Temporal broadening of attosecond photoelectron wavepackets from solid surfaces: supplementary material

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1. SHIRLEY SECONDARY ELECTRON BACKGROUND SUBTRACTION

The secondary scattered electron background contribution to the photoelectron spectrum in the vicinity of the valence band was estimated using the Shirley method [1]. To allow an appraisal of the uncertainty in the Shirley background, two independent approaches were employed for its calculation, as described in the following.

Approach 1

The secondary electron background was calculated iteratively between energy bounds $\mathcal{E}_L = 73$ eV and $\mathcal{E}_H = 100$ eV, using the procedure in [1].

Approach 2

Decomposing the photoelectron spectrum into a unscattered part and a scattered part, the unscattered valence band part of the photoelectron spectrum can be closely described by a Gaussian, $f_{vb}(\mathcal{E}) = h_1 \exp[-(\mathcal{E} - \mathcal{E}_{vb})^2/w^2]$, where h_1 , $\mathcal{E}_{vb}$, and w are the height, central energy, and width of the valence band feature, respectively. The Shirley background of scattered electrons at energy $\mathcal{E}$ is proportional

to the integrated number of unscattered electrons in the valence band at energies $> \mathcal{E}$. Thus, for a photoelectron feature described by $f_{vb}(\mathcal{E})$ the scattered part of the spectrum is

$$f_{se}(\mathcal{E}) = h_2 \int_{\mathcal{E}_H}^{\mathcal{E}} d\mathcal{E}' \exp\left[-\left(\frac{\mathcal{E}' - \mathcal{E}_{vb}}{w}\right)^2\right], \quad (\text{S1})$$

where h_2 is the maximum height of the secondary electron background, and $\mathcal{E}_H$ is an energy above which the intensity of the spectrum can be considered negligible.

An independent estimate of the Shirley background can then be made using a fitting procedure. Each photoelectron spectrum in the raw streaking trace (no Fourier filtering applied) was fitted using a nonlinear least-squares procedure in the range from $\mathcal{E}_L = 73$ eV to $\mathcal{E}_H = 100$ eV, using the fit function $f(\mathcal{E}) = f_{vb}(\mathcal{E}) + f_{se}(\mathcal{E})$ with h_1 , h_2 , $\mathcal{E}_{vb}$, and w as fitting parameters. The secondary electron background is then given by $f_{se}(\mathcal{E})$ from the fit. An example fitted photoelectron spectrum, and a comparison between the electron backgrounds calculated using the two different approaches, is shown in figure S1.

Fig. S1. Comparison of Shirley backgrounds calculated using two different approaches. Experimental WO_3 photoelectron spectrum (black), fitted spectrum from approach 2 (red), and Shirley secondary electron background calculated using an iterative procedure in approach 1 (dashed green), and a fitting procedure in approach 2 (blue).

2. FROG-CRAB TRACES AND ERROR ANALYSIS

FROG-CRAB was used to retrieve the photoelectron wavepackets from the experimental streaking traces, with the secondary electron background subtracted but with no Fourier filter applied. Negative count numbers, resulting from subtracting the secondary electron background from a noisy streaking trace, were set to zero. The algorithm error in the retrieved photoelectron wavepacket was determined following the approach in [2].

Fig. S2. Error analysis of wavepacket duration for WO_3 , showing the retrieved wavepacket duration as a function of spectral window size with secondary electron background subtraction using approach 1 (black data points), and approach 2 (red data points). The error bars indicate the algorithm errors for each retrieval. The median of the retrieved wavepacket durations (359 asec) is indicated by the dashed blue line. The overall experimental error on the wavepacket duration, taken as the total range of retrieved wavepacket, durations is indicated by the shaded area. The circled data point corresponds to the retrieved wavepacket in figure 2 of the main paper, and the retrieved trace in figure S4.

The low signal-to-noise of features lying close to the extrema of the valence band peak complicates the identification of the energy bounds

Fig. S3. Error analysis of wavepacket duration for Au. The median retrieved wavepacket duration is 319 asec. The legend is the same as for figure S2. The circled data point corresponds to the retrieved wavepacket in figure 3 of the main paper, and the retrieved trace in figure S5.

Fig. S4. FROG-CRAB reconstruction of WO_3 streaking trace.

Fig. S5. FROG-CRAB reconstruction of Au streaking trace.

at which the intensity of the valence band feature drops to zero. To determine the resulting uncertainty in the retrieved wavepacket duration, the size of the spectral window of the input streaking trace was varied symmetrically around the valence band peak, with sizes from 18 – 22 eV. The uncertainty in the secondary electron background is potentially another source of error. We investigated this uncertainty by using the two independent approaches described earlier for calculating the secondary electron background. The FROG-CRAB retrieval was performed for all combinations of spectral window size and secondary electron background. The wavepacket duration was taken as the median of the retrieved durations. The overall experimental error on the wavepacket duration was taken as the total range of retrieved pulse durations. The retrieval results are summarised in figures S2 and S3 for WO₃ and Au, respectively. The retrieved wavepackets displayed in figures 2 and 3 of the main paper correspond to the circled data points in figures S2 and S3, respectively, which lie close to the median wavepacket durations. The FROG-CRAB reconstructed streaking traces corresponding to these data points are shown in figures S4 and S5 for WO₃ and Au, respectively.

