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Biexcitons do not Form in MoS₂ Monolayers from Optical Pumping at 6 K

Ryan E. Wood^{1,2,3*}, Lawson T. Lloyd^{1,2,3*}, Fauzia Mujid¹, Lili Wang^{1,2,3+}, Marco A. Allodi^{1,2,3}, Hui Gao^{1,2,4,5}, Richard Mazuski^{1,2,3}, Po-Chieh Ting^{1,2,3}, Saïen Xie^{1,2,6}, Jiwoong Park^{1,2,4} and Gregory S. Engel^{1,2,3**}

¹ Department of Chemistry, University of Chicago, Chicago, IL, 60637, USA

² James Franck Institute, University of Chicago, Chicago, IL, 60637, USA

³ Institute for Biophysical Dynamics, Chicago, IL, 60637, USA

⁴ Pritzker School of Molecular Engineering, Chicago, IL, 60637, USA

⁵ Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY, 14853, USA

⁶ Kavli Institute at Cornell for Nanoscale Science, Cornell University, Ithaca, NY 14853, USA

⁺ Present Address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA

* These authors contributed equally to this work

** Corresponding Author; e-mail gsengel@uchicago.edu

ABSTRACT:

Transition metal dichalcogenides (TMDs) have attracted much interest in recent years due to their emerging material properties. In monolayer TMDs, such as MoS₂, extreme quantum confinement is achieved in the monolayer limit. Although monolayer TMDs represent an ideal platform to explore excitonic physics using ultrafast spectroscopy, this exploration is currently limited by confusion regarding the origin of certain spectral features, including the below-bandgap PIA feature observed in pump-probe experiments. In this work, we document an absence of PIA features immediately after photoexcitation, indicating a lack of strong optically-induced biexciton formation. Below-bandgap PIA features are observed to grow in with a time constant of 110 ± 10 fs, indicative of other factors responsible for their origin. These results indicate that optically-induced biexciton formation is most likely not responsible for the previously observed PIA features in MoS₂ monolayers.

INTRODUCTION:

Transition Metal Dichalcogenides (TMDs) realize distinct optoelectronic properties from their bulk counterparts in the monolayer limit.^{1,2} While reminiscent of graphene in this regard, semiconducting TMDs are markedly different from graphene in that they are semiconductors which undergo a transition from indirect to direct bandgap in the monolayer limit, due to the extreme quantum confinement achieved.^{1,3} Based on their semiconducting nature and small size, TMDs are a natural choice for the next generation of miniature optoelectronic devices.⁴ TMDs have been used as the active element in optoelectronic devices including light emitting diodes,^{5,6} photodetectors,⁷⁻⁹ transistors¹⁰⁻¹² and solar cells.¹³ Quasiparticle formation is highly favored in TMDs, mainly because of reduced screening in the monolayer limit.^{14,15} Additionally, in the monolayer limit, inversion symmetry is broken, resulting in the formation of non-equivalent valleys at K and K' in the band structure.^{16,17} These non-equivalent valleys have given rise to a new field of "valleytronics", exploiting the new valley degree of freedom for device applications.¹⁸ Many studies have also reported the formation of higher-lying quasiparticle complexes in TMDs including biexcitons, enabled by this reduced screening.¹⁹⁻²³ However, the role of these higher-lying quasiparticles in relation to the role of more conventional dynamics and effects is not yet known.

Ultrafast spectroscopy uses femtosecond laser pulses separated by time delays to interrogate dynamics in the system of interest.²⁴ Most notably, pump-probe spectroscopy has been used to study many aspects of dynamics in TMDs, including bandgap renormalization^{25,26}, intervalley biexciton formation,²⁰ and exciton-exciton annihilation.^{27,28} Pump-probe experiments often encounter problems associated with overlapping spectral signals. One notable example of

controversy arising from potentially overlapping signals revolves around photoinduced absorption (PIA) features observed below the bandgap in TMDs. These features have been assigned to optically-induced biexciton formation^{20, 29} or to a mixture of carrier-induced bandgap renormalization and exciton binding energy change (BGR/EBE).^{25, 26} Optically-induced biexciton formation should require no delay between excitations, thus a technique with sub-100fs time resolution that preserves excitation frequency information should be able to determine if these PIA features originate from optically-induced biexciton formation.

