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Darien J. Morrow, Daniel D. Kohler, Yuzhou Zhao, Song Jin, and John C. Wright Phys. Rev. B **100**, 235303 — Published 4 December 2019 DOI: 10.1103/PhysRevB.100.235303

Pump-triple sum-frequency-probe spectroscopy of transition metal dichalcogenides

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(Dated: November 15, 2019)

Triple sum-frequency (TSF) spectroscopy measures multidimensional spectra by resonantly exciting multiple quantum coherences of vibrational and electronic states. In this work we demonstrate pump-TSF-probe spectroscopy in which a pump excites a sample and some time later three additional electric fields generate a probe field which is measured. We demonstrate pump-TSF-probe spectroscopy on polycrystalline, smooth, thin films and spiral nanostructures of both MoS₂ and WS₂. The pump-TSF-probe spectra are qualitatively similar to the more conventional transient-reflectance spectra. While transient-reflectance sensitivity suffers under low surface coverage, pump-TSF-probe sensitivity is independent of the sample coverage and nanostructure morphologies. Our results demonstrate that pump-TSF-probe is a valuable methodology for studying microscopic material systems.

I. INTRODUCTION

Pump-probe spectroscopy is a ubiquitous methodology for investigating the dynamics and energetics of excited systems on sub-picosecond time scales. In a pump-probe experiment, a pump excites the system of interest and a probe interrogates the evolved system at a later time, T. The differences in the probe signal with and without the pump inform on system evolution. Most analytical merits of a pump-probe experiment, such as sensitivity and selectivity, are determined by the choice of a specific probe methodology, of which there are many.[1–10] The development of Coherent Multidimensional Spectroscopy (CMDS) offers promising possibilities for new probes because CMDS methods can have increased selectivity compared to conventional methods.[11–17] CMDS uses multiple optical interactions to create a multiple quantum coherence within the material whose optical emission is measured. The ability/requirement to couple multiple quantum states together leads to the selectivity inherent within CMDS. By preceding a CMDS pulse sequence by a pump, the selectivity of CMDS can be leveraged as a probe in a "pump-CMDS-probe" measurement. [2, 3, 6, 18, 19] In this paper we introduce triple sum-frequency (TSF) spectroscopy as a new fullycoherent probe for material systems by measuring the pump-induced TSF response of model semiconductor systems: transition metal dichalcogenides (TMDCs).

TSF spectroscopy uses three electric fields, E_1 , E_2 , and E_3 , to create coherences at increasingly higher energies. These coherences cooperatively emit a new electric field with frequency $\omega_{\text{out}} = \omega_1 + \omega_2 + \omega_3$ in a direction defined by phase-matching. Scanning the multiple driving laser frequencies enables collection of a multidimensional spectrum whose cross-peaks identify dipole coupling among probed states. The selectivity of TSF is due to the increase in output intensity achieved when the driving fields are resonant with one or more states; multiple resonance conditions can act as a spectral fingerprint of an analyte.[20] TSF has been used to investigate vibrational and electronic coupling in molecules,[21–26] and recently, TSF has revealed the electronic states of MoS₂ and the mixed-vibrational-electronic coupling of organic-inorganic perovskites.[27, 28] We believe TSF is a promising probe methodology for several reasons: TSF offers complementary information compared to standard techniques like reflection and absorption;[27] TSF is usable across many different sample morphologies; multiresonant TSF can examine interactions between multiple electronic and/or vibrational states; and pump-TSFprobe is easily extended to microscopy due to the groundwork already laid for multiphoton microscopy.[29–31]

In this paper, we use MoS_2 and WS_2 as model systems to demonstrate some of the capabilities of pump-TSFprobe spectroscopy. MoS_2 and WS_2 are well-studied, layered semiconductors in the TMDC family.[32] The bandedge optical spectrum of MoS_2 has two excitonic features labeled A ($\hbar\omega_{\rm A} \approx 1.8 \text{ eV}$) and B ($\hbar\omega_{\rm B} \approx 1.95 \text{ eV}$) while WS_2 is dominated near the bandedge by a single excitonic feature labeled A ($\hbar\omega_{\rm A} \approx 2 \text{ eV}$). These features originate from high binding energy excitonic transitions between spin-orbit split bands (cf. absorption spectrum of MoS_2 and inset diagram in Figure 1).[33–38] The present work expands upon our previous work on the unpumped TSF response of MoS_2 , [27] the extensive body of harmonic generation work on TMDCs (cf. the review by Autere *et al.* [39] and references therein), and the innovative pump-second-harmonic-generation probe work accomplished on semiconductors.[40-47]

In our previous work on the unpumped TSF response of MoS₂ we noted important differences between the nonlinear TSF probe and conventional linear probes, such as absorption or reflection.[27] One important difference is the scaling with transition dipole, μ , and state density, J: TSF intensity scales as $\mu^8 J^2$, while absorption and reflection scale as $\mu^2 J$. The steep scaling of TSF with transition dipole compared to state density depresses continuum signals and enhances large dipole

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FIG. 1. Normalized amplitude 1D spectra of MoS_2 thin films. The absorption measurement was originally shown in Czech *et al.* [48]. The TSF and reflection contrast measurements were originally shown in Morrow *et al.* [27]. Vertical bars are guides to the eyes set at 1.80 and 1.95 eV. The inset is a cartoon of the band dispersion of MoS_2 about the K point. Only the valence bands are shown as spin-orbit-split because the splitting of the conduction bands is generally too small to be observed for MoS_2 .

transitions. The dipole scaling of other CMDS techniques has enabled the measurement of protein structure against large backgrounds when conventional absorption measurements fail.[49, 50] The ability of TSF to isolate large dipole transitions is highlighted in Figure 1 for the example of MoS₂. The absorption and reflection spectra of the MoS₂ thin film are dominated by higher energy transitions with large joint density of states and low transition moments. Conversely, the TSF spectrum (in this case $\omega_1 = \omega_2 = \omega_3 = \omega_{out}/3$, a third harmonic generation, THG, spectrum) is dominated by the large transition dipole A and B excitonic transitions.

Another important difference between TSF and linear probes is the nature of backward propagating light. For linear probes, the amount of backward propagating light (reflection) depends not only on resonance, but also on refractive index mismatch, which can result in large background contributions, especially for samples with incomplete surface coverage, or rough morphologies. This limitation is important for optically thick samples, where reflection is the only viable linear probe. On the other hand, TSF is well-suited for a reflection geometry, where non-linear pulse propagation effects due to phase mismatch, group velocity mismatch, and absorption are negligible.[51] Furthermore, non-linear emission in the backwards direction is qualitatively different than the direct reflection of incident light, and the refractive index mismatch does not control the measured intensities.[52] For example, we have found that the ratio of reflected TSF emission from MoS_2 films to pure substrate TSF emission is beyond the dynamic range of our our experiment as determined by our analog-to-digital-converter (>65,000:1).[27] As a result, a TSF probe provides high contrast signal, resulting in better signal-to-noise, lower detection limits, and sensitivity to a variety of sample morphologies. This paper highlights these advantages by examining different sample morphologies and surface coverage levels.

The structure of this paper is as follows. In the Theory section we describe the pump-TSF-probe response and compare it to the familiar pump-reflection-probe method. In the Experimental section we describe our spectrometer and our various TMDC samples. In the Results section we present our pump-TSF-probe measurements on TMDCs. We first examine how the multidimensional TSF spectrum is affected by an optical pump. We find that the multidimensional TSF spectrum can be fully described by the one-dimensional pump-THG-probe spectrum. We compare pump-THG-probe to pump-reflectance-probe spectroscopy and we demonstrate that the same pump-induced physics explains both spectra. We then compare the pump-TSF-probe of several TMDC samples that differ in morphology and composition, both demonstrating the versatility of pump-TSF-probe and revealing the strong dependence of morphology on several layer TMDC dynamics. Finally, we discuss how transient-TSF might be used in the future on other systems.

II. THEORY

A. The linear and non-linear probe

In this section we present the correspondence between the reflectance and TSF of a material. We investigate the phenomenological, microscopic properties that are responsible for the susceptibility and also how the susceptibility dictates the electric field output. Readers interested in first-principle calculations of TMDC nonlinear susceptibility should consult refs.[53–57]. Our analysis uses standard perturbation theory.[58, 59] The material polarization, P, is expanded in orders of the electric field, E:

$$P = \epsilon_0 \left(\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \cdots \right), \qquad (1)$$

where $\chi^{(n)}$ is the n^{th} -order susceptibility and ϵ_0 is the permittivity of free space. The linear susceptibility, $\chi^{(1)}$, determines the response of linear spectroscopies such as absorption and reflection. The third-order susceptibility, $\chi^{(3)}$, determines the response of non-linear spectroscopies such as TSF.

Within the dipole approximation, $\chi^{(1)}$ is constructed from a sum over all initial and final states:

$$\chi^{(1)}(\omega_1) = \sum_{a,g} \frac{\mu_{ag}^2}{\Delta_{ag}^1},$$
 (2)

where $\Delta_{ag}^1 \equiv \omega_{ag} - \omega_1 - i\Gamma$, μ_{ag} and ω_{ag} are the transition dipole and frequency difference between states a and g, Γ is a damping rate which accounts for the finite width of the optical transitions, and ω_1 is the driving frequency. We see from Equation 2 that when the driving field is resonant ($\omega_1 = \omega_{ag}$), $\chi^{(1)}$ is large and the interaction with light is strong.

Like Equation 2, the TSF susceptibility is a sum over states, but we must consider three sequential excitations $g \rightarrow a \rightarrow b \rightarrow c$:

$$\chi^{(3)} \left(-\omega_{321}, \omega_1, \omega_2, \omega_3 \right) = \mathcal{P} \sum_{c, b, a, g} \frac{\mu_{gc} \mu_{cb} \mu_{ba} \mu_{ag}}{\Delta_{gc}^{123} \Delta_{gb}^{12} \Delta_{ga}^{1}}, \quad (3)$$
$$\Delta_{ga}^1 \equiv \omega_{ag} - \omega_1 - i\Gamma,$$
$$\Delta_{gb}^{12} \equiv \omega_{bg} - \omega_{21} - i\Gamma,$$
$$\Delta_{gc}^{123} \equiv \omega_{cg} - \omega_{321} - i\Gamma,$$
$$\omega_{21} \equiv \omega_2 + \omega_1,$$
$$\omega_{321} \equiv \omega_3 + \omega_2 + \omega_1,$$

where \mathcal{P} is a permutation operator which accounts for all combinations of field-matter interactions. If only the triple sum transition is resonant, we can approximate all other resonance (Δ) terms as constant and arrive at an expression similar to Equation 2:[27]

$$\chi^{(3)}(\omega_{123}) \propto \sum_{a,g} \frac{\mu_{ag}^4}{\Delta_{ag}^{123}}.$$
 (4)

We now consider how the linear and third-order susceptibilities dictate the reflectance and TSF response, respectively. Both relations are formulated using Maxwell's equations via continuity relations (boundary conditions) between the incident, reflected, and transmitted fields. For ease of comparison, we will analyze the simple limit of an extremely thin film (thickness much less than the wavelength of light) on a transparent substrate. We also restrict consideration to normal incidence. Including thickness and angular dependence is straightforward but needlessly complex for our intent of illustrating qualitative differences between methodologies. These conditions are reasonable for many of the samples and experiments we consider here.

