Photoluminescence Kinetics of Dark and Bright Excitons in Atomically Thin MoS$_2$

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The fine structure of the exciton spectrum, containing optically allowed (bright) and forbidden (dark) exciton states, determines the radiation efficiency in nanostructures. Time-resolved microphotoluminescence in MoS$_2$ monolayers (MLs) and bilayers (BLs), both unstrained and compressively strained, in a wide temperature range (10–300 K), is studied to distinguish between exciton states optically allowed and forbidden, both in spin and in momentum, as well as to estimate their characteristic decay times and contributions to the total radiation intensity. The decay times are found to either increase or decrease with increasing temperature, indicating the lowest bright or lowest dark state, respectively. The results unambiguously show that, in an unstrained ML, the spin-allowed state is the lowest for a series of A excitons (1.9 eV), with the dark state being <2 meV higher, and that the splitting energy can increase several times at compression. In contrast, in the indirect exciton series in BLs (1.5 eV), the spin-forbidden state is the lowest, being about 3 meV below the bright one. The strong effect of strain on the exciton spectrum can explain the large scatter among the published data and must be taken into account to realize the desired optical properties of 2D MoS$_2$.

1. Introduction

Atomically thin transition metal dichalcogenides (TMDs) such as MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$ have great potential for use in next-generation electronic and nanophotonic devices. They exhibit strong exciton oscillator strength, an enhanced luminescence quantum yield up to room temperature (RT), and interesting valley physics.$^{[1,2]}$ The key issue for realization of such benefits is the kinetics of radiative recombination,$^{[3]}$ which is controlled by the fine structure of the exciton spectrum comprising optically allowed (bright) and forbidden (dark) exciton states. The TMDs have a complex band structure that leads to the existence of both spin- and momentum-forbidden excitons. When optically dark states have lower energies than bright ones, this arrangement reduces the radiation efficiency,$^{[4]}$ which is critical for many applications.

As was first demonstrated for MoS$_2$$^{[5,6]}$ and later adopted for other TMDs, their monolayers (MLs) are direct-bandgap semiconductors, in which the lowest-energy optical transitions occur at the K± points of the Brillouin zone. In contrast, bulk, few-layer, and bilayer (BL) TMDs are indirect-gap semiconductors, in which the lowest-energy transitions occur between the top of the valence band at point Γ and the bottom of the conduction band, which is either at point K or at the midpoint Λ.$^{[7–10]}$ Recent research has challenged this simplistic picture. In particular, momentum-indirect nature of the optical bandgap is proposed for the MLs of MoS$_2$, WS$_2$, and WSe$_2$ based on the exciton dynamics$^{[11,12]}$ and resonant exciton–phonon scattering.$^{[13]}$ Thus, only the direct bandgap of MoSe$_2$ MLs is beyond doubt by now.

In an atomically thin layer, the transition of band structure type from direct to indirect can naturally occur when it is subjected to tensile or compressive deformation.$^{[14–19]}$ The direct bandgap in a MoS$_2$ ML is realized only in a quite narrow range of the lattice parameter deviation (ε) from the unstrained value (ε from −1.3% to 0.3%).$^{[17]}$ It should be noted that strong tensile strain arises when atomically thin TMD layers are encapsulated with hexagonal boron nitride (hBN), which is widely used to protect them from environmental influences and improve their optical properties.$^{[20,21]}$ In this case, direct–indirect crossover and a possible change in the energies of exciton states can complicate the interpretation of experimental data.

Strong resonances of A and B excitons, separated mainly due to spin–orbit splitting of the valence band and the influence of dielectric environment,$^{[22]}$ are well pronounced in the optical spectra of bulk, few-layer, and ML TMDs.$^{[5,8,23–25]}$ For a ML, fine structure of the exciton energy levels has been studied in detail using the methods of symmetry analysis.$^{[26–28]}$ In particular, the A exciton series is formed with the participation of a hole from

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the upper sub-band of the valence band and electrons from the two lowest sub-bands of the conduction band. It comprises the following excitons: bright (Γ_u), “gray” (Γ_d), which is an out-of-plane z-polarized state, and dark (Γ_f), representing an optically inactive linear combination orthogonal to Γ_u. The difference in energy between the Γ_u and Γ_f states is small, less than 1 meV[20]; therefore, with normal incidence of light on the ML, they are often collectively called “dark” (we will follow this simplification later). Several external factors may influence the fine structure of the exciton energy levels, among which strain is of particular interest.[10]