RESULTS:

In this work, we use two-dimensional electronic spectroscopy (2DES) to probe the sub-100 fs dynamics of chemical vapor deposition (CVD)-grown MoS₂ monolayers at cryogenic temperature (6K). The all-reflective 2DES setup used provides 10 fs time resolution while retaining excitation frequency resolution. This time resolution allows us to directly observe signals immediately after photoexcitation, when other processes have yet to happen in the sample. We observe no PIA signals corresponding to biexciton formation at cryogenic temperature and fluences of 4×10^{12} excitons per cm². 2DES has been previously conducted on MoS₂ monolayers, documenting an exchange-driven mixing of the A and B excitonic states.³⁰ However, this study did not distinguish between positive and negative features in the 2DES spectra, and was thus unable to comment on the PIA signals observed in the pump-probe spectra. The phased 2DES spectra obtained using our all-reflective 2DES setup (described in detail previously)³¹ are capable of distinguishing positive ground state bleach (GSB) and stimulated emission (SE) signals from negative PIA features and as such can resolve the controversy around interpretation of the PIA features. To promote biexciton formation, cryogenic temperatures and higher sub-Mott fluences are chosen, consistent with reports of biexciton formation in the literature.^{20, 21, 23}

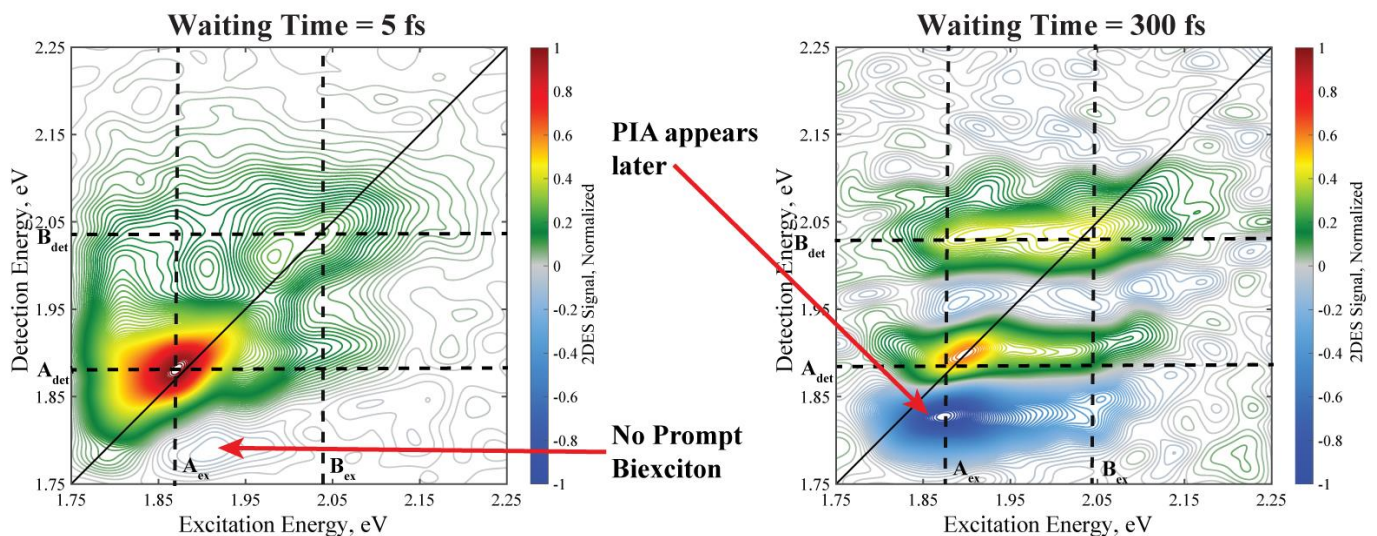


Figure 1. 2DES spectra of MoS₂ monolayers at 6K. At early waiting times (5 fs) negative PIA features are not visible over the positive features of the spectrum. At later waiting times (300 fs), strong PIA features are observed. Cross-peaks are also observed in the spectra, corresponding to excitonic coupling (above-diagonal) and excitonic coupling and energy transfer (below-diagonal).

Cryogenic 2DES data outlining the excitonic coupling and dynamics of MoS₂ monolayers are shown in Figure 1. We observe positive features, corresponding to the A and B excitons, along the diagonal at all waiting times. We also observe an above-diagonal cross-peak, corresponding to coupling between the A and B excitonic states, at all waiting times. The appearance of this cross peak has been documented previously, with a variety of proposed explanations.³² We do not observe strong signals of biexciton formation at early waiting times, as evidenced by the lack of PIA features corresponding to biexciton formation. We observe growth of the below-bandgap PIA feature at later waiting times, as shown in Figure 2. This time trace is obtained by taking the 2DES spectral intensity for all waiting times, then fitting to a double exponential. The double exponential fit yields a growth time constant for the PIA feature, as well as one which reports on the population of the excited state. We obtain a time constant of 110 ± 10 fs for growth of the PIA feature.