With these conditions, the reflectance, R, is related to the thin film linear susceptibility, $\chi^{(1)}$, by[60, 61]

$$R \equiv \frac{I_{\text{reflected}}}{I_{\text{incident}}} = \frac{(1 - n_s - A)^2 + B^2}{(1 + n_s + A)^2 + B^2},$$
 (5)

in which n_s is the substrate refractive index,

$$A \equiv \frac{\omega_1 \ell}{c} \operatorname{Im} \left[\chi^{(1)} \right], \tag{6}$$

$$B \equiv \frac{\omega_1 \ell}{c} \operatorname{Re}\left[\chi^{(1)}\right],\tag{7}$$

 ℓ is the film thickness (propagation length), and c is the speed of light in vacuum.

Expanding Equation 5 and keeping only terms linear in $\chi^{(1)}$, shows that the imaginary component of the thin film susceptibility is responsible for contrast from the substrate background:

$$R \approx \frac{(1-n_s)^2 - 2(1-n_s)A}{(1+n_s)^2 + 2(1+n_s)A}.$$
(8)

Equation 8 can be further simplified by Taylor expansion around A = 0:

$$R \approx R_0 \left(1 - \frac{2}{1 + n_s^2} A \right),\tag{9}$$

where $R_0 \equiv \frac{(1-n_s)^2}{(1+n_s)^2}$ is the reflectance of the substrate-air interface.

Equations 5-9 show that reflectance is largely determined by the substrate refractive index, which results in large background. As an example, consider properties appropriate for TMDC thin films encountered here: $\ell \sim 10$ nm and $n_s = 1.45$. Under the optimal conditions of resonant excitaton (excitation wavelength ~ 600 nm and $\chi^{(1)} = i$), $A \approx 0.1$ so the thin film gives a maximum contrast from the substrate of $(R - R_0)/R_0 \sim 0.4$. This level of background is typical for reflection studies of TMDC samples.[62] Note that the contrast becomes considerably worse in the case of incomplete sample coverage, where the observed reflection amplitude would be a weighted average of the reflection coefficients. Rough samples introduce scattering which also distort resonance effects of specular reflection.

TSF emission, or non-linear frequency conversion in general, is qualitatively different from reflectance (or transmittance) because the TSF wave originates from inside the thin film. This difference brings two important consequences to the measured beam: (1) TSF emission is dark in regions where the thin film is not present, and (2) the continuity relations are acutely sensitive to the thin film non-linear polarization, rather than an incident field.[52] For the aforementioned thin film conditions, the TSF output intensity satisfies the proportionality

$$\frac{I_{\text{TSF}}}{I_1 I_2 I_3} \propto \left| \chi^{(3)} \right|^2 (\omega \ell)^2, \tag{10}$$

where I_i is the intensity of the *i*th excitation field.[52] Unlike reflectance, thin film TSF emission obeys the same $\chi^{(3)}$ scaling as the thick film emission case,[22] where the film thickness is larger than or close to the wavelength of light, but phase mismatch effects are still small.

B. Pump-TSF-probe and TR spectroscopy

We now consider how the different nature of the reflectance and TSF probe result in different, yet similar, pump-probe measurements. For both linear and nonlinear probes, we can describe the pump-induced susceptibility as a perturbation to the unpumped susceptibility:

$$\chi_{\text{pumped}}^{(n)} = \chi_{\text{unpumped}}^{(n)} + \mathrm{d}\chi^{(n)}, \qquad (11)$$

where $d\chi^{(n)} = \chi^{(n+2)}I_{pump}$ is the small pump-induced perturbation. Pump-probe methodologies often look at relative changes in the probe:

signal metric =
$$\frac{X_{\text{pumped}} - X_{\text{unpumped}}}{X_{\text{unpumped}}}$$
 (12)

in which X is the probed quantity. This normalization removes the probe intensity dependence from the signal.

Using reflectance as our probe (Equation 9) gives a transient response of

$$\frac{\Delta R}{R} \approx -\frac{R_0}{R} \frac{4\omega\ell}{(1+n_s^2)c} \text{Im}\left[d\chi^{(1)}\right].$$
(13)

This expression shows that our signal metric scales as Im $[d\chi^{(1)}]$ which is the same as transient transmittance in a bulk sample (see Appendix A 2 for a derivation). In other words, in the extremely thin film limit, transient reflectance will have lineshapes which are intuitive to those who are used to interpreting bulk transient transmittance (absorption) measurements. The intuitive correspondence between transient reflectance and transient transmittance spectroscopies will break down as $\frac{\omega_1 \ell}{c} |\chi^{(1)}|$ increases—thick samples require a full Fresnel analysis to understand the transient reflectance lineshapes.

With TSF intensity as our probe, we use Equation 11 and Equation 10 to arrive at

$$\frac{\Delta I_{\rm TSF}}{I_{\rm TSF}} = \frac{\left| d\chi^{(3)} \right|^2 + 2 \left| d\chi^{(3)} \right| \left| \chi^{(3)} \right| \cos(d\theta)}{\left| \chi^{(3)} \right|^2}, \qquad (14)$$

where we have used phasor representations of the susceptibilities: $\chi^{(3)} \equiv |\chi^{(3)}| e^{i\theta}$ and $d\chi^{(3)} \equiv |d\chi^{(3)}| e^{i(\theta+d\theta)}$, in which θ can be dependent on probe frequency. If $|d\chi^{(3)}| \ll |\chi^{(3)}\cos(d\theta)|$ we can write

$$\frac{\Delta I_{\rm TSF}}{I_{\rm TSF}} \approx 2 \frac{\left| d\chi^{(3)} \right|}{\left| \chi^{(3)} \right|} \cos(d\theta), \tag{15}$$

If the pump changes only the amplitude of $\chi^{(3)}$ (d $\theta = 0, \pi$), the relative change in TSF intensity tracks the relative change in susceptibility. However, if the pump also changes the phase, the amplitude changes can be suppressed. Note that in the case of a $\pi/2$ phase shift, our assumption behind Equation 15 is invalid. It is important, then, to understand when $\cos(d\theta)$ can be small.

In general, θ changes rapidly near resonances; if pump induced changes shift or broaden a resonance to an extent similar to its linewidth, $d\theta$ will strongly influence the pump-TSF-probe spectrum. In the absence of dramatic resonance changes, lineshapes will closely approximate $d\chi^{(3)}/\chi^{(3)}$.

To anticipate the spectra of each technique, it is useful to consider the case of a single Lorentzian resonance perturbed by the pump. For a small perturbation to lineshape parameter $\lambda \in \{\Gamma, \omega_{ag}, \mu\}$, we can construct $d\chi^{(n)}$ using the derivative

$$\mathrm{d}\chi^{(n)} = \frac{\partial\chi^{(n)}}{\partial\lambda}\mathrm{d}\lambda.$$
 (16)

In the appendices we derive analytical expressions for the lineshapes expected from transient-TSF, transientreflectance, and transient-transmittance spectroscopies in this single resonance limit. Numerically calculated spectra are shown in Figure 2 for three different types of perturbations:

- An increase in the transition dipole, $d\mu > 0$. Statefilling and Coulomb-screening lead to a decrease in exciton transition dipoles (opposite of change shown in the figure). Note that changes in state density will cause the same lineshape as transition dipole changes.
- An increase in the resonance frequency, $d\omega_{ag} > 0$. Bandgap renormalization or Coulomb-screening can decrease or increase an exciton resonance frequency.
- An increase in the dephasing rate, $d\Gamma > 0$. Pumpexcited carriers can scatter with probe excitations, causing the dephasing rate of a transition to increase.

The transient-reflectance spectra (see Figure 2a) are easily interpreted because changes in Im $[\chi^{(1)}]$ correlate with changes in absorptive cross-section (Equation 9). Interpretation of $\Delta R/R$ line shapes mirrors the traditional interpretation of differential transmission, $\Delta T/T$, for bulk samples obeying Beer's law. Increasing the dipole strength (red line) increases reflectance (positive $\Delta R/R$), with a line shape mirroring the unpumped transition. Resonance red-shifts (green line) increase reflectance to the red and decreases reflectance to the blue. Line shape broadening (blue line) decreases reflectance in the center of the resonance but increases reflectance on the wings.

The transient-TSF lineshapes (Figure 2b) have similar interpretations. Increases in transition dipole (red line) increases TSF (positive $\Delta I/I$). Unlike reflectance, the increase results in a constant $\Delta I/I$ offset. This is because the unpumped I_{TSF} lineshape has no background from substrate and so its lineshape is sharply peaked and matches that of ΔI . Line shape broadening (blue line) and blue-shifting (green line) again mirror the behavior of $-\Delta T/T$, but the $\Delta I/I$ line shapes are noticeably broader than $\Delta R/R$. Since TSF is sensitive not only to imaginary component, but also the dispersive real component of $\chi^{(3)}$



FIG. 2. Calculated transient lineshapes for a single, complex Lorentzian resonance (see Appendices A 1-A 2). (a) The transient-reflectance spectrum. (b) The transient-TSF spectrum. The spectra are produced by perturbing μ , ω_{ag} , or Γ by a factor of 10^{-5} .

(Equation 15), the resulting lineshapes are intrinsically broader. In general, for the same dephasing rate, the transient-TSF lineshapes are broader than the transienttransmittance and transient-reflectance lineshapes.