The distributions of wavepacket durations as a function of time delay, determined from the streaking traces using the approach in [2], are illustrated in figures S6 (a) - (b) and S7 (a) - (b). For both WO₃ and Au, the distribution of retrieved wavepacket durations is single-peaked, and there is no correlation outside the scatter of the data points between the wavepacket duration and the instantaneous electric field at the ionisation time. While variations in the spectral width of the wavepacket can be induced by the streaking field [3] this effect is not very pronounced in our traces due to the relatively low streaking amplitude (< 1 eV), as shown by figures S6 (c) and S7 (c). The absence of strong correlations in figures S6 (d) and S7 (d) indicates that the distribution of wavepacket durations is not directly related to the spread of spectral widths.

3. SAMPLE FABRICATION AND CHARACTERISATION

A 20 nm W film was coated onto a Si (100) substrate using sputter deposition, and a 52 nm-thick Au film was deposited onto a Si (100) substrate by thermal evaporation. The samples were stored in ambient conditions before being installed in the UHV surface streaking experimental chamber. The samples were characterised *ex-situ* using x-ray photoelectron spectroscopy (XPS) (SPECS Mg K α X-ray source, Phoibos 150 hemispherical analyser, data analysis with CasaXPS, Casa Software Ltd), x-ray diffraction (XRD) (Rigaku SmartLab), and atomic force microscopy (AFM) (Veeco Dimension Icon, data analysis with Gwyddion).

XPS and XRD measurements of the WO₃ and Au samples are shown in figures S8 and S10, respectively. The XPS spectra were calibrated using the C 1s peak at 285 eV. The C and O peaks are a clear indication of surface contamination, and are present in all measurements for both samples, at binding energies in agreement with the literature values [4].

The prominent 4f peaks in the XPS spectrum of the W film are shifted by 4.7 eV compared to the metallic W 4f 7/2 peak, from 31.7 eV to 36.4 eV binding energy (BE). This shift corresponds to WO₃ [4]. The substructure at 30.5 - 31.5 eV BE contains a contribution from pure W [5]. The thickness of the WO₃ layer was estimated as 8.5 nm by comparing the peak intensity ratios after subtraction of a Shirley background [6]. This is more than an order of magnitude larger than the $\sim 4.9\text{\AA}$ mean free path of 84 eV photoelectrons. Photoelectron spectra measured using the attosecond XUV pulses will therefore be almost entirely from WO₃.

To determine the crystallinity of the WO₃ sample, XRD was performed in ambient conditions, on both the pure Si (001) substrate and

Fig. S6. Distribution of wavepacket durations and spectral widths for WO₃. (a) Retrieved wavepacket durations (data points) as a function of time-delay between the NIR and XUV pulses, corresponding to the circled data point in figure S2. The retrieved streaking field at the sample surface is also shown (red curve). (b) Histogram of retrieved wavepacket durations from (a). (c) Measured spectral width of valence band peak as a function of time-delay. (d) Plot of spectral width versus wavepacket duration.

Fig. S7. Distribution of wavepacket durations and spectral widths for Au. See figure S6 caption for an explanation of the figure panels. The retrieved durations in (a) correspond to the circled data point in figure S3.

on the sample itself. The dominant narrow peaks in both XRD spectra are from the single crystalline Si substrate, while no characteristic tungsten peaks are present. Peaks from WO_3 , which would appear in the $23^\circ < 2\Theta < 25^\circ$ region [7] (where 2Θ is the angle of the diffracted beam relative to the incident beam), are also absent. Thus, we can confirm that the WO_3 film is amorphous.

The AFM image of the WO_3 surface topology is shown in figure S9. The sample surface has an average roughness of 65nm. This roughness corresponds to several WO_3 layers (lattice parameters monoclinic WO_3 $a = 5.3 \text{ \AA}$, $b = 7.2 \text{ \AA}$, $c = 7.7 \text{ \AA}$).

The XPS analysis of the Au sample reveals a metallic Au film with carbon and oxygen surface contamination caused by storage and transport under ambient conditions. The prominent Au 4f peaks are detected without any shift confirming the presence of pure metallic Au.

The XRD analysis of the Au sample shows intense narrow peaks from the single crystalline Si substrate and weaker broadened peaks from the Au layer. The relative broadness of the Au diffraction peaks in the XRD trace, and the presence of diffraction peaks from different crystal orientations, confirms the polycrystalline nature of the Au film. The ratio of the peak areas from the Au(111) and the other crystal orientations indicates a preferred Au(111) orientation in the sample. The Si(200) and Si(400) peaks originate from the Si(100) substrate.

The AFM image of the surface topology of the Au film is shown in figure S11. On the flat surface with an average roughness of 0.7 nm the formation of discs can be seen. The disc profiles, shown in figure S12, have an average width of 20 – 30 nm and a height of 5 – 10 nm. The focal spot diameter of the XUV pulses used for the streaking measurements is on the order of a couple of μm . The photoelectron signal from the ~ 50 discs within the area of the XUV focal spot is expected to make up less than 1 % of the total signal, based on their relative area compared to the underlying plane Au surface.

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Fig. S8. Upper: XPS measurement on WO_3 sample. The inset shows the 4f region of the spectrum, and the expected positions of the 4f 5/2 and 4f 7/2 peaks for pure W. Lower: XRD measurement on WO_3 sample. The inset region $23^\circ < 2\Theta < 25^\circ$ (where 2Θ is the angle of the diffracted beam relative to the incident beam) is the expected region of WO_3 diffraction peaks [7]. The XRD trace of the Si (100) substrate is also shown.

Fig. S9. AFM measurement of WO_3 sample.

Fig. S10. Upper: Au XPS measurement. The inset shows the 4f region of the spectrum, and the expected positions of the 4f $5/2$, and 4f $7/2$ peaks for pure Au. Lower: Au XRD measurement.

Fig. S11. AFM measurement of Au sample.

Fig. S12. Disc profiles along the lines indicated in figure S11.