

Unravelling Strong Electronic and Interlayer Correlations in a Transition Metal Dichalcogenide – Supplementary Information

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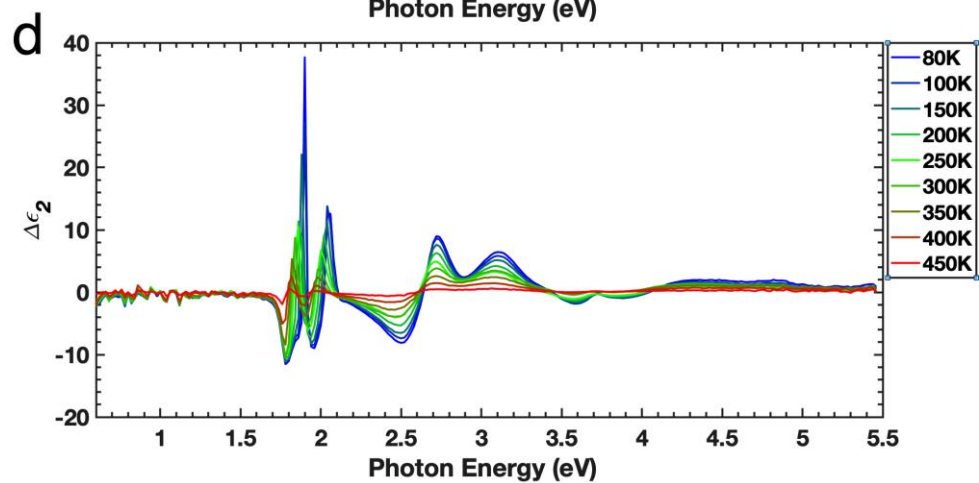
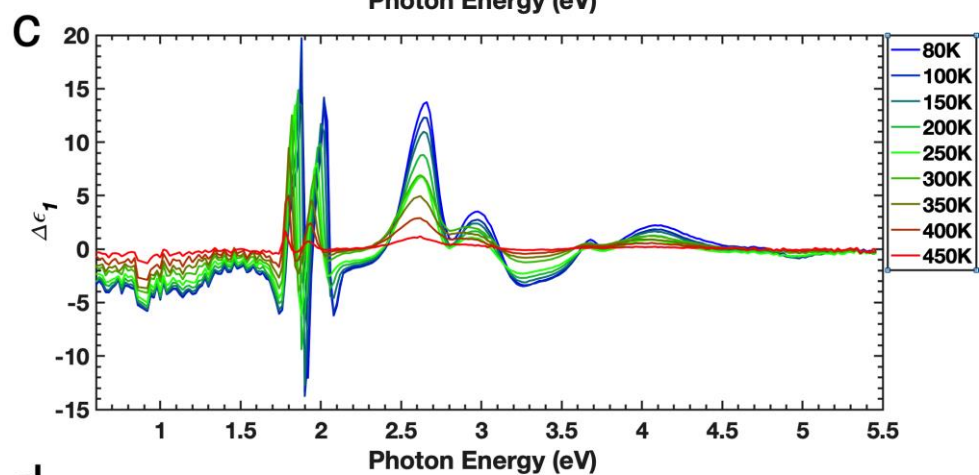
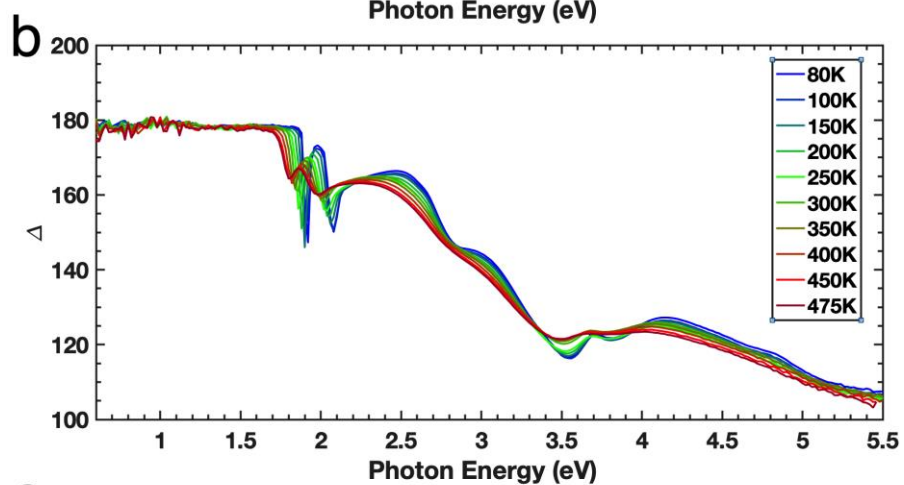
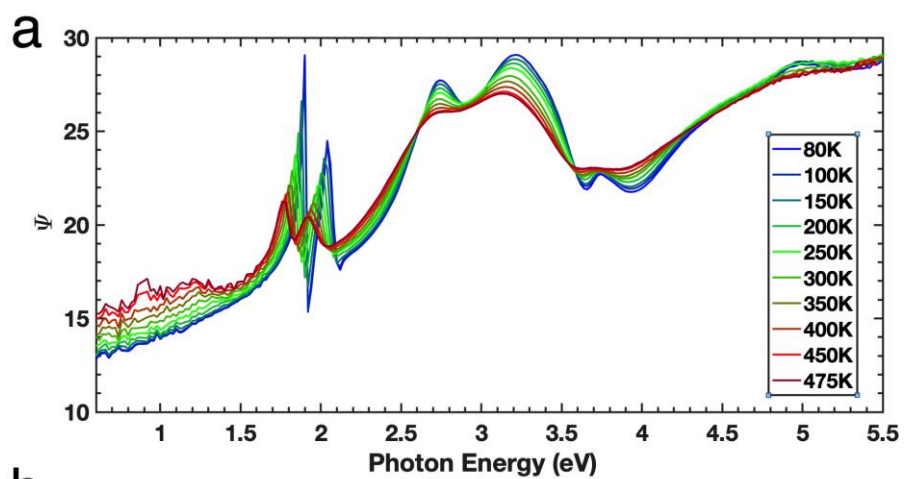