III. EXPERIMENTAL

A. Ultrafast measurements

Our experimental setup uses an ultrafast oscillator seeding a regenerative amplifier (Spectra-Physics Tsunami and Spitfire Pro, respectively) to produce ~ 35 fs pulses centered at 1.55 eV at a 1 kHz repetition rate. The amplifier output separates into three arms. Not all arms are used in every experiment. Two arms are optical parametric amplifiers (Light-Conversion TOPAS-C) which create tunable pulses of light from ~ 0.5 to ~ 2.1 eV with spectral width on the amplitude level of FWHM ≈ 46 meV, absorptive filters and wire grid polarizers are used to isolate light of the desired color.[63] The third arm frequency doubles the output of the amplifier to create pulses centered at 3.1 eV in a β -barium-borate crystal. Each arm has its own mechanical delay stage and optical chopper. All pulses are then focused onto the sample with a 1 m focal length spherical mirror. The spatially coherent output (either the reflected probe or the triple sum of the probe) is isolated with an aperture in the reflected direction (sometimes referred to as an epi experiment), focused into a monochromator (Horiba Micro-HR) and detected with a thermoelectrically cooled photomultiplier tube (RCA C31034A). Figure 3 diagrams

the focusing and collection geometry used in this work. A dual-chopping routine is used to isolate the desired differential signal.[64] The color-dependent time-of-flight for

A dual-chopping routine is used to isolate the desired differential signal.[64] The color-dependent time-of-flight for each arm is corrected by offsetting the mechanical delay stages for each combination of pump and probes colors. We use a reflective geometry for our TSF measurements in order to minimize phase-mismatch effects. [51, 65] Unless otherwise noted, the pump fluence in these measurements is $\sim 100 \ \mu J/cm^2$. In Appendix D we show that this pump fluence is sufficiently small such that higherorder non-linear pump-induced effects can be neglected. The visible probe beam for the reflectance-probe experiments has a fluence of $\sim 2 \ \mu J/cm^2$ while the NIR probe lasers for the TSF-probe experiments have a fluence of $\sim 1000 \ \mu J/cm^2$. All beams are hundreds of microns wide at the sample. All raw data, workup scripts, and simulation scripts used in the creation of this work are permissively licensed and publicly available for reuse.[66] Our acquisition[67] and workup[68] software are built on top of the open source, publicly available Scientific Python ecosystem.[69-71]



FIG. 3. Overview of the pump-probe experiments in this work. (a) Schematic of the focusing and collection assembly (not to scale). The optical axis is ~ 9° from the sample surface normal. "PMT": photomultiplier tube. Also shown are the three excitation geometries used in this work: (b) pump-reflection-probe, in which the specular probe (ω_1) reflection is measured, (c) pump-THG-probe, in which the third harmonic signal ($3\omega_1$) travels in the same direction as the fundamental incident probe, and (d) pump-TSF-probe, in which signal is isolated in the $2k_1 + k_2$ direction. The \triangleleft symbol denotes the collected beam direction (isolated with an aperture). For sake of clarity, some reflections are not shown.

B. Sample preparation and characterization

Polycrystalline MoS_2 (WS₂) films were prepared by first e-beam evaporating 2 nm of Mo (W) onto a fused silica substrate and subsequent sulfidation in a tube furnace at 750 °C for 10 (30) minutes.[48] Note that this exact MoS₂ thin film sample was previously explored in Morrow *et al.* [27]. Following the methods detailed in Zhao and Jin [72], WS₂ (MoS₂) nanostructure samples on 300 nm SiO₂/Si substrates were prepared using water vapor assisted chemical vapor transport growth by heating 100 mg WS₂ (MoS₂) powder to 1200 °C at 800 torr in a tube furnace in which water vapor was produced by heating 1 g CaSO₄·2H₂O powder to 150 °C (120 °C) using heating tape wrapped around the tube furnace. 100 sccm argon was used as the carrier gas during the reaction.

Figure 4 shows optical microscope (Olympus BX51M) images, atomic force microscope (Agilent 5500) data, and Raman spectra (LabRAM Aramis, Confocal Raman/PL Microscope, 2.33 eV excitation) of the samples. The Raman spectra show the common E_{2g}^1 and A_{1g} modes seen in WS_2 and MoS_2 at the frequencies expected for many-layer to bulk morphologies.[73-75] The polycrystalline thin films (~ 10 nm thick) are continuous, flat, and smooth samples that are much larger than the spot size of our lasers (see Figure 4a). Each MoS_2 nanostructure (Figure 4b) is a few microns wide and sparsely scattered across the substrate. The nanostructures exhibit a wide range of morphologies from screw-dislocation spirals to stacked plates. The WS_2 nanostructure (Figure 4c and d) is a single screw-dislocation spiral which is 84 nm (\sim 120 layers) thick and \sim 150 μ m wide. TMDC screw-dislocation spirals are known to have excellent optical harmonic generation abilities. [76–79] Note that the perceived colors of the nanostructures in Figure 4b and Figure 4c are due to thin-film interference effects from the combination of the pyramid nanostructures, which have a large change in height across the structure, and the SiO_2/Si substrates; this class of effects have previously been explored for monolayers and nanostructures.[80-82]

IV. RESULTS AND DISCUSSION

A. MoS_2 thin film: transient-TSF

We first examine the effect of a pump on the multidimensional TSF spectrum, in which ω_1 and ω_2 are independently scanned. The output frequency of the TSF probe, $\omega_m = \omega_1 + 2\omega_2$, covers the range of the A and B excitons (1.65 - 2.25 eV). We explore this dependence with a MoS_2 thin film. In this film, the unpumped multidimensional spectra exhibit singly resonant features that depend only on the output triple sum frequency (e.g. Equation 4).[27] There are no cross peaks in the unpumped TSF spectrum because MoS_2 A and B excitons do not have the correct symmetry for our excitation beams to couple together. Like the unpumped spectrum, we found that the pump-TSF-probe spectra depends only on the triple sum frequency, regardless of pump-probe delay time. Pump-TSF-probe spectra of the MoS2 thin film at two different delays are shown in Fig-



FIG. 4. TMDC Sample characterization. (a) Photograph of the WS₂ film explored in this work. (b) Optical microscope image of the MoS₂ nanostructures explored in this work. (c) Optical microscope and (d) atomic force microscope image of the WS₂ nanostructure explored in this work. (e) Raman spectra of each sample; the maximum of each Raman spectrum is normalized to 1 and then offset for ease of comparison.

ure 5 ($\hbar\omega_{\text{pump}} = 3.1 \text{ eV}$). At both delay times, all features run along lines of constant output color (slope of -1/2). We explored the multidimensional probe spectra at other frequency and T combinations (output energies up to 3 eV and population times up to 100 ps); all features found are defined solely by the output color.

Given the similarities in band structure, we expect this result to be general to all TMDCs. The simplicity of the TSF and pump-TSF-probe spectra motivate the use of Equation 4 and its associated pump-THG-probe analysis which was discussed in the Theory section. Since the output color seems to uniquely determine the observed spectra, we restrict ourselves to the case $\omega_1 = \omega_2 = \omega_m/3$ (pump-THG-probe) for the rest of this work. We will understand the lineshapes present in Figure 5 by understanding the lineshapes of the pump-THG-probe spectroscopy presented in the next section.



FIG. 5. Pump-TSF-probe spectra of an MoS₂ thin film at 0 ps (a) and 0.90 ps (b) delay between pump and probe interactions. In both frames $\hbar\omega_{\text{pump}} = 3.1 \text{ eV}$ with a fluence of $120 \ \mu\text{J/cm}^2$, $\omega_m = \omega_1 + 2\omega_2$, and $\vec{k}_{\text{out}} = \vec{k}_1 + 2\vec{k}_2$.

B. MoS₂ thin film: transient-THG and transient-reflectance

Here we consider the pump-reflectance-probe and the pump-TSF-probe side-by-side to understand the differing selectivities of both methods. We first compare both probe methodologies using a single pump color. Figure 6 shows both the pump-reflectance-probe (left) and the pump-TSF-probe (right) response of the MoS₂ thin film with pump excitation at the B exciton. Note that horizontal $3\omega_1$ slices through Figure 6b are almost equivalent to the diagonal, $\omega_1 = \omega_2$ slices of Figure 5; they differ only in the use of different pump colors.

The TR and pump-THG-probe responses of Figure 6 are qualitatively similar. Our analysis in the Theory section indicates that phenomena like shifting and broadening will lead to similar lineshapes between the two spectroscopies while state density and dipole decreases will look different between the two spectroscopies—so our observed response is likely due to shifting and broadening of the underlying excitonic resonances. In both spectra, the measured intensity at the A and B excitons decreases when the pump is on $(\Delta I/I < 0)$. The intensity decreases dominate at T = 0, then decay over ~500 fs to form spectra that undulate between positive and negative values. These undulating spectra persist for several picoseconds (data not shown).

The minima of the transient-THG spectra are blueshifted relative to the corresponding minima observed in the transient-reflectance spectrum, but roughly agree with the peak positions of the unpumped THG spectrum (Figure 1). The A and B peaks of the unpumped THG spectrum are blue-shifted by ~ 50 meV compared to the absorption/reflection spectrum. We cannot explain why the maxima of the THG and absorption/reflection spectra are different by ~ 50 meV, but we note that Wang *et al.* [83] also observed this same unexplained blue-shift in their THG measurements.



FIG. 6. Comparison of transient-reflectance spectroscopy (a) to transient-TSF spectroscopy (b) for a MoS₂ thin film. In both frames $\hbar\omega_{\text{pump}} = 1.98 \text{ eV}$, as indicated by the vertical gray line. Each plot has its own colormap extent, red (dotted contours) signifies $\Delta I/I > 0$, white (solid contour) signifies $\Delta I/I = 0$, and blue (dashed contours) signifies $\Delta I/I < 0$.

To understand the spectral and temporal information in Figure 6, we examine transients at fixed probe frequencies and spectra at fixed time delays in Figure 7. For both cases, we use simple models to ensure standard physical arguments can explain our observations. Specifically, we show that the behavior of both probes can be understood with the same underlying system changes.

We first consider the spectral slices. The technical details of the spectral lineshape model (results shown as solid lines in Figure 7a and Figure 7b) are discussed in Appendix B. In both spectroscopies, the lineshape at $T \approx 0$ (Figure 7a) can be explained by a ~10 meV redshift, slight broadening, and slight amplitude decreases of the A and B resonances. In order to describe the pump-TSF-probe lineshape in Figure 7b we incorporated an additional ESA background. We attribute the additional ESA to excitation of near band edge carriers (conduction band electrons, valence band holes, or excitons) upon pump photoexcitation and subsequent relaxation. We attribute the redshift to carrier-induced bandgap renormalization (BGR), which was previously predicted and observed by many in monolayer TMDCs).[8, 84–87] The lineshape broadening upon excitation is common in semiconductors and has been previously observed by refs. [88, 89] in TMDCs. The amplitude decrease is likely due to state/band filling from the photocarriers.

A short time after excitation, T = 0.55 ps, the probe spectra change (Figure 7b): the line shapes are reproduced by a few meV redshift, no broadening, and no amplitude decrease. The simultaneous decrease in broadening, BGR, and state/band filling suggests that the majority of photocarriers have relaxed within several hundred femtoseconds, a curious dynamic that will be explored throughout this paper. Importantly, the interpretation of both probe methodologies is consistent.

