

Time-resolved ARPES Determination of a Quasi-Particle Band Gap and Hot Electron Dynamics in Monolayer MoS₂

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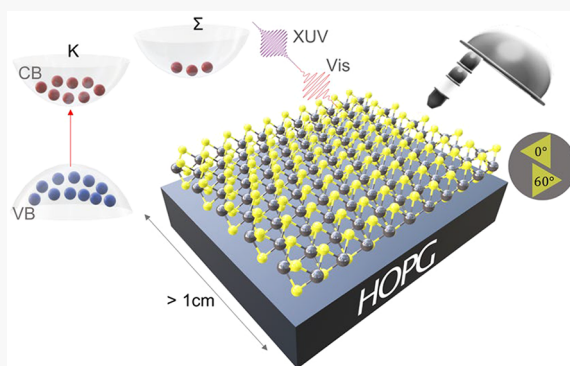
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Supporting Information

ABSTRACT: The electronic structure and dynamics of 2D transition metal dichalcogenide (TMD) monolayers provide important underpinnings both for understanding the many-body physics of electronic quasi-particles and for applications in advanced optoelectronic devices. However, extensive experimental investigations of semiconducting monolayer TMDs have yielded inconsistent results for a key parameter, the quasi-particle band gap (QBG), even for measurements carried out on the same layer and substrate combination. Here, we employ sensitive time- and angle-resolved photoelectron spectroscopy (trARPES) for a high-quality large-area MoS₂ monolayer to capture its momentum-resolved equilibrium and excited-state electronic structure in the weak-excitation limit. For monolayer MoS₂ on graphite, we obtain QBG values of ≈ 2.10 eV at 80 K and of ≈ 2.03 eV at 300 K, results well-corroborated by the scanning tunneling spectroscopy (STS) measurements on the same material.

KEYWORDS: Transition metal dichalcogenide (TMD), MoS₂, monolayer, XUV-trARPES, electronic structure, exciton



The emergence of monolayer (ML) transition metal dichalcogenides (TMDs) has opened up new frontiers for materials science and novel devices.^{1–7} As a consequence of the extreme two-dimensional (2D) geometry, Coulomb or dielectric screening is significantly reduced, which results in remarkably large exciton binding energies as well as important implications for the formation of exotic quantum states. Reduced Coulomb or dielectric screening also impacts the quasi-particle electronic structure, including the quasi-particle band gap (QBG), which is also referred to as the quasi-particle renormalization effect. Accurate knowledge of the quasi-particle electronic structure is critical for designing novel electronic and photonic devices. Moreover, any error incurred in the QBG determination directly translates into an error in the determination of the exciton binding energy, another key parameter in designing photonic systems to realize novel quantum phenomena such as exciton condensates. The quasi-particle renormalization effect, on the one hand, adds to diverse toolsets to tailor electronic structures of TMDs.^{8–20} On the other hand, however, it presents challenges to achieving an accurate determination of the QBG of TMDs since the QBG determined on one sample structure cannot be directly translated to another sample structure.

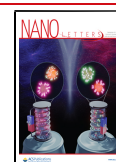
Previous extensive efforts to determine the QBG have not yielded consistent results. For example, in the case of monolayer WS₂ on SiO₂, substantial differences in the QBG

were reported^{21,22} when derived from optical luminescence and absorption spectroscopy. Moreover, in the case of MoS₂ on SiO₂, optical studies based on the excitonic Rydberg series²³ yielded a smaller QBG than the value acquired from gate-tuned photoluminescence excitation (PLE) spectra.¹⁸ It is unclear whether such a discrepancy reflects the difference in the measurements themselves which incur effects that are not yet accurately accounted for or it is simply due to the sample variability. Regardless, neither techniques probe quasi-particle band structures directly. In principle, scanning tunneling microscopy (STM) can probe the QBG directly. In this case, however, the literature shows a QBG value ranging from 1.9 to 2.4 eV, even for monolayer MoS₂ on graphite (the same sample structure).^{8,24–30} As analyzed by Zhang et al.,³¹ the tunneling decay constants for different critical points (e.g., Γ vs K) in the TMD monolayer differ significantly, resulting in orders of magnitude difference in the tunneling probability. Thus, a conventional approach may not have enough sensitivity to accurately determine the band edge location.