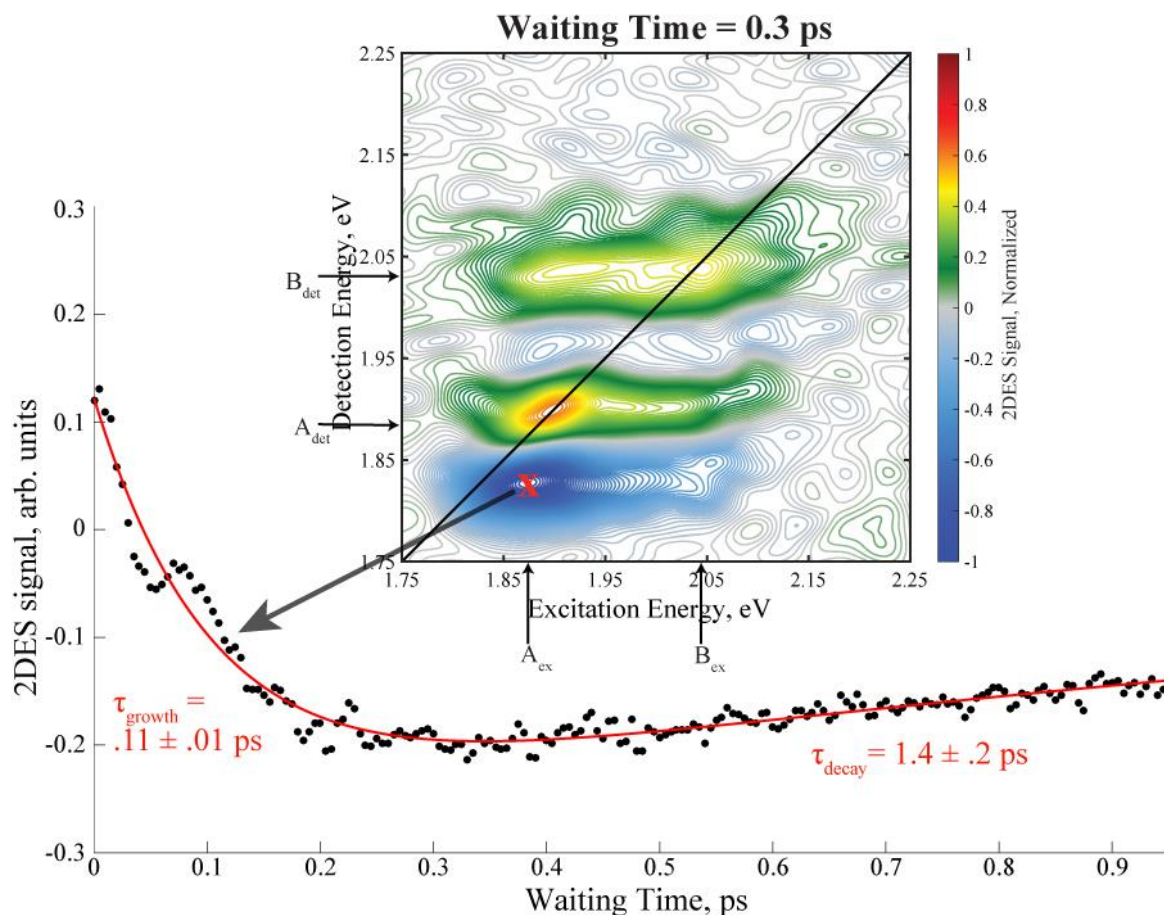


Figure 2. Time trace for the PIA feature observed below the band edge. This feature is observed to grow in as a function of waiting time, making biexciton formation most likely not responsible. The decay of this PIA feature occurs on the same timescale as the decay of the excited state.