Dynamics were described by an exponential decay and



FIG. 7. Comparison of spectral and temporal lineshapes with $\hbar\omega_{\text{pump}} = 1.98 \text{ eV}$ (gray vertical line). Spectral lineshapes in (a) and (b) are acquired with delay times of 0.05 and 0.55 ps, respectively. Dynamics in (c) are acquired at probe energies indicated by the vertical lines in (a) (1.97 and 2.02 eV for pump-refl-probe and pump-TSF-probe, respectively). Solid lines in each plot are calculated from the models described in the main text and Appendix B.

a static offset:

$$\frac{\Delta I}{I}(T) = \left(A_0 \exp\left(-\frac{T}{\tau}\right) + A_1\right) \Theta\left(T - t_0\right), \quad (17)$$

in which Θ is the Heaviside step function. We convolve Equation 17 with an instrument response function, which we approximate as Gaussian. Results are shown as solid lines in Figure 7c). Like the spectral line-shapes, the dynamics of both probe methods are consistent (Table I). The fast dynamic that changes the probe spectra in Figure 7a,b have a time constant of ~200 fs .[90] Dynamics on this timescale have previously been attributed to several mechanisms, including carrier trapping,[91–93] carrier-carrier scattering,[88, 94] carrier-phonon scattering,[95–97] free-carrier screening effects,[89, 98] and exciton formation.[98] The longer dy-

namic in Figure 7c, which we treat as an offset, A_1 , is common in single crystal ultrathin TMDC samples.[92, 98]

TABLE I. Results from fitting Equation 17 to the dynamics shown in Figure 7b. FWHM = full width at half maximum of the instrument response function.

	pump-refl-probe	pump-TSF-probe		
$\hbar\omega_m \ (eV)$	1.97	2.02		
τ (ps)	0.22 ± 0.02	0.21 ± 0.01		
FWHM (ps)	0.125 ± 0.009	0.095 ± 0.006		

Figure 8 shows the response from both TR and transient-THG spectroscopies for different combinations of pump and probe frequencies when T = 50 fs. Figure 8a is a very similar measurement to refs. [48, 99–105] where "traditional" coherent multidimensional spectroscopies were accomplished on TMDCs using a single electric field interaction as a probe; this measurement similarity is not the case for Figure 8b in which TSF acts as the probe with three electric field interactions. Nevertheless, both of our spectroscopies in Figure 8 have a similar dependence on the pump frequency—this can be seen by comparing vertical slices of Figure 8a and b (these horizontal slices are analogous to horizontal slices of Figure 6.).[106] The lineshapes of our two spectroscopies change smoothly as a function of $\hbar \omega_{pump}$ —there are no distinct contributions from the A or B resonances along the pump axis. The lack of structure along the pump axis mirrors the results of transient grating measurements on a MoS_2 thin film. [48] The general insensitivity to pump color suggests band gap renormalization (BGR) is a large contributor to the pump-induced changes. BGR is determined by Coulomb interactions, which are less sensitive to the explicit electron and hole occupation than, for instance, Pauli blocking effects.

Conversely, small, but noticeable, dependencies on $\omega_{\rm pump}$ suggest secondary contributions to the TR and transient-TSF spectra. For instance, when $\hbar \omega_{\text{pump}} \approx$ 1.8 eV $\approx \hbar \omega_A$, the decreases in intensity at $\omega_{out} = \omega_A$, are \sim 15% larger than at $\omega_{\rm out}$ = ω_B for both TR and pump-TSF-probe. When $\hbar\omega_{pump} \approx \hbar\omega_{B}$, however, both A and B have similar decreases in intensity. We believe band/state filling (bleaching) can account for the observed asymmetries in the decreases in intensity. The MoS_2 valence band is energetically split for different hole spins, but the conduction band is energetically degenerate for electron spins (cf. the inset in Figure 1). The A transition and B transition share neither valence nor conduction bands, so state/band filling is not shared between transitions. When the pump is resonant with the A transition, the bleach of the B transition is not direct and is expected to be smaller, in agreement with our measurements. Some bleaching is allowed through intervalley scattering, but valley depolarization measurements suggest these timescales are much longer than our pump probe delay time (50 fs) and is thus not significant.[107–109] When the pump is resonant with the B transition, it will also directly excite hot excitons or free electons/holes from the A band, which explains why the effects on the A and B transitions are similar for these pump colors. These observations are all consistent with line shape analysis of Figure 7a, in which redshifts (BGR) played a significant, but not complete, role in the line shape.

Guo *et al.* [105] also found asymmetries in the cross peaks of their multidimensional spectra of monolayer MoS₂ at 40 K. They attribute the asymmetric crosspeaks and their dynamics to be due to an exchange interaction between A and B excitons. This effect does not explain our results because the exchange interaction requires simultaneous populations of A and B excitons, which is not the case for $\omega_{pump} \approx \omega_A$.



FIG. 8. Comparison between transient-reflectance spectroscopy (a) and transient-TSF spectroscopy (b) of a MoS_2 thin film. In both frames T = 50 fs.

C. MoS₂ and WS₂ nanostructures

In this section we investigate the effects of sample morphology on pump-TSF-probe spectroscopy by comparing all the samples shown in Figure 4. We first compare spectra of the previously discussed thin film with an ensemble of spiral nanostructures grown via a screw dislocation driven growth method (Figure 4b). The goal of this comparison is to broadly demonstrate that the spectra and dynamics observed with transient-TSF are sensitive to the specifics of sample morphology. We then compare the transient-TSF and TR response of both a WS₂ thin film and a single WS₂ screw-dislocation nanostructure.

1. Transient-THG of a MoS_2 thin film vs. nanostructures

Figure 9 shows the probe frequency vs. delay time response of the thin film (Figure 9a) and nanostructure (Figure 9b). Both spectra show similar spectral lineshapes near zero delay with decreases at the A and B features. The nanostructures spectrum (Figure 9b) demonstrate narrower peaks and greater increase in TSF intensity to the red of the A exciton resonance compared to the thin film (Figure 9a). The nanostructures exhibiting narrower features indicates that the thin film has more structural inhomogeneity. While both samples show similar lineshapes at T = 0, they exhibit drastically different dynamics.



FIG. 9. Pump-TSF-probe spectra of a MoS₂ thin film (a) and a MoS₂ spiral nanostructure ensemble (b). The temporal axis has linear scaling until 1 ps (horizontal green line) and then logarithmic scaling until the end (50 ps). In both frames $\hbar\omega_{\rm pump} = 3.1$ eV with a fluence of 120 μ J/cm².

Figure 10 shows a single temporal trace through the data shown in Figure 9 for each sample morphology. The thin lines are the measured data and the thick lines are fits using Equation 17. We recover exponential decay time constants of 0.34 ± 0.02 ps for the thin film and 12.7 ± 0.8 ps for the nanostructures. The morphology strongly affects dynamics. We speculate that the dramatic differences in timescales are related to the density of grain boundaries, which can affect carrier scattering, recombination, and/or trapping.[91] The grain size of the thin film is on the order of 100 nm^2 while that of the nanostructures is on the order of 10-100 μ m². We believe that carrier trapping or defect assisted annihilation is the main source of dynamics in Figure 10; a carrier once it has been trapped/annihilated is not able to efficiently screen the electron-hole Coulomb interaction, so BGR is lessened and the observed differential response is decreased.

There is a low amplitude, rapid dynamic present for each sample in Figure 10 that is not captured by our single exponential fit; we attribute this rapid dynamic to hot carriers (the carriers have $\sim 1 \text{ eV}$ excess energy upon photoexcitation) cooling to form excitons.[89, 98] In TMDCs, hot carriers bleach excitonic transitions more effectively than excitons; so a hot carrier cooling will reduce the bleach observed at the A and B transitions.[89, 98, 110] Taken together, we believe defect/grain-boundary assisted quenching of carriers along with hot carrier cooling can explain the dynamics observed in Figure 9 and Figure 10.



FIG. 10. Pump-TSF-probe of a MoS₂ thin film and an ensemble of spiral nanostructures. The temporal axis has linear scaling until 1 ps (green line) and then logarithmic scaling until the end (50 ps). This figure displays 1D slices out of Figure 9 in which the pump is set to $\hbar\omega_{\text{pump}} = 3.1 \text{ eV}$ while the probe is set to $3\hbar\omega_1 = \hbar\omega_m = 1.87 \text{ eV}$.

2. Unified description of pump induced dynamics in MoS_2

Our measurements support the following description of carrier dynamics in multilayer MoS₂. The pump creates electrons (holes) in the valence (conduction) band and excitons. These carriers affect the optical transitions that a probe observes. At T = 0, the excited carriers screen the electron-hole Coulomb interaction causing BGR and lowering exciton transition energy. The excited carriers also scatter with each other leading to faster dephasing rates and therefore broadening of the exciton transition. The excited carriers can also Pauli-block the bandedge transitions leading to a small decrease in transition amplitude.

After photoexcitation, the carriers are rapidly annihilated, trapped, or scattered to other momentum points (recall that few-layer MoS_2 is an indirect semiconductor). The exact timescale for this relaxation depends on extrinsic properties such as defects: for our polycrystalline thin film the timescale is hundreds of femtoseconds, while for nanostructures the timescale is roughly ten picoseconds. An electron and hole, once annihilated or trapped, does not scatter or Pauli-block transitions, so the probe sees the original exciton linewidth and transition amplitude. Importantly, a trapped carrier or an indirect exciton can still screen the electron-hole Coulomb interaction,[111, 112] so a long-lived redshift of the exciton transition is commensurate with residual BGR caused by trapped/indirect carriers. The T = 0.55 ps spectrum shown in Figure 7b represents this residual BGR.

3. Transient-THG vs. transient-reflectance for WS₂ thin film vs. single nanostructure

To further investigate the abilities of pump-TSF-probe, we performed pump-TSF-probe and pump-reflectanceprobe experiments on two different morphologies of WS₂: a thin film on a fused silica substrate (photo shown in Figure 4a), and a single, isolated, spiral nanostructure grown on a 300 nm SiO₂ on Si substrate (optical microscope and atomic force microscope characterization shown in Figure 4c, and Figure 4b, respectively). Our probe beam area is small compared to the area of the thin film, but much larger than the single nanostructure.

In Figure 11 we use a NIR pump to drive mid-gap or 2-photon transitions and probe the A exciton transition of WS_2 . Appendix C describes experiments on our MoS_2 thin film which demonstrate our ability to drive midgap transitions with a NIR pump. The full spectra and a discussion of these NIR pump measurements will be the subject of another publication. The unpumped THG spectra of the thin film and nanostructure are shown in Figure 11a, and the differential spectra (T = 120 fs) for each morphology are shown in Figure 11b. In both cases, the thin film exhibits a broader and redder A feature than the nanostructure—structural inhomogeneity from the small grain size of the polycrystalline film likely causes the increased linewidth of the thin film. The differing amount of spectral inhomogeneity causes the transientreflectance and transient-TSF spectra between the two samples to look slightly different.

While the transient-TSF spectra from both the thin film and the single nanostructure are comperable in signal strength, the same is not true for transient-reflectance measurements. Figure 11c shows that the nanostructure significantly reduces the transient reflectance signal (~ 5x less signal). This is largely due to the indiscriminate nature of reflectivity (Equations 5–9): since the bare substrate has a substantial reflectivity and covers a large portion of the illumination area, a correspondingly large portion of the reflected probe does not represent the nanostructure. As a result, the relative changes in reflectivity of the nanostructure is diminished. Furthermore, reflected light from bare substrate interferes with reflected light of the nanostructure signals, significantly complicating comparisons between the spectra of the two structures.

