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SUPPORTING INFORMATION

Relative Photoionization Cross-Sections of SAMOs in C_{60}

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1. Full Data Series

The complete series of angle-integrated photoelectron spectra used to extract the data shown in Figures 2 and 4 of the paper are shown in Figure S1. The thermal background has not been subtracted from these plots but the fit used to determine the background contribution is shown as a red line.

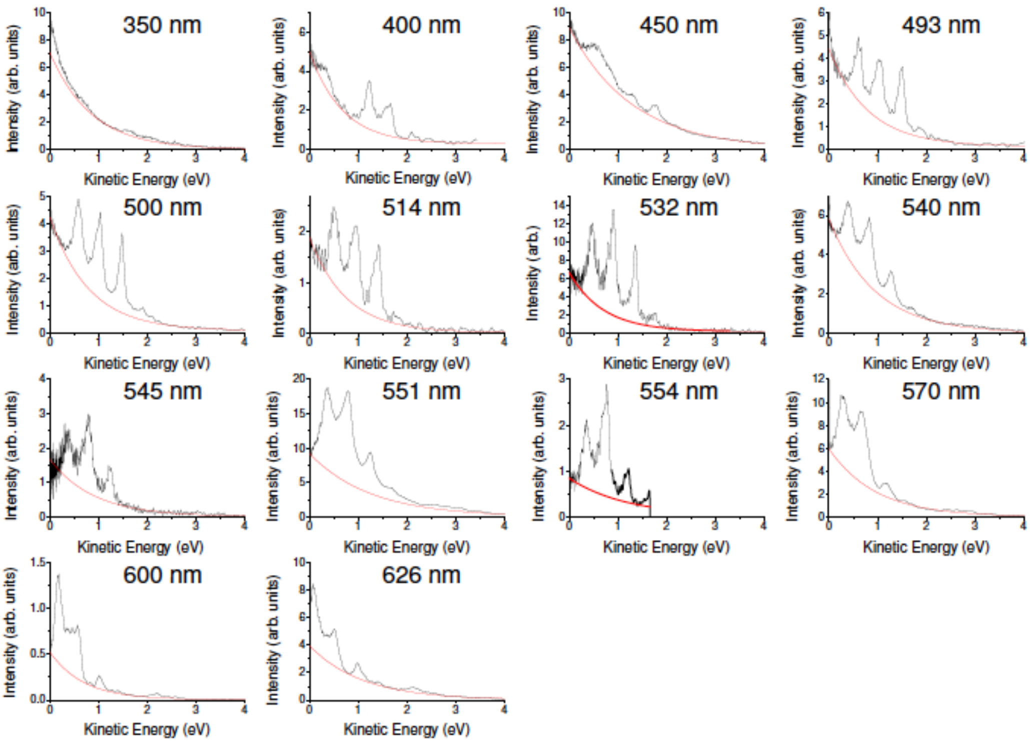

Fig. S1. Photoelectron spectra for different laser wavelengths. The red line shows the fit used to subtract the thermal background.

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2. Dependence on Experimental Parameters

The following tests were carried out to ensure that the results did not depend critically on fullerene oven temperature, laser pulse duration or laser pulse intensity within the ranges typically used in the photoionization experiments.

A. – LASER PULSE DURATION DEPENDENCE

Measurements were performed at a set wavelength and oven temperature (542 nm (corresponding to 2.3 eV), 505 °C) to ascertain the influence of laser pulse duration upon the relative s-SAMO, p-SAMO and d-SAMO signals. The results are reported in Figure S2. The data plotted in black correspond to a laser pulse duration of 38±1 fs and the data plotted in red to 99±2 fs, in both cases the laser pulse fluence was 0.4 Jcm^{-2}.

