ fs.

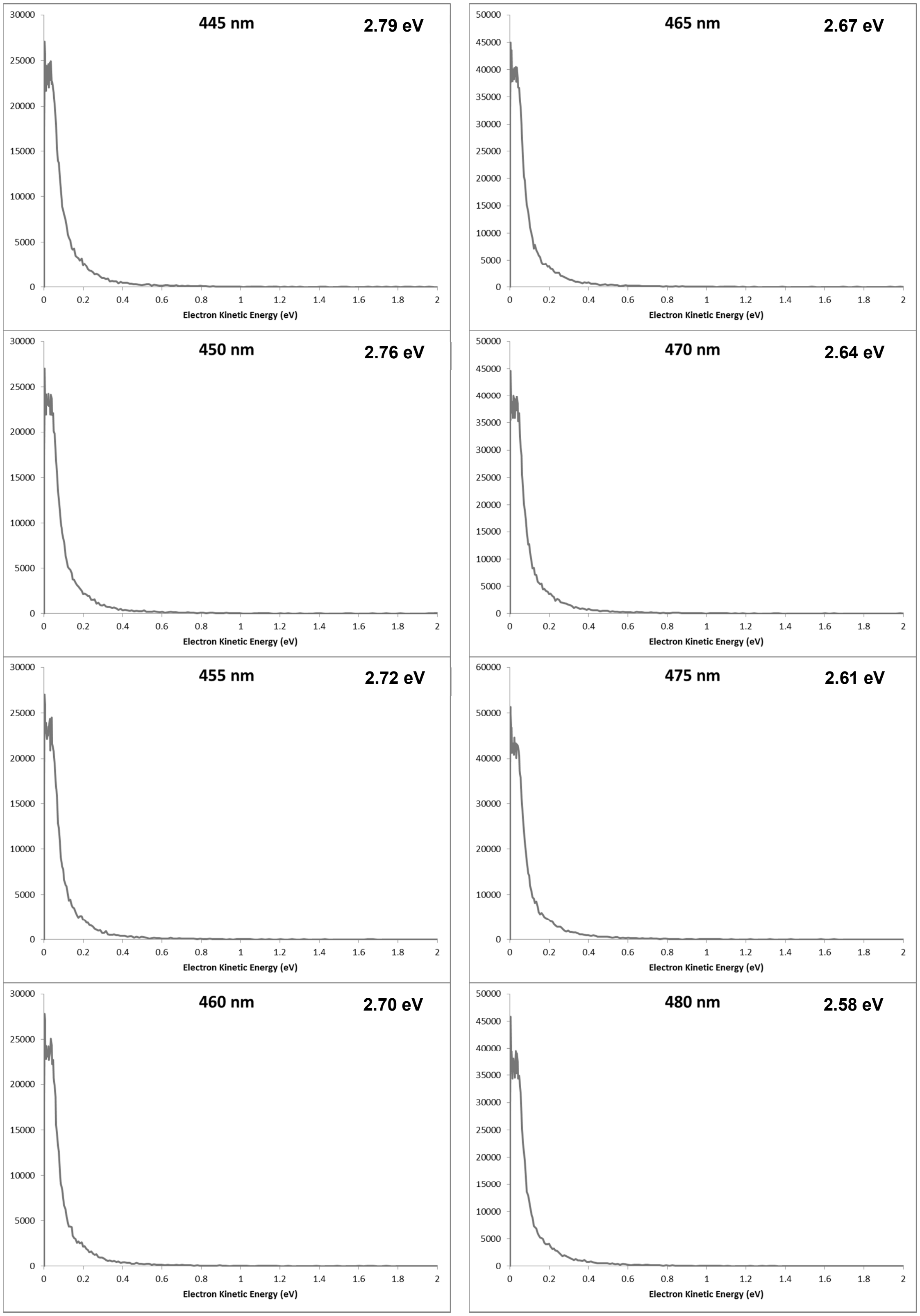
Individual Photoelectron Spectra included in Figure 1e

