Ultrafast Electron and Hole Relaxation Pathways in Few-Layer MoS₂

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Supporting Information

ABSTRACT: Femtosecond optical pump–probe spectroscopy is employed to elucidate the band-selective ultrafast carrier dynamics of few-layer MoS₂. Following narrowband resonant photoexcitation of the exciton A transition, the subpicosecond to picosecond relaxation dynamics of the electron and the hole at the K valley are separately interrogated by a broadband probe pulse. The temporal evolution of the spectral first moment reveals nonexponential intravalley relaxation dynamics in the conduction band. Fluence dependence measurements suggest that this relaxation process is predominantly mediated by acoustic phonon emission. Intervally scattered carriers from the K valley to the extrema of the conduction and valence bands is also observed via the decay of the spectral zeroth moment. In addition, second-order Raman scattering leads to the emergence of sidebands in the normalized differential transmission spectra. The observed two-phonon energies and the associated band-edge photoluminescence from the visible to the near-infrared make these materials well-suited to a variety of optoelectronic applications. Moreover, in the case of monolayer TMDs, there exists two inequivalent but energetically degenerate valleys at the corners of the first Brillouin zone, labeled K and K', as well as opposite spin projections for the two spin–orbit-split valence bands at the K and K' valleys; the energy gap between the spin–orbit-split valence bands has been measured by steady-state optical spectroscopy. The above implies coupled spin and valley degrees of freedom.

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INTRODUCTION

Few-layer two-dimensional transition metal dichalcogenides (TMDs) have recently emerged as promising candidates for atomically thin semi-conducting electronic materials, with molybdenum disulfide (MoS₂) being the most commonly studied to date. Good electron mobilities of ~200 cm² V⁻¹ s⁻¹ and on/off ratios exceeding 10⁸, for example, have been demonstrated in field-effect transistors based on monolayer MoS₂. In addition, the existence of a direct band gap transition in the monolayer regime along with the chemical tunability of the associated band-edge photoluminescence from the visible to the near-infrared make these materials well-suited to a variety of optoelectronic applications. Moreover, in the case of monolayer TMDs, there exists two inequivalent but energetically degenerate valleys at the corners of the first Brillouin zone, labeled K and K', as well as opposite spin projections for the two spin–orbit-split valence bands at the K and K' valleys; the energy gap between the spin–orbit-split valence bands has been measured by steady-state optical spectroscopy. The above implies coupled spin and valley degrees of freedom.
which are addressable by circularly polarized light, thus heralding the potential application of monolayer TMDs to spintronics and valleytronics.\textsuperscript{10,14}

In the specific realm of carrier transport and electrical switching, earlier studies suggest that field-effect transistors (FETs) based on multilayer MoS\textsubscript{2} exhibit superior performance characteristics compared to those that employ single-layer MoS\textsubscript{2}. The carrier mobility has been shown to increase with the number of layers in a nonmonotonic fashion, with a record-high mobility of 700 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1} achieved for a FET that comprises 10 nm thick MoS\textsubscript{2} overcoated by an Al\textsubscript{2}O\textsubscript{3} dielectric layer.\textsuperscript{15} The enhanced mobility supports higher on-state currents, which in turn enable larger operation bandwidths.\textsuperscript{16} Moreover, single-layer devices have been shown to suffer from high \(\sim 0\Omega\) resistance, possibly due to the large Schottky barrier between the electrode and the TMD monolayer.\textsuperscript{17} The higher electrical noise associated with monolayer devices further limits their application to sensing,\textsuperscript{19} for example. Finally, phototransistors that employ multilayer MoS\textsubscript{2} have one to two-orders of magnitude higher photoresponse at visible wavelengths\textsuperscript{20} than their single-layer counterparts.\textsuperscript{18} As a result of its indirect band gap, multilayer MoS\textsubscript{2} also allows the responsivities of phototransistors to extend to the near-infrared.\textsuperscript{20,22} Taken together, these studies suggest that additional investigations of the electronic properties of multilayer MoS\textsubscript{2} are desired to further increase its technological relevance.