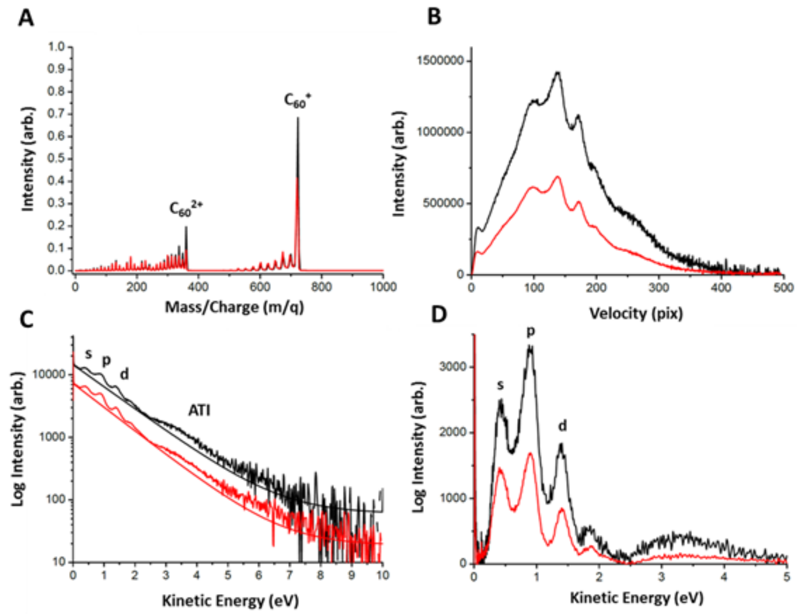

Figure S2 - (A) TOF mass spectra, (B) Photoelectron velocity distribution, (C) PES (intensity plotted on a log scale) with fitted thermal electron background, (D) PES with thermal electron background subtracted. The spectra in black and red correspond to a pulse duration of 38 ±1 fs (10.5 $TWcm^{-2}$) & 99±2 fs (4 $TWcm^{-2}$) respectively. The signal above 2.5 eV is due to above threshold ionization (ATI).

The comparison between the data at the two pulse durations is shown in Figure S3.

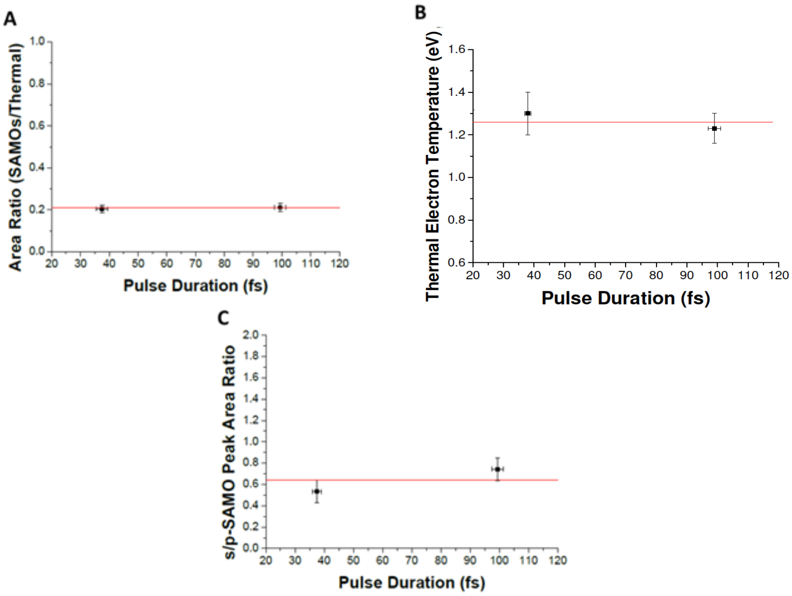

Figure S3 - Plots showing the pulse duration dependence of (A) overall s, p and d-SAMO photoionization intensity relative to thermal electron emission, (B) thermal electron temperature and (C) s/p-SAMO photoionization intensity ratio. Data taken from spectra in Fig. S2. Red lines are horizontal lines to guide the eye.

From these results it was deduced that the pulse duration is not a significant factor determining the relative intensity of the SAMO states. Although there appears to be a slight increase of the s/p ratio for the longer pulse duration, this is still, just, within the experimental error bars.