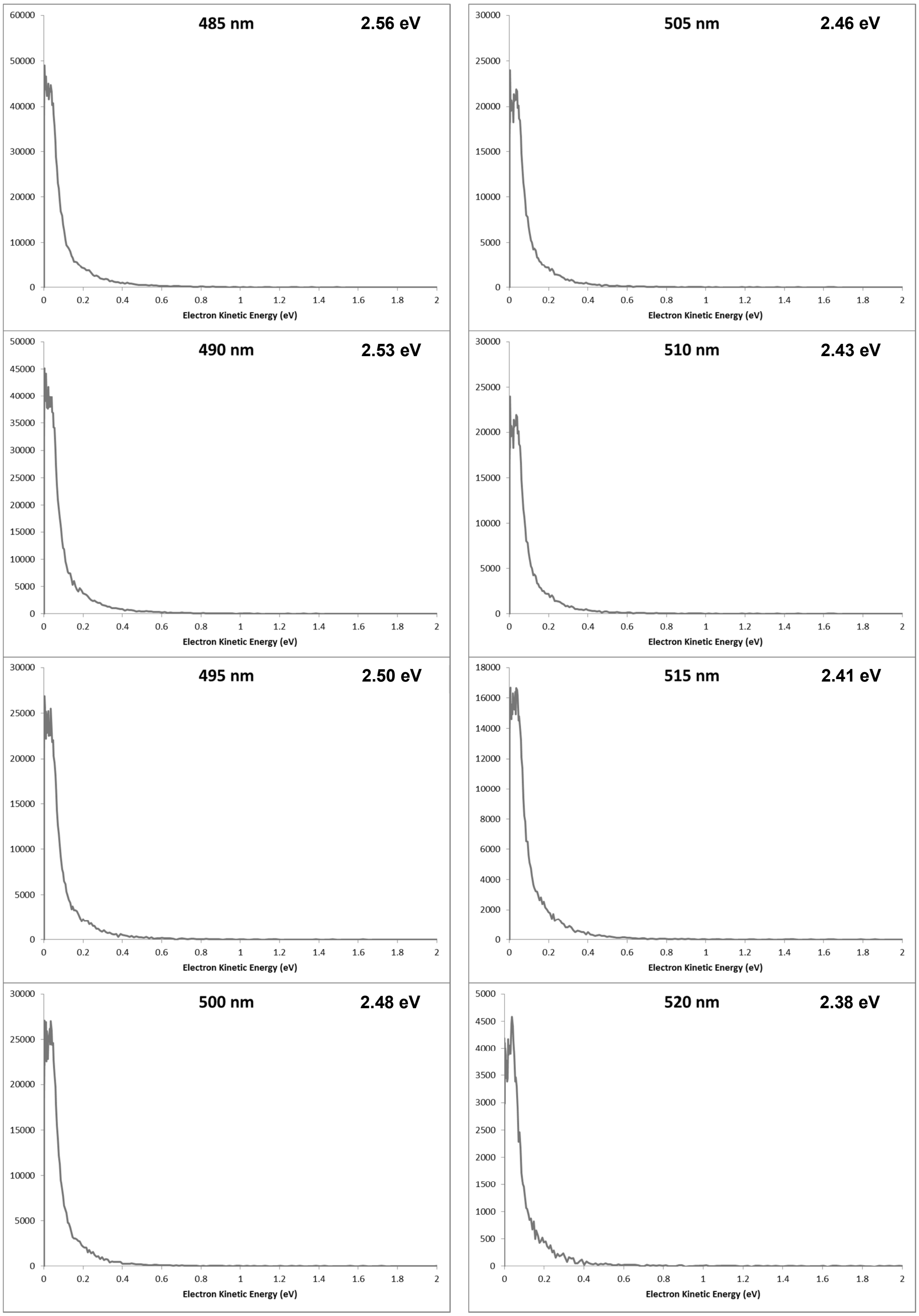



325 nm
3.81 eV
345 nm
3.59 eV
330nm
3.76 eV
350 nm
3.54 eV
335 nm
3.70 eV
355 nm
3.49 eV
340 nm
3.65 eV
360 nm
3.44 eV
Electron Kinetic Energy (eV)


365 nm
3.40 eV
385 nm
3.22 eV
370 nm
3.35 eV
390 nm
3.18 eV
375 nm
3.31 eV
395 nm
3.14 eV
380 nm
3.26 eV
400 nm
3.10 eV
Electron Kinetic Energy (eV)


405 nm
3.06 eV
Electron Kinetic Energy (eV)
425 nm
2.92 eV
Electron Kinetic Energy (eV)
410 nm
3.02 eV
Electron Kinetic Energy (eV)
430 nm
2.88 eV
Electron Kinetic Energy (eV)
415 nm
2.99 eV
Electron Kinetic Energy (eV)
435 nm
2.85 eV
Electron Kinetic Energy (eV)
420 nm
2.95 eV
Electron Kinetic Energy (eV)
440 nm
2.82 eV
Electron Kinetic Energy (eV)


445 nm
2.79 eV
465 nm
2.67 eV
450 nm
2.76 eV
470 nm
2.64 eV
455 nm
2.72 eV
475 nm
2.61 eV
460 nm
2.70 eV
480 nm
2.58 eV
Electron Kinetic Energy (eV)


485 nm
2.56 eV
Electron Kinetic Energy (eV)
505 nm
2.46 eV
Electron Kinetic Energy (eV)
490 nm
2.53 eV
Electron Kinetic Energy (eV)
510 nm
2.43 eV
Electron Kinetic Energy (eV)
495 nm
2.50 eV
Electron Kinetic Energy (eV)
515 nm
2.41 eV
Electron Kinetic Energy (eV)
500 nm
2.48 eV
Electron Kinetic Energy (eV)
520 nm
2.38 eV
Electron Kinetic Energy (eV)