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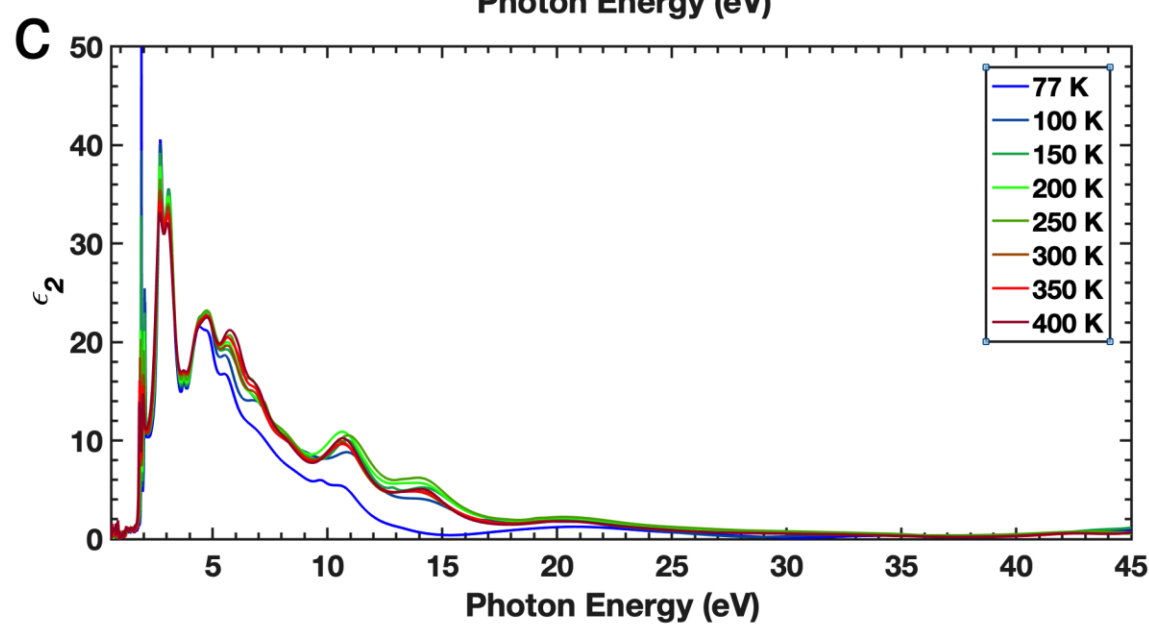
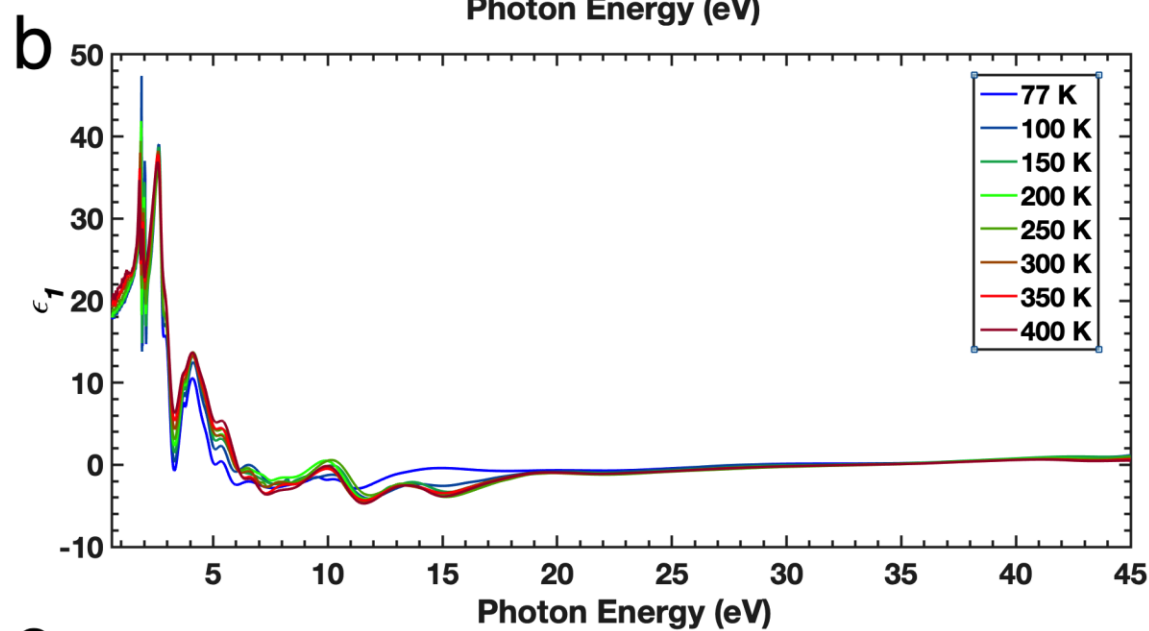
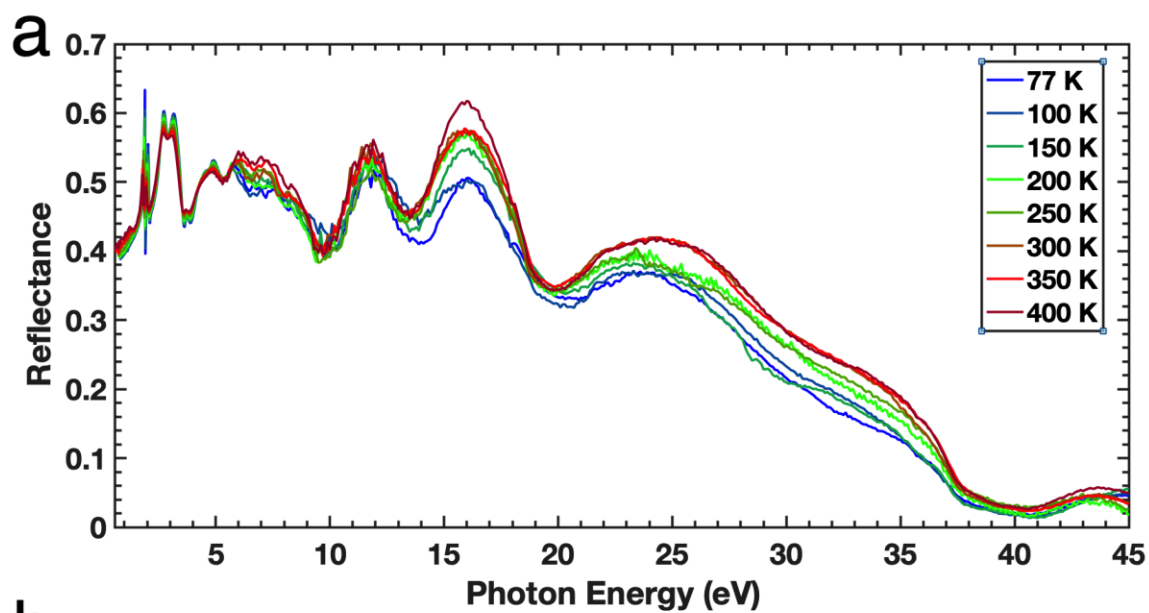
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Supplementary Figure 1 | Spectroscopic Ellipsometry measurements of MoS₂. The output data of the spectroscopic ellipsometry measurements, **a** ψ and **b** Δ , the ratio of the amplitude and the difference in phase between the incident and reflected light respectively. The difference in the **c** real and **d** imaginary parts of the dielectric function between 475 K and the colder measurements.