B. – INITIAL INTERNAL ENERGY DEPENDENCE

Since earlier studies have shown the importance of initial vibrational energy for the population and detection of the SAMO peaks [1], measurements were performed at a set wavelength, pulse duration and laser intensity (540 nm (corresponding to 2.3 eV), 35 fs, and 8.20 ± 0.05 $TWcm^{-2}$) for a number of different oven temperatures, although still for significantly higher vibrational temperatures than the low temperature beam studied in Ref 1, to investigate any influence the oven temperature and hence the internal energy of C_{60} may have on the SAMO ratios. Figure S4 details the results of these measurements.

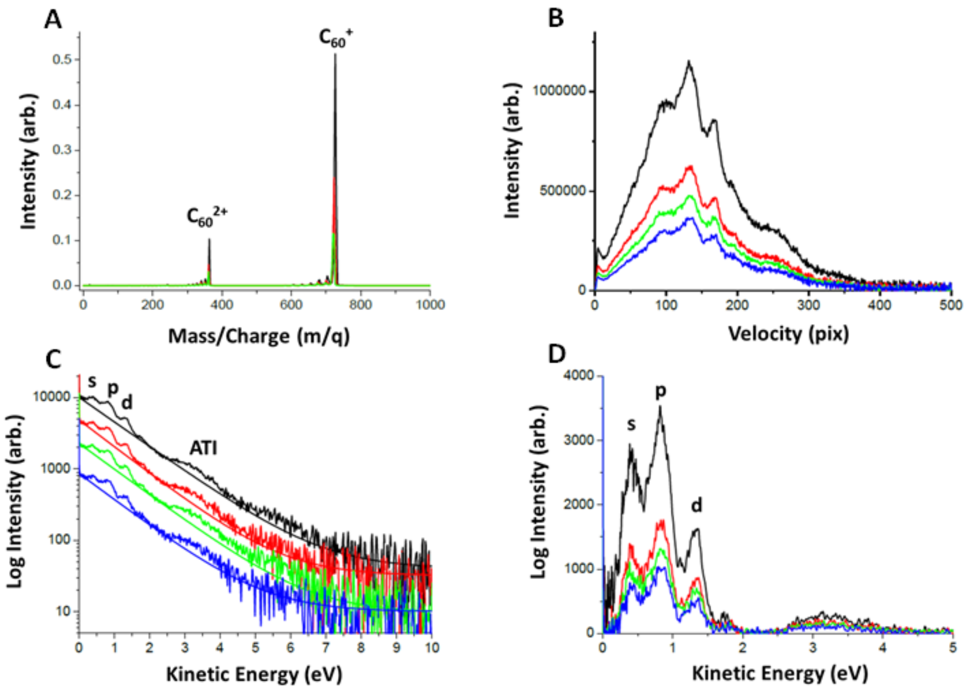

Figure S4 - (A) TOF mass spectra, (B) Photoelectron velocity distribution, (C) PES (intensity plotted on a log scale) with fitted thermal electron background, (D) PES with thermal electron background subtracted. The spectra are coloured black, red, green and blue to differentiate the different oven temperatures of 505 °C, 485 °C, 460 °C & 435 °C respectively.

The comparison between the different oven temperatures is presented in Figure S5.

