Supplementary material for K-edge paper

1 Spectral Dispersion

Calibration shots using parylene-C as a back-lighter were taken which produces a spectrum with three dominant lines, see figure S1. These are the chlorine He_α resonance line (2p $^1P_1$-1s^2 $^1S_0$ at 2789.8 eV), the inter-combination lines (2p $^3P_1$-1s^2 $^1S_0$ at 2775.1 eV) [**Thompson et al 2009**] and the lithium-like satellite transitions which have a less certain energy. Since the He_α line is well defined in literature and often used when diagnosing hot plasmas, this was used together with the nickel-like $(3d^{-1}_{5/2}4f_{7/2})_{J=1}$ bismuth line (see figure S2) which is also well defined at 2854.4 $\pm$ 0.4 eV [**Bradley et al 1987**, **Elliott et al 1993**], to calibrate the energy dispersion across the spectrometers (we have shots with both the parylene-C and bismuth back-lighters for which the geometry of the experimental setup was the same). This is achieved by least squares fitting the maximum peaks of these lines to the literature recorded energies based on adjusting the source to crystal distance and the crystal angle to within error of the measured values on experiment. The energy spectrum is calculated using Bragg's Law since we know the pixel position of the maximum peaks along with the associated geometry of the experimental setup. We now have an energy spectrum fitted to the bismuth emission and can identify the energies of the four strongest bismuth lines. These lines can be used to identify further bismuth spectra on shots were the geometry of the experiment was different, again using linear regression to fit the four strongest lines using the peak values.

