Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for:

The valence electron affinity of uracil determined by anion cluster photoelectron spectroscopy

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Calibration of electron-binding energies

Our extracted electron binding energy for the DBS of U was: EA_D = +75 ± 6 meV. Other experimental studies are in agreement with this value,[1,2] but some report a slightly higher binding energy (~90 meV).[3,4] Details of our calibration process are included below.

Atomic iodide, I^-, was the selected calibrant. Following photodetachment with 266 nm laser pulses ($h\nu$ = 4.661 eV), two peaks are observed in the photoelectron spectrum (Fig. S1(a)), corresponding to formation of neutral I in either the $^2P_{3/2}$ (ground) or $^2P_{1/2}$ (excited) state. The electron affinity of I is EA = 3.0590 eV,[5] and the spin-orbit splitting between the two peaks is E_{SO} = 0.9427 eV.[6] The two peaks were fit with Gaussian functions, providing calibration for the velocity map imaging spectrometer.

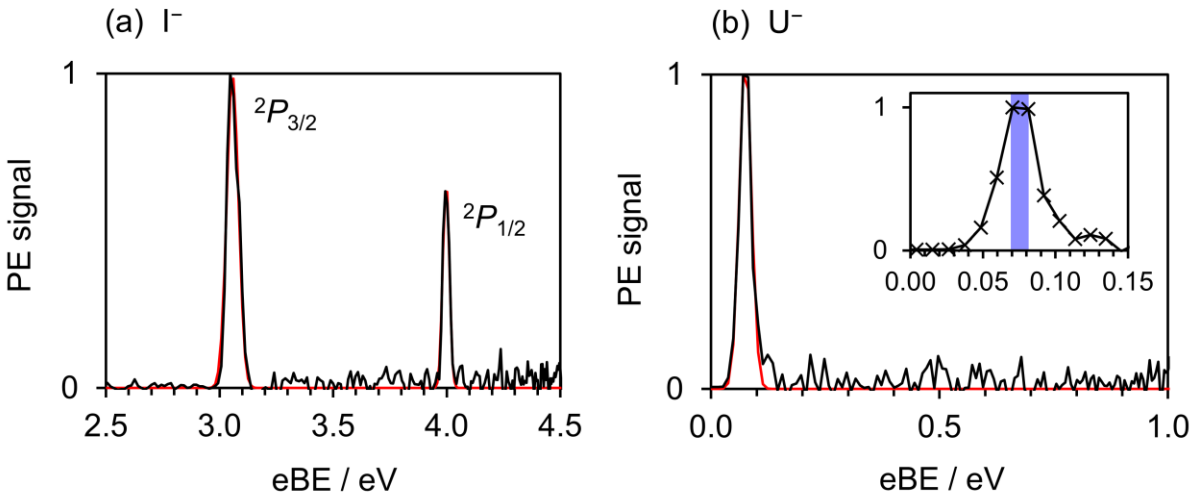

Fig. S1. Photoelectron spectra of (a) I^- and (b) U^-. Gaussian fits to each peak are shown in red. Inset of (b) shows an expanded view of the DBS peak, with the stated range for EA_D highlighted in blue.

Immediately after measurement of I^-, the photoelectron spectrum of U^- (Fig. S1(b)) was acquired with 1064 nm laser pulses ($h\nu$ = 1.165 eV). The photon energy was lowered due to the smaller electron binding energy for U^-. Resultantly, the central eKE of the DBS peak was between the eKEs of the two I^- peaks, ensuring that the calibration was appropriate (and not subject to radial dependencies in the image). The fitted central eBE was found to be EA_D =

+75 meV. Although the DBS peak has a notable width (σ = 13 meV), the peak center can be determined to a greater precision. We extract an uncertainty of ±6 meV, which is displayed in inset of Fig. S1(b). Repeated measurements at different wavelengths have also given consistent values for EA_D.

Dominant vibrational excitation

In the calculated vibronic spectrum from the π_1* valence state of U^-, the vibrational progression is dominated by the excitation of the ν_{15} vibrational mode. Fig. S2 shows the displacement vectors for this vibrational mode. The corresponding motion clearly connects the planar neutral uracil molecule with the non-planar geometry of the π_1* valence state anion.

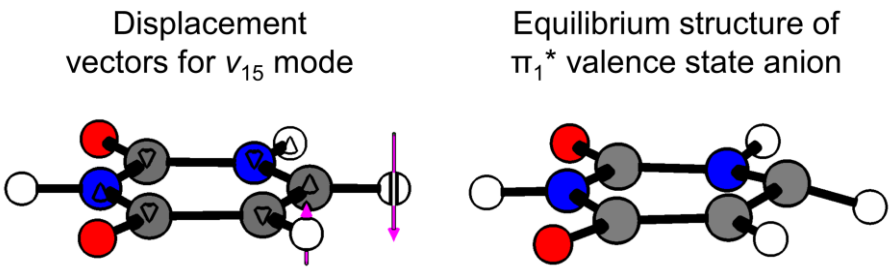

Fig. S2. Calculated displacement vectors (pink) for the ν_{15} vibrational mode (left), that contributed most to the calculated vibronic spectrum. For comparison, the calculated, optimized geometry of U^- in its π_1* valence state is also shown (right).

References

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