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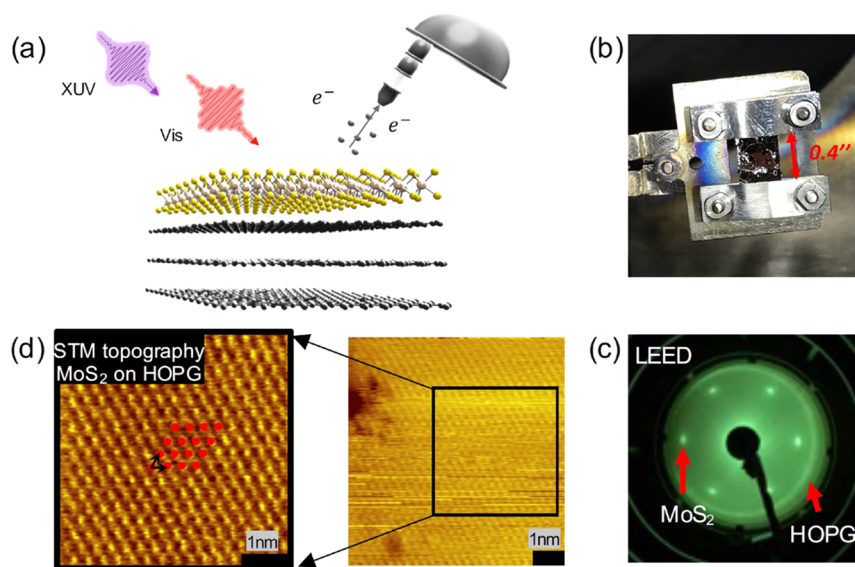


Figure 1. Large-scale oriented MoS₂ monolayers on HOPG and the transient probe scheme. (a) Illustration of the time-resolved ARPES of the photoexcited monolayer's electronic structure. (b) Sample mounted for photoemission with a ≈ 1 cm (0.4 in.) accessible lateral width. (c and d) LEED images (68 eV bias voltage) and STM topography, respectively, of the MoS₂ monolayer, confirming a high surface quality and crystalline orientation.

Although this difficulty can be overcome by employing a sophisticated variable-*z* tunneling spectroscopic approach,³¹ it has not been widely adopted. Moreover, it is not a direct *k*-space measurement, and the band edge location is inferred only indirectly from the behaviors of different thresholds. In this regard, time-resolved angle-resolved photoelectron spectroscopy (trARPES) would be an ideal tool since it can reveal the *k*-resolved electronic states in both the valence and conduction bands. We emphasize, however, that there are several caveats. In the trARPES measurements of excited states, one needs to disentangle quasi-particle electrons from other forms of many-body states such as excitons. Moreover, one needs to separate the additional renormalization effect due to photoexcited carriers other than the substrate.

To implement the trARPES measurement of quasi-particle band structures for monolayer TMDs, there are several technical challenges. First, to resolve the equilibrium and excited states at the K-valley, extreme-UV (XUV) photons are necessary for photoemission, precluding the use of the more common trARPES approaches using a 6 eV probe. Second, high-quality trARPES requires large-area ML samples that are laterally homogeneous with an atomically clean surface and well-defined in-plane crystallographic orientation. Finally, strong excitation can lead to strong energy renormalization, which would preclude a reliable QBG determination. Due to these challenges, only a few studies of ML-TMDs using XUV trARPES have been reported.^{32–37} In the previous investigations, ML-TMD samples were either prepared by physical vapor deposition (PVD) or chemical vapor deposition (CVD) on graphene or metallic substrates,^{32–34,37} or as large-area exfoliated MLs derived from single crystals.^{35,36} While this enabled important insights into electronic dynamics, the sensitivity or resolution has so far been insufficient to enable a precise determination of the QBG. We note that the recent use of micro-trARPES with an ultrahigh repetition rate has achieved successful characterizations of exciton dynamics with a high sensitivity on mechanically exfoliated monolayer WSe₂.³⁸

In this work, by utilizing a wafer-scale MoS₂ monolayer with a well-aligned in-plane orientation along with sensitive XUV-trARPES with high energy and momentum resolution, we resolve the quasi-particle equilibrium and excited electronic structures at different critical points. From such measurements, the QBG in monolayer MoS₂ on graphite is unambiguously determined. Interestingly, the QBG is well corroborated by scanning tunneling spectroscopy (STS) measurements on the same sample structure.

Panels a and b in Figure 1 depict the sample structure and size of the wafer-scale well-aligned monolayer MoS₂ and the transient probe scheme, respectively. We first epitaxially grow a MoS₂ ML on a 2 in. diameter sapphire wafer using CVD. The “substrate guided growth” procedure is then utilized,^{39–41} providing significant improvements in terms of reducing the defect density and obtaining monolayers with a well-aligned orientation (cf. Figure S2). HOPG was chosen as a conductive support substrate to prevent the buildup of a surface photovoltage during photoemission^{35,38,42} and to eliminate tip-induced band bending during STM measurements.^{43–46} After removing the poly(methyl methacrylate) (PMMA) polymer used for the transfer, the sample was further annealed in ultrahigh-vacuum (UHV) to remove the PMMA residue. Additional details of the sample preparation are provided in Supporting Information Figure S3. We note that while large-area TMD MLs with a similar transfer method were previously used in static ARPES,^{47–49} orientational variations of the ML flakes in those studies resulted in an admixture of different momentum-space structures that complicated the band structure determination.

As shown in Figure 1c, low-energy electron diffraction (LEED) measurements of our sample reveal a well-defined pattern that confirms the high crystalline quality of the transferred MoS₂ monolayer, corresponding to a high orientational alignment of the domains and their twin pairs. The ring pattern is produced by the HOPG. The LEED pattern remained stable while the electron beam was scanned across the sample, indicating an aligned and clean surface over the