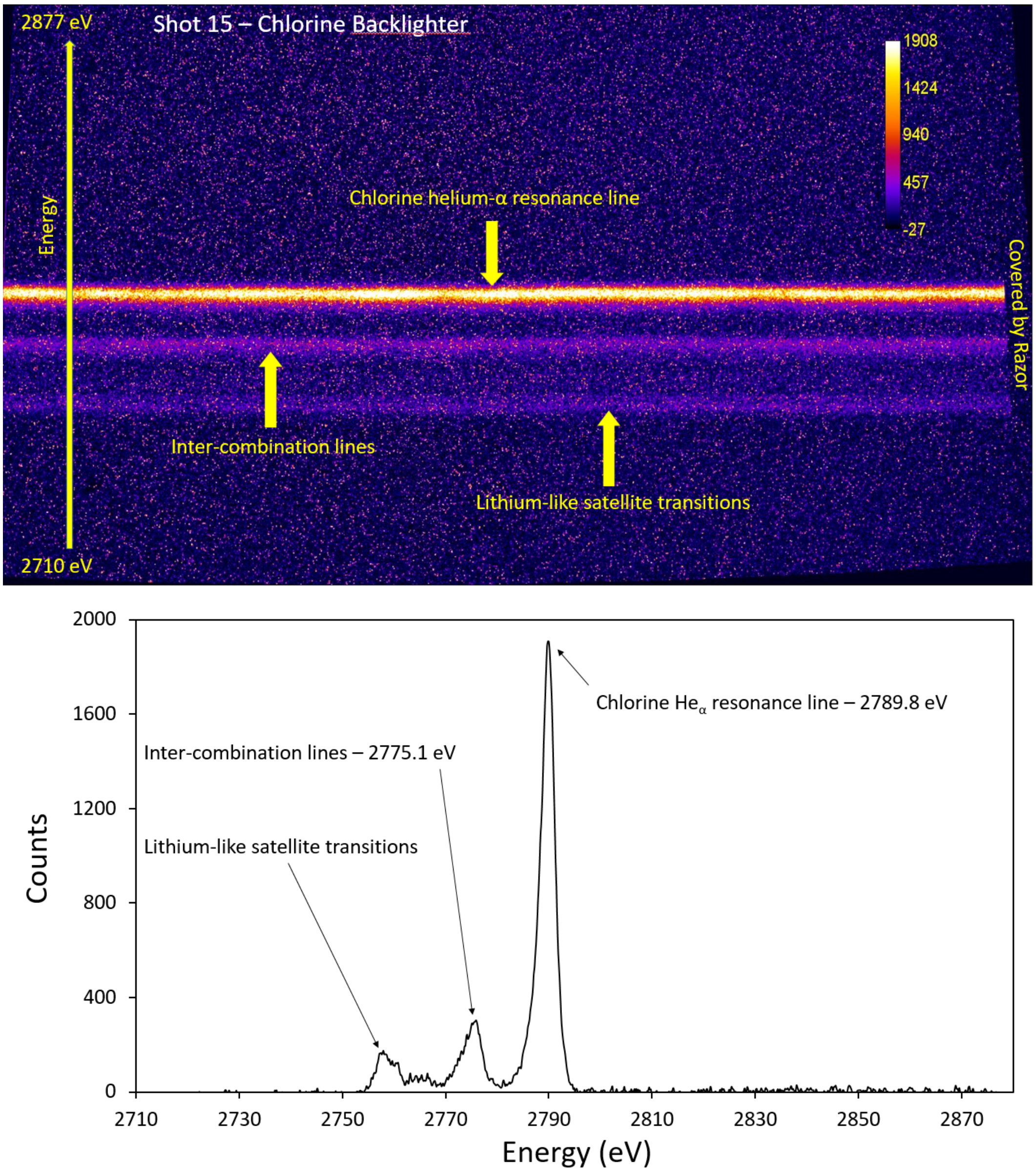

FIGURE S1: Top: Background corrected raw data image of a parylene-C backlighter (shot 15) from the west spectrometer. The image area is 2048 × 1024 pixels, or 26.6 mm × 13.3 mm. An aluminium layer has been divided out from the left half of the image, corrected for defects and straightened (hence the black curvature at the bottom of the image). Bottom: Spectral line-out after background subtraction taken vertically along the length of the raw data image and averaged over the spatial axis (horizontal axis) between pixels 41 and 1952.

