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

Supplementary information Ultrafast evolution of the complex dielectric function of monolayer WS_2 after photoexcitation

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1 Microscope images of the samples

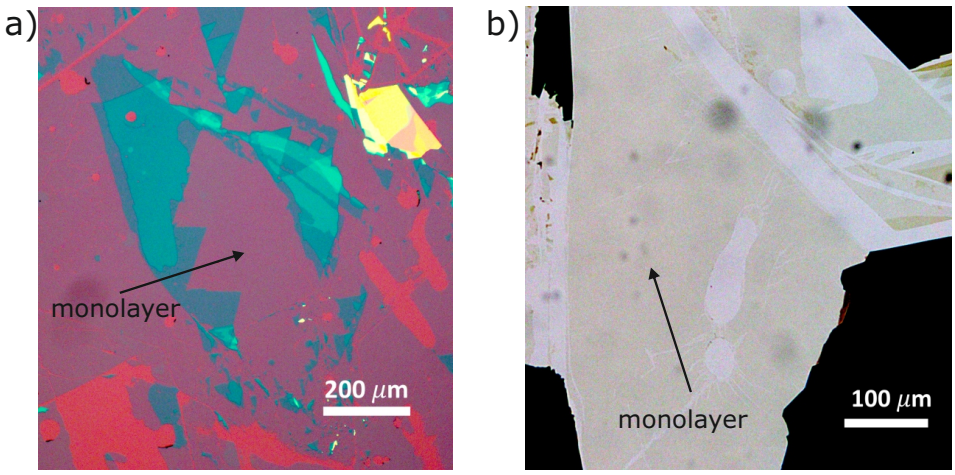

Figure S1: The optical microscope images are shown for WS_2 samples deposited on a) Si/SiO_2 and b) FS substrates respectively. Areas of hundreds by hundreds of micrometers of clean monolayer are visible and are indicated by the arrows. Areas with different color are the substrates or multilayer areas. Both samples are exfoliated using Au assisted exfoliation as described in detail in Ref. [1, 2]

2 Comparison of the TC background modeling and error estimation

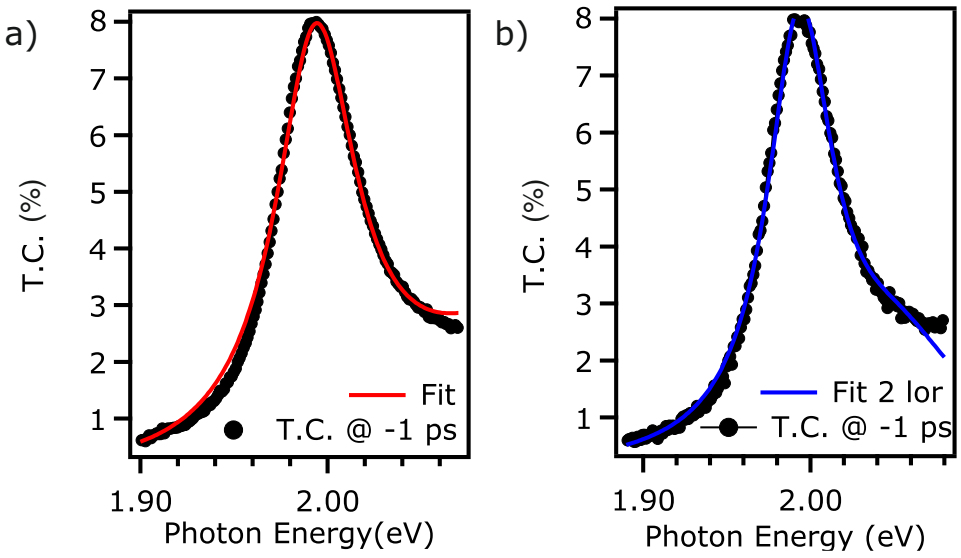

Figure S2: a) Steady state TC contrast spectra of monolayer WS_2 deposited on a thick FS substrate (black trace). Best fit using the function including the polynomial background: Eq. 1 (red trace). This figure correspond to Fig. 1.a) from the main text. b) Steady state TC contrast spectra of monolayer WS_2 deposited on thick FS substrate (black trace). Best fit using the function including the two Lorentzians fit function: Eq. 3 (blue trace).