The electronic and optoelectronic characteristics of semiconductors are, to a large extent, governed by their fundamental carrier dynamics.\textsuperscript{23} For example, carrier–carrier and carrier–phonon scattering processes are known to limit carrier mobilities. In high-field transport, these scattering processes also participate in the cooling of carriers that are heated by the presence of large external electric fields. For valleytronic materials, possible loss of valley polarization due to carrier–carrier and carrier–phonon scattering must be taken into account. The above considerations have motivated recent studies of the ultrafast carrier dynamics of single-layer and few-layer TMDs. Results from optical pump–probe spectroscopy on MoS\textsubscript{2} performed with circularly polarized pulses suggest the preservation of valley polarization on a few-picosecond time scale,\textsuperscript{24,25} in agreement with results obtained from time-resolved photoluminescence measurements.\textsuperscript{26,27} Subpicosecond dynamics that are associated with the coherent coupling of electrons in different valleys\textsuperscript{25} exciton–exciton scattering,\textsuperscript{28} carrier thermalization, and cooling\textsuperscript{29} have also been observed by optical pump–probe spectroscopy, in addition to rapid exciton–exciton annihilation\textsuperscript{30} in MoS\textsubscript{2} and ultrafast charge transfer in MoS\textsubscript{2}/WS\textsubscript{2} van der Waals heterostructures.\textsuperscript{31} By augmenting a spatial dimension to optical pump–probe studies, optical pump–probe microscopy has yielded exciton lifetimes and diffusion coefficients for a variety of TMDs.\textsuperscript{32} Spatially resolved ultrafast exciton trapping and carrier-phonon scattering dynamics of single-layer to bulk MoS\textsubscript{2} have been observed as well.\textsuperscript{33} The above optical measurements are complemented by optical-pump terahertz-probe measurements, which reveal photoconductivity responses of monolayer MoS\textsubscript{2} that can be explained by trion formation followed by their decay over tens of picoseconds via nonradiative recombination at defect sites.\textsuperscript{34} On subpicosecond time scales, the decay of terahertz photoconductivity is assigned to defect-mediated carrier recombination.\textsuperscript{35}

The aforementioned time-resolved optical pump–probe studies of TMDs have yielded information on the combined dynamics of the electrons and the holes. This is because pump–probe spectroscopy is inherently sensitive to absorption saturation induced by phase-space filling, such that the normalized differential transmission signal \(\Delta T/T \propto f_e + f_h\) is proportional to the sum of the electron \((f_e)\) and the hole \((f_h)\) distribution functions.\textsuperscript{36} It remains desirable, however, to discern the separate time evolution of the electrons and the holes. Beyond their fundamental interest, the individual ultrafast dynamics of the electron and the hole also provide the conceptual framework for understanding the electron and hole transport properties of TMD-based electronic devices.

Here, we report the use of optical pump–probe spectroscopy to elucidate the separate ultrafast relaxation dynamics of electrons and holes of a five-layer MoS\textsubscript{2} sample. Our experimental approach (Figure 1a) is inspired by earlier optical pump–probe studies of GaAs, in which photoexcitation of the heavy- and light-hole valence bands was followed by probing the interband transition from the higher-energy spin–orbit split-off valence band \(\Gamma_{v,so}\).\textsuperscript{37,38} As the low-energy pump excitation does not create holes at \(\Gamma_{v,so}\), the probe pulse interrogates only the electronic dynamics in the conduction band \(\Gamma_c\). In the present work, narrowband resonant excitation of the A exciton transition by the pump pulse (Figure 1b) promotes electrons from \(K_{\text{v,so}}\) to \(K_c\), following which the differential transmission of a broadband probe pulse that spans

![Figure 1. (a) Schematic illustration for the band-selective probing of ultrafast electron and hole relaxation dynamics in MoS\textsubscript{2}. Following resonant excitation of the exciton \(A\) transition, the exciton \(B\) probe interrogates only the electron dynamics at \(K_c\). With knowledge of the electron dynamics, the hole dynamics at \(K_{\text{v,so}}\) can be extracted from the exciton \(A\) probe signal, which reflects both electron and hole dynamics. (b) UV/visible absorption spectrum of the five-layer MoS\textsubscript{2} sample collected at 300 K (solid line). The A and B excitonic transitions are located at 684 and 631 nm, respectively. The normalized spectral densities of the narrowband (dotted line) and broadband (dashed line) laser pulses employed for pump and probe, respectively, are also shown.](image-url)
the A and B exciton transitions is collected as a function of pump-probe time delay. The B exciton probe transition, which promotes electrons from the spin-orbit split-off \( K_2 \) band to \( K_\Gamma \), is insensitive to the time-dependent hole distribution function at \( K_\Gamma \) that is created by the pump pulse. Therefore, its temporal evolution only reflects the electron dynamics at \( K_\Gamma \). With knowledge of the electron dynamics, the hole dynamics can then be recovered from the temporal evolution of the A exciton probe transition, which bears contributions from both electron and hole dynamics. This approach contrasts with the nonselective, broadband excitation by 10 fs pulses that was employed in our previous work, which creates an energetically broad carrier distribution and therefore obfuscates the separation of electron and hole dynamics. 29

It is important to note that the pump fluences employed in this work yield two-dimensional carrier densities that span \((0.5-2.4) \times 10^{13} \text{cm}^{-2}\), which is comparable to the Mott density of MoS\(_2\) \((\sim 10^{13} \text{cm}^{-2})\). As such, the ultrafast dynamics that are reported herein are those of free carriers in an electron-hole plasma rather than excitons. Since the optical band gap of trilayer MoS\(_2\) (1.35 eV) \(^{22}\) already approaches the extrema of the valence and conduction bands and momentum conservation requirements. In the case of few-processes are mediated by phonon emission to fulfill scattering of carriers to other valleys (Figure 2). 42 Both cooling can occur via intravalley relaxation and intervalley

**Figure 2.** Schematic illustration of the various phonon-mediated carrier relaxation pathways following the photoexcitation of few-layer MoS\(_2\) at the exciton A transition. Intravalley relaxation (blue arrows) confines the carriers to the K valley, whereas intervalley scattering (green arrows) results in the transfer of electrons and holes to the \( \Gamma \) and \( \Gamma_v \) valleys, respectively. Carrier cooling via intravalley relaxation modifies the valence-to-conduction band transition energy, which in turn leads to a shift in the spectral first moment with time. On the other hand, intervalley scattering removes carriers from the K valley probe region, thereby resulting in a decrease in the spectral zeroth moment with time.

where \( t \) is the pump-probe time delay, and \( \lambda_i \) and \( \lambda_f \) correspond to the limits of the integral. On the other hand, time scales for the intervalley scattering of carriers away from the K valley are obtained by analyzing the decay of the spectral zeroth moment, given as

\[
(\lambda^{(0)}(t)) = \frac{\int_{\lambda_i}^{\lambda_f} d\lambda \Delta T(\lambda, t)/T(\lambda)}{\lambda_f - \lambda_i}
\]

(2)

Intuitively, \( (\lambda^{(0)}) \) is related to the energy gap between the bands which are optically coupled by the probe pulse, whereas \( (\lambda^{(0)}) \) yields the carrier populations at the initially excited Franck-Condon region. 39 Note that by virtue of its long time scale \((\geq 100 \text{ ps})\) carrier recombination in few-layer MoS\(_2\) is not expected to contribute significantly to the picosecond decay of \((\lambda^{(0)}(t)) \) observed in this work.

The normalized differential transmission spectra \( \Delta T/T \) collected at 300 K as a function of pump-probe time delay for excitation pump fluences of 0.06, 0.14, and 0.29 mJ/cm\(^2\) are shown in Figures 3a, 3b, and 3c, respectively. At low pump fluence, the \( \Delta T/T \) spectra reveal positive \( \Delta T/T \) features that are ascribed to ground-state bleaching of the exciton A and B transitions and stimulated emission at the exciton A transition. A negative \( \Delta T/T \) feature that is especially prominent on the low-energy side of the probe spectrum is also observed and is assigned to excited-state absorption involving intersubband transitions. 35,28,29 Employing higher pump fluences results in the emergence of positive \( \Delta T/T \) features on the low-energy side of the exciton A and B probe transitions (Figure 3c).

The time evolution of \((\lambda^{(1)}(t)) \) in the spectral region of the exciton B probe yields the intravalley electronic relaxation dynamics at Kc. The computed \((\lambda^{(1)}(t)) \) traces for excitation pump fluences of 0.06, 0.14, and 0.29 mJ/cm\(^2\) are shown in Figure 4. The observed blueshift with increasing time delay is due to the dynamic Burstein-Moss effect that accompanies intravalley carrier relaxation. 36,47 The nonequilibrium behavior of the spectral blueshift points to electron cooling dynamics that cannot adequately be described in terms of a single rate constant, as prescribed by the Fermi Golden Rule. On the other hand, the excellent fit of the spectral blueshift to the Gaussian decay profile (see Supporting Information Table 1 for the fit
parameters) suggests the need for a quantum dynamical description of electron cooling in few-layer MoS₂. The Gaussian decay time constant $\tau_e$ (1), equivalent to the standard deviation of a Gaussian function, decreases from 1.77 ± 0.08 ps at a pump fluence of 0.06 mJ/cm² to 1.34 ± 0.02 ps for both 0.14 and 0.29 mJ/cm² pump fluences.

Ab initio studies of monolayer MoS₂ show that intravalley relaxation at K_c is primarily mediated by the emission of the A₁g longitudinal optical (LO) phonon. The cooling power of LO phonons is also predicted to be 2 orders of magnitude larger than acoustic phonons, thereby favoring LO phonon emission as the more efficient carrier relaxation pathway. In light of these theoretical findings, LO phonon emission might be expected to be the major contributor to the intravalley electronic relaxation observed here. The fluence dependence exhibited by $\tau_e$ (1), however, is incompatible with the participation of LO phonons in intravalley relaxation. This is because carrier cooling via LO phonon emission is highly susceptible to the hot phonon effect, which leads to a drastic reduction in cooling power at higher carrier densities due to the buildup of a large, nonequilibrium LO phonon population. On the other hand, the following considerations point to acoustic phonon emission as the dominant route to electronic cooling in the present work. First, the observed fluence dependence of $\tau_e$ (1) can be explained by the increase in cooling power of acoustic phonons with carrier density. Moreover, the acoustic phonons can be assumed to be in thermal equilibrium with the lattice and the substrate, thus rendering them relatively insensitive to the hot phonon effect. Second, the excess electronic energy of $E_e \sim 620 \pm 230$ cm⁻¹ (see Supporting Information Figure S1) is comparable to the LO phonon frequency of $\omega_{LO} \sim 400$ cm⁻¹ under our experimental conditions. Because the dissipation of excess energies below $h\omega_{LO}$ cannot proceed via the emission of LO phonons, acoustic phonon emission is expected to account for a sizable fraction of the electronic energy loss.

Besides intravalley carrier relaxation, carriers that are initially generated at the K valley can also relax to other valleys via intervalley scattering. In few-layer MoS₂, the $K_c \rightarrow Q_\nu$ and $K_v \rightarrow \Gamma_v$ scattering pathways are available for the electrons and holes, respectively. The spectral zeroth moment time traces $\langle \lambda^{(0)}(t) \rangle$ computed about the exciton B transition are shown in Figure 3.

Figure 3. Normalized differential transmission $\Delta T/T$ spectra collected as a function of time delay following photoexcitation of five-layer MoS₂ with pump fluences of (a),(b) 0.06 mJ/cm², (c),(d) 0.14 mJ/cm², and (e),(f) 0.29 mJ/cm².

Figure 4. Time evolution of the spectral first moment $\langle \lambda^{(1)}(t) \rangle$ computed at the exciton B probe transition (dashed lines). The spectral blueshift with time delay, which reflects intravalley relaxation of the electrons, can be adequately fit to a Gaussian function (solid lines).
The decrease in \( \langle \lambda_{B}^{(0)}(t) \rangle \) on the picosecond time scale is a result of intervalley scattering of electrons from the K valley of the conduction band. On the other hand, the temporal evolution of the hole population at the K valley is reflected in the difference signal \( \langle \lambda_{A, B}^{(0)}(t) \rangle = \langle \lambda_{A}^{(0)}(t) \rangle - \langle \lambda_{B}^{(0)}(t) \rangle \) (Figure 5b). Both \( \langle \lambda_{B}^{(0)}(t) \rangle \) and \( \langle \lambda_{A, B}^{(0)}(t) \rangle \) traces can be fit to exponential decays to give time constants \( \tau_{A}^{(0)} \) and \( \tau_{B}^{(0)} \), respectively (Table 1). The exponential decay dynamics of intervalley scattering is consistent with the indirect band gap nature of few-layer MoS\(_2\), which presents a high density of states into which the carriers at the K valley can scatter, hence ensuring the validity of the Fermi Golden Rule. Furthermore, \( \tau_{A}^{(0)} \) and \( \tau_{B}^{(0)} \) are found to exhibit opposite trends in their pump fluence dependence: \( \tau_{A}^{(0)} \) increases with excitation pump fluence, whereas \( \tau_{B}^{(0)} \) decreases. Employing the same considerations that account for the observed fluence dependence of the intravaleley electronic relaxation time scales (see above),\(^{32}\) we can tentatively infer that intervalley scattering in the conduction band is primarily mediated by LO phonons, whereas intervalley scattering in the valence band involves the participation of acoustic phonons.

The sidebands in the \( \Delta T/T \) spectra that emerge under high-excitation fluence conditions (Figure 3c) provide further evidence for the participation of LO and acoustic phonons in the intervalley scattering processes in the conduction and valence bands, respectively. The sidebands develop on the low-energy side of the exciton A and B transitions and evolve concomitantly with the primary peaks. The latter observation suggests that the sidebands are not a product of carrier cooling. Here, the origin of these sidebands is assigned to second-order Raman scattering (Figure 6a).\(^{35,56}\) Starting from the initial electron and hole distributions generated by the pump pulse, the successive emission of two phonons of opposite momenta \(-\hbar q + \hbar q\) leads to the reappearance of carriers in the original K valley. By the conservation of energy, these carriers are lower in energy than the initial distributions by \( 2\hbar \omega_{\nu} \). The subset of lower-energy carriers gives rise to additional ground-state bleaching and stimulated emission transitions which result in the sidebands in the \( \Delta T/T \) spectra. The characteristic energy of the two-phonon transition is consequently given by the energetic separation between the primary exciton peak and its sideband, whose positions can be delineated from the second-derivative \( \Delta T/T \) spectra (Figure 6b). At a time delay of 200 fs, the second-derivative spectrum shows an energy separation of \( \Delta E_{A} = 550 \pm 13 \text{ cm}^{-1} \) between the exciton A transition and its sideband, whereas for the exciton B transition and its sideband is \( \Delta E_{B} = 462 \pm 13 \text{ cm}^{-1} \) (Figure 6c, also see Supporting Information Figure S2). These two-phonon energies are in good agreement with the \( 2E_{1g}(\Gamma) \) and \( 2\text{LA}(\text{M}) \) two-phonon peaks that appear in the spontaneous resonant Raman spectrum at 565 and 450 cm\(^{-1}\), respectively (see Supporting Information Figure S3).\(^{35,57,58}\) Our result therefore indicates that the two-phonon carrier-phonon scattering processes in the conduction and valence bands are mediated by the \( E_{1g} \) LO phonon and the LA phonon, respectively.

From the above analysis, we infer that two-phonon carrier-phonon scattering processes in the conduction and valence bands involve the \( E_{1g} \) LO phonon and the LA phonon, respectively. For an initial population of carriers at the K valley with excess energies of \( E_{e} \sim 620 \pm 230 \text{ cm}^{-1} \) and \( E_{h} \sim 820 \pm 290 \text{ cm}^{-1} \), respectively, the energetically accessible two-phonon scattering pathways are \( K_{e} \rightarrow Q_{e} \rightarrow K_{e} \) for the conduction band and \( K_{h} \rightarrow \Gamma_{h} \rightarrow K_{v} \) for the valence band.\(^{43,44}\) It is conceivable that the same phonons are primarily responsible for the net depopulation of carriers from the K valley via one-phonon \( K_{e} \rightarrow Q_{e} \) and \( K_{h} \rightarrow \Gamma_{h} \), intervalley scattering. That is, the intervalley scattering that leads to the observed decay in the \( \langle \lambda_{B}^{(0)}(t) \rangle \) and \( \langle \lambda_{A, B}^{(0)}(t) \rangle \) time traces is mediated by the \( E_{1g} \) LO and LA phonons, respectively. Because the cooling power of optical phonons decreases with carrier density whereas that of acoustic phonons increases, \( \tau_{B}^{(0)} \) is found to increase with carrier density, opposite to the fluence dependence observed for \( \tau_{A}^{(0)} \). Furthermore, the presence of second-order Raman sidebands even at early time delays \((t < 200 \text{ fs})\) implies the onset of

![Figure 5](image-url)

Figure 5. (a) Zeroth moment \( \langle \lambda_{B}^{(0)}(t) \rangle \) time traces obtained at different excitation fluences. The solid lines are obtained from fitting the data to the convolution of a monoexponential decay function with a Gaussian function of 83 fs fwhm. The latter models the instrument response function. The monoexponential decay constant corresponds to \( \tau_{B}^{(0)} \), the intervalley scattering time constant for electrons. (b) Zeroth moment \( \langle \lambda_{A, B}^{(0)}(t) \rangle \) time traces obtained at different excitation fluences. The solid lines are obtained from fitting the data to the convolution of a biexponential decay function with a Gaussian function of 83 fs fwhm. The latter models the instrument response function. The slow decay component, with a time constant \( \tau_{B}^{(0)} \), results from the intervalley scattering of holes. The origin of the fast decay component \((t \sim 40 \text{ fs})\) is unknown, although its time constant is reminiscent of the time scale for carrier thermalization.

<table>
<thead>
<tr>
<th>Fluence (mJ/cm(^2))</th>
<th>Carrier Density (10(^{13}) cm(^{-2}))</th>
<th>( \tau_{A}^{(0)} ) (ps)</th>
<th>( \tau_{B}^{(0)} ) (ps)</th>
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<tbody>
<tr>
<td>0.06</td>
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<td>0.51 ± 0.01</td>
<td>1.21 ± 0.03</td>
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<tr>
<td>0.14</td>
<td>1.2</td>
<td>0.62 ± 0.01</td>
<td>0.80 ± 0.01</td>
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<tr>
<td>0.29</td>
<td>2.4</td>
<td>0.67 ± 0.01</td>
<td>0.62 ± 0.01</td>
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intervalley scattering immediately upon photoexcitation, which in turn raises the possibility that the same phonon modes might be responsible for the previously observed sub-20 fs intervalley scattering dynamics in few-layer MoS2.29

Ab initio nonadiabatic molecular dynamics simulations are performed to elucidate the various electronic relaxation channels that are available in photoexcited few-layer MoS2. Starting from a population of electrons in the Kc valley with an initial excess energy of 1000 cm\(^{-1}\), relaxation via intervalley scattering is found to occur with time constants of 75 fs and 0.72 ps (Figure 7a). The latter is in good agreement with the present experimental results, while the fast component is consistent with the time scale for carrier thermalization in few-layer MoS2.29 The simulation also agrees with the experiment in showing that the intravalley electron–phonon scattering requires longer time than the intervalley scattering. However, the simulated time trace for the intravalley relaxation of the conduction band electrons is different from those obtained from experiment. The simulated time trace is well represented by an exponential decay with a time constant of 0.80 ps (Figure 7a), whereas the experimental data strongly suggest non-exponential dynamics (Figure 4). Moreover, experiments show that the time required for the hot electron population to reach 1/e of its initial energy is 1.9 ps, approximately a factor of 2 longer than the simulated time. These discrepancies can be attributed to the excess energy being higher in the simulations (1000 cm\(^{-1}\)) than in the experiments (620 cm\(^{-1}\), as indicated by sample calculations. The additional phonon-mediated relaxation pathways that arise from the higher excess energy effectively enhance energy dissipation and suppress nonexponential relaxation behavior.

It is interesting to note that the simulated intravalley and intervalley relaxation time traces reveal the existence of weak oscillatory features. The FFT power spectra (Figure 7b) yield the frequencies of phonons which mediate the intravalley and intervalley relaxation processes. present experimental results, while the fast component is consistent with the time scale for carrier thermalization in few-layer MoS2.29 The simulation also agrees with the experiment in showing that the intravalley electron–phonon scattering requires longer time than the intervalley scattering. However, the simulated time trace for the intravalley relaxation of the conduction band electrons is different from those obtained from experiment. The simulated time trace is well represented by an exponential decay with a time constant of 0.80 ps (Figure 7a), whereas the experimental data strongly suggest non-exponential dynamics (Figure 4). Moreover, experiments show that the time required for the hot electron population to reach 1/e of its initial energy is 1.9 ps, approximately a factor of 2 longer than the simulated time. These discrepancies can be attributed to the excess energy being higher in the simulations (1000 cm\(^{-1}\)) than in the experiments (620 cm\(^{-1}\), as indicated by sample calculations. The additional phonon-mediated relaxation pathways that arise from the higher excess energy effectively enhance energy dissipation and suppress nonexponential relaxation behavior.

It is interesting to note that the simulated intravalley and intervalley relaxation time traces reveal the existence of weak oscillatory features. The FFT power spectra (Figure 7b) yield the frequencies of phonons which participate in the electronic cooling process. Both power spectra exhibit a low-frequency band (<100 cm\(^{-1}\)) as well as a high-frequency peak at 800 cm\(^{-1}\). The latter is consistent with the first overtone frequency of the A\(_{1g}\) LO phonon; its fundamental frequency at 400 cm\(^{-1}\) is apparent in the FFT power spectrum of the intervalley relaxation trajectory. The low-frequency band likely arises from acoustic phonons, although contributions from interlayer shearing modes are also possible.59 These simulation results indicate that the phonon modes which mediate the electronic cooling process in few-layer MoS2 are similar to those observed in bulk MoS2, suggesting that similar electronic relaxation mechanisms are at play in both systems.
should be compared with the experimental results, which suggest that intravalley and intervalley electronic relaxation are dominated by the emission of acoustic phonons and the $E_{2g}$ LO phonon, respectively. It is likely that the larger excess energies employed in the simulations than in the experiments enhance the contributions of the higher-frequency LO phonons to the electronic cooling.

Finally, we note that the second-derivative $\Delta T/T$ spectra reveal an electronic transition at 729 nm that is Stokes shifted by $\Delta E_A \sim 1200$ cm$^{-1}$ from the exciton A transition (see arrow in Figure 6b). This feature becomes more prominent with increasing time delay (Figure 8a) and is apparent even with the lowest excitation fluence (0.06 mJ/cm$^2$) employed in our experiments. The absence of spectral features at such high frequencies in the room-temperature Raman spectrum of MoS$_2$ excludes the possibility of associating $\Delta E_A'$ with a multiphonon Raman scattering process.$^{50}$ We instead consider an electronic origin for $\Delta E_A'$ due to its similarity to the 0.15 eV spin–orbit splitting of the valence band at the K valley.$^{5,6}$ Here, the electronic transition at 729 nm is tentatively assigned to a radiative shake-up satellite, in accord with its appearance on the low-energy side of the exciton A transition. Its existence as a peak atop the negative-going signal in the $\Delta T/T$ spectra is consistent with the stimulated emission nature of the transition. On the basis of the $Q_c \rightarrow K_{v1}$, $K_c \rightarrow \Gamma_{v1}$, and $Q_c \rightarrow \Gamma$, indirect transitions can be ruled out as a possible explanation for the observed feature at 729 nm, for which the Stokes shift relative to the exciton A transition is only $\sim 1200$ cm$^{-1}$.

In the radiative shake-up process, originally uncovered in Auger transitions in the X-ray,$^{51}$ the radiative recombination of carriers accompanies the simultaneous excitation of the system. The conservation of energy requires the energy of the emitted photon to be downshifted from the band gap by the quantum of excitation. Shake-up satellites have previously been observed in the photoluminescence spectra of CdZnSe/ZnSe core–shell nanocrystals$^{62}$ and doped semiconductors.$^{63,64}$ In the latter, the radiative recombination of excitons or free carriers is accompanied by the excitation of the dopant atoms. For the CdZnSe/ZnSe nanocrystals, radiative recombination of positive trions occurs concomitantly with the excitation of the remaining hole into higher-energy valence states. In the case of MoS$_2$, we postulate that the excitation of holes from $K_{v1}$ to $K_{v2}$ accompanies the probe pulse-stimulated radiative recombination of carriers at the band edge (Figure 8b). Because part of the energy released by band-edge radiative recombination $E_r$ is used to excite the hole from $K_{v1}$ to the spin–orbit-excited $K_{v2}$ level, the final energy of the emitted photon is $\Delta E_{\text{sat}} = h\nu = E_r - \Delta E_{\text{sat}}$ where $\Delta E_{\text{sat}}$ is the energy gap between $K_{v1}$ and $K_{v2}$. Such a two-electron transition, in which a single photon drives the excitation and/or de-excitation of two electrons, is a hallmark of strong electron correlation.$^{65}$ While the observation of two-electron transitions in layered two-dimensional materials is unprecedented, their appearance in the present work is perhaps unsurprising in view of the few-nanometer spacing between adjacent carriers (corresponding to two-dimensional carrier densities of $\sim 10^{13}$ cm$^{-2}$). The proximity between carriers leads to strong carrier–carrier interactions from which the two-electron transitions emerge. Interestingly, the energetic separation $\Delta E_A'$ is found to be time-dependent, starting from an initial value of 1218 ± 10 cm$^{-1}$ and asymptotically approaching 1166 ± 1 cm$^{-1}$ with a time constant of 0.66 ± 0.11 ps (Figure 8c). This time constant matches the picosecond carrier cooling time scale and suggests that the spin–orbit splitting is weakly dependent on the carrier temperature. Moreover, it is noteworthy that the asymptotic value of 1166 ± 1 cm$^{-1}$ provides a measure of the $K_{v1} - K_{v2}$ spin–orbit splitting of five-layer MoS$_2$.

**CONCLUSION**

Femtosecond optical pump–probe spectroscopy has been employed to unravel, for the first time, the separate electron and hole relaxation dynamics following photoexcitation of five-layer MoS$_2$, as well as the nature of phonons that participate in
intra- and intervalley carrier-phonon scattering. Analysis of the first and zeroth spectral moments computed from the normalized differential transmission spectra yields time scales for intravalley and intervalley relaxation, respectively. Intravalley relaxation of the electron at K, exhibits nonexponential decay kinetics. The Gaussian decay constant decreases from 1.77 ± 0.08 ps to 1.34 ± 0.02 ps with increasing pump fluence, suggesting the dominant role played by acoustic phonons in mediating the intravalley relaxation. With increasing pump fluence, intervalley scattering time scales are found to increase from 0.51 ± 0.01 ps to 0.67 ± 0.01 ps for scattering in the conduction band and decrease from 1.21 ± 0.03 ps to 0.62 ± 0.01 ps for scattering in the valence band. The observed fluence dependence points to the participation of LO phonons and acoustic phonons in intervalley scattering in the conduction and valence bands, respectively. In support of this result, the second-order Raman scattering sidebands that emerge in the ΔT/T spectra under high-fluence excitation conditions suggests carrier-phonon scattering in the conduction and valence bands that involve the E_{1g} LO phonon and the LA phonon, respectively. The experimentally determined time scales for intervalley electronic relaxation are substantiated by ab initio nonadiabatic molecular dynamics simulations. Finally, close examination of the ΔT/T spectra reveals a two-electron radiative shake-up satellite that arises from radiative band edge carrier recombination and the concomitant excitation of holes from K_{1} to K_{2}. The observed two-electron transition points to the high degree of electron correlation that exists in photoexcited few-layer MoS_{2}.

## EXPERIMENTAL AND THEORETICAL METHODS

The preparation of the five-layer MoS_{2} sample by chemical vapor deposition (CVD) and its extensive characterization by various spectroscopic, microscopic, and electrical methods have been detailed previously.66 The use of a chlorine-based precursor (MoCl_{5}) in the growth of the five-layer MoS_{2} sample favors the creation of the 3R polytype.67 Whereas the more commonly studied 2H polytype has a centrosymmetric structure, the 3R polytype is noncentrosymmetric. The different symmetry properties, however, do not significantly impact the band structure of the few-layer samples.67 Characterization of the MoS_{2} sample by atomic force and Raman microscopies reveals a spatially homogeneous, five-layer sample.29 Optical pump–probe spectroscopy is performed with narrowband pump pulses centered at 684 nm and broadband probe pulses that span the exciton A and B transitions. The broadband probe pulses of 10 fs duration are centered at 660 nm with a spectral bandwidth of ~200 nm. The narrowband pump pulse is generated by inserting a 10 nm bandpass filter into the original broadband pump pulse. A second-order intensity cross-correlation between pump and probe pulses, performed in a 10 μm thick BBO crystal located at the position of the sample target, reveals a time resolution of 83 fs fwhm for the apparatus (Supporting Information Figure S4). Typical pulse energies for pump and probe beams are 100 and 20 nJ, respectively. The focal spot diameter (1/e²) of the pump beam (400 μm) is twice that of the probe beam (200 μm). The pump and probe beams are orthogonally polarized to minimize the contribution of coherent artifacts to the measured signal, which can be further suppressed by singular-value decomposition of the two-dimensional probe wavelength–time delay data set.68 The transmitted probe beam is spectrally dispersed in a 300 mm spectrograph and detected on a 1024-element linear array detector. The detector has a read-out rate of 1 kHz and is synchronized to the 500 Hz optical chopper positioned in the path of the pump beam. The differential transmission signal exhibits a linear fluence dependence in the range of pump fluences used in the experiments (Supporting Information Figure S5). All measurements are performed at 300 K. To minimize sample degradation by potential atmospheric oxidation, the MoS_{2} sample is housed in a vacuum cryostat that is evacuated to <10^-8 mbar.

We applied ab initio nonadiabatic molecular dynamics (NAMD) implemented within time-domain density functional theory (TD-DFT)69–71 in the Kohn–Sham (KS) framework72 to model the inter- and intravalley electron–phonon relation in the K valley in a bilayer MoS_{2}. The simulations were performed using the Vienna ab initio simulation package (VASP)73,74 augmented with the NAMD functionality.75–77 The generalized gradient approximation (GGA) functional of Perdew–Burke–Ernzerhof (PBE)78 was used to describe the electronic exchange-correlation interactions, while the projector augmented wave (PAW)79 method was employed to represent the electron–ion interaction. An amount of 15 Å of vacuum was added perpendicular to the bilayer to avoid spurious interactions between the periodic images. The optimized bilayer MoS_{2} was heated to 300 K by repeated velocity rescaling. A microcanonical molecular dynamics trajectory of 4 ps was run in the ground state with a 1 fs time step. The DFT-D2 method of Grimme80 was used to describe the van der Waals interactions stabilizing the bilayer MoS_{2} during geometry optimization and molecular dynamics simulation.

To model the photoinduced inter- and intravalley electron–phonon scattering dynamics within the experimental excess energy range, we utilized the classical path approximation76 combined with the fewest switches surface hopping (FSSH)81 into the time-domain KS scheme72 and including a semiclassical correction for quantum decoherence.82 The decoherence times were computed using the optical-response formalism, as described in ref 83. The approach has been applied to study electron transfer and relaxation in many systems, including graphene,84 carbon nanoribbons,85 and quantum dot–TiO_{2} interfaces.86 FSSH is a NAMD method using a stochastic algorithm that generates trajectory branching83 and satisfies detailed balance.87 In the experiment, the electron–phonon scattering processes start with 620 cm⁻¹ (~0.08 eV) of excess electron energy. To capture the dynamics within this energy range, we had to include multiple k-points. Among the 600 k-points, there were 36 k-points within the K valley. Ten k-points outside the K valley were used to describe the intervalley electron–phonon relaxation.

## ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b05048.

Fit parameters for intravalley electronic relaxation, calculation of the excess energies of the carriers, reconstructed transmission spectrum of the photoexcited MoS_{2} sample, sample characterization by resonant Raman spectroscopy, optical pump–probe cross-correlation, and fluence-dependence measurement results (PDF)