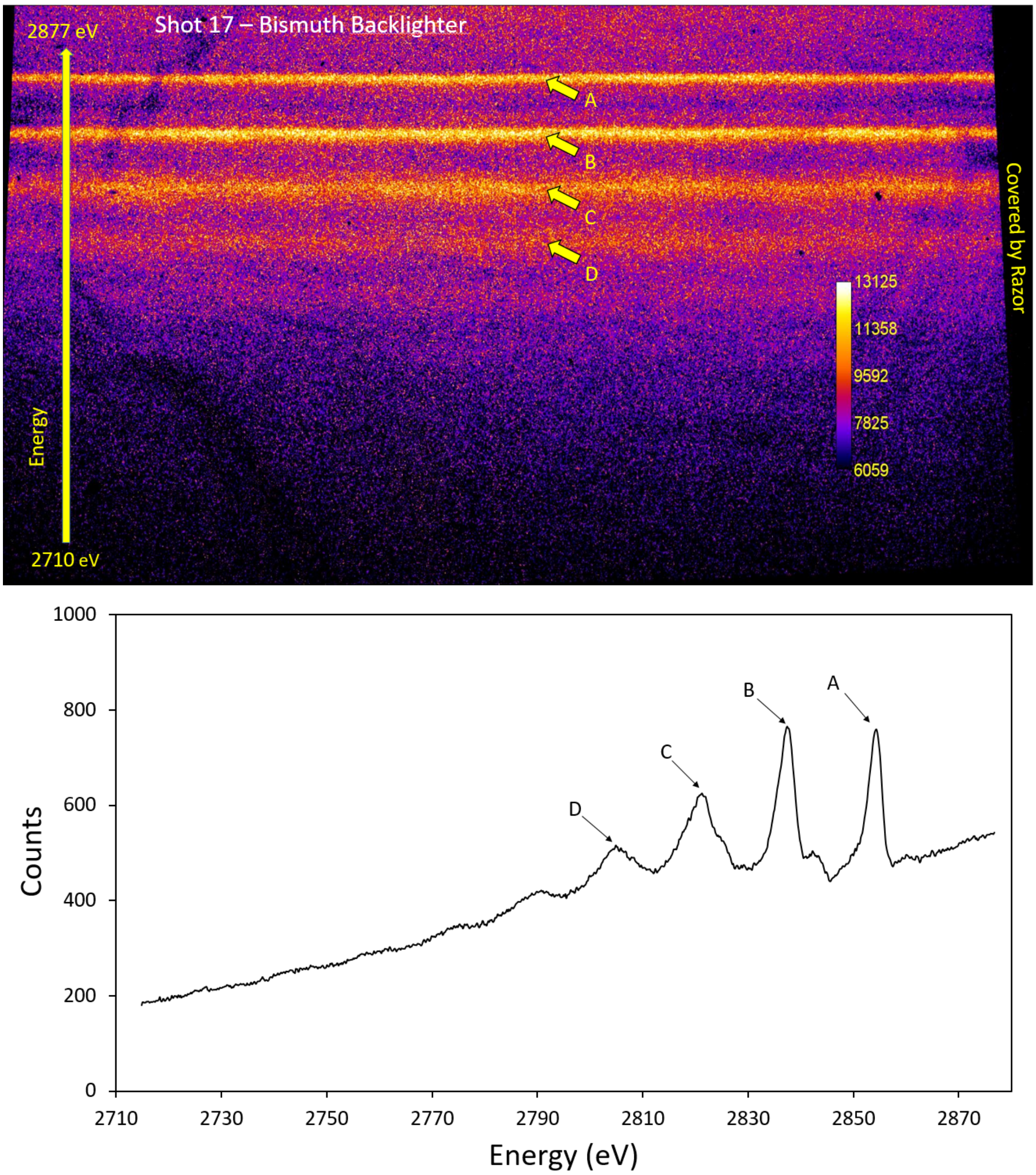

FIGURE S2: Top: Background corrected raw data image of a bismuth back-lighter (shot 17) from the west spectrometer. The image area is 2048 × 1024 pixels, or 26.6 mm × 13.3 mm. An aluminium layer has been divided out from the left half of the image, corrected for defects and straightened (hence the black curvature at the bottom of the image). Bottom: Spectral lineout taken vertically along the length of the raw data image and averaged over the spatial axis (horizontal axis) between pixels 41 and 1952. Line A is the nickel-like $(3d^{-1}_{5/2}4f_{7/2})_{J=1}$ bismuth line at an energy of 2854.4 eV together with lines B = 2837.5 eV, C = 2821.3 eV and D = 2804.9 eV.

2 Shift in bismuth energy spectrum

Although we are dealing with embedded chlorine in both sample cases, and we would not necessarily expect the K-edge position of embedded chlorine to give the same edge position as non-embedded chlorine i.e. at 2822.4 eV [**Thompson et al 2009**], we would however not expect it to be shifted by the amount we are seeing in both cases of parylene-C $\approx$ 2825.6 eV and KCl $\approx$ 2828 eV. As a check on the cold edge positions for both materials we referred to a similar experiment that was carried out in September/October 2015 at at VULCAN target area west at the Central Laser Facility, UK. The experimental setup is shown in figure S3. Here we used a 1.3 ns FWHM long pulse (527 nm) (as the short pulse through the CPA system failed) focused to $\approx 500\ \mu$m onto the same bismuth back-lighter with CH layer as we used in the present experiment to generate the x-ray back-lighter probe. The bismuth drive pulse was incident onto the bismuth from an east to west position. The M-shell x-rays passed through the target at 45° and the spectra recorded onto a Silicon (111) CCD (Andor DX436) spectrometer with 13.5 μm square pixels that sat in a north-east position. Reducing the data with the same methods applied herein, the K-edges for the cold samples came out at 2822.3 eV and 2823.8 eV for parylene-C and KCl respectively. These edge positions would be much closer to what we would expect to see. This discrepancy in the edge led to looking at the spectra for the 2017 data more closely. Taking the ratio of the difference between two bismuth peaks and the difference between one bismuth peak and the K-edge, we would expect the ratio for both sets of experimental data for 2017 and 2015 to come out the same. This was not the case with the 2017 data having a ratio of 0.62, whilst the ratio of the 2015 data was 0.55. This led to the belief that the bismuth spectrum must be red/blue shifting. If the bismuth plasma is blowing back from the irradiated side at high velocity this could result in a shift of the spectrum and since the K-edge position due to absorption of the sample would hold in the same place the K-edge would appear to move in the opposite energy direction to the shift. Since we are using very different probe drive pulses to generate the x-rays on both experiments this could lead to very different shifts, along with the effect of the different geometries of each experiment. In fact due to the geometry of the 2015 experiment we would see a resultant blue shift as the blow-off from the plasma comes towards the sample and spectrometer at an angle of 45°. For the 2017 experiment (see figure of 2017 set-up) both probe beams would result in a red-shift as the blow-off from the bismuth plasma is in the opposite direction to that of the sample and spectrometer at an angle of 30°.