In contrast, TSF emission is strongly dependent on resonance enhancement and dipole strength (Equations 3 and 10). These dependencies strongly suppress both glass substrates (no resonant enhancement) and bulk semiconductor substrates (small dipoles for resonant transitions). As a result, our TSF probe is virtually background free, with contrast similar to that of fluorescence imaging.



FIG. 11. Comparison of pump-TSF-probe and pumpreflectance-probe for two morphologies of WS₂: a thin film and a single, ~150 μ m wide spiral nanostructure. (a) normalized TSF spectrum for each sample, these spectra are not normalized for the frequency dependent intensity of the probe OPA. (b) pump-TSF-probe spectra for each sample. (c) pump-refl-probe spectra for each sample. In (b) and (c) the sub-band edge pump has frequency of $\hbar\omega_{pump} = 1.054 \text{ eV}$ and a fluence of ~7000 μ J/cm². All spectra were acquired for the same number of laser shots. Each spectra is composed of 7 spectra averaged together at $T \approx 0.12$ ps. (b) and (c) each show the standard deviation of the averaged spectra for each sample morphology as a filled spread around the average.

V. OUTLOOK AND CONCLUSION

Using the examples of MoS₂ and WS₂, this work shows that pump-TSF-probe spectroscopy can elucidate the dynamics and energetics of photoexcited semiconductor thin films and nanostructures. We demonstrated that this new spectroscopy (specifically the degenerate case of pump-TSF-probe, pump-THG-probe) is complementary to the more mature spectroscopy, transient-reflectance. While pump-THG-probe and transient-reflectance have different dependencies on variables like transition dipole strength and state density, we showed that the two spectroscopies can be understood in tandem from the same underlying excited-state physics. These differences in dependencies allow pump-TSF-probe to offer a complementary view on excited state physics, which in some cases will be more definitive than a transient-reflectance measurement. We found that transient-TSF is robust to extrinsic nanocrystal properties, such as size and surface coverage, that dramatically affect transient-reflectance spectra. This robustness allowed us to measure the transient-TSF spectrum of nanostructures much smaller than the excitation spot size, while at the same time maintaining a high signal-to-noise ratio. We predict that with pump-TSF-probe spectroscopy, researchers can avoid the reflectance artifacts which have complicated recent ultrafast work (cf. refs [113, 114]) because the measured TSF and pump-TSF-probe intensities are easily connected to the sample's susceptibility.

Previous studies have shown that TSF can be used to measure coupling between states.[21, 28] Isolating cross peaks is a strategy not explored in this work that could further increase the selectivity of pump-TSFprobe spectroscopy in the future. We believe that samples with states/bands of the correct symmetry would yield insightful dynamical coupling information. For instance, since TSF can measure the energy separations of up to four states, it could resolve how bands change their dispersion upon photo-excitation. Crucially, unlike other multidimensional probes which are not fullycoherent,[2, 6, 18, 19] TSF is not susceptible to population relaxations during the multiple electric field interactions, it is therefore a more direct probe of the underlying quantum states.

Another area that could benefit from the proof-ofconcept measurements in this work is multi-photon microscopy. Multiphoton microscopy uses a diverse set of techniques, including THG/TSF,[29–31] to predominantly measure biologically relevant samples. These multiphoton microscopies could easily incorporate a pump and a delay stage in order to measure spatially resolved dynamics.

SUPPLEMENTARY MATERIAL

All data and the workup/representation/simulation scripts used to generate the figures in this work are available for download at http://dx.doi.org/10.17605/OSF.IO/UMSXC.

ACKNOWLEDGMENTS

We acknowledge support from the Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under award DE-FG02-09ER46664. D.J.M. acknowledges support from the Link Foundation. We thank Kyle Czech for synthesizing the MoS_2 thin film sample. D.J.M., D.D.K., and J.C.W. have filed a patent application on some of the work described herein.

Appendix A: Single resonance simulations of pump-probe responses

Here we examine the spectra produced by small changes in a system described by one Lorentzian resonance. We assume the system changes are small (Equation 16).

1. Pump-THG-probe

The single resonance third-order susceptibility is given by

$$\chi^{(3)} = \frac{\mu^4}{\omega_{ag} - \omega_{321} - i\Gamma}.$$
 (A1)

The parital derivatives of Equation A1 are

$$\frac{\partial \chi^{(3)}}{\partial \mu} = \frac{4\mu^3}{\omega_{ag} - \omega_{321} - i\Gamma} \tag{A2}$$

$$\frac{\partial \chi^{(3)}}{\partial \Gamma} = i \frac{\mu^4}{\left(\omega_{ag} - \omega_{321} - i\Gamma\right)^2} \tag{A3}$$

$$\frac{\partial \chi^{(3)}}{\partial \omega_{ag}} = -\frac{\mu^4}{\left(\omega_{ag} - \omega_{321} - i\Gamma\right)^2} \tag{A4}$$

Using Equation 12 and Equation 16 we can calculate the change in TSF intensity due to a perturbation:

$$\frac{\Delta I}{I} = \left| 1 + \frac{1}{\chi^{(3)}} \frac{\partial \chi^{(3)}}{\partial \lambda} d\lambda \right|^2 - 1$$
(A5a)

$$\approx 2 \operatorname{Re}\left[\frac{1}{\chi^{(3)}} \frac{\partial \chi^{(3)}}{\partial \lambda}\right] \mathrm{d}\lambda,$$
 (A5b)

where in Equation A5b we used the fact that the perturbation is small, $d\chi^{(3)} \ll \chi^{(3)}$ (Equation A5b is equivalent to Equation 15). Combining Equations A1 - A5b, we have

$$\frac{\Delta I}{I} \approx 8 \frac{\mathrm{d}\mu}{\mu} \tag{A6}$$

$$\frac{\Delta I}{I} \approx -\frac{2\Gamma}{\left(\omega_{ag} - \omega_{321}\right)^2 + \Gamma^2} d\Gamma \quad \left(\propto \operatorname{Im}\left[\chi^{(3)}\right]\right) \qquad \lambda = \Gamma \qquad (A7)$$

$$\frac{\Delta I}{I} \approx -\frac{2\left(\omega_{ag} - \omega_{321}\right)}{\left(\omega_{ag} - \omega_{321}\right)^2 + \Gamma^2} d\omega_{ag} \quad \left(\propto \operatorname{Re}\left[\chi^{(3)}\right]\right) \qquad \lambda = \omega_{ag}.$$
(A8)

This is the desired result which was discussed in the main text (Figure 2).

2. Transient transmittance and transient reflectance

The single resonance linear susceptibility is given by

$$\chi^{(1)} = \frac{\mu^2}{\omega_{ag} - \omega - i\Gamma}.$$
(A9)

The partial derivatives are

$$\frac{\partial \chi^{(1)}}{\partial \mu} = \frac{2\mu}{\omega_{ag} - \omega - i\Gamma} \quad \left(\propto \chi^{(1)}\right) \tag{A10}$$

$$\frac{\partial \chi^{(1)}}{\partial \Gamma} = i \frac{\mu^2}{\left(\omega_{ag} - \omega - i\Gamma\right)^2} \quad \left(\propto i \frac{\mathrm{d}}{\mathrm{d}\omega} \chi^{(1)}\right) \tag{A11}$$

$$\frac{\partial \chi^{(1)}}{\partial \omega_{ag}} = -\frac{\mu^2}{\left(\omega_{ag} - \omega - i\Gamma\right)^2} \tag{A12}$$

Using Equation 12 and the thin film limit Equation 13, the differential reflectivity for a small change in parameter λ is

$$\frac{\Delta R}{R} = -\frac{R_0}{R} \frac{4\omega\ell}{\left(1+n_s^2\right)c} \operatorname{Im}\left[\frac{\partial\chi^{(1)}}{\partial\lambda}\mathrm{d}\lambda\right].$$
(A13)

Since the quantity $\frac{R_0}{R} \frac{4\omega\ell}{(1+n_s^2)c}$ is relatively insensitive to frequency, the differential reflectance lineshape can be inferred by examining the imaginary projections of Equations A10-A12. The lineshape for $\lambda = \mu$ corresponds to the imaginary component of the original Lorentzian lineshape. The lineshape for $\lambda = \Gamma$ corresponds to the first derivative lineshape of the real (dispersive) part of the resonance. The lineshape for $\lambda = \omega_{ag}$ corresponds to the first derivative lineshape of the original Lorentzian.

Finally, note that for transmission that obeys Beer's law $(I = I_0 \exp(-\alpha \ell)$ with $\alpha \equiv \frac{\omega}{cn} \text{Im} [\chi^{(1)}]$, where *n* is the refractive index of the volume), the expression for small differential signal differs from Equation A13 only by prefactors:

$$\frac{\Delta T}{T} = \frac{\exp\left(-\alpha_{\text{pumped}}\ell\right) - \exp\left(-\alpha_{\text{unpumped}}\ell\right)}{\exp\left(-\alpha_{\text{unpumped}}\ell\right)} \tag{A14}$$

$$\approx -\ell \left(\alpha_{\text{pumped}} - \alpha_{\text{unpumped}} \right) \tag{A15}$$

$$= -\frac{\omega\ell}{nc} \mathrm{Im} \left[\frac{\partial \chi^{(1)}}{\partial \lambda} \mathrm{d}\lambda \right]$$
(A16)

$$=\frac{R}{R_0}\frac{1+n_s^2}{4n}\frac{\Delta R}{R},\tag{A17}$$

so $\Delta T/T$ and $\Delta R/R$ are proportional to the extent that R, n, and n_s are frequency invariant. Therefore the transient reflection lineshapes of Figure 2a can be interpreted as the absorption cross section lineshape changes seen in $\Delta T/T$ measurements.

Appendix B: Lineshape modeling

In this appendix we describe our simple model for building the spectral lineshapes shown in Figure 7. The general implementation is:

- 1. For both spectroscopies construct an unexcited $\chi^{(n)}$ spectrum from a sum of oscillators.
- 2. Calculate the unexcited reflectance or TSF spectrum from $\chi^{(1)}$ and $\chi^{(3)}$, respectively.
- 3. Create a $\chi^{(n)'}$ spectrum to perturb the central frequencies, linewidths, and amplitudes of the oscillators used to construct $\chi^{(n)}$.
- 4. Calculate the excited reflectance or TSF spectrum from $\chi^{(1)\prime}$ and $\chi^{(3)\prime}$, respectively.
- 5. Use Equation 12 to calculate $\frac{\Delta I}{I}$ for both spectroscopies.
- 6. Iterate through previous steps to fit observed lineshapes.

