Electronic Supplemental Information for

The influence of aqueous solvent on the electronic structure and non-adiabatic dynamics of indole explored by liquid-jet photoelectron spectroscopy

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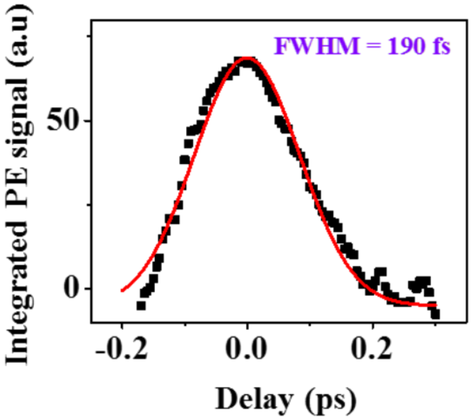
Cross-correlation measurement for determining instrument response function

The cross-correlation between pump and probe was measured by recording non-resonant two photon ionization of 100 mM sodium iodide in water. For both 266 nm and 292 nm, the wavelengths are off-resonant with the iodide charge-transfer-to-solvent (CTTS) band, although 266 nm is very nearly resonant.[1] The vertical detachment energy of iodide is 8.1 eV[2] so ejected electron signal should require absorption of two photons, either both coming from the 292 nm beam, both from the 266 nm beam, or one from each. The pre-resonance at 266 nm will strongly favor the latter two paths; only the last path will depend on the pump-probe delay. Therefore, at each delay point, time of flight (TOF) spectrum was recorded and the time-invariant signal of pump alone and probe alone were subtracted from the total photoelectron signal. In order to extract the cross-correlation width, the integrated signal at each delay point with increment of 5 fs was plotted as a function of pump-probe delay time and was fitted with a Gaussian function (Figure S1).

Figure S1: Cross-correlation between pump and probe pulses in the liquid-jet.



R2PI measurement of aqueous tryptophan

The vertical ionization energies (VIE) of aqueous tryptophan corresponding to D_0-S_0 and D_1-S_0 using two photon ionizations from 266 nm and 292 nm are 7.5 ± 0.1 eV and 8.4 ±0.1 eV (Table S1) after correction for inelastic scattering, which are not significantly different to the values reported for aqueous indole in this article (7.4 and 8.4 ±0.1 eV). From Table S1, it is clear that solvation has had a large impact on the ionization corresponding to D_0-S_0 while the D_1-S_0 ionization energy remains relatively unchanged in comparison to the gas phase values. This implies a large change in the D_0-D_1 gap in aqueous solution.

Figure S2: Resonant one-color two-photon ionization spectra of aqueous tryptophan (10 mM) recorded with (a) 266 nm and 292 nm ionization (b) pulses. Individual Gaussian fits are shown in red and green. Note that the R2PI spectra are affected by the instrument cut-off function at eKE < 0.5 eV.

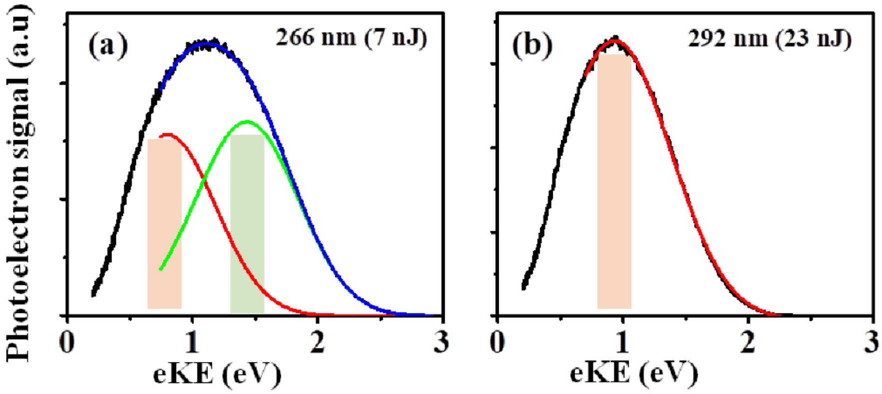


Table S1: Photoionization of aqueous tryptophan. All energies are in eV.

Ionized orbital	eKE[a] (266 nm/292 nm)	Corrected eKE[b] (266 nm/292 nm)	VIE[c] (266 nm/292 nm)	VIE[d] (gas phase)
HOMO (π_3)	1.4 / 0.9	1.8 / 1	7.5 / 7.5	7.9
HOMO-1(π_2)	0.8 / -	0.9 / -	8.4 / -	8.3

[a] eKE - electron kinetic energy

[b] eKE reported after correcting for electron inelastic scattering.

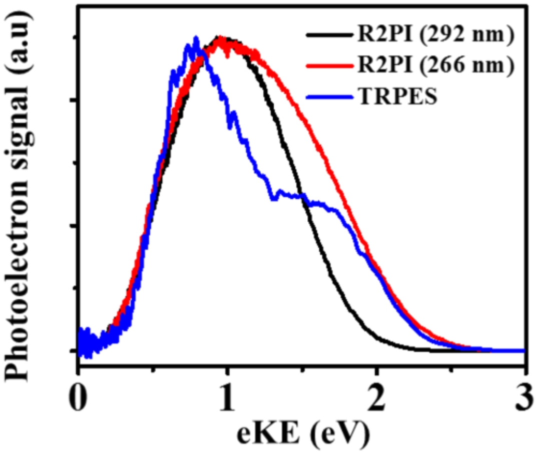
[c] VIE - vertical ionization energy

[d] VIE reported in gas phase[3-5]

Comparison between R2PI spectra and TRPES spectrum near zero pump-probe delay

Figure S3 shows the resonant two-photon enhanced photoelectron spectrum ionized 1+1 with one-color 266 nm and one-color 292 nm, respectively, in comparison with resonant two-color 266/292 nm 1+1' PE spectrum obtained at zero pump-probe delay in the TRPES for aqueous indole. Aqueous indole absorbs at the one-photon level at both 266 and 292 nm, and hence the 1+1' spectrum has contributions from both time-orderings. The total photon energies involved are 8.5 eV, 9.4 eV and 8.9 eV, respectively. The 266 nm R2PI spectrum is shifted towards higher eKE because of extra photon energy. The time-resolved spectrum clearly shows a well resolved shoulder in higher eKE and nowhere close in shape with either of R2PI spectrum.

Figure S3: Comparison between R2PI spectra with different one-color excitation along with time-resolved spectrum obtained near zero pump-probe delay (resonant 1+1' ionization). The 266 nm beam was horizontally polarized while 292 nm beam was vertically polarized with respect to the laboratory frame.



Influence of inelastic scattering on photoelectron kinetic energy

eKE peak (in experimental spectra)	Shift towards high eKE (correction for inelastic scattering)
0.75	0
0.83	0.08
1	0.15
1.15	0.35
1.4	0.4
1.5	0.45

The effect of inelastic scattering of electrons before leaving the liquid depends on the kinetic energy of the outgoing electrons. Recently, Luckhaus *et al.* carefully examined this issue and reported the contribution of inelastic scattering in the experimental data by comparing the experimental photoelectron spectra (3.6 eV ≤ hν ≤13.6 eV) of the same aqueous species with the Monte Carlo simulations that include inelastic scattering.[6] We referred to the supplementary information of this paper and tabulated the kinetic energy shift between the experimental spectra and the simulated spectra for given ionization photon energies.

References for the Supplemental Information

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6. D. Luckhaus, Y.-i. Yamamoto, T. Suzuki and R. Signorell, *Sci. Adv.*, 2017, **3**, 1603224.