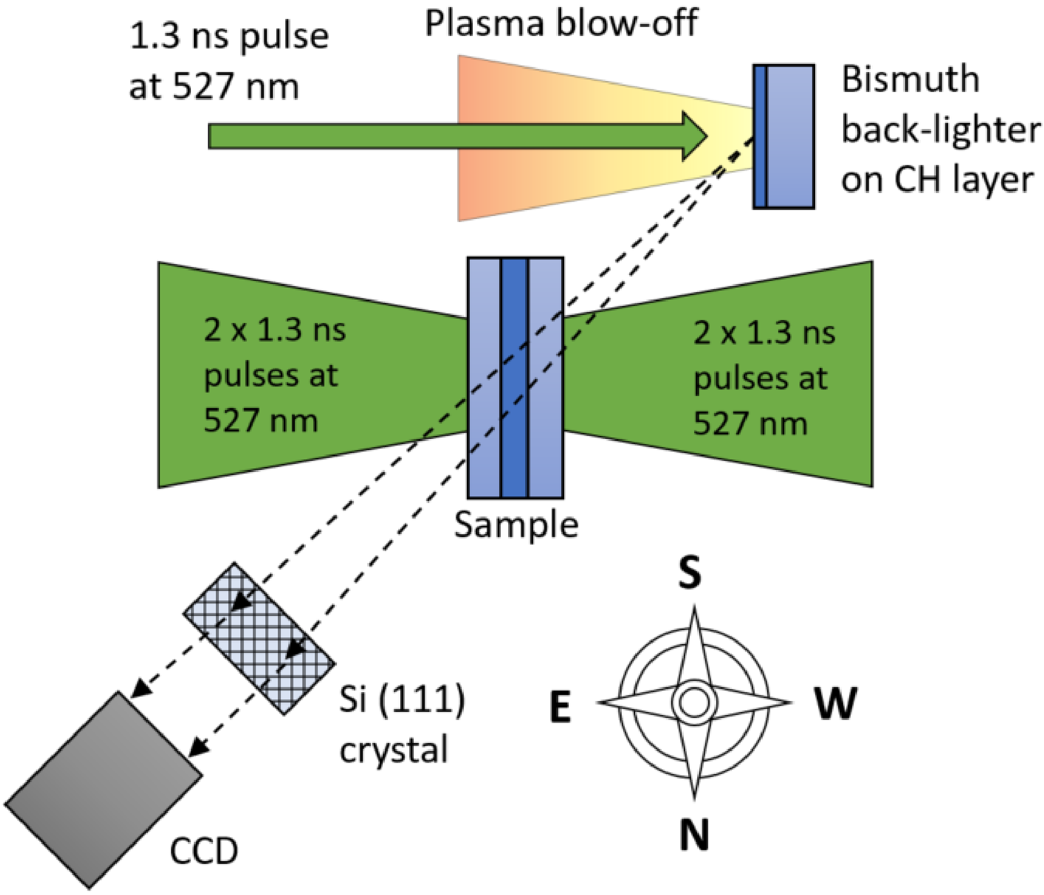

FIGURE S3: Top down schematic view of the 2015 experimental set-up (not to scale). The four shock drive beams incident on the embedded chlorine sample are not present during a cold K-edge shot. The bismuth and sample target centres were positioned approximately 7 mm apart. The two targets were pre-aligned on a target alignment rig which ensured that the line of sight from back-lighter to spectrometer passed through the shock compressed region of the sample. The spectrometer set-up (composing of the silicon (Si) crystal and CCD) is at 45° to the bismuth normal.