Muller-matrix spectroscopic ellipsometry measurements were carried out using a variable-angle spectroscopic ellipsometer (V- VASE, J.A. Woollam Co.) with a rotating analyser and compensator at the Singapore Synchrotron Light Source (SSLS). The output data from the spectroscopic ellipsometry measurements are ψ and Δ , which are shown in Supplementary Figs. 1a and 1b respectively, as a function of temperature. The measurement ψ , is the ratio of the amplitudes of the polarised light incident on the target and the polarised light reflected from the target, whilst the measurement Δ , is the phase difference between the incident and reflected polarised light.

Using the W-VASE analysis program, a model of the sample is created which includes the MoS₂ bulk material and surface effects (e.g. roughness, oxidation etc.). As the sample thickness is very large, the complex dielectric function of the MoS₂ can be determined through the best fits to the output data ψ and Δ . Single crystal MoS₂ is known to be anisotropic so the spectroscopic ellipsometer was used in the Mueller-Matrix mode with a rotational sample stage.^{1,2} Supplementary Fig. 1 also shows the difference in the real, Supplementary Fig. 1c, and imaginary, Supplementary Fig. 1d, parts of the complex dielectric function between the highest temperature of 475 K measured and the lower temperatures. There is clearly a very large change in the spectral weight as the sample is cooled with the biggest changes occurring between 1.70eV and 3.40eV.



Supplementary Figure 2 | Reflectance measurements and complex dielectric function of MoS₂. **a** Measurements of the reflectance of the bulk MoS₂ sample as a function of temperature from near-IR (0.6eV) up to X-ray (45eV) using the SUV beam-line at SSLS, log scale. The **b** real (ϵ_1) part and **c** imaginary (ϵ_2) part of the complex dielectric function of MoS₂ modelled from spectroscopic ellipsometry and X-ray reflectance data as a function of temperature, linear scale.

Supplementary Fig. 2a shows the combined Muller-Matrix spectroscopic ellipsometry and soft X-ray reflectivity measurements of MoS₂ as a function of temperature from 0.6eV – 45eV in the log scale. Supplementary Figs. 2b and 2c show the real, ϵ_1 , and imaginary, ϵ_2 , parts of the complex dielectric function, respectively, on a linear scale. The reflectivity data taken from the SUV beamline are selected in the range 3.5eV – 45eV, whilst the ellipsometry results cover the range 0.6eV – 5.5eV, providing ~3.0eV overlap for normalization. Spectroscopic ellipsometry allows us to determine the complex dielectric function of a material from which the self-normalised reflectivity can be calculated using the following:

$$R = \frac{((n - 1)^2 + k^2)}{((n + 1)^2 + k^2)} \quad (S1)$$

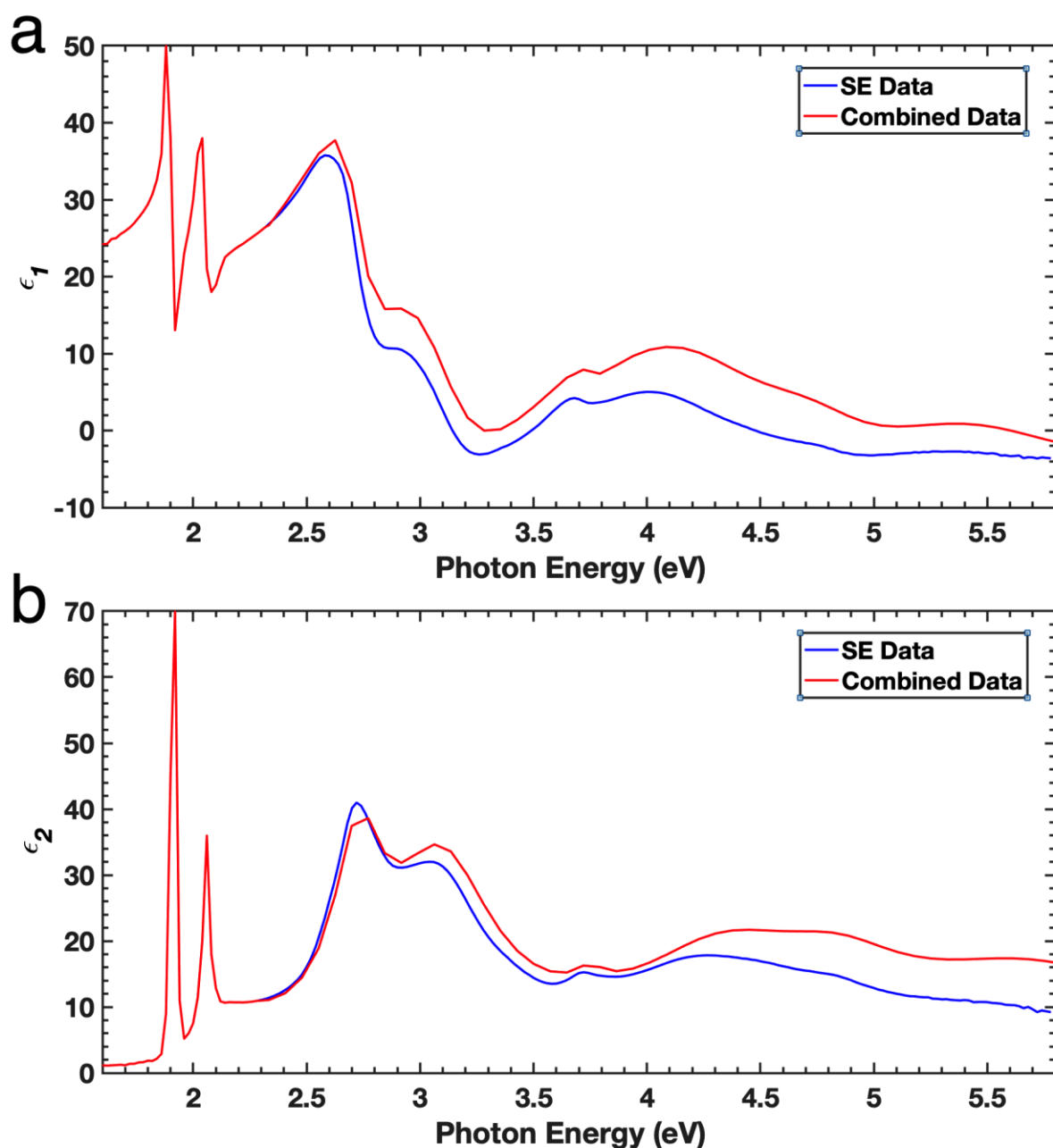
where n and k are the refractive index and absorption coefficient respectively and can be calculated from the real (ϵ_1) and (ϵ_2) imaginary parts of the complex dielectric function using:

