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# Electron dynamics in transition metal dichalcogenides utilizing attosecond transient absorption spectroscopy

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**Abstract:** Strong enhancement of exciton binding has been observed in valence-excitons in the optical regime of 2D materials. We report direct observation of long-lived core-exciton states in transition metal dichalcogenides by attosecond transient absorption spectroscopy in the XUV. © 2018 The Author(s)  
**OCIS codes:** (320.7150) Ultrafast spectroscopy; (160.6000) Semiconductor materials; (320.7120) Ultrafast phenomena.

## 1. Introduction

Two-dimensional transition metal dichalcogenides (TMDCs) exhibit a wide variety of novel electronic properties. Specifically, the electronic structure of TMDCs can change drastically when the thickness of the material is thinned to single or few layers [1]. For example, bulk molybdenum disulfide (MoS<sub>2</sub>) is an indirect gap semiconductor. However, as the thickness decreases, optical exciton features are substantially enhanced due to the diminished screening and when the thickness is reduced to one monolayer, the material becomes a direct gap semiconductor with a strong exciton transition at approximately 1.8 eV [2].

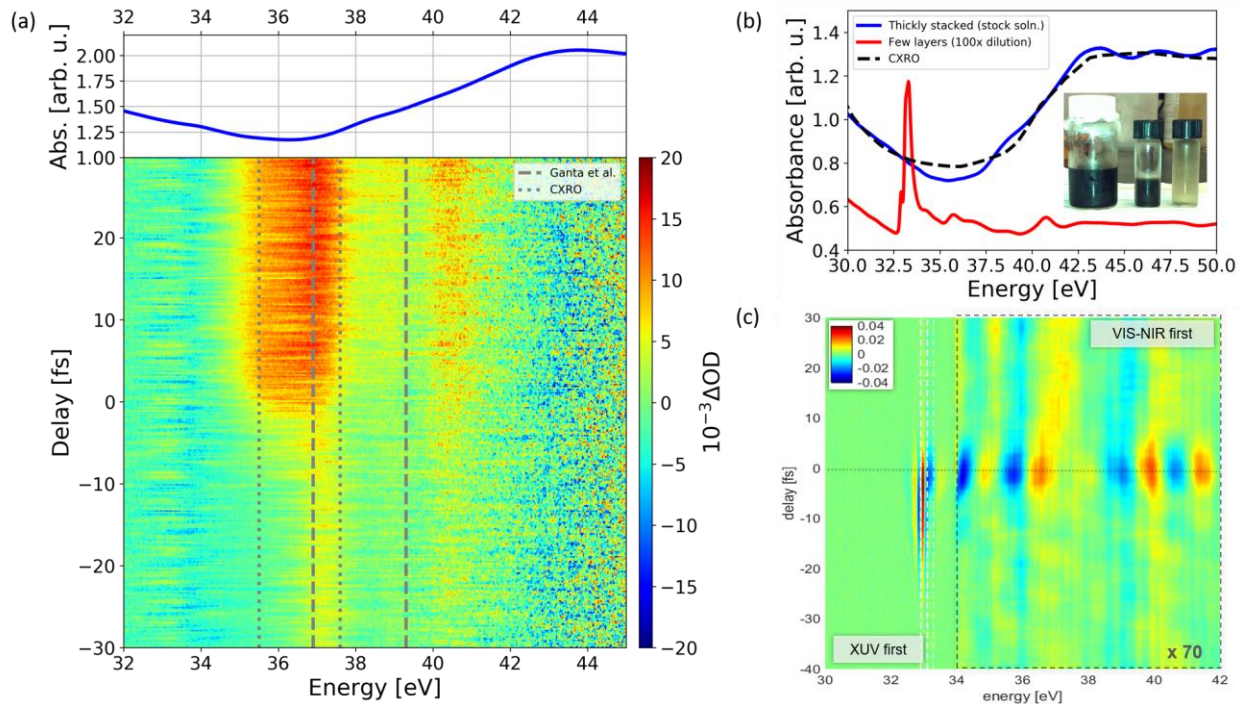
The dimensionality of TMDCs plays an important role in the valence electronic structure, as the screening of electrons changes drastically when the material is thinned from a three-dimensional bulk down to a two-dimensional monolayer [3]. This leads to strong enhancement in excitonic transitions that can be studied element specific in the extreme ultraviolet photon range (XUV) as well as time-resolved with attosecond pulses produced by high-harmonic generation. The study of specific exciton states (e.g. dark [4], core [5]) has attracted much interest in the past years and became experimentally possible very recently [6]. While valence excitons are rather well-studied the study of strongly bound core excitons extends the investigations from valence states to the core levels. TMDCs open access to those unique electronic states when being investigated with ultrafast attosecond transient absorption spectroscopy.

## 2. Experiment

Attosecond transient absorption (ATA) measurements were carried out in the extreme ultraviolet (XUV) on two-dimensional TMDCs such as molybdenum-disulfide (MoS<sub>2</sub>). Thin films of MoS<sub>2</sub> (on a transparent Si<sub>3</sub>N<sub>4</sub> membrane) are pumped by few-cycle VIS-NIR pulses (~4 fs) and probed by attosecond XUV pulses generated by means of high harmonic generation in argon (Ar). The change in absorbance (optical density) is measured as a function of the temporal delay of the few-cycle VIS-NIR and attosecond XUV pulses. In typical semiconductors the (pumping) few-cycle VIS-NIR excites electrons from the valence to the conduction band where the density of empty electronic states is probed by a broadband attosecond XUV pulse by means of a time-resolved variant of x-ray absorption near-edge structure spectroscopy (XANES) [7]. The underlying dynamics can be observed in the data in the positive delay region (Figure 1a), which is defined as the VIS-NIR pulse arriving first. Minimizing the contributing layers (reducing the thickness) usually minimizes the detected signal, since fewer states contribute to the measurement. In contrast reducing the bulk MoS<sub>2</sub> system to mono/few-layers shows a strongly modified static absorption spectrum (Figure 1b) as well as a very dominant change in optical density region (dynamics) in the negative delay region, which is related to the XUV pulse arriving first (Figure 1c). There the polarization by the (pumping) XUV is manipulated by the perturbing (probing) VIS-NIR to reveal the core-excitons and their lifetimes.

Probing at the Mo N<sub>2,3</sub> edge between 30 and 40 eV, an approximately 4 eV red shift of the edge is observed along with a drastic narrowing and enhancement of the new absorption peaks in mono/few layer MoS<sub>2</sub> compared to bulk samples. This is, to the best of our knowledge, the first observation of strongly enhanced core-excitons due to a

dimensionality change. Few-layer MoS<sub>2</sub> data reveal exceptionally long lifetimes between 3 to 5 fs for the core-excited states compared to most bulk solids, which typically exhibit core excitation lifetimes below 1 fs [6]. The observed very strong binding of approximately 4 eV is also in stark contrast to previous experiments on solids [8].



**Fig. 1.** (a) Transient absorption spectrum of bulk MoS<sub>2</sub> indicating carrier excitation from the valence band to the conduction band. (b) Static absorption spectrum of a bulk system in comparison to a mono/few layer system (the small inset depicts the solutions being used for drop-casting sample preparation). (c) Transient absorption spectrum of mono/few layer MoS<sub>2</sub> revealing strong XUV-excited features related to core-excited states.

### 3. Conclusion

The lifetime of the core-exciton states in few-layer (2D)-dichalcogenides was measured by attosecond transient absorption spectroscopy in conjunction with ab initio calculations. Furthermore, we observe transient Stark shifts, coherences, and population transfer between different core-exciton states. With the observation of strongly enhanced core-excited states in two-dimensional semiconductors, this work paves the way for further exploration into the properties and dynamics of core-excited states in two-dimensional materials.

### 4. References

- [1] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, "Electronics and optoelectronics of two-dimensional transition metal dichalcogenides," *Nature Nanotechnology* **7**, 699–712 (2012).
- [2] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, "Atomically Thin MoS<sub>2</sub>: A New Direct-Gap Semiconductor," *Physical Review Letters* **105**, 136805 (2010).
- [3] Diana Y. Qiu, Felipe H. da Jornada, and Steven G. Louie, "Screening and many-body effects in two-dimensional crystals: Monolayer MoS<sub>2</sub>," *Physical Review B* **93**, 235435 (2016).
- [4] X.-X. Zhang, T. Cao, Z. Lu, Y.-C. Lin, F. Zhang, Y. Wang, Z. Li, J. C. Hone, J. A. Robinson, D. Smirnov, S. G. Louie, and T. F. Heinz, "Magnetic brightening and control of dark excitons in monolayer WSe<sub>2</sub>," *Nature Nanotechnology* **12**, 883–888 (2017).
- [5] H. P. Hjalmarson, H. Büttner, and J. D. Dow, "Theory of core excitons," *Physical Review B* **24**, 6010 (1981).
- [6] A. Moulet, J. B. Bertrand, T. Klostermann, A. Guggenmos, N. Karpowicz, E. Goulielmakis, "Soft x-ray excitonics," *Science* **357**(6356), 1134–1138 (2017).
- [7] M. Schultze, K. Ramasesha, C. D. Pemmaraju, S.A. Sato, D. Whitmore, A. Gandman, J. S. Prell, L. J. Borja, D. Prendergast, K. Yabana, D. M. Neumark, S. R. Leone, "Attosecond band-gap dynamics in silicon," *Science* **346**(6215), 1348–1352 (2014).
- [8] J. F. Morar, F. J. Himpsel, G. Hollinger, G. Hughes, and J. L. Jordan, "Observation of a C-1s Core Exciton in Diamond," *Physical Review Letters* **54**(17), 1960–1963 (1985).