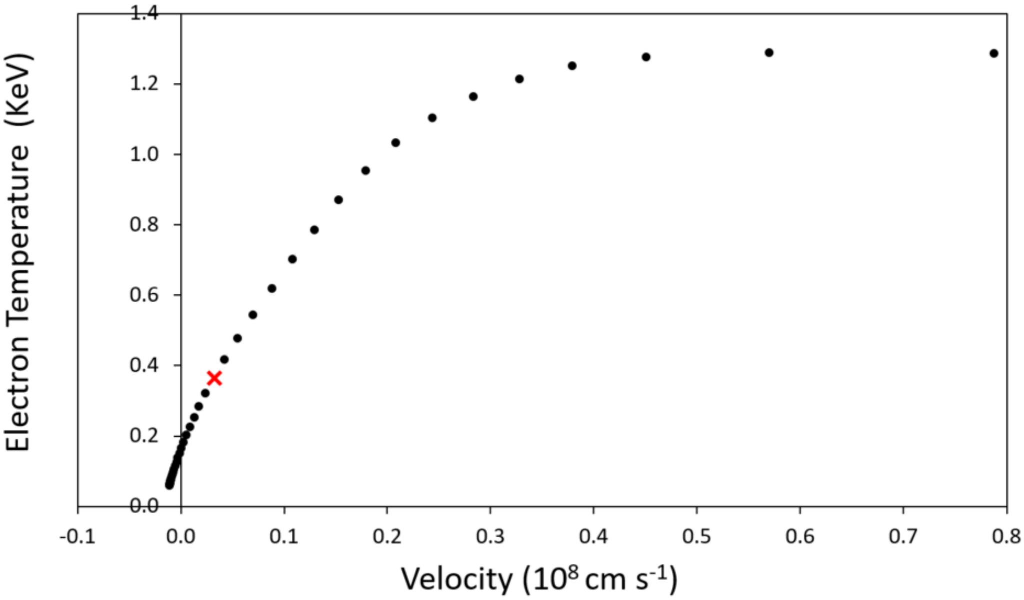

FIGURE S4: HYADES simulation for irradiated bismuth, from the 2015 experimental data-set (shot 14 2015/10/27). Taken at the peak of the probe pulse (1.1 ns at an intensity of 2.4×10^{13} W cm^{-2}). The data point represented by the red x is the position where the intensity of the emission peaks (see figure S6), implying that the shift in the bismuth energy spectrum is dominated by material at this lower temperature (327 eV)/higher density(2.44×10^{-2} g cm^{-2}) region, with a velocity of 3.27×10^6 cm s^{-1}. The positive velocity represents the direction that the plasma is moving, which is opposite to the direction of the incident probe pulse.