In general, the energy splitting Δ_AF between the allowed (A) and forbidden (F) excitons can have a different sign and magnitude, as it is determined by three contributions Δ_AF = Δ_M + Δ_b + Δ_es, where Δ_M denotes the single-particle spin splitting of the conduction band, Δ_b is related to the binding energy of an exciton, mainly controlled by the spin-orbit-induced splitting, and Δ_es is due to the exchange interaction between the electron and hole. These contributions can have the same or opposite signs; in the latter case, they partially compensate each other. It was predicted that the lowest-energy exciton state in Mo-based materials is bright due to the opposite signs of Δ_e and Δ_es. On the contrary, the lowest state for W-based materials is dark and the splitting value can be significant (several tens of meV) due to the same sign of these contributions.[11,12]

In contrast to a ML, a pristine MoS₂ BL, like other TMDs with an even number of layers, is characterized by the combination of the spatial inversion and time-reversal symmetry, which lifts off spin-orbit splitting. This constraint leads to the appearance of two spin-degenerate sub-bands in both conduction and valence bands.[33,34] The exciton states in the entire Brillouin zone should be spin degenerate to the extent that this is determined by the spin-orbit splitting. The degeneracy of the bands can be lifted in magnetic and electric fields or under other external influences that break the symmetry.[10,33,35] In particular, helicity-resolved magnetoreflectance experiments confirmed the degeneracy and elucidated the evolution of direct-bandgap K-excitons in MoS₂ BL.[36] Observation of two indirect transitions was conducted using temperature-dependent continuous wave (cw) photoluminescence (PL) but their exciton spectrum has not been clarified. The landscape of the exciton states in MoS₂ BLs is enriched with interlayer excitons, which include an electron and a hole located in different layers.[36,38]

Experimental confirmation of the theoretical prediction for the excitons in MLs was obtained by measuring the temperature dependence of the PL intensity, which shows the thermally activated contribution of the dark state to the radiation in WSe₂.[4,25] Polarization-resolved PL experiments with light propagating along a ML showed the bright-dark exciton splitting of 40 meV in WSe₂ and 55 meV in WS₂.[32] Brightening of the dark state in a magnetic field that mixes the electronic wave functions and thus makes the dark exciton states visible is a strong argument in favor of the theory’s predictions. This effect was repeatedly observed for the W-based MLs,[29,39,40] which made it possible to reliably establish their fine exciton spectrum.

In contrast to W-based materials, the experimental results on MoS₂ look rather contradictory. The PL temperature dependence, which is characteristic of the lower dark state, when the intensity increases with increasing temperature, was never observed in MoS₂ MLs.[44,45] Moreover, the temperature dependences for the hBN-encapsulated MoS₂ MLs showed that the dark trion state is 2 meV above the bright one,[42] and the neutral exciton states would likely have similar arrangement. These temperature PL dependences contradict the data of magneto-PL spectroscopy, which, in turn, are highly dispersive. Molas et al.[42] reported that the MoS₂ ML has a dark exciton ground state with a dark–bright exciton splitting energy of 98 meV. In a more recent work, the splitting energy in a ML encapsulated with hBN decreased significantly: in a transverse magnetic field, a dark exciton appeared 14 meV below the bright one under an in-plane magnetic field.[43] We emphasize that the main results and supporting information in the cited articles are very reliable; thus, additional factors must be sought that can provide such a huge spread.

Time-resolved (TR) PL (TRPL) spectroscopy can provide valuable information about exciton states in atomically thin materials. Currently, it is well established that the high oscillator strength of the direct exciton in MoS₂ MLs results in ultrafast radiative recombination with a characteristic time of few ps.[44,45] However, data on the radiative lifetimes of spin- and momentum-forbidden excitons in TMDs are scarce. It was predicted theoretically that the radiative decay of the dark excitons should be ≈100 times slower than that of the bright ones.[46] This agrees with the measured 110 ps radiative time of the out-of-plane exciton in WSe₂.[28] Measurements of differential transmission transients showed that the carrier lifetime increases rapidly from ≈50 ps in a ML to 1 ns in ten layers of MoS₂,[47] which may reflect the contribution of momentum-forbidden transitions in multilayer indirect-gap structures. Even in a ML, the radiation window inside the light cone is very narrow in TMDs, and excitons leaving the window must also have a long decay time, as they are indirect in momentum. It should be noted that the time domains, in which previous TRPL measurements were carried out, might not be wide enough to correctly determine the long decay time characteristic of various dark states. Thus, the TRPL method must be adapted to analyze the rich landscape of excitons in TMDs.