We choose to use complex, Lorentzian oscillators to construct our spectra:

$$\chi^{(n)} = \sum_{j=1} \sqrt{\frac{\Gamma_j}{\pi}} \frac{A_j}{E_{0,j} - \hbar\omega_m - i\Gamma_j}$$
(B1)

in which j = 1 and j = 2 are the A and B transitions, and the other oscillators are high-lying non-resonant transitions. To create $\chi^{(n)'}$ we replace $\Gamma_j \to \Gamma_j + \Delta \Gamma_j$, $E_{0,j} \to E_{0,j} + \Delta E_{0,j}$, and $A_j \to (1 - \% \text{ decrease})A_j$. ESA-like additional transitions are incorporated by adding a phased offset to $\chi^{(n)'}$; the pump-TSF-probe spectrum in Figure 7b has a slight offset with phase described by exp $[i\theta]$ with $\theta = 1$ radian. Table II codifies the parameters we found, by hand, to give acceptable fits to the data shown in Figure 7.

We construct a TSF spectrum by merely calculating the square magnitude of $\chi^{(3)}$ as indicated by Equation 10. We construct a reflectance spectrum by converting $\chi^{(1)}$ to a complex refractive index, \bar{n} and then using a Fresnelcoefficient-like analysis, specifically as discussed in Anders [115], which takes into account the influence of multiple reflections and the substrate. This treatment is slightly more holistic than merely using Equation 5 because it takes into account the finite thickness of the sample (while the derivation of Equation 5 assumes a delta function sample).

$$R = \left| \frac{\bar{r}_1 + \bar{r}_2 \exp\left[-i\phi_1\right]}{1 + \bar{r}_1 \bar{r}_2 \exp\left[-i\phi_1\right]} \right|^2 \tag{B2}$$

$$\bar{r}_1 = \frac{\bar{n}_0 - \bar{n}_1}{\bar{n}_0 + \bar{n}_1} \tag{B3}$$

$$\bar{r}_2 = \frac{\bar{n}_1 - \bar{n}_2}{\bar{n}_1 + \bar{n}_2} \tag{B4}$$

$$\phi_1 = \frac{4\pi\ell\bar{n}_1}{\lambda} \tag{B5}$$

in which \bar{n}_0 is the refractive index of air, \bar{n}_1 is the constructed refractive index of the MoS₂ thin film with thickness ℓ , \bar{n}_2 is the refractive index of the fused silica substrate, and λ is the vacuum wavelength of the interrogating electric field.

TABLE II. Parameters used to produce the lineshapes shown in Figure 7.Note that the model in Figure 7b for pump-TSF-probe has a slight offset with phase described by $\exp[i\theta]$ with $\theta = 1$ radian and amplitude of 1% of the maximum feature.

transition	$E_0 (\mathrm{eV})$	$\Delta E_0 ({\rm eV})$	Γ (eV)	$\Delta \Gamma$ (eV)	relative A	% A decrease
		transient	reflectance mo	del $T = 0.05$ ps		
А	1.807	-0.01	0.1	0.002	1	2
В	1.98	-0.009	0.12	0.005	1.1	2
	2.7	-0.008	0.25	0	4	5
	3.2	0	0.25	0	8	0
	6	0	0.25	0	40	0
		transient	reflectance mo	del $T = 0.55$ ps		
А	1.807	-0.005	0.1	0	1	2
В	1.98	-0.005	0.12	0	1.1	2
	2.7	0	0.25	0	4	5
	3.2	0	0.25	0	8	0
	6	0	0.25	0	40	0
		transie	ent TSF model	$T = 0.05 \ ps$		
А	1.81	-0.012	0.085	0.005	1	2
В	1.95	-0.009	0.1	0.005	0.91	2
		transie	ent TSF model	$T = 0.55 \ { m ps}$		
А	1.81	-0.003	0.085	0	1	0
В	1.95	-0.002	0.1	0	0.91	0

Appendix C: Sub-bandgap pump, reflectance probe of a MoS₂ thin film

TMCDs have weak but finite absorption well below the bandgap.[116] To investigate this sub-band edge response, we tuned our pump to NIR colors, using fluence an order of magnitude higher than the visible pump. The effects of this sub-band edge pump on the band-edge reflectance spectrum are shown in Figure 12. We observe similar spectral and temporal lineshapes for both the visible and NIR pump, indicating the NIR pump generates photocarriers in a similar manner to a visible pump.



FIG. 12. Transient-reflectance spectroscopy on a MoS₂ thin film with a NIR pump. (a) shows the transient-reflectance spectrum for different combinations of pump and probe frequencies for T = 50 fs. This spectrum is not normalized for the frequency dependence of the pump laser intensity. (b) shows the measured dynamics for different probe colors with $\hbar\omega_{pump} = 0.99$ eV

Given the strong two-photon absorption in TMDCS, [117–121] it is possible that the signals in Figure 12 arise from two-photon absorption of sub-bandgap light. To identify the presence of two-photon transitions, we examined the fluence scaling. Figure 13 shows the TR signal scaling for the sub-bandgap pump (orange down-pointing triangles). We observe linear scaling of the probe metric with respect to the NIR pump fluence. This linear scaling is commensurate with the work of Völzer *et al.* [122] who observe linear response in bulk MoS₂ up to a pump fluence of ~200 μ J/cm². These observations rule out two-photon absorption as the dominant contribution to Figure 12. Instead, it is likely that our NIR pump excites electrons/holes to/from midgap states that have small optical cross-sections. Midgap states exist in synthetically grown MoS₂ and are generally attributed to sulfur vacancies and edge defects.[91, 123–128] We believe mid-gap excitations can induce BGR and band-filling in a manner similar to direct, allowed transitions, which explains the similarity in lineshape between visible and NIR pumps (compare Figure 8a with Figure 12a or Figure 6a with Figure 12b). The insensitivity to pump wavelength reflects the large dispersion of mid-gap states and their transitions to valence and conduction bands.

Appendix D: Pump-fluence dependence of pump-TSF-probe

Here we investigate the scaling of pump-TSF-probe signal with respect to pump fluence. Figure 13 shows the fluence dependence of $|\Delta I_{\text{TSF}}|/I_{\text{TSF}}$ when pumping and probing near the B exciton resonance (purple squares), and compares the response to pump-reflection-probe pumping and probing the same resonance (orange up-pointing triangles).

The $|\Delta I_{\text{TSF}}|/I_{\text{TSF}}$ shows sublinear behavior at higher fluences (> 50 μ J/cm²). Since the reflection probe exhibits linear response for far higher pump fluences than the onset of THG sublinear scaling, we cannot attribute the sublinear trend to traditional explanations like band saturation or many-body effects caused by the pump interaction. Rather, we attribute this unique power dependence to the competition between quadratic scaling, difference intensity signal, $|d\chi^{(3)}|^2$, and the linear scaling, heterodyne signal, $|\chi^{(3)}||d\chi^{(3)}|\cos(d\theta)$ (cf. Equation 14). For low pump fluence, $d\chi^{(3)} \ll \chi^{(3)}$ so $|\Delta I_{\text{TSF}}|/I_{\text{TSF}}$ scales linearly. As the pump fluence is increased to the point where $|\Delta I_{\text{TSF}}|/I_{\text{TSF}} \sim$ 1, the intensity level differential signal becomes similar to the heterodyne signal, so the quadratic term becomes important. The observed power scaling in this regime depends on the sign of $\cos(d\theta)$, which can be inferred by the sign of ΔI in the linear fluence regime. When $\cos(d\theta) > 0$ (and $\Delta I > 0$ for low fluence), the quadratic terms adds to the linear term and superlinear scaling is observed (as simulated in Figure 13, hashed line). When $\cos(d\theta) < 0$ (and $\Delta I < 0$ for low fluence, as is the case in Figure 13), the quadratic term and linear scaling terms destructively interfere and sublinear scaling is observed (as simulated in Figure 13, dotted line). Note that the Equation 14 fit of our pump-TSF-probe fluence data recovers the phase and amplitude of $\chi^{(5)} = d\chi^{(3)}/\mathcal{F}_{pump}$: we find that



FIG. 13. Comparison of transient-reflectance spectroscopy (orange) to transient-TSF spectroscopy (violet) pump fluence scaling for a MoS₂ thin film. The y-axis is maximum extent of the bleach measured (near T = 0). The pump and probe combinations are as follows: (\blacktriangle , $\hbar\omega_1 = \hbar\omega_m = \hbar\omega_{pump} = 1.98 \text{ eV}$); (\blacktriangledown , $\hbar\omega_1 = \hbar\omega_m = 1.98 \text{ eV}$, $\hbar\omega_{pump} = 0.99 \text{ eV}$); and (\blacksquare , $3\hbar\omega_1 = \hbar\omega_m = 2.05 \text{ eV}$, $\hbar\omega_{pump} = 1.98 \text{ eV}$). Gray solid lines show linear scaling to guide the eye. The gray dotted line is a fit of Equation 14 to the THG probe data. Also shown is an example of Equation 14 for the case of constructive interference (dashed line).

 $|\chi^{(5)}| / |\chi^{(3)}| = 0.003 \text{ cm}^2/\mu \text{J}$ and $\cos(d\theta) = -0.6$.

Theoretically, a similar power scaling competition as Equation 14 can occur in linear probe experiments if $d\chi^{(1)}$ becomes large enough, but this regime is uncommon because in linear experiments the unpumped probe (reflection or transmission) is usually more intense, so higher-order pump processes often contribute before this onset. For example in Figure 13, a pump-fluence of ~100 μ J/cm² produces only a ~ 1% change in reflectivity, while under the same conditions the TSF intensity changes by ~ 20%.

To reiterate, the pump-TSF-probe fluence scaling is both non-linear and well-understood; the trend is *not* due to higher-order non-linear effects (e.g. $\chi^{(7)}$). The pump fluence trends observed here are well-described by a fluence-independent absorption cross-section for the pump. Note that the lineshape simulations in Figure 2 assume linear scaling of pump fluence. Our main results were acquired at a pump fluence of ~100 μ J/cm² which is in the regime of nonlinear scaling of $|\Delta I_{\rm TSF}|/I_{\rm TSF}$ with pump fluence. Importantly, the lineshape fitting of our data (Figure 7) accounts for the possible nonlinear scaling of $|\Delta I_{\rm TSF}|/I_{\rm TSF}$ with pump fluence because Equation 12 is explicitly used in our model. If we had used Equation 15 in our analysis this nonlinear pump scaling would not have been taken into account.