As discussed in the main text, the fit function used to reproduce the TC spectra in Fig 1.a) includes a polynomial to model the background signal, and it is given by the following formula:

$$TC = -Re\left[\frac{2}{1+n_{sub}}\right] Z_0\sigma^s(\varepsilon_{WS_2}) + A + B(x-x_p) + C(x-x_p)^2 \tag{1}$$

where $\varepsilon = \varepsilon_{\text{inf}} + \frac{I}{x_0^2 - x^2 - igx}$.

A more precise method to model the background would be to use other resonances at higher energies. In the following, another fit is performed to model the dielectric function, using two Lorentzians, one of which lying at high energies, and compared to the fit function used in the main text. In this case the dielectric function can be written as:

$$\varepsilon_{WS_2} = \varepsilon_{\text{inf}} + \frac{I}{x_0^2 - x^2 - igx} + \frac{I_1}{x_1^2 - x^2 - ig_1x} \tag{2}$$

The second Lorentzian does not reproduce any physical meaningful feature of the optical spectrum, but is simply used to approximate the background. The resulting fit function is:

$$TC = -Re\left[\frac{2}{1+n_{sub}}\right] Z_0\sigma^s(\varepsilon_{WS_2}) \tag{3}$$

The comparison between the two fit functions is shown in Fig. S2 where the polynomial background fitting using Eq. 1, is reported in the left panel and the double Lorentzian fit using Eq. 3 on the right panel. In both cases the fit is restricted to the energy range between 1.85 and 2.07 eV. The fit shows a qualitatively good agreement in both cases. In particular, the approach using two Lorentzians is slightly better in reproducing the tails of the resonance. Table 1 reports the fit parameters. They differ relative to each other of a minimal amount, with a maximum relative error of 4%. This demonstrates the fit function's reliability of the polynomial approach in the main text to isolate and quantify the excitonic feature in the transmittance contrast spectrum.

The comparison of the two different backgrounds can also be used to estimate the error of the exciton resonance fit parameters. The statistical errors from the respective fits are one order of magnitude smaller

Parameters	**Polynomial fit**	**Two Lorentzian fit**
x_0	1.9942±0.0002 eV	1.9937±0.0003 eV
g_0	50±1 meV	48±1 meV
I_0	1.29±0.02	1.23±0.04

Table 1: Fit parameters. Statistical errors corresponding to 4σ confidence interval of the fit.

than the difference between the parameters extracted from the two fits, which is why the variation due to the choice of background seems like a good approximation for the experimental error. The the extracted parameters of the fit using the polynomial background, with the respective errors, are then: x_0=1.994±0.001 eV, g_0=50±3 meV and I_0=1.29±0.06. The same errors on the fit parameters are considered for the fit to the steady state RC discussed in the main text.