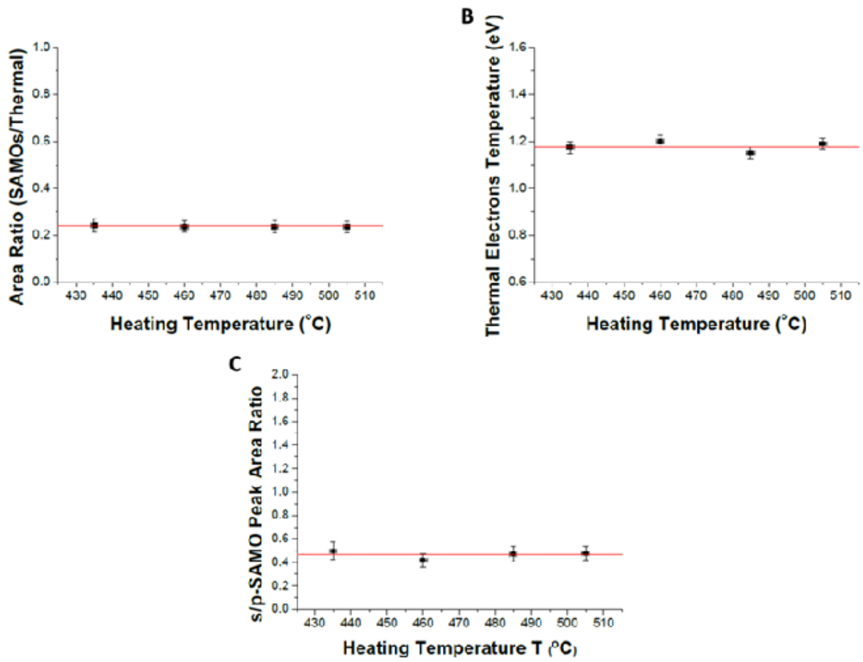

Figure S5 - Plots showing the oven temperature dependence of (A) overall s, p and d-SAMOs photoionization intensity relative to thermal electron emission, (B) thermal electron temperature and (C) s/p-SAMOs intensity ratio. Data from the spectra in Fig. S4. Horizontal red lines to guide the eye.

From these measurements it was determined that the oven temperature, whilst an important factor in optimising the total count rate (by controlling the target density), is not a critical factor, for the temperature range studied, in determining the relative difference in the observed photoelectron intensities of the SAMO states.

C. – LASER INTENSITY DEPENDENCE

Measurements were performed at a set wavelength, pulse duration and oven temperature (540 nm (corresponding to 2.3 eV), 35 fs, and 505 °C) for a number of different laser intensities to investigate the effects of laser power density on the relative observed signal levels from the SAMO states. Figure 5 details these results taken at 5.8 ± 0.1, 4.7 ± 0.1, 3.9 ± 0.06, 3.2 ± 0.05 and 1.8 ± 0.03 $TWcm^{-2}$.

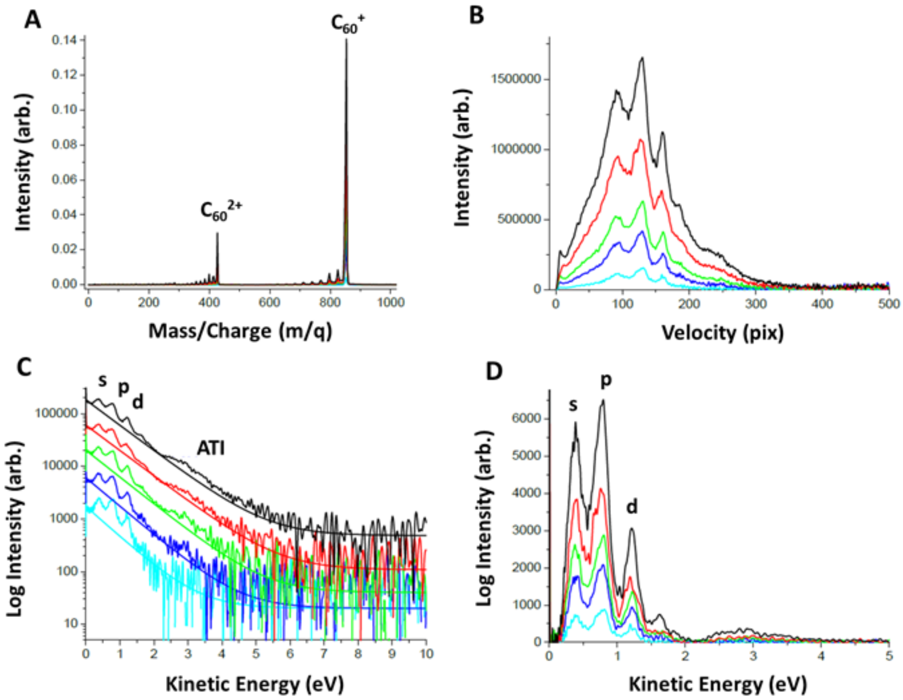

Figure S6 - (A) TOF mass spectra, (B) Photoelectron velocity distribution, (C) PES (intensity plotted on a log scale) with fitted thermal electron background, (D) PES with thermal electron background subtracted. The spectra are colour coded as black, red, green, blue and cyan for the measurements recorded at 5.77, 4.70, 3.93, 3.20, 1.82 $TWcm^{-2}$ respectively.