- R. Ulbricht, E. Hendry, J. Shan, T. F. Heinz, and M. Bonn, Rev. Mod. Phys. 83, 543 (2011).
- [2] W. Xiong, J. E. Laaser, P. Paoprasert, R. A. Franking, R. J. Hamers, P. Gopalan, and M. T. Zanni, J. Am. Chem. Soc. 131, 18040 (2009).
- [3] D. R. Dietze and R. A. Mathies, ChemPhysChem 17, 1224 (2016).
- [4] A. E. Bragg, W. Yu, J. Zhou, and T. Magnanelli, J. Phys. Chem. Lett. 7, 3990 (2016).
- [5] F. Ceballos, M.-G. Ju, S. D. Lane, X. C. Zeng, and H. Zhao, Nano Lett. 17, 1623 (2017).
- [6] A. Mandal, J. D. Schultz, Y.-L. Wu, A. F. Coleman, R. M. Young, and M. R. Wasielewski, J. Phys. Chem. Lett. 10, 3509 (2019).
- [7] E. J. Sie, C. M. Nyby, C. D. Pemmaraju, S. J. Park, X. Shen, J. Yang, M. C. Hoffmann, B. K. Ofori-Okai, R. Li, A. H. Reid, S. Weathersby, E. Mannebach, N. Finney, D. Rhodes, D. Chenet, A. Antony, L. Balicas, J. Hone, T. P. Devereaux, T. F. Heinz, X. Wang, and A. M. Lindenberg, Nature 565, 61 (2019).
- [8] F. Liu, M. E. Ziffer, K. R. Hansen, J. Wang, and X. Zhu, Phys. Rev. Lett. **122**, 246803 (2019).
- [9] F. Langer, C. P. Schmid, S. Schlauderer, M. Gmitra, J. Fabian, P. Nagler, C. Schüller, T. Korn, P. G. Hawkins, J. T. Steiner, U. Huttner, S. W. Koch, M. Kira, and R. Huber, Nature 557, 76 (2018).
- [10] Z. Wang, H. Park, Y. H. Lai, J. Xu, C. I. Blaga, F. Yang, P. Agostini, and L. F. DiMauro, Nat. Commun. 8, 1686 (2017).
- [11] J. C. Wright, Annu. Rev. Phys. Chem. 62, 209 (2011).
- [12] J. C. Wright, Annu. Rev. Anal. Chem. 10, 45 (2017).
- [13] P. C. Chen, Appl. Spectrosc. **70**, 1937 (2016).
- [14] C. L. Smallwood and S. T. Cundiff, Laser Photonics Rev. 12, 1800171 (2018).
- [15] S. T. Cundiff and S. Mukamel, Physics Today 66, 44 (2013).
- [16] M. Cho, Chem. Rev. **108**, 1331 (2008).
- [17] M. Cho, ed., Coherent Multidimensional Spectroscopy (Springer Singapore, 2019).
- [18] J. Bredenbeck, J. Helbing, R. Behrendt, C. Renner, L. Moroder, J. Wachtveitl, and P. Hamm, J. Phys. Chem. B 107, 8654 (2003).
- [19] B. Abraham, L. G. C. Rego, and L. Gundlach, J. Phys. Chem. C 123, 23760 (2019).
- [20] N. A. Neff-Mallon and J. C. Wright, Analytical Chemistry 89, 13182 (2017).
- [21] J. D. Handali, K. F. Sunden, B. J. Thompson, N. A. Neff-Mallon, E. M. Kaufman, T. C. Brunold, and J. C. Wright, J. Phys. Chem. A **122**, 9031 (2018).
- [22] E. S. Boyle, A. V. Pakoulev, and J. C. Wright, J. Phys. Chem. A 117, 5578 (2013).
- [23] E. S. Boyle, N. A. Neff-Mallon, and J. C. Wright, J. Phys. Chem. A 117, 12401 (2013).
- [24] E. S. Boyle, N. A. Neff-Mallon, J. D. Handali, and J. C. Wright, J. Phys. Chem. A 118, 3112 (2014).
- [25] M. Grechko, T. Hasegawa, F. D'Angelo, H. Ito, D. Turchinovich, Y. Nagata, and M. Bonn, Nat. Commun. 9, 885 (2018).
- [26] M. Bonn, C. Hess, J. H. Miners, T. F. Heinz, H. J. Bakker, and M. Cho, Phys. Rev. Lett. 86, 1566 (2001).
- [27] D. J. Morrow, D. D. Kohler, K. J. Czech, and J. C.

Wright, J. Chem. Phys. **149**, 091101 (2018).

- [28] M. Grechko, S. A. Bretschneider, L. Vietze, H. Kim, and M. Bonn, Angew. Chem. 57, 13657 (2018).
- [29] A. M. Hanninen, R. C. Prince, and E. Potma, IEEE J. Sel. Top. Quantum Electron. 25, 1 (2018).
- [30] A. M. Hanninen, R. C. Prince, R. Ramos, M. V. Plikus, and E. O. Potma, Biomed. Opt. Express 9, 4807 (2018).
- [31] H. Segawa, M. Okuno, H. Kano, P. Leproux, V. Couderc, and H. o Hamaguchi, Opt. Express 20, 9551 (2012).
- [32] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Phys. Rev. Lett. **105**, 136805 (2010).
- [33] G. Wang, A. Chernikov, M. M. Glazov, T. F. Heinz, X. Marie, T. Amand, and B. Urbaszek, Rev. Mod. Phys. 90, 021001 (2018).
- [34] A. Molina-Sánchez, D. Sangalli, K. Hummer, A. Marini, and L. Wirtz, Phys. Rev. B 88, 045412 (2013).
- [35] D. Y. Qiu, F. H. da Jornada, and S. G. Louie, Phys. Rev. Lett. **111**, 216805 (2013).
- [36] K. He, N. Kumar, L. Zhao, Z. Wang, K. F. Mak, H. Zhao, and J. Shan, Phys. Rev. Lett. **113**, 026803 (2014).
- [37] N. Saigal, V. Sugunakar, and S. Ghosh, Appl. Phys. Lett. 108, 132105 (2016).
- [38] J. Kopaczek, M. P. Polak, P. Scharoch, K. Wu, B. Chen, S. Tongay, and R. Kudrawiec, J. Appl. Phys. 119, 235705 (2016).
- [39] A. Autere, H. Jussila, Y. Dai, Y. Wang, H. Lipsanen, and Z. Sun, Adv. Mater. **30**, 1705963 (2018).
- [40] Y. M. Chang, L. Xu, and H. W. K. Tom, Phys. Rev. Lett. 78, 4649 (1997).
- [41] C. Guo, G. Rodriguez, and A. J. Taylor, Phys. Rev. Lett. 86, 1638 (2001).
- [42] A. McClelland, V. Fomenko, and E. Borguet, J. Phys. Chem. B 108, 3789 (2004).
- [43] D. Hsieh, F. Mahmood, J. W. McIver, D. R. Gardner, Y. S. Lee, and N. Gedik, Phys. Rev. Lett. **107**, 077401 (2011).
- [44] W. A. Tisdale, K. J. Williams, B. A. Timp, D. J. Norris, E. S. Aydil, and X.-Y. Zhu, Science **328**, 1543 (2010).
- [45] H. Park, M. Gutierrez, X. Wu, W. Kim, and X.-Y. Zhu, J. Phys. Chem. C 117, 10974 (2013).
- [46] C. A. Nelson, J. Luo, A. K.-Y. Jen, R. B. Laghumavarapu, D. L. Huffaker, and X.-Y. Zhu, J. Phys. Chem. C 118, 27981 (2014).
- [47] E. M. Mannebach, K.-A. N. Duerloo, L. A. Pellouchoud, M.-J. Sher, S. Nah, Y.-H. Kuo, Y. Yu, A. F. Marshall, L. Cao, E. J. Reed, and A. M. Lindenberg, ACS Nano 8, 10734 (2014).
- [48] K. J. Czech, B. J. Thompson, S. Kain, Q. Ding, M. J. Shearer, R. J. Hamers, S. Jin, and J. C. Wright, ACS Nano 9, 12146 (2015).
- [49] J. P. Lomont, K. L. Rich, M. Maj, J.-J. Ho, J. S. Ostrander, and M. T. Zanni, J. Phys. Chem. B 122, 144 (2017).
- [50] A. M. Alperstein, J. S. Ostrander, T. O. Zhang, and M. T. Zanni, Proc. Natl. Acad. Sci. U.S.A. **116**, 6602 (2019).
- [51] D. J. Morrow, D. D. Kohler, and J. C. Wright, Phys. Rev. A 96, 063835 (2017).
- [52] N. Bloembergen and P. S. Pershan, Phys. Rev. 128, 606 (1962).

- [53] A. Taghizadeh and T. G. Pedersen, Phys. Rev. B 99, 235433 (2019).
- [54] A. Taghizadeh and T. G. Pedersen, Phys. Rev. B 97, 205432 (2018).
- [55] A. Taghizadeh, F. Hipolito, and T. G. Pedersen, Phys. Rev. B 96, 195413 (2017).
- [56] T. G. Pedersen, Phys. Rev. B 92, 235432 (2015).
- [57] D. B. S. Soh, C. Rogers, D. J. Gray, E. Chatterjee, and H. Mabuchi, Phys. Rev. B 97, 165111 (2018).
- [58] R. W. Boyd, Nonlinear Optics, 3rd ed. (Academic Press, 2008).
- [59] N. Bloembergen and Y. R. Shen, Phys. Rev. 133, A37 (1964).
- [60] L. A. Falkovsky, J. Phys. Conf. Ser. **129**, 012004 (2008).
- [61] E. J. Sie, A. J. Frenzel, Y.-H. Lee, J. Kong, and N. Gedik, Phys. Rev. B 92, 125417 (2015).
- [62] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, Nano Lett. 10, 1271 (2010).
- [63] A crucial filter for our TSF probe experiments is a 1000 nm longpass filter (ThorLabs FGL1000M) which ensures no visible light from secondary OPA processes reach the sample. Notably, double side polished silicon was not a suitable filter because it created non-negligible THG as well as lossy transmission.
- [64] K. Furuta, M. Fuyuki, and A. Wada, Appl. Spectrosc. 66, 1475 (2012).
- [65] J. D. Handali, K. F. Sunden, E. M. Kaufman, and J. C. Wright, Chemical Physics 512, 13 (2018).
- [66] D. J. Morrow, Open Science Framework (2019), 10.17605/OSF.IO/UMSXC.
- [67] B. J. Thompson, K. F. Sunden, D. J. Morrow, and N. A. Neff-Mallon, "PyCMDS," (2018).
- [68] B. Thompson, K. Sunden, D. Morrow, D. Kohler, and J. Wright, J. Open Source Softw. 4, 1141 (2019).
- [69] E. Jones, T. Oliphant, and P. Peterson, "SciPy: Open source scientific tools for Python," (2001), [Online; accessed 2017-09-28].
- [70] S. van der Walt, S. C. Colbert, and G. Varoquaux, Comput. Sci. Eng. 13, 22 (2011).
- [71] J. D. Hunter, Comput. Sci. Eng. 9, 90 (2007).
- [72] Y. Zhao and S. Jin, "Controllable water vapor assisted chemical vapor transport synthesis of WS2-MoS2 heterostructure," (2019), arXiv:1909.01390.
- [73] C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone, and S. Ryu, ACS Nano 4, 2695 (2010).
- [74] H. Li, Q. Zhang, C. C. R. Yap, B. K. Tay, T. H. T. Edwin, A. Olivier, and D. Baillargeat, Advanced Functional Materials 22, 1385 (2012).
- [75] A. Berkdemir, H. R. Gutiérrez, A. R. Botello-Méndez, N. Perea-López, A. L. Elías, C.-I. Chia, B. Wang, V. H. Crespi, F. López-Urías, J.-C. Charlier, H. Terrones, and M. Terrones, Sci. Rep. 3, 1755 (2013).
- [76] M. J. Shearer, L. Samad, Y. Zhang, Y. Zhao, A. Puretzky, K. W. Eliceiri, J. C. Wright, R. J. Hamers, and S. Jin, J. Am. Chem. Soc. **139**, 3496 (2017).
- [77] X. Fan, Y. Zhao, W. Zheng, H. Li, X. Wu, X. Hu, X. Zhang, X. Zhu, Q. Zhang, X. Wang, B. Yang, J. Chen, S. Jin, and A. Pan, Nano Lett. 18, 3885 (2018).
- [78] X. Fan, Y. Jiang, X. Zhuang, H. Liu, T. Xu, W. Zheng, P. Fan, H. Li, X. Wu, X. Zhu, Q. Zhang, H. Zhou, W. Hu, X. Wang, L. Sun, X. Duan, and A. Pan, ACS Nano **11**, 4892 (2017).
- [79] L. Zhang, K. Liu, A. B. Wong, J. Kim, X. Hong, C. Liu,