3 Time-dependent fitting accuracy

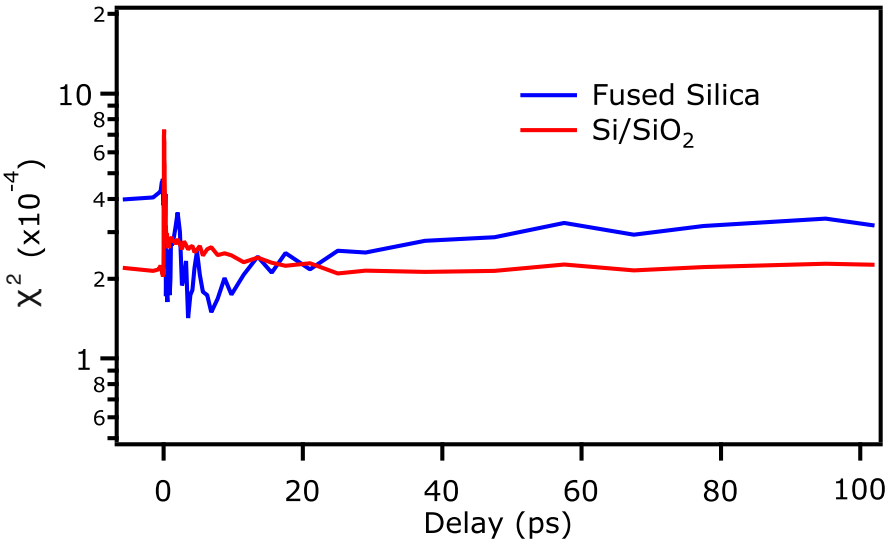

Figure S3: Time-dependent χ^2 of the fits of tr-TC data (blue) and tr-RC data (red), confirming that the fits of the TC and RC spectra upon photoexcitation are accurate.

4 Time-dependent spectral weight

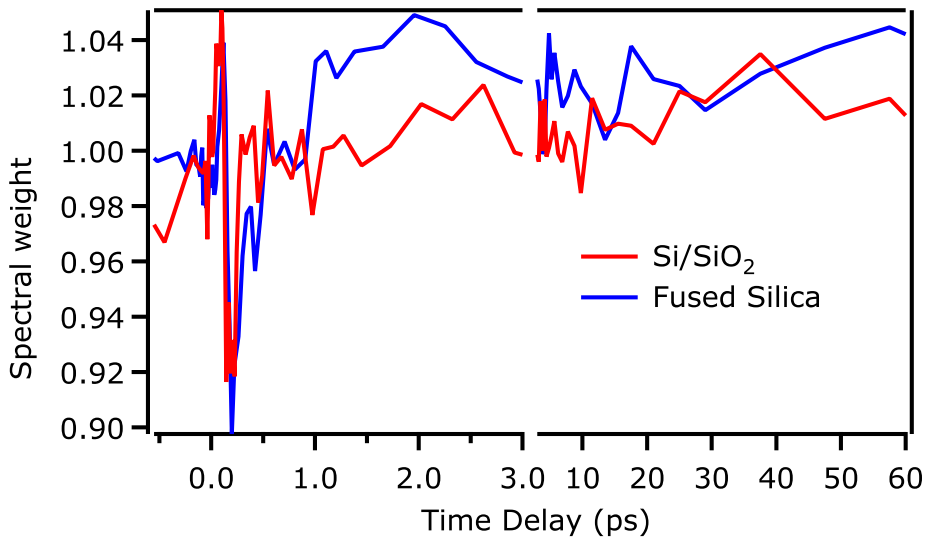

Figure S4: Time-evolution of the normalized spectral weight (I/I_{eq}) of the fits of tr-TC data (blue) and tr-RC data (red). Within the noise level, the spectral weight does not show any significant dynamics beyond some fluctuations around t=0 within the cross correlation of pump and probe pulses (100fs).

5 Calculation of absorbance and photoexcited particle density

For the case of the transparent FS substrate, starting from the extracted dielectric function and making use of the 2D linearized model [3], we can calculate the absorbance of the WS_2 sample by:

$$A = \frac{4}{|\,1 + n_{sub}\,|^2}\,[-i2\pi(\varepsilon_{WS_2} - 1)(d/\lambda)] \tag{4}$$

Where n_{sub} and ε_{WS_2} are the complex refractive index of the substrate and the complex dielectric function of the monolayer WS_2, respectively. d is the thickness of the monolayer and λ the wavelength.