$$\epsilon_1 = n^2 - k^2, \quad \epsilon_2 = 2nk. \quad (S2)$$

The soft X-ray reflectivity is then normalised using spectroscopic ellipsometry at the lower energy range,³ and X-ray data is tabulated at the high energy range from 30 eV onward.⁴ In order to determine the complex dielectric function of the MoS₂ across the whole energy range, we use a model based on Kramers-Kronig-transformable Drude-Lorentz oscillators of the form:

$$\varepsilon(\omega) = \varepsilon_{\infty} + \sum_{\mathbf{k}} \frac{\omega_{p,\mathbf{k}}^2}{\omega_{0,\mathbf{k}}^2 - \omega^2 - i\Gamma_{\mathbf{k}}\omega} \quad (S3)$$

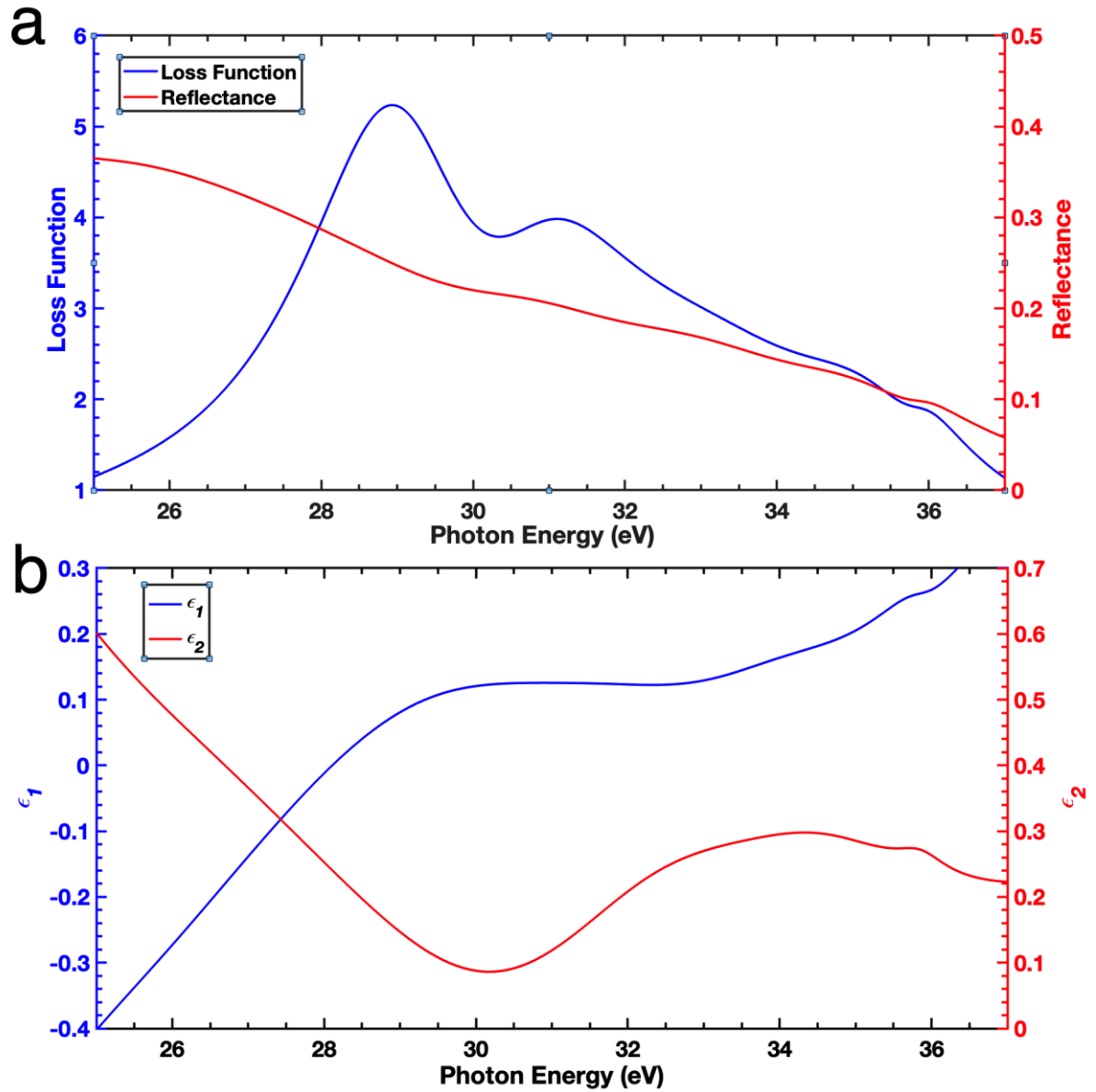
where ε_{∞} is the high-frequency dielectric constant and $\omega_{p,\mathbf{k}}$, $\omega_{0,\mathbf{k}}$ and $\Gamma_{\mathbf{k}}$ are the plasma frequency, the transverse frequency (eigenfrequency), and the line width (scattering rate) of the $\mathbf{k}$ -th oscillator, respectively. Using the new methodology introduced here, our model is constrained by the complex dielectric function measured with spectroscopic ellipsometry. Therefore, we are able to obtain reflectivity with very high accuracy and resolution as a function of temperature in such a broad energy range.