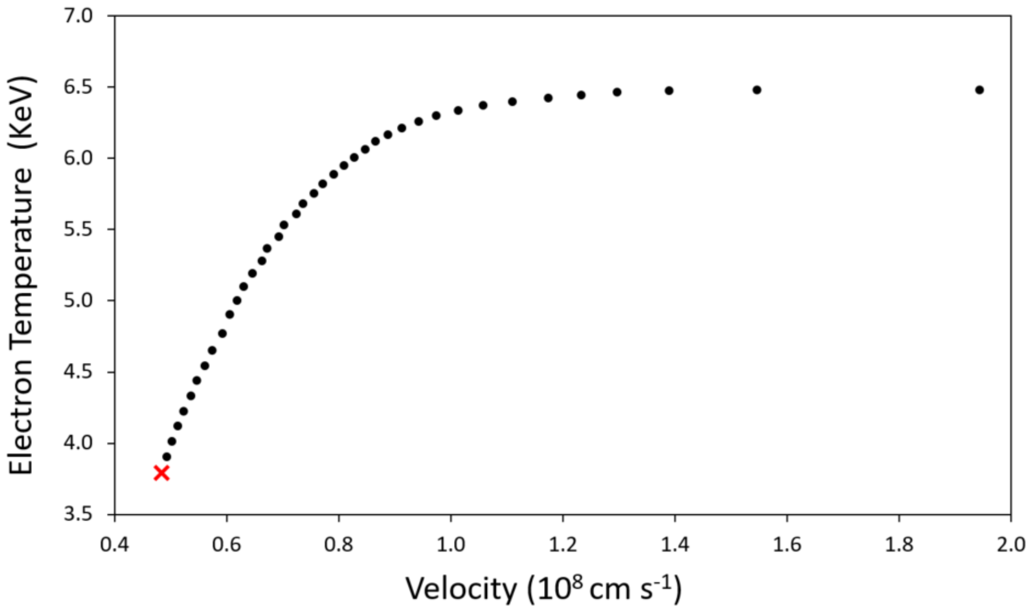

FIGURE S5: HYADES simulation for irradiated bismuth, from the 2017 experimental data-set (shot 79). Taken at the peak of the probe pulse (0.7 ns at an intensity of 2.2×10^{15} W cm^{-2}). The data point represented by the red x is the position where the intensity of the emission peaks (see figure S7), implying that the shift in the bismuth energy spectrum is dominated by material at this lower temperature (3800 eV)/higher density(2.79×10^{-2} g cm^{-2}) region, with a velocity of 4.83×10^{7} cm s^{-1}. The positive velocity represents the direction that the plasma is moving, which is opposite to the direction of the incident probe pulse.

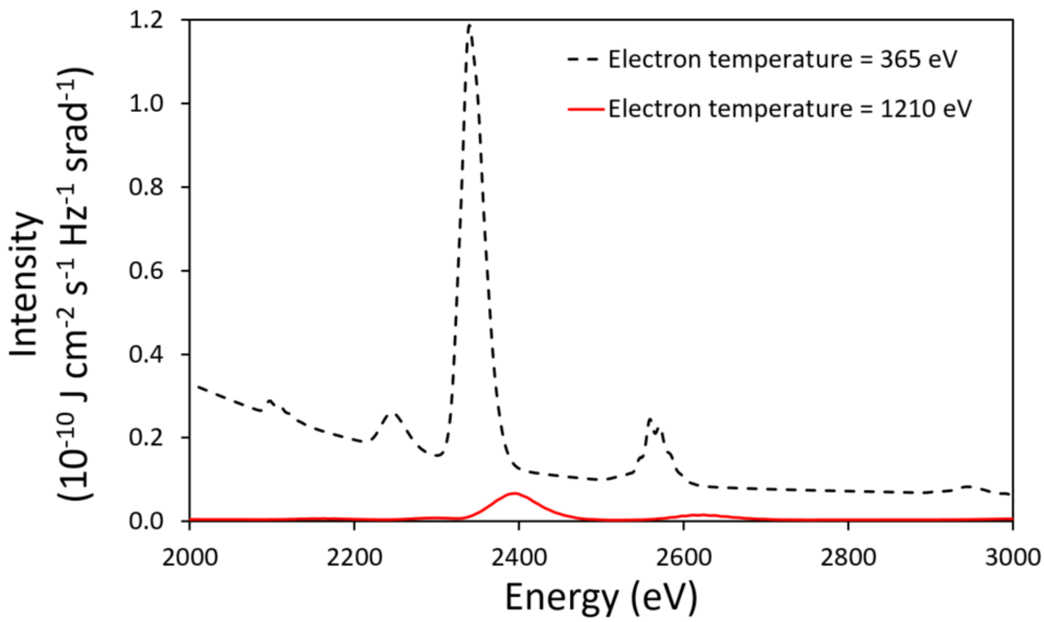

FIGURE S6: FLYCHK simulation of the 2015 data showing the intensity of emission from two points at extreme conditions from each other in figure S4. Here we use gold to show the general plot and conditions of bismuth.