The dielectric function of the monolayer WS_2 is given by the Lorentzian with the parameters reported in the Table 1. The calculated absorption spectrum is shown in Fig. S5 a. In this graph, we report the absorbance of the monolayer WS_2 on top of a thick substrate of fused silica (red trace) and the normalized pump spectrum (blue trace). The effective absorbance (i.e. the number of photons absorbed by the WS_2) is calculated by the integral of the multiplication of the absorbance and the normalized pump lineshape. The latter returns a value of 4.1%. The photoexcited particle density of 3.2 E+12 cm^{-2} is then obtained by multiplying the incident fluence (0.025 mJ/cm^2) and the effective absorbance.

For the monolayer WS_2 deposited the Si/SiO_2, the calculation of the absorbance is more complicated, because of the layered structure of the sample. We employed a Matlab script that allows the calculation of the selective absorption of a layer in a heterostructure, as introduced and discussed in detail by Jannin et al. in [4]. The script is based on the same transfer matrix formalism used in this text and extended to more general use for calculating optical observables of complex heterostrutures starting from the dielectric functions of the constituents materials. The script has been changed to feed the dielectric function of the WS_2 given by the Lorentzian with the parameters retrieved in the fitting. The script calculates the monolayer's selective absorption and returns the absorption spectrum, which is reported in Fig. S5b with the red trace. The normalized pump lineshape is depicted in the same figure (blue trace), and the procedure to calculate the initial photoexcited particle density is analogous to the case reported for the FS substrate.

The effective absorbance of the WS_2 layer is given by the integral of the multiplication of the absorbance by the normalized pump's line-shape and gives a value of 4.6%. Finally, the photoexcited particle density is then given once again by the multiplication of the incident fluence (0.022 mJ/cm^2) and the effective absorbance returning a value of 3.2 E+12 cm^{-2}.

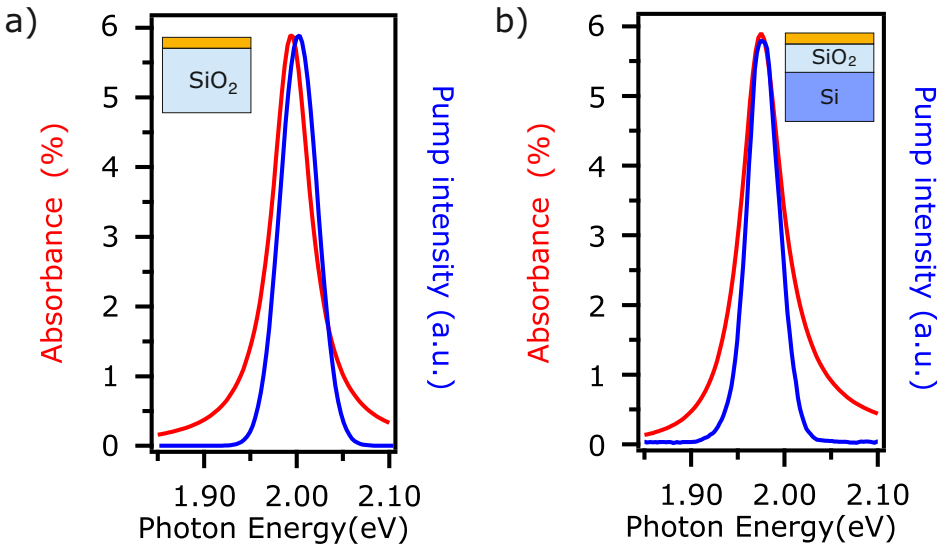

Figure S5: a)Absorbance of monolayer WS_2 deposited on a FS substrate (red trace) as a function of photon energy, calculated using Eq. 4. Pump spectra (blue trace) as a function of photon energy. b) Selective absorbance of monolayer WS_2 deposited on a layered Si/SiO_2 substrate (red trace) as a function of photon energy, calculated using a Matlab script. Pump spectra (blue trace) as a function of photon energy.

References

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