Supplementary Figure 3 | Spectral Weight Comparison of MoS₂. The **a** real and **b** imaginary parts of the complex dielectric function of MoS₂ at 40 K using just the spectroscopic ellipsometry data (blue) and from the data using a combination of spectroscopic ellipsometry and high-energy reflectance (red).

Within a single measurement, spectroscopic ellipsometry measures the change in phase and amplitude of polarised light after being transmitted or reflected from a material,

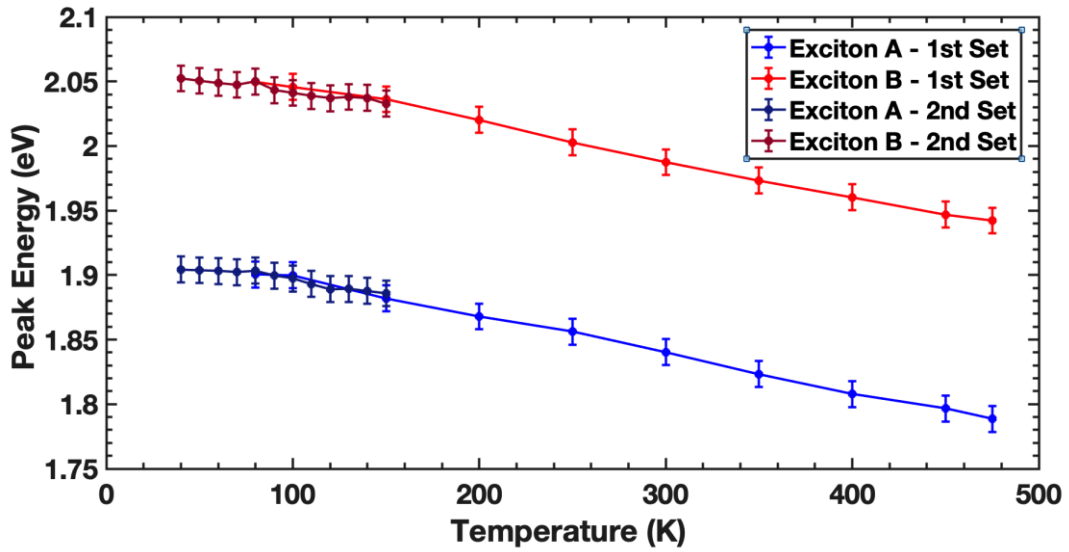
from these we can simultaneously determine the complex dielectric function, loss function and reflectivity. For data that cover a limited spectral range, the derived complex dielectric function towards these limits is not accurate. Supplementary Fig. 3 shows the complex dielectric function determined from a small energy range (SE data) compared to a large energy range (Combined SE and high-energy reflectivity data). It is clear that the complex dielectric function is severely underestimated above 2.5eV using data from only a limited energy range. Therefore, low energy measurements, especially those trying to determine the complex dielectric function and spectral weight transfer, are not always valid. Higher energy band measurements must also be taken into consideration.