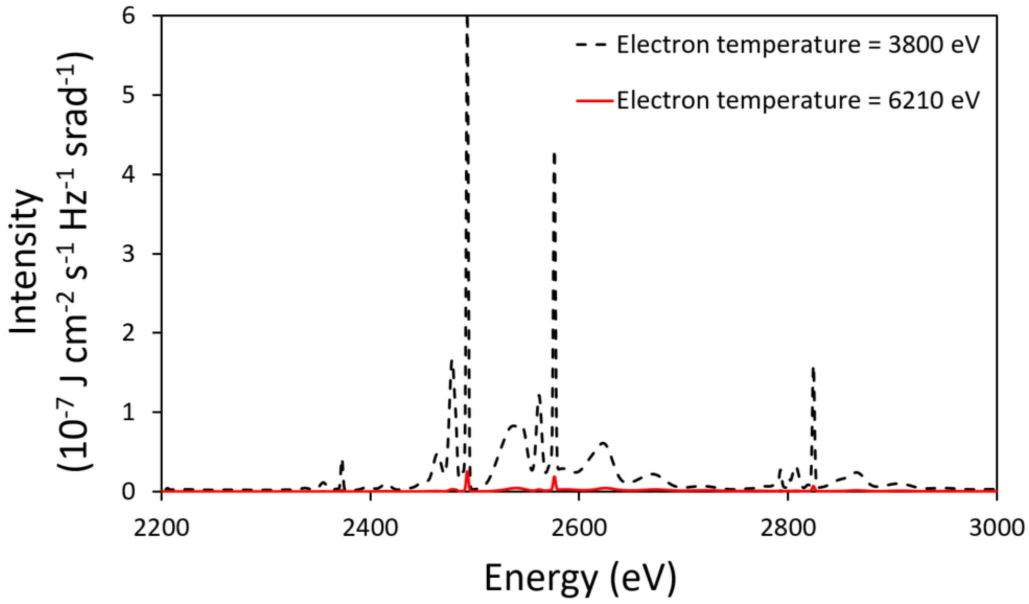

FIGURE S7: FLYCHK simulation of the 2017 data showing the intensity of emission from two points at extreme conditions from each other in figure S5. Here we use gold to show the general plot and conditions of bismuth

Simulations of the irradiated bismuth for both experimental cases were carried out using the 1D hydrodynamic software HYADES, for which the results can be seen in figures S4 and S5, from these it is clear that the 2017 data due to the short pulse gives a higher velocity of the plasma blow-off. In both cases the dominant emission is coming from the lower temperature/higher density regions where the velocity is lower. This can be approximately demonstrated using the generalised population kinetics code FLYCHK [**Chung et al 2005**]. Here we are using gold to show the general plot of bismuth due to this being the maximum limit of the nuclear charge in FLYCHK. However gold has a similar atomic mass to bismuth and gives an order of magnitude approximation for the plasma blow-off in bismuth. Figures S6 and S7 show the intensity of emission for both experimental cases at two extreme points in plots S4 and S5. In both cases the intensity of emission from the lower temperature/high density regions peak a lot higher than the higher temperature/low density regions. This implies that the shift in the bismuth is dominated by material at this lower temperature. This sounds reasonable since as the temperature gets higher and the density falls off the collisional rates for excitation would drop. Using the velocity at these higher intensity peaked regions we get a red-shift value of ≈ 3.9 eV for the 2017 data resulting in a cold K-edge for parylene-C of ≈ 2821.7 eV and the cold KCl edge at ≈ 2824.1 eV. For the 2015 data set, since the velocity is not so great due to the longer pulse we get a very slight blue shift of ≈ 0.2 eV, resulting in a parylene-C cold K-edge position of ≈ 2822.5 eV and cold KCl edge at ≈ 2824 eV. These cold K-edge positions compare better to what we see in other literature for both parylene-C and KCl i.e. [**Riley et al 1989**, **Bradleyet al 1987**, **Zhao et al 2013**, **Zhao et al**, **2015**, **Trischka 1945**]

Again we stress that this is an order of magnitude approximation for the blow-off plasma that gives us a general idea of the shifts that would occur in bismuth. A more in depth calculation of this process would not be trivial. The probe pulse would need to be weighted over, along with an integration across all of the blow-off material to get an average. This would be hard to do as FLYCHK only does one set of conditions at a time. Also the radiation transport would be difficult to model, from one part of the plasma to the other. In the 2017 data-set we are looking through the rear of the target and some of the emission could get reabsorbed before re-emitting as it is coming through the rest of the bismuth back-lighter.