DISCUSSION:

The data in this proceeding suggest that at the high-carrier sub-Mott limit, optically-induced biexciton formation is not present. We base this assignment on the absence of strong PIA features in the 2DES spectrum immediately after photoexcitation. It is possible that some PIA features from biexciton formation are indeed present, but they are not visible over the positive features of the spectrum. We are unable to electrically dope the sample during the 2DES experiment, which has been previously documented to promote biexciton formation.³³ It has also been previously documented that spontaneous biexciton formation is furthered by the presence of edge states in the sample.³⁴ Therefore, it is possible that the lack of edge states in this continuous wafer-scale CVD-grown sample make it unfavorable towards biexciton formation. However, while this sample lacks edge states, it does have grain boundaries on the 1 μm scale which are highly likely to serve as sites for spontaneous biexciton formation. The optically-induced biexciton formation observed in ultrafast spectroscopic experiments is distinct from the spontaneous biexciton formation observed in photoluminescence experiments. In the optically-induced biexciton formation process, the single exciton state is forced into the higher-lying biexciton state by excitation of another exciton in the opposite valley.³⁵ By contrast, in the spontaneous biexciton formation process, two excitons diffuse throughout the sample and encounter each other to form a biexciton. The findings of this manuscript regarding the optically-induced biexciton formation are thus distinct from the spontaneous biexciton formation process. We do not see any signatures of spontaneous biexciton formation in this sample in our 2DES experiments. We do see signals corresponding to second-order processes in this sample, which have been previously assigned to exciton-

exciton annihilation.²⁸ We note that the kinetics of these processes do indeed match the expected kinetics of spontaneous biexciton formation. We do not see any signatures of stimulated emission from a spontaneously formed biexciton in this experiment, although we would expect such a stimulated emission signal to appear in the same spectral location as the below-bandgap PIA feature observed at later waiting times.

CONCLUSION:

In this work, we have exploited the simultaneous time and excitation energy resolution of 2DES to demonstrate a lack of optically-induced biexciton formation in the high-carrier sub-Mott limit at cryogenic temperatures in MoS₂ monolayers. 2DES allows us to make this assignment based on the lack of PIA features observed in the spectrum at $T = 5$ fs. We document that the previously observed PIA features grow in with a 110 ± 10 fs time constant at 6 K. These PIA features could correspond to Bandgap renormalization and Exciton Binding Energy change, similar to previous reports in the literature.^{25, 26} PIA signals from BGR/EBE change should reflect a delay from initial excitation as the BGR/EBE change process requires time for the carriers to be thermalized and fill the bands,³⁶ thus making BGR/EBE change a plausible explanation for the observed PIA features.

METHODS:

Ultrafast Spectroscopic Methods:

A 5kHz Ti:sapphire regenerative amplifier seeded by an 80MHz mode-locked Ti:sapphire oscillator (Coherent Inc., Legend Elite USP) produced 38 fs pulses centered at 800 nm. Continuum white light spanning ~500 to 900 nm was generated via self-phase modulation in a 2 m tube of Ar gas at 16 psi. Light red of 700 nm was rejected with a dielectric short pass filter. A pulse shaper (MIIPS, Biophotonics Inc.) compressed the pulses to a time-bandwidth limited product of 9 fs. The 2DES experiments were performed in an all-reflective setup described previously.³¹ In the 2DES interferometer, the initial beam is split into four pulses aligned in the BOXCARS geometry and focused to a ~120 μm spot on the sample, with the fourth beam attenuated by $\sim 10^5$ and used as a local oscillator for heterodyne detection. The waiting time (T) and coherence time (τ) delays are controlled by motorized delay stages (Aerotech Inc.). The third-order signal and local oscillator co-propagate into a spectrograph and are spectrally resolved onto a CCD array camera (Andor Inc). A custom exchange-gas helium flow cryostat (RC-151, Cryo Industries of America) is used to cool and maintain the sample at 6 K. The 2DES spectra are phased to separately acquired pump-probe measurements using the same broadband pulses to determine the absolute phase and produce fully absorptive spectra.

Sample growth and characterization:

The MoS₂ monolayers used in this study were grown on fused SiO₂ substrates using a metal-organic CVD methodology in a home-built hot-walled horizontal tube furnace. The method used for this growth has been described in detail previously.¹⁰ Characterization was conducted via scanning electron microscopy (SEM), Raman microscopy, photoluminescence, and UV-visible spectroscopy. SEM characterization was carried out using a commercially-available scanning electron microscope (Merlin, Zeiss Inc.) using a secondary-electron imaging technique. Accelerating voltages were maintained between 1-3 kV. Raman and PL spectra were collected in the reflected geometry using 532 nm laser excitation on a confocal microscope (LabRamHR, Horiba Inc.). Absorption spectra were collected in the transmission geometry in a UV-visible spectrophotometer (Cary, Agilent Inc.).

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