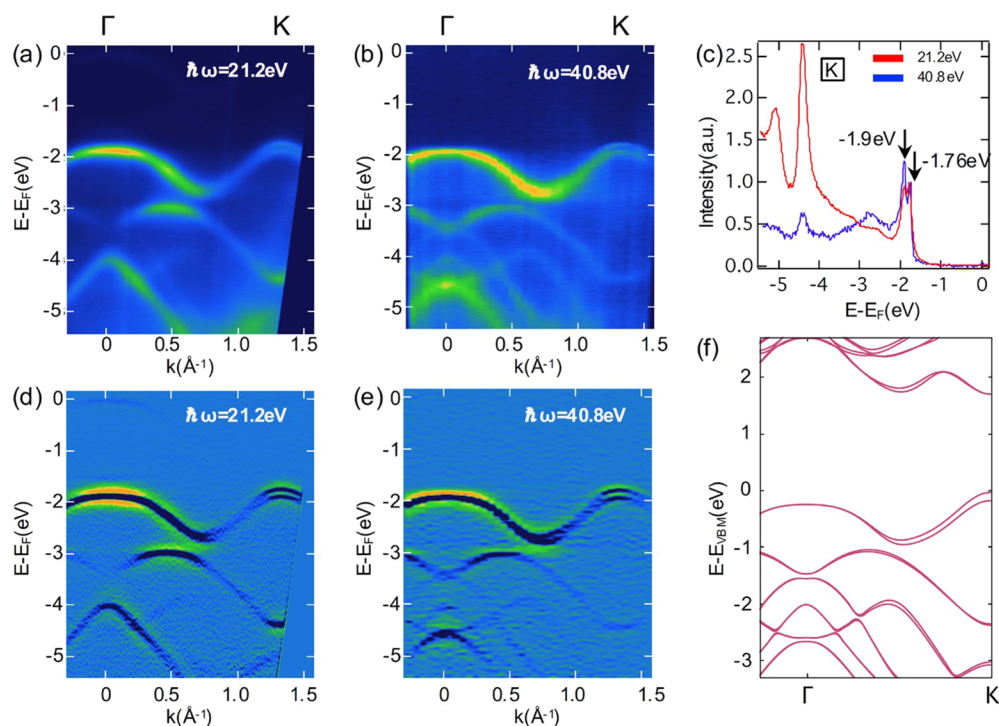


Figure 2. Static ARPES maps of ML MoS₂ on HOPG. Occupied band structure obtained with a He lamp source at (a) 21.2 and (b) 40.8 eV photon energies. (c) EDCs at the K-point integrated over $\pm 0.025 \text{ \AA}^{-1}$ for 21.2 eV (red) and 40.8 eV (blue) photon energy. The data indicates a spin–orbit splitting of $140 \pm 4 \text{ meV}$. (d and e) Second-derivative images corresponding to panels a and b, respectively, for better visualization of the dispersion. (f) Electronic band structure of a free-standing MoS₂ monolayer calculated via DFT using the Quantum ESPRESSO package.

whole sample area. STM images shown in Figure 1d were obtained at 77 K, revealing a lattice constant of $3.17 \pm 0.03 \text{ \AA}$ that is in agreement with the well-accepted value of $3.16 \text{ \AA}$. We note that while the cleaning procedure left minimal traces of residue on the surface, the amounts were too small to impact ARPES, trARPES, and STM/S investigations of the quasi-particle electronic structure.^{35,36,47–50}

Panels a and b of Figure 2 show ARPES maps of the momentum-space electronic structure in the valence band, which we probed via static ARPES using a He lamp excitation source with 21.2 and 40.8 eV photon energies, respectively. Corresponding K-point energy distribution curves (EDCs) are indicated in Figure 2c. Each photon energy offers distinct advantages and drawbacks; the 21.2 eV line is brighter but has different sensitivities for dissimilar bands, whereas the 40.8 eV line is about two orders of magnitude weaker yet yields a more uniform photoionization cross-section for all bands.⁵¹ Panels d and e of Figure 2 show the respective second-derivative images for improved contrast. The states near the valence band maximum (VBM) at Γ and K are resolved well, revealing a K-valley spin–orbit splitting of $140 \pm 4 \text{ meV}$ and the Γ valley located $\approx 130 \text{ meV}$ below the VBM. The deeper valence bands were better revealed with the 40.8 eV photons, resulting in a band structure that compares very well with that calculated via density functional theory (DFT). The latter is shown in Figure 2f for a free-standing single-layer MoS₂. Importantly, we also find that the atomically clean surface can be recovered through UHV annealing even after exposure to ambient air. This results in consistent ARPES spectra (see Figure S4) and enables straightforward transfer between experimental setups.

We investigated the excited-state electronic structure and dynamics of the MoS₂ monolayers using a high-repetition-rate XUV-trARPES setup,⁵² which provided direct access to the

electronic bandgap via excitation into otherwise unoccupied levels. In these experiments, the MoS₂ ML was excited above the gap with 2.2 eV pump pulses from a frequency-doubled optical parametric amplifier at a 25 kHz repetition rate with an absorbed fluence of $\approx 26 \text{ \mu J/cm}^2$. Subsequently, *p*-polarized XUV probe pulses at 22.3 eV were used for the photoemission. Figure 3a shows the transient band structure at 300 K measured at a pump–probe delay time of $\Delta t = 0.13 \text{ ps}$, evidencing the observation of both the valence band and the pump-excited states near the conduction band minimum (CBM).

Figure 3b shows plots of corresponding EDCs around the K-point for a later time delay of $\Delta t = 1.27 \text{ ps}$ when the carriers have relaxed toward the CBM for two different sample temperatures of 80 and 300 K. We noted that near $\Delta t = 0$ there is a rapid downshift of the K-point valence band edge by $\approx 0.1 \text{ eV}$ within about 200 fs (see Figure 4), with the conduction band edge shifting in the same direction. The energies then remain nearly steady on the longer picosecond time scale. Since both valence and conduction band states are concurrently affected, the shifts nearly cancel out, as shown in Figure 4c and d, and the determination of the quasi-particle bandgap is not significantly influenced by this effect. The origin of this downward shift and other many-body effects (including the excitonic effect) in the trARPES process are outside the scope of the current paper and will be presented elsewhere. Here we primarily focus on the determination of the QBG. The valence band spin–orbit splitting of $\approx 140 \text{ meV}$ at the K-point is well resolved at 80 K and broadened at 300 K. The CBM energy at the K-point decreases with temperature from 0.25 eV at 80 K to 0.18 eV at 300 K while, within the energy resolution, the K-point VBM remains steady at -1.85 eV . The energy differences between the VBM and the transiently