Supplementary Figure 4 | Loss function, complex dielectric function and reflectivity of 40K MoS₂. A comparison of **a** the loss function and reflectivity, and **b** the complex dielectric function of 40 K MoS₂ in the energy range 25 – 37eV in order to show the properties of soft X-ray correlated-plasmons.

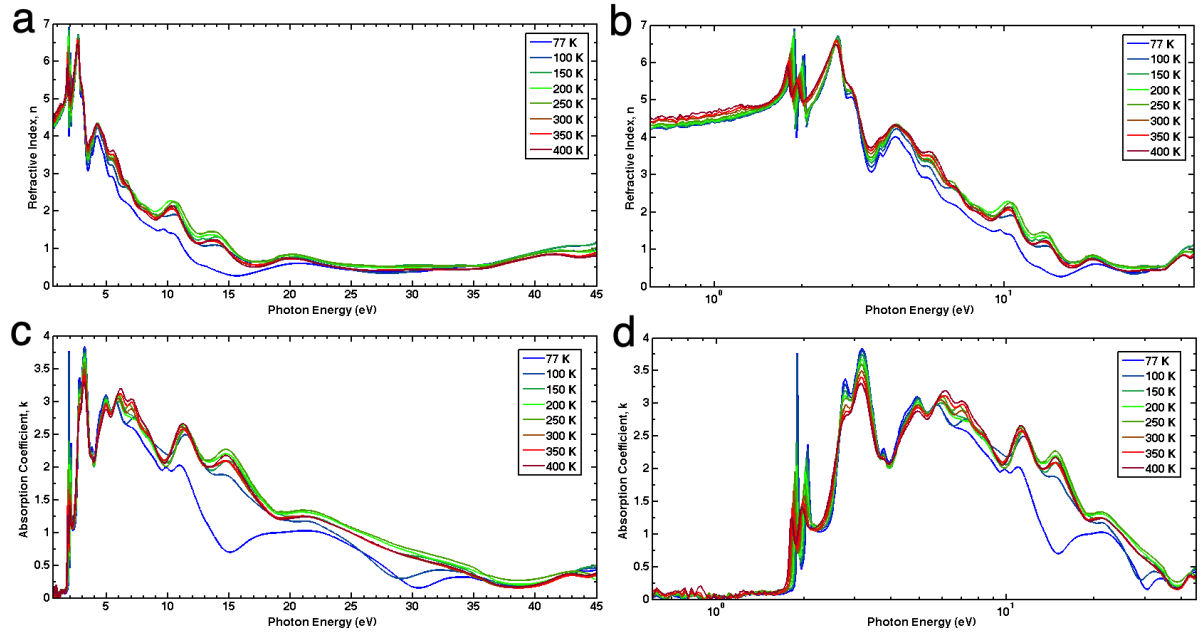
Supplementary Fig. 4 shows the loss function, reflectivity, and complex dielectric function of MoS₂ cooled to 40K. Correlated plasmons have the following characteristics; (1) peaks in loss function as seen at 30eV in Supplementary Fig 4a, (2) local minimums in

reflectivity, and (3) near zero values of ε_l as seen at the same energy in Supplementary Fig 4b. What makes it different from metal is the value of ε_l . Unlike conventional plasmons in metal that have negative values of ε_l , the ε_l in correlated-plasmons have values that are near zero due to electronic correlations.