In this article, we present experimental evidences that the spin-allowed bright exciton is the lowest in the series of A excitons in MoS₂ MLs and BLs that are unstrained or under compressive strain; on the contrary, the spin-forbidden exciton is the lowest in the momentum-indirect exciton series (1.5 eV) in BLs. This conclusion is based on detailed time-resolved micro-PL measurements in a wide temperature range (10–300 K) and in an extended time domain (25 ns) of samples on planar and patterned substrates, in which the strain values were determined using a micro-Raman study. The temperature dependencies of characteristic PL decay times, which we assigned to the spin-allowed, spin-forbidden, and momentum-forbidden excitons, are nonmonotonic; they begin either to increase or decrease at certain temperatures due to a change in the thermalized population of the upper state. This behavior makes it possible to estimate the sign of the bright–dark exciton splitting (negative when the dark is upper) and its magnitude. These estimates are additionally confirmed by the temperature-dependent contribution of the corresponding component to the integrated emission intensity. The splitting energy of A excitons in unstrained
samples turns out to be rather low (<2 meV); however, in structures subjected to compressive deformation, it increases several times. Our data unambiguously show a strong effect of strain not only on the band structure as a whole, but also on the fine spectrum of exciton states, which can explain the scatter of literature data on this matter.

2. Samples

Atomically thin MoS\(_2\) flakes were mechanically exfoliated from a bulk crystal and transferred either onto planar substrates, SiO\(_2\)/Si and Si\(_3\)N\(_4\)/Si, or onto a patterned Al\(_2\)O\(_3\) substrate with pyramids on their surface, as described in Section 7.1. Figure 1 shows optical images of the structures fabricated on the patterned (a) and planar (b) substrates. The regions of ML and BL thicknesses were determined by micro-Raman spectroscopy, described in Section 7.2. Focusing the laser beam into a spot with diameter <1 \(\mu\)m allows us to measure separately the regions of different thicknesses and to focus on the top of the pyramids and in inter-spaces between them.

A nonresonant Raman spectrum of high-quality MoS\(_2\) in the range of 50–500 cm\(^{-1}\) consists of two main lines usually referred to as E\(_{2g}\) (380 cm\(^{-1}\)) and A\(_{1g}\) (405 cm\(^{-1}\)) and an asymmetric 2LA peak (Figure 1c). The E\(_{2g}\) and A\(_{1g}\) lines correspond to the in-plane and out-of-plane vibrations of the S atoms, respectively, whereas the 2LA line is an overtone of the longitudinal acoustic mode. The difference between the E\(_{2g}\) and A\(_{1g}\) line positions is a well-known way of determining the number of layers. The typical \(\omega(\text{A}_{1g}) - \omega(\text{E}_{2g})\) frequency difference lies in the range of 18–20 cm\(^{-1}\) for ML\([51,54]\) and 21–22.3 cm\(^{-1}\) for BL\([51,54]\) MoS\(_2\). However, positions of these lines can be affected by different factors such as strain and doping.\([51,54]\) Thus, the most unambiguous way to distinguish between the ML and BL is to analyze the low-frequency part of the spectrum (0–50 cm\(^{-1}\)). In case of BL, the in-plane and out-of-plane motion of the MoS\(_2\) layers with respect to each other cause the appearance of shear (C, 23 cm\(^{-1}\)) and layer-breathing (LB, 40 cm\(^{-1}\)) modes, respectively.\([55]\) In the spectrum of ML MoS\(_2\) these lines are obviously absent due to the lack of the second layer.

Figure 1c shows typical Raman spectra measured in the different areas on the planar structures on the Si-based substrates. In the areas denoted as BL, the C and LB lines are present on their classical positions, and the frequency difference ranges from 21.7 cm\(^{-1}\) for MoS\(_2\) on Si\(_3\)N\(_4\)/Si to 22 cm\(^{-1}\) on SiO\(_2\)/Si. This allows us to unequivocally determine the BL areas. In other
spectra, the C and LB lines are absent in the low-frequency part, and the frequency difference $\omega(A_{1g}) - \omega(E_{2g})$ is 19.8 cm$^{-1}$ for MoS$_2$ on the planar substrate and 18.3 cm$^{-1}$ on the patterned substrate. This verifies that MoS$_2$ is a ML in corresponding areas. Analysis of the Raman mapping data (details of the analysis are described in the next section) obtained on MoS$_2$ MLs on the planar substrate shows that the areas under study are practically strain free (Figure 1d).