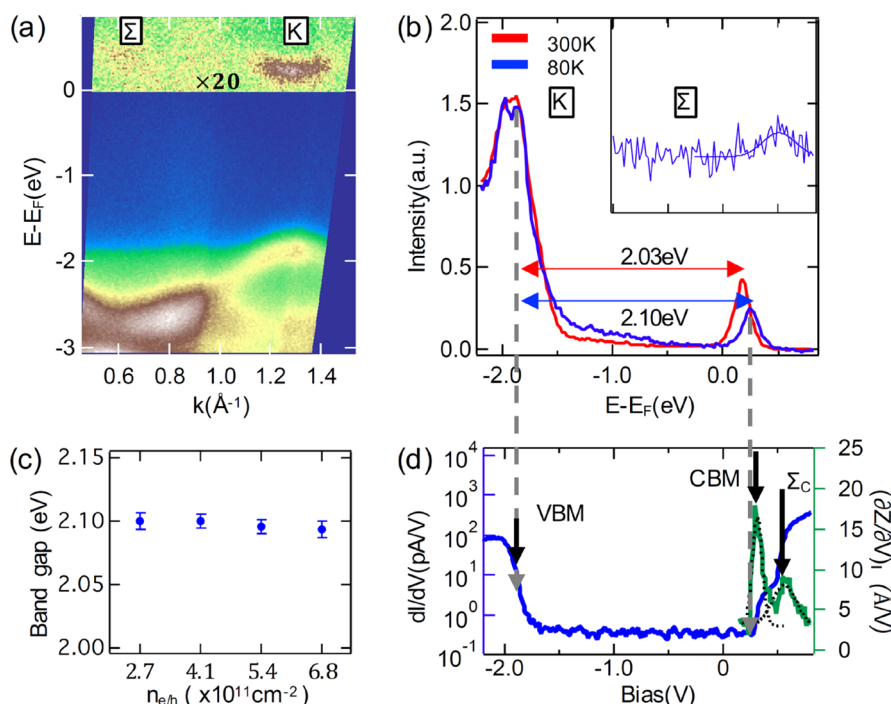


Figure 3. Time-resolved ARPES and scanning tunneling spectroscopy (STS) of monolayer MoS₂ on HOPG. (a) Energy-momentum dispersion along $\Gamma - K$ of the photoexcited monolayer for a $\Delta t = 0.13$ ps time delay (integrated over ± 0.2 ps) and a 300 K lattice temperature. The sample was excited with 2.2 eV pump pulses and probed via extreme-UV (XUV) pulses around 22.3 eV. The transiently occupied conduction band is clearly visible at the K- and Σ -points. (b) EDCs around the K-point for two sample temperatures and a longer time delay of $\Delta t = 1.27$ ps, integrated over ± 0.5 ps, and $\Delta k = 0.05 \text{ \AA}^{-1}$. A quasi-particle band gap of 2.03 ± 0.02 eV at 300 K was obtained, based on Gaussian fits with the standard deviation, increasing to 2.10 ± 0.02 eV at 80 K. The inset shows the EDC at the Σ -point measured 0.13 ps after excitation with 1.8 eV pump pulses, integrated over ± 0.15 ps, and $\Delta k = 0.25 \text{ \AA}^{-1}$. (c) Pump-power dependence of the K-point quasi-particle band gap at 80 K. (d) STS measured at 77 K representing the differential conductance dI/dV (blue) acquired at a constant height and the $(\partial Z/\partial V)_I$ signal (green) acquired at a constant current in comparison to the valence band maximum (VBM) and the conduction band minimum (CBM) derived from the trARPES measurements; $(\partial Z/\partial V)_I$ is used to distinguish thresholds (in this case Σ -point versus K-point). A detailed description can be found in Figure S6 as well as ref 31.

occupied CBM, indicated also in Figure 3b, thus allow us to directly determine the bandgap. This results in QBG values of 2.10 ± 0.02 eV at an 80 K lattice temperature and 2.03 ± 0.02 eV at 300 K for the MoS₂ monolayer.