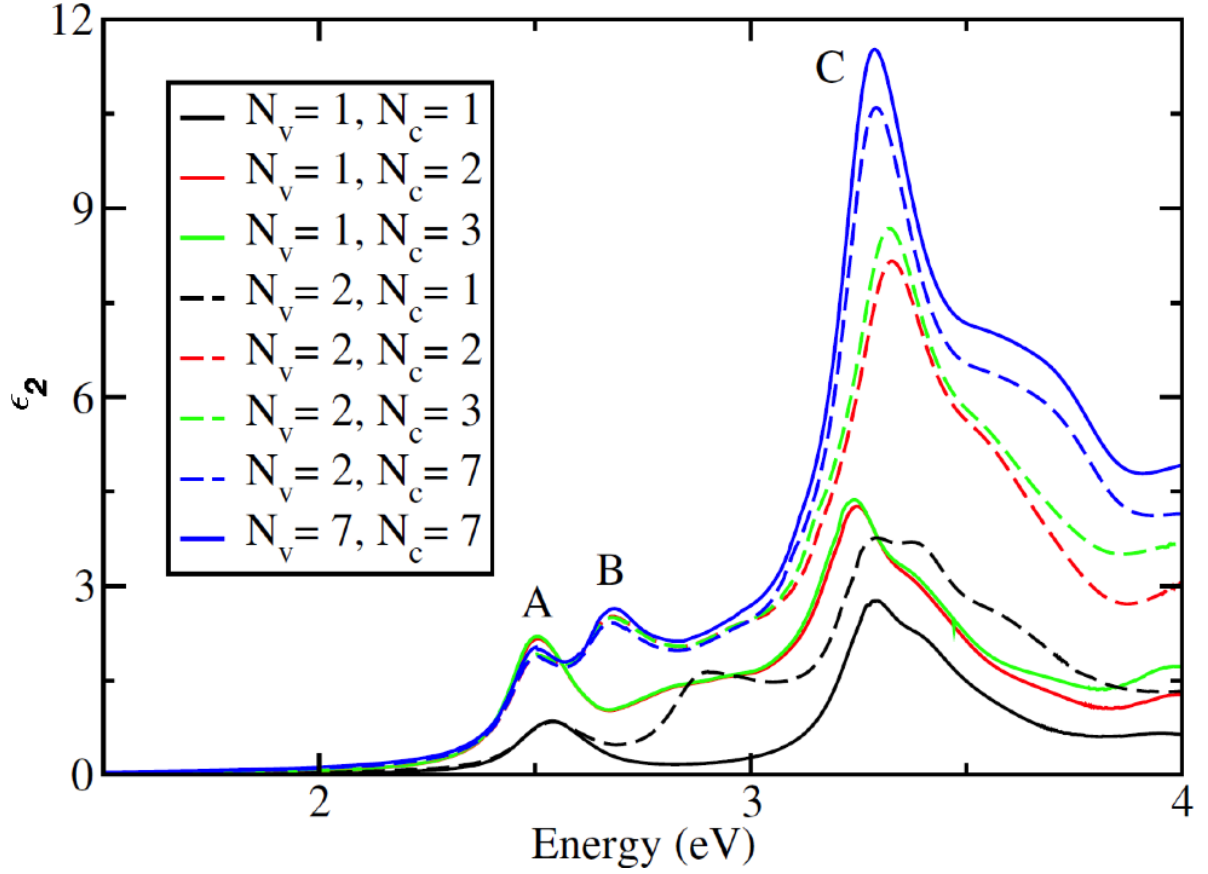
Supplementary Figure 5 | Peak position of excitons A and B. The peak positions of excitons A and B as a function of temperature from 475K to 40K for both sets of measurements. Error bars are calculated using a 2meV shift.

Supplementary Fig. 5 shows the peak positions of excitons A and B measured from the spectroscopic ellipsometry results in Fig. 1c of the main text. These include measurements from the first set of results seen in Figs. 1a-c and the second set of results with temperatures measured from 150K down to 40K at 10K intervals, both of which are in excellent agreement with each other. There is a steady blue-shift of the peak position as the temperature is decreased from 475K to 40K.



Supplementary Figure 6 | Complex refractive index of MoS₂. The refractive index, n , of MoS₂ as a function of temperature **a** linear scale, **b** log scale. The absorption coefficient, k , of MoS₂ as a function of temperature **c** linear scale, **d** log scale.

Supplementary Fig. 6 shows the complex refractive index of MoS₂ as a function of temperature from 0.6eV – 45eV. Supplementary Figs. 6a and 6b show the linear and log plots of the refractive index, n , respectively and Supplementary Figs. 6c and 6d show the linear and log plots of the absorption coefficient, k .



Supplementary Figure 7 | Calculated ϵ_2 as a function of the number of bands. Theoretical calculations based on GW+BSE for different number of valence bands N_v and conduction bands N_c .

We perform theoretical calculations by varying the number of valence bands ($N_v = 1, 2$ and 7) and conduction bands ($N_c = 1, 2, 3$ and 7) of MoS₂ and calculate ϵ_2 by incorporating electron-electron and electron-hole interactions using GW Bethe-Salpeter equation (BSE) calculations.⁵ More numbers of valence and conduction bands mean that there are more higher energy bands involved and a higher number of valence and conduction bands is needed to properly calculate the spectrum in the energy range of interest. We utilize $N_v = N_b = 7$ to give a converging result.

From Supplementary Fig. 7, we see that the single-band transition $N_v = N_c = 1$ can already form the excitonic peaks A and C but the excitonic peak B is missing. By increasing the number of conduction bands at high energies, we can see that low-energy excitations are enhanced, including these excitons. This further supports that the low-energy excitations are determined by high-energy bands. We note that our calculated values for the three excitonic peaks are in average overestimated by ~ 0.57 eV, which is due to the limited number of k -points in the GW calculations.

Supplementary References:

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