Micro-PL spectra are measured in ML and BL regions using cw excitation by a 532 nm line of Nd:YAG laser (Figure 1e). They are fully consistent with the published spectra of MoS$_2$ samples placed on different substrates. The peak of the A exciton dominates the spectra in the MLs, whereas the peak of the B exciton is markedly smaller. An additional peak associated with the indirect exciton IX appears at 1.5 eV in BLs. In the thicker parts of the flakes (three layers and more), this IX peak is shifted toward 1.3 eV. Thus, such measurement of PL spectra is an independent way to confirm our determination of the atomically thin regions.

3. Strain in Atomically Thin MoS$_2$

We conduct the combined micro-Raman and micro-PL measurements to analyze the strain in the structures under study. For our planar samples, the $E_{2g}$ and $A_{1g}$ modes are found at 384.3 and 404.4 cm$^{-1}$ in MLs, whereas for BLs, they are at 383.6 and 405.3 cm$^{-1}$. In the limits of experimental accuracy, these values are in good agreement with previously published data for structures with negligible strain and doping levels. Therefore, we assume our planar samples as strain and doping free and take these mode frequencies as references to determine the strain in MLs and BLs on the patterned substrate. The correlation analysis of the $A_{1g}$ and $E_{2g}$ line positions, that allows one to separate the strain and doping contributions to the shift of these lines, was conducted out using the Expressions (1) and (2) from the work of Kim et al. We used the Gruneisen parameters for the case of biaxial strain and electron density shift rates for ML and BL MoS$_2$ given in this article. By this analysis, we derived the values of carrier concentration and biaxial strain for each spectrum. For planar and patterned MLs and BLs, the estimated doping level varied in the range $2 \times 10^{12}$ cm$^{-2}$, which is low in comparison with the values that can provide a noticeable shift of the PL lines. According to the Raman mapping analysis, the scatter of the strain values for planar ML in the area of interest was negligible, $\varepsilon_{||} = (0 \pm 0.01)\%$, (see Figure 1d), and the same statement holds for BL (map not shown here).

The site-selective micro-Raman spectra of ML and BL measured in the pyramids and between them are shown in Figure 2, together with those of the reference planar samples. Previous experimental studies of the samples, strained mechanically, showed that the tensile strain provides a lower-energy shift of both $E_{2g}$ and $A_{1g}$ modes. For the more strain-sensitive $E_{2g}$ mode, the shift induced by the tensile deformation is about $5 \times 10^{-2}$ cm$^{-1}$ %$^{-1}$. Under compressive strain,
the modes are shifted to higher energy. The Raman data obtained in our experiments indicate that at the top of the pyramids, the MoS$_2$ ML is compressed by an average of 0.12% compared with the planar one, whereas the compressive strain in the BL is higher, about 0.28%. It is useful to compare these data with those obtained by similar Raman studies of the MoS$_2$ ML and BL, where the strain appears after hBN encapsulation. The derived strains are $-0.06\%$ and $-0.29\%$, respectively, being of the same order of magnitude, but with a negative sign due to tensile deformation. Thus, we can conclude that the strain is not caused by the lattice mismatch with a substrate, as in conventional semiconductor heterostructures, but rather by fabrication methods in both cases. A possible reason of the greater strain in the BLs is that the thicker the film, the more difficult it is for it to relax elastically.

With selective study of micro-PL in the tops and interspaces between the pyramids, we faced an intricate situation. Everywhere in the compressively strained regions, the energy of the PL peak was shifted to lower energy with respect to the planar strain-free structure. At RT with 532 nm line excitation, it was on average at 1.815 eV on the top of the pyramids, whereas on the flat substrate it was at 1.837 eV. There is also a difference between the regions suspended and contacted with the Al$_2$O$_3$ tops (Figure 2c,f), which is higher than what can be induced by a change in the dielectric environment. Note that these areas belong to the same flake, where the carrier concentration is uniform.

Generally speaking, a shift of the PL energy can occur due to modification of the band structure, which can be caused by both tensile and compressive strain. In a ML under tensile strain, the valence band at the $\Gamma$ point rises up, and the conduction band in the $K$ point shifts downward. As a result, the momentum-indirect transition $\Gamma K\Gamma$ turns out to be the lowest in energy. Under compression, the minimum of the conduction band is in the $\Lambda$ point, whereas the valence band at the $\Gamma$ point goes down, and the lowest-energy transition is $\Lambda K$. Thus, the MoS$_2$ ML is undoubt- edly a direct-gap semiconductor only within a rather narrow strain range, in which the PL line exhibits a linear redshift under tension and weaker blueshift under compression (Figure 3b). Outside this range, compressive deformation can lead to a decrease in the PL energy due to the admixture of the indirect AK transitions.

Theoretical studies predicted that such a decrