Monolayers of transition metal dichalcogenides (TMDs) have attracted much attention in current research due to their remarkable optical and electronic properties making them interesting nanomaterials for both fundamental science and technological applications [1–6]. As atomically thin materials, they show a reduced screening of the Coulomb potential resulting in an extraordinarily strong Coulomb interaction and the formation of tightly bound excitons [7–10]. Furthermore, they exhibit an efficient light-matter interaction giving rise to pronounced features in optical spectra [1, 4, 11, 12]. Very recently, the presence of dark exciton states, which are located energetically below the optically bright state, has been experimentally demonstrated [11–17]. A recent scanning tunneling spectroscopy study has revealed that monolayer WSe₂ exhibits an indirect electronic gap of approximately 80 meV below the direct gap [18]. So far, only one class of such dark states has been considered in literature, namely spin-forbidden states, where the Coulomb-bound electron and hole states have opposite spin [19, 20]. However, the formation of excitons is not limited to the same high-symmetry point in the Brillouin zone allowing for a different class of dark states with a non-zero center-of-mass momentum [21–25]. Since these momentum-forbidden intervalley dark excitonic states can lie below the optical bright excitons [23], exciton-phonon scattering into these states is highly efficient even at very low temperatures and determines the excitonic dephasing time and the homogeneous linewidth of these materials [23]. In contrast to the previously studied spin-forbidden dark states [26], they do not require a spin-flip and thus, exciton-phonon scattering into these states can occur on a femtosecond time scale. Furthermore, also the topological properties of the Bloch bands [27, 28] as well as the excitonic angular momentum quantum number [29] dictate the optical selection rules in two dimensional semiconductors.

Here, we present a sophisticated many-particle study of the time- and energy-resolved exciton dynamics in monolayer TMDs. In particular, we shed light on the phonon-assisted formation and thermalization of excitons as well as on their impact on the photolumi-
nescence yield. Besides the bright excitons, where the Coulomb bound electron and hole are both placed at the K valley, we also take into account dark excitonic states with a center-of-mass momentum exceeding the light cone. This includes intervalley dark excitons, where the hole lies at the K valley, while the electron is located either at the Λ, Λ′, or K′ valley, see figure 1. We find that first on a timescale of 100 fs a coherent exciton population is generated within the light cone decaying via radiative recombination and exciton-phonon scattering. Then on a sub-picosecond timescale, incoherent exciton populations in K–K, K–Λ, and K–K′ states are located at the Λ, Λ, and K point in the excitonic Brillouin zone that is characterized by the center-of-mass momentum Q. (b) Intra- and intervalley exciton–phonon scattering leads to thermalization of incoherent exciton populations. Excitons located within the light cone (blue shaded) can decay via radiative recombination Nrad resulting in photoluminescence. nα denotes the occupation of the involved phonon from the i = Γ, Λ, K, M point in the 1. BZ.

Figure 1. Exciton formation, thermalization, and luminescence. (a) After optically exciting a coherent exciton population P, incoherent excitons are formed in different valleys assisted by emission and absorption of phonons. We take into account intravalley excitons, where the Coulomb bound electron and hole are both placed at the K valley as well as intervalley excitons, where the hole lies at the K point, while the electron is either at the Λ, or K′ valley. The corresponding states denoted as K–K, K–Λ, and K–K′ excitons are located at the Γ, Λ, and K point in the excitonic Brillouin zone that is characterized by the center-of-mass momentum Q. (b) Intra- and intervalley exciton–phonon scattering leads to thermalization of incoherent exciton populations. Excitons located within the light cone (blue shaded) can decay via radiative recombination Nrad resulting in photoluminescence. nα denotes the occupation of the involved phonon from the i = Γ, Λ, K, M point in the 1. BZ.
After resonant optical excitation with a delta-shaped pulse, a coherent exciton occupation \( |P_0(t)|^2 \) at the \( \Gamma \) valley is formed with an approximately zero kinetic energy (energies are shown with respect to the corresponding valley minimum) at the exemplary temperature of 77 K for the (a) K–K, (b) K–A, and (c) K–K' excitonic states. Logarithmic time snapshots are shown in the insets and illustrate the exciton formation (increase of \( N_k^\mu(t) \) up to approximately 100 fs) followed by exciton thermalization on a picosecond timescale.

Figure 2. Exciton dynamics in WSe₂. Time-dependent incoherent exciton occupation \( N_k^\mu \) as a function of the excitonic kinetic energy (energies are shown with respect to the corresponding valley minimum) at the exemplary temperature of 77 K for the (a) K–K, (b) K–A, and (c) K–K' excitonic states. Logarithmic time snapshots are shown in the insets and illustrate the exciton formation (increase of \( N_k^\mu(t) \) up to approximately 100 fs) followed by exciton thermalization on a picosecond timescale.
phonon scattering within the excitonic decays due to radiative recombination and exciton–as into dark excitonic $K'$ resulting in a decay time in the range of tens of femtoseconds. This process is a conserved quantity provided that the radiative recombination is negligibly small. Figure 2 illustrates the time- and energy-dependent dynamics of the incoherent exciton occupations due to non-radiative phonon absorption is proportional to the Bose distribution $n_q^\mu$ with the phonon mode $\alpha$ and momentum $q$, this feature is less pronounced than the emission peaks that are proportional to $(1 + n_q^\mu)$. Note that the energetic position of these peaks does not exactly correspond to the phonon energy, since exciton thermalization sets in even before the exciton formation has been finalized. As a result, excitons relax to lower kinetic energies and scatter from there with phonons. The features characterizing the spectral distribution of the K–$K'$ exciton occupation can be explained in an analogous way.

After the characteristic phonon-induced formation time of approximately 100 fs, thermalization of incoherent exciton occupations takes over and determines the dynamics of excitons. The generated hot K–K, K–$\Lambda$, and K–$K'$ excitons scatter towards the energetically lowest states. This process is again driven by phonon-assisted scattering to dark intra- and inter-valley excitonic states. The steady-state exciton occupations correspond to degenerate Bose–Einstein distributions.

To further study the thermalization dynamics, we determine the temporal evolution of exciton densities $N_\mu = \sum_q N_{\mu q}$ for different excitonic states $\mu = K–K, K–\Lambda, K–K'$ including the coherent exciton density $|P_0^\mu|^2$, see figure 3(a). Here, the center-of-mass momentum is restricted to the corresponding valley in the excitonic Brillouin zone, i.e. $Q \in (\Gamma, \Lambda, or K)$. We reveal a thermalization time of approximately 2 ps, after which the incoherent exciton occupations remain constant. Remarkably, the reached steady state occupation of K–K excitons is negligibly small. In contrast, the K–$\Lambda$ excitons show the largest density followed by K–$K'$ excitons, where $N_{K–\Lambda}$ is more than three times larger than $N_{K–K'}$. At first sight, this is surprising, since the energy separation between the K–$K'$ and the K–$\Lambda$ excitons is only about $\Delta E_{K\Lambda} = 3$ meV (figure...
excitons. However, since their occupation of the K point occurs three times in the Brillouin zone, while there is only one K' point. Furthermore, the K–K' exciton occupation is interestingly not mainly driven by the decay of the coherent exciton occupation \( |P_{0}|^2 \), but is rather formed indirectly through the exciton-phonon scattering with KA excitons (dashed line in figure 1(a)). This is due to the very efficient scattering of K–Λ to K–K' excitons assisted by acoustic and optical Λ phonons. We have also taken into account the dynamics of K–Λ' excitons. However, since their energy separation from the bright state is 130 meV in WSe\(_2\) and 150 meV in MoSe\(_2\), their impact on the dynamics is very small.

So far, we have discussed the exciton formation and thermalization for the exemplary TMD material WSe\(_2\) and at the exemplary temperature of 77 K. Our calculations reveal that at room temperature, the same qualitative behavior can be observed, see supplementary material. At the elevated temperature, the higher occupation of Λ and zone edge phonons leads to several additional features: First, the region for the formation of incoherent K–K excitons is larger reflecting the broader spectral width of the coherent exciton states. Second, the relaxation to lower energetic states, driven mainly by phonon emission, becomes faster due to the \( (1 + n_{\Lambda}'^2) \) dependence of the emission rates, which increase at enhanced phonon occupations. Third, the thermalized exciton distribution becomes broader, which is consistent to expectations from a simple free Bose gas, where the width of the Bose distribution is given by the thermal energy \( kT \).

Furthermore, the exciton dynamics in MoSe\(_2\) turns out to be qualitatively different, see figure 3(b) (and the supplementary material for the time- and energy-dependent dynamics of exciton occupations). Here, most excitons are formed in the K–K states via scattering with optical and acoustic Λ phonons. In contrast to tungsten-based TMDs [23, 42], the K–K excitons are energetically lowest states in MoSe\(_2\). Here, the K–Λ excitons are located approximately 130 meV higher in energy. As a result, the steady state density of K–Λ excitons is rather small, since these exciton states are only accessible with multiple phonon scattering events. However, we find a relatively large incoherent K–K' exciton occupation, since the K–K' excitons lie only approximately 7 meV above the K–K excitons enabling more phonon-induced scattering channels. In both tungsten- and molybdenum-based TMDs, the total density of created incoherent excitons is lower than the optically induced coherent exciton density. The reason lies in the radiative decay of the coherent excitons that takes part at the same time as the formation of incoherent excitons and is therefore in direct competition with this process. At lower temperatures, the radiative recombination becomes the dominant channel drastically reducing the efficiency of the formation of incoherent excitons.

Having determined the dynamics of coherent and incoherent excitons, we can now investigate the temporal evolution of the light emitted from TMDs. The total photoluminescence is given by both coherent \( |P_{0}|^2 \) and incoherent excitons \( N_{\text{rad}} = \sum_{Q < K} N_{Q} \) within the light cone, see equation (2). We reveal that at 77 K and for times shorter than approximately 1 ps the photoluminescence in WSe\(_2\) is dominated by coherent light emission exceeding the incoherent contribution by orders of magnitude, see figure 4(a) (note the logarithmic scale of the y axis). This is in line with the calculated exciton densities in figure 3. The coherent part of the luminescence decays rapidly on a timescale of a few tens of femtoseconds. This excitonic coherence lifetime \( T_{2} \) is determined by the radiative decay and phonon-induced dephasing of the excitonic polarization [23]. It is reduced from approximately 60 fs at 77 K to 30 fs at 300 K. This is due to a stronger exciton-phonon scattering at higher temperatures [23, 42]. For comparison, figure 4(b) shows the luminescence in MoSe\(_2\). Here, we find a dominant coherent emission up to 0.5 ps. The coherence lifetime is approximately 60 fs at 77 K and decreases to 15 fs at room temperature. This very short lifetime can be ascribed to the very efficient formation of incoherent K–K excitons via emission and absorption of acoustic and optical Λ phonons [23]. We find the radiative contribution to the \( T_{2} \) time in both materials to be around 200 fs (corresponding...
to a FWHM of 4 meV in linear spectroscopy, which is in excellent agreement with recent theoretical [43, 44] and experimental studies [45, 46].

The incoherent part of the photoluminescence decays on a much slower timescale of a few tens of nanoseconds and corresponds to the exciton radiative lifetime \( T_1 \). The reason for this slow decay is the complex interplay between radiative recombination and exciton-phonon scattering, see equation (2) in the supplementary material: first, phonon-driven thermalization of the incoherent exciton occupation \( N_Q \) takes place and is then followed by a radiative decay of incoherent excitons within the light cone \( N_{rad} \). Since now the incoherent excitons are not thermalized any more, exciton-phonon scattering again refills the empty states within the light cone. Following this mechanism on longer timescales, this leads to an effective decay of the total exciton occupation and thus to a decay of the exciton density within the light cone.

Now, we investigate the temperature dependence of the exciton radiative lifetime \( T_1 \) and the photoluminescence yield for WSe\(_2\) in direct comparison with MoSe\(_2\), see figure 5. We find an opposite temperature behavior for the two considered TMDs: For MoSe\(_2\) (WSe\(_2\)), the \( T_1 \) time increases (decreases) with temperature ranging from 210 ps (260 ms) at 50 K to 1.3 ns (33 ns) at 300 K, see figure 5(a). The increased \( T_1 \) in MoSe\(_2\) can be traced back to the reduced exciton density within the light cone at elevated temperatures resulting in a less efficient radiative decay and thus a longer exciton lifetime. In the case of WSe\(_2\), the situation is different, since the energetically lowest states are dark. Thus, higher temperatures are favorable for filling up the bright states within the light cone resulting in a faster radiative coupling and a shorter \( T_1 \) time. Note that we focus here on intrinsic exciton properties in the low excitation regime neglecting non-radiative relaxation or defect-assisted exciton recombination channels. In many experimentally accessible situations, the relaxation of the exciton occupation will be much faster than the radiative recombination rates [11, 13, 47], and therefore the predicted intrinsic \( T_1 \) time has not been measured yet. Recent experimental studies have determined that non-radiative decay by exciton–exciton annihilation becomes important for exciton density above \( 10^{12} \) cm\(^{-2} \) [48, 49]. This presents the limiting range for our calculations, which are valid in the weak excitation limit.

The yield of the luminescence is defined as the ratio of the time-integrated luminescence intensity to the number of optically generated excitons. Assuming comparable non-radiative recombination channels for all excitons, we estimate the luminescence yield by the ratio between the density of bright excitons \( N_{bright} \) and all generated excitons \( N_{all} \). Our calculations reveal that interestingly the yield in WSe\(_2\) increases with temperature figure 5—in contrast to the behavior of conventional semiconductors. This can be directly attributed to the existence of energetically lower lying dark excitonic states in tungsten-based TMDs [23, 42]. While at low temperatures, most excitons are located at the K–\( \Lambda \) states (figure 3(a)), at enhanced temperatures more and more excitons are occupying the bright states within the light cone increasing the efficiency for photoemission. In contrast, in MoSe\(_2\), where bright states are the energetically lowest, the luminescence yield exhibits the temperature dependence expected from conventional materials, i.e. a decreased luminescence yield at higher temperatures. Since the exciton distribution generally becomes broader at elevated temperatures, the occupation of the bright states becomes smaller reducing the luminescence yield. Our findings are in excellent agreement with recent experimental studies [11–13]. The observed opposite behavior of WSe\(_2\) and MoSe\(_2\) is the remarkable consequence of an extraordinary exciton landscape in TMD materials. Note that for samples at elevated excitation densities, the dark relaxation rate could exhibit an additional temperature dependence [13, 47], which would require a more careful analysis of the luminescence yield. Exemplarily, the decay constant \( T_1 \) was found to decrease as a function of temperature in MoSe\(_2\) in a recent study [47], which is the inverse behavior to the radiative lifetime shown in figure 5(a). Such a decay would further decrease the emission at elevated temperatures and thus support the already observed temperature trend for the luminescence yield.
In conclusion, we have presented a microscopic study revealing time- and energy-resolved formation and thermalization of bright and dark excitons in monolayer transition metal dichalcogenides. Exploiting the gained insights, we shed light on many-particle processes behind the photoluminescence in two representative TMD materials. In particular, we demonstrate the presence of dark intervalley excitonic states that are located below optically accessible bright excitons in tungsten-based TMDs. In contrast to conventional semiconductors, these materials show an enhanced luminescence quantum yield and a reduced exciton lifetime at elevated temperatures.

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ORCID iDs

Malte Selig https://orcid.org/0000-0003-0022-412X
Marten Richter https://orcid.org/0000-0003-4160-1008
Rudolf Bratschitsch https://orcid.org/0000-0002-2368-2548

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