The comparison of the different laser intensities is shown in Figure S7.

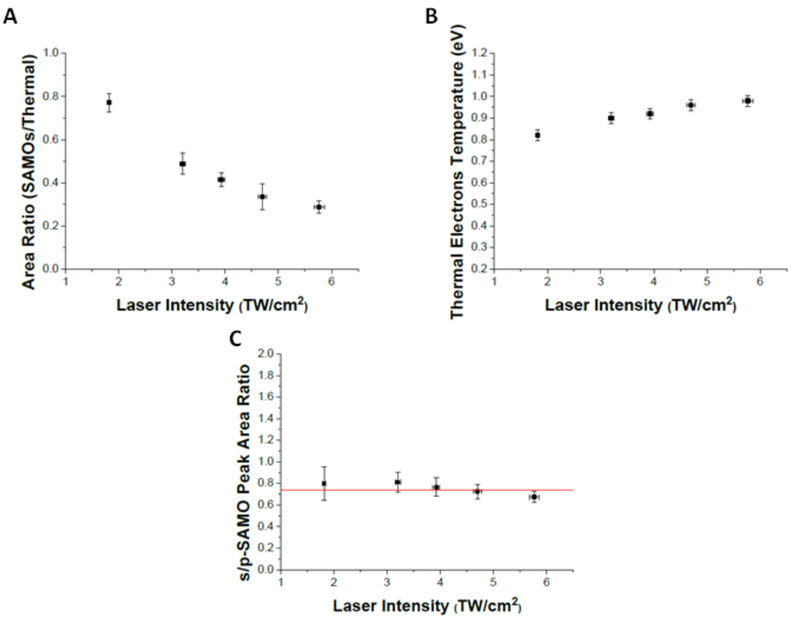

Figure S7 - Plots showing the laser intensity dependence of (A) overall s, p and d-SAMO photoionisation intensity relative to thermal electron emission, (B) thermal electron temperature and (C) s/p-SAMOs photoionization intensity ratio. Horizontal red line to guide the eye. Data from the spectra in Fig S6.

From this comparison it can be seen that there is a significant dependence of the relative magnitude of the SAMO states with respect to the total thermal background on laser pulse intensity. The trend shows that the total thermal background signal increases more rapidly with increasing laser intensity (fluence), and hence increasing electron temperature [2,3], than the SAMO signal. However the relative intensities of the SAMO states with respect to each other remain constant as a function of laser intensity for the range investigated.

3. Ratio of d and 2s SAMO Intensities

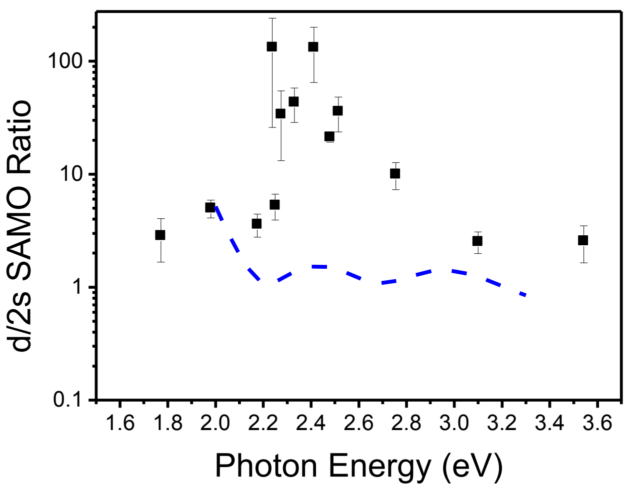

Fig. S8. Comparison of relative experimental d and 2s SAMO peak intensities with theoretical ionization width ratios (average band values) as a function of photon energy.

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