Importantly, as shown in Figure 3c, the quasi-particle gap value remains nearly constant as a function of the excitation density. This highlights the negligible influence of pump-induced bandgap renormalization and attests to the validity of our analysis in Figure 4; in the time-delayed spectra, the transient incident pump fluence after $\Delta t = 0$ will increase in $\Delta t = 200$ fs due to the finite pulse width, during which time the trend of the gap size should be equivalent to the one shown in Figure 3c. Unlike the previous study of MoS₂/graphene, which exhibited a large bandgap renormalization as a function of the excitation fluence,³³ our measurements were performed at significantly smaller excitation levels. To be specific, in such a small photoexcitation, the dielectric screening effect^{10,11} from the HOPG substrate becomes predominant rather than the screening from photoexcited free carriers.

Despite the distinctive capability of trARPES to verify unoccupied electronic structures directly, it is nontrivial to distinguish the exciton and free carrier states from photoemission signals (especially when energy resolution is limited). The theoretical work of Rustagi and Kemper⁵³ showed that the exciton dispersion obtained from the photoemission has a downward parabolic shape at low temperatures. This suggests that exciton and free carrier states can be distinguished using

the shape of their dispersion. However, concurrently they showed that at high temperatures, thermally excited exciton states with a nonzero center-of-mass can form an upward parabolic dispersion like free carriers so that under limited-energy resolution a CB photoemission signal can be weighted with a hot exciton signal. In our experimental work, we check the “apparent” effective masses at two different temperatures, 80 and 300 K, and find an effective mass of $\sim 0.7 m_0$ at 80 K and that of $\sim 1.2 m_0$ at 300 K. The value of $0.7 m_0$ is consistent with the electron effective mass derived from the measurement of the temperature dependence of Shubnikov–de Haas (SdH) oscillations as a function of the magnetic field.⁵⁴ This confirms that the observed dispersion at 80 K corresponds to that of the free electrons, with minimal contributions from hot excitons carrying nonzero center-of-mass (COM) momentum. On the other hand, at 300 K a larger “apparent” effective mass suggests a mixture of free electrons and hot excitons (hot excitons would have an apparent effective mass of $m^* = m_e + m_h = 1.4 m_0$). See Supporting Information Figure S5 for more details. This might be due to the fact that “hot excitons” decay slower at 300 K than that at 80 K. Nevertheless, as we discussed in Supporting Information Figure S6, at the above-gap excitation (2.2 eV), the zero-COM momentum exciton population is always much smaller than the free carrier contribution. Thus, the determination of the CBM position is not significantly affected by the presence of the hot exciton. Since the scope of this paper is on the accurate determination of the quasi-particle

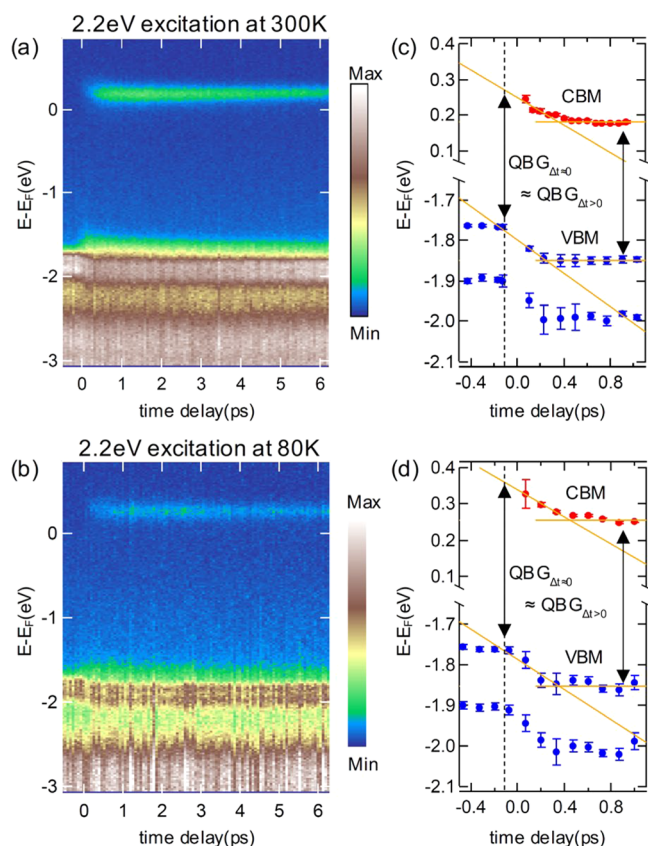


Figure 4. (a and b) Time-dependent VB downward shift at the K-point at 300 and 80 K, respectively, as seen in trARPES maps of the energy-dependent photoelectron intensity versus the pump–probe time delay. The downward VB shift on the order of 0.1 ± 0.02 eV occurs near time zero (near -2 eV). (c and d) Extracted peak position at the K-point conduction (red) and valence (blue) bands near time zero at 300 and 80 K respectively. The size of the CB shift was obtained by extrapolating (orange solid lines) the peaks near time zero. From the extrapolation, the QBG at 300 K was obtained as 2.04 ± 0.07 eV and that at 80 K QBG was obtained as 2.12 ± 0.03 eV, which is consistent with the QBG in the main text within the error bar. Also, the invariant QBG value when the pump power in Figure 3c was varied supports that the QBG change is negligible in the lower fluence regime (corresponding to times near time zero).

band structure, a more in-depth discussion of excitonic effects as well as other forms of many-body effects will be presented elsewhere.

We now compare the MoS₂ monolayer electronic structure derived from trARPES at 80 K with that determined from STS measurements acquired at 77 K. As shown in Figure 3d, in the STS measurements the VBM occurs at -1.84 eV and the CBM occurs at 0.31 eV. This results in an STS-derived bandgap of 2.15 ± 0.06 eV, which is in excellent agreement with the value determined from trARPES. These mutually consistent results also provide a resolution to the controversies regarding the QBG initiated by different STM studies.^{8,24–31,43} In addition, the STS measurements further identify a second threshold located at 0.2 ± 0.05 eV above the CBM. The two thresholds can be more clearly identified in the $(\partial Z/\partial V)_I$ spectrum (shown as green curve), which is acquired by keeping the current constant and sweeping the bias while observing the change in the tip-to-sample separation. As discussed previously in ref 31 (also briefly summarized in Supporting Information Figure S7), the sharp peaks in the $(\partial Z/\partial V)_I$ spectrum are

associated with the thresholds originating from different valleys in the BZ (albeit not a direct k -resolved method). The lower threshold is simply the CBM at the K-point, while the second threshold above it is assigned as Σ_c (often referred to as Q_c). In turn, the trARPES signals in the inset of Figure 3b also reveal the Σ state at 0.55 ± 0.03 eV, although the count rate and thus the transient quasi-particle occupation is much lower than those at the K-point.

Finally, we discuss the excited-state dynamics. Figure 5a shows the transient ARPES signals at 80 K around the K-point