T. Cao, S. G. Louie, F. Wang, and P. Yang, Nano Lett. 14, 6418 (2014).

- [80] H. Zhang, Y. Wan, Y. Ma, W. Wang, Y. Wang, and L. Dai, Appl. Phys. Lett. 107, 101904 (2015).
- [81] M. M. Benameur, B. Radisavljevic, J. S. Héron, S. Sahoo, H. Berger, and A. Kis, Nanotechnology 22, 125706 (2011).
- [82] P. Blake, E. W. Hill, A. H. Castro Neto, K. S. Novoselov, D. Jiang, R. Yang, T. J. Booth, and A. K. Geim, Appl. Phys. Lett. **91**, 063124 (2007).
- [83] R. Wang, H.-C. Chien, J. Kumar, N. Kumar, H.-Y. Chiu, and H. Zhao, ACS Appl. Mater. Interfaces 6, 314 (2013).
- [84] E. A. A. Pogna, M. Marsili, D. D. Fazio, S. D. Conte, C. Manzoni, D. Sangalli, D. Yoon, A. Lombardo, A. C. Ferrari, A. Marini, G. Cerullo, and D. Prezzi, ACS Nano 10, 1182 (2016).
- [85] A. Chernikov, C. Ruppert, H. M. Hill, A. F. Rigosi, and T. F. Heinz, Nat. Photonics 9, 466 (2015).
- [86] A. Steinhoff, M. Rösner, F. Jahnke, T. O. Wehling, and C. Gies, Nano Lett. 14, 3743 (2014).
- [87] L. Meckbach, T. Stroucken, and S. W. Koch, Appl. Phys. Lett. **112**, 061104 (2018).
- [88] S. Sim, J. Park, J.-G. Song, C. In, Y.-S. Lee, H. Kim, and H. Choi, Phys. Rev. B 88, 075434 (2013).
- [89] P. D. Cunningham, A. T. Hanbicki, K. M. McCreary, and B. T. Jonker, ACS Nano 11, 12601 (2017).
- [90] Because these lineshapes are not merely caused by amplitude changes $(J \text{ or } \mu)$, fitting different probe colors results in different decay rates, with τ up to 0.4 ps.
- [91] P. D. Cunningham, K. M. McCreary, A. T. Hanbicki, M. Currie, B. T. Jonker, and L. M. Hayden, J. Phys. Chem. C 120, 5819 (2016).
- [92] H. Shi, R. Yan, S. Bertolazzi, J. Brivio, B. Gao, A. Kis, D. Jena, H. G. Xing, and L. Huang, ACS Nano 7, 1072 (2013).
- [93] P. Schiettecatte, P. Geiregat, and Z. Hens, J. Phys. Chem. C 123, 10571 (2019).
- [94] D. Tsokkou, X. Yu, K. Sivula, and N. Banerji, J. Phys. Chem. C 120, 23286 (2016).
- [95] Z. Nie, R. Long, L. Sun, C.-C. Huang, J. Zhang, Q. Xiong, D. W. Hewak, Z. Shen, O. V. Prezhdo, and Z.-H. Loh, ACS Nano 8, 10931 (2014).
- [96] N. Kumar, J. He, D. He, Y. Wang, and H. Zhao, J. Appl. Phys. **113**, 133702 (2013).
- [97] Z. Nie, R. Long, J. S. Teguh, C.-C. Huang, D. W. Hewak, E. K. L. Yeow, Z. Shen, O. V. Prezhdo, and Z.-H. Loh, J. Phys. Chem. C 119, 20698 (2015).
- [98] F. Ceballos, Q. Cui, M. Z. Bellus, and H. Zhao, Nanoscale 8, 11681 (2016).
- [99] A. Singh, G. Moody, S. Wu, Y. Wu, N. J. Ghimire, J. Yan, D. G. Mandrus, X. Xu, and X. Li, Phys. Rev. Lett. **112**, 216804 (2014).
- [100] G. Moody, C. K. Dass, K. Hao, C.-H. Chen, L.-J. Li, A. Singh, K. Tran, G. Clark, X. Xu, G. Berghäuser, E. Malic, A. Knorr, and X. Li, Nat. Commun. 6, 8315 (2015).
- [101] A. Singh, G. Moody, K. Tran, M. E. Scott, V. Overbeck, G. Berghäuser, J. Schaibley, E. J. Seifert, D. Pleskot, N. M. Gabor, J. Yan, D. G. Mandrus, M. Richter, E. Malic, X. Xu, and X. Li, Phys. Rev. B 93, 041401 (2016).
- [102] K. Hao, G. Moody, F. Wu, C. K. Dass, L. Xu, C.-H. Chen, L. Sun, M.-Y. Li, L.-J. Li, A. H. MacDonald,

and X. Li, Nat. Phys. 12, 677 (2016).

- [103] K. Hao, L. Xu, P. Nagler, A. Singh, K. Tran, C. K. Dass, C. Schüller, T. Korn, X. Li, and G. Moody, Nano Lett. 16, 5109 (2016).
- [104] K. Hao, J. F. Specht, P. Nagler, L. Xu, K. Tran, A. Singh, C. K. Dass, C. Schüller, T. Korn, M. Richter, A. Knorr, X. Li, and G. Moody, Nat. Commun. 8, 15552 (2017).
- [105] L. Guo, M. Wu, T. Cao, D. M. Monahan, Y.-H. Lee, S. G. Louie, and G. R. Fleming, Nat. Phys. 15, 228 (2018).
- [106] The decrease in $\Delta I/I$ at high pump frequencies in the TR experiment Figure 8a is likely caused by a decrease in the I_{pump} at those frequencies. The two spectra in Figure 8 were collected at different times and do not share the same pump intensity spectrum.
- [107] F. Mahmood, Z. Alpichshev, Y.-H. Lee, J. Kong, and N. Gedik, Nano Lett. 18, 223 (2017).
- [108] L. Yang, N. A. Sinitsyn, W. Chen, J. Yuan, J. Zhang, J. Lou, and S. A. Crooker, Nat. Phys. 11, 830 (2015).
- [109] G. Moody, J. Schaibley, and X. Xu, J. Opt. Soc. Am. B 33, C39 (2016).
- [110] S. Schmitt-Rink, D. S. Chemla, and D. A. B. Miller, Phys. Rev. B 32, 6601 (1985).
- [111] P. W. Juodawlkis and S. E. Ralph, Appl. Phys. Lett. 76, 1722 (2000).
- [112] G. Mak and H. M. van Driel, Phys. Rev. B 49, 16817 (1994).
- [113] J. Liu, J. Leng, S. Wang, J. Zhang, and S. Jin, J. Phys. Chem. Lett. 10, 97 (2019).
- [114] T. Ghosh, S. Aharon, A. Shpatz, L. Etgar, and S. Ruhman, ACS Nano 12, 5719 (2018).
- [115] H. Anders, Thin Films in Optics (The Focal Press, 1967).
- [116] S. Bikorimana, P. Lama, A. Walser, R. Dorsinville,

S. Anghel, A. Mitioglu, A. Micu, and L. Kulyuk, Opt. Express **24**, 20685 (2016).

- [117] S. Zhang, N. Dong, N. McEvoy, M. O'Brien, S. Winters, N. C. Berner, C. Yim, Y. Li, X. Zhang, Z. Chen, L. Zhang, G. S. Duesberg, and J. Wang, ACS Nano 9, 7142 (2015).
- [118] Z. Ye, T. Cao, K. O'Brien, H. Zhu, X. Yin, Y. Wang, S. G. Louie, and X. Zhang, Nature 513, 214 (2014).
- [119] T. C. Berkelbach, M. S. Hybertsen, and D. R. Reichman, Phys. Rev. B 92, 085413 (2015).
- [120] N. Dong, Y. Li, S. Zhang, N. McEvoy, R. Gatensby, G. S. Duesberg, and J. Wang, ACS Photonics 5, 1558 (2018).
- [121] Q. Cui, Y. Li, J. Chang, H. Zhao, and C. Xu, Laser Photonics Rev. 13, 1800225 (2018).
- [122] T. Völzer, M. Lütgens, F. Fennel, and S. Lochbrunner, J. Phys. B 50, 194003 (2017).
- [123] A. M. van der Zande, P. Y. Huang, D. A. Chenet, T. C. Berkelbach, Y. You, G.-H. Lee, T. F. Heinz, D. R. Reichman, D. A. Muller, and J. C. Hone, Nat. Mater. 12, 554 (2013).
- [124] W. Zhou, X. Zou, S. Najmaei, Z. Liu, Y. Shi, J. Kong, J. Lou, P. M. Ajayan, B. I. Yakobson, and J.-C. Idrobo, Nano Lett. **13**, 2615 (2013).
- [125] Z. G. Yu, Y.-W. Zhang, and B. I. Yakobson, Nano Lett. 15, 6855 (2015).
- [126] J. Hong, Z. Hu, M. Probert, K. Li, D. Lv, X. Yang, L. Gu, N. Mao, Q. Feng, L. Xie, J. Zhang, D. Wu, Z. Zhang, C. Jin, W. Ji, X. Zhang, J. Yuan, and Z. Zhang, Nat. Commun. 6, 6293 (2015).
- [127] H. Qiu, T. Xu, Z. Wang, W. Ren, H. Nan, Z. Ni, Q. Chen, S. Yuan, F. Miao, F. Song, G. Long, Y. Shi, L. Sun, J. Wang, and X. Wang, Nat. Commun. 4, 2642 (2013).
- [128] C.-P. Lu, G. Li, J. Mao, L.-M. Wang, and E. Y. Andrei, Nano Lett. 14, 4628 (2014).