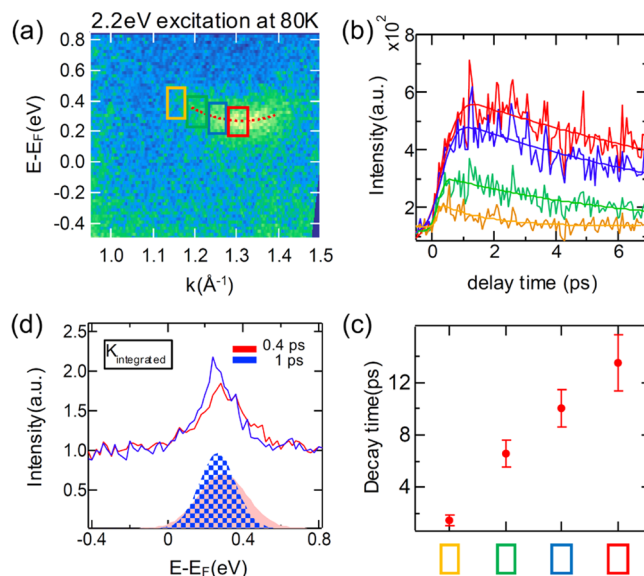


Figure 5. Intravalley dynamics around K-point. (a) Parabolic shape of the E – k dispersion at the K-point conduction band observed with trARPES. (b) Photoelectron intensity versus time delay spectra for different points along the parabolic shape dispersion per the colored box areas of panel a. (c) Decay time of the states in the colored boxes. (d) Momentum-integrated EDC around K. The area of the curve, which represents the photoexcited electrons in the K-valley conduction band, changes less than $\sim 3\%$ during the initial relaxation.

for a representative time delay of $\Delta t = 0.4$ ps, clearly evidencing an upward parabolic dispersion corresponding to the conduction band minimum. To understand the early dynamics, we plot the time-dependent photoemission signals from four different momentum regions near the K-point and its decay time in panels b and c of Figure 5. Carriers at high energies (yellow box) exhibit dynamics that peak at an early time delay of ≈ 0.3 ps, with a subsequent rapid decay on a ≈ 1.5 ps time scale. Approaching the K-point minimum, the dynamics systematically peak at later times and then decay with longer time constants (green and blue box). Finally, at the K-point CBM the dynamics exhibit a peak density around ≈ 1.2 ps, followed by a decay with a ≈ 13 ps time constant. This trend indicates the successive electron scattering from higher to lower energies, which is consistent with a hot electron decay down to the local minimum in momentum space.⁵⁵

Figure 5d shows two K-valley-integrated EDC spectra acquired at $\Delta t = 0.4$ and 1.0 ps, respectively. The areas below each spectral peak are identical within 3%, indicating that nearly all the hot electrons in the K-valley are cooled to the CBM and additional contributions from intervalley-scattered Σ -valley (Σ_c) electrons are minor. We notice that the strength of the Σ_c occupation will vary with the

experimental conditions.³⁸ For the transient photoelectron signal at Σ_c that reveals efficient ultrafast intervalley scattering near time zero with a fast decay of ~ 500 fs,^{56,57} see [Supporting Information Figure S8](#).

In conclusion, the successful fabrication of large-scale monolayer MoS₂ on HOPG was combined with static and time-resolved surface probes to investigate its equilibrium and excited-state electronic structure. Equilibrium measurements evidence a uniform in-plane orientation and an atomically clean surface across the sample, with a band structure consistent with DFT calculations. Sensitive time-resolved XUV ARPES provided concurrent access to the valence band and transiently excited conduction band states, yielding a direct measure of the quasi-particle bandgap in ML MoS₂. We found the resulting value to be in remarkable agreement with the electronic bandgap determined from STS measurements on the same sample structure. Furthermore, XUV-trARPES reveals ultrafast intra- and intervalley dynamics and a parabolic conduction band minimum around the K-point with the excitonic influence. Future experiments utilizing the combination of wafer-scale TMDs and sensitive trARPES can fully access their complex electron dynamics in time, energy, and momentum to guide the search for the new valley and exciton physics and devices based on TMD monolayers and heterostructures.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.1c02674>.

Regular and time-resolved ARPES experimental methods, computational methods, a large discrepancy of the bandgap size in STM studies, optical characterization of ML-MoS₂, wet-transfer procedure, ML-MoS₂ air stability, effective masses measured at the K-point, bandgap determination in the trARPES measurements, $(\partial Z/\partial V)_I$ technique for critical points identification, and transient photoelectron intensity (exciton and free carrier mixture) (PDF)

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Notes

The authors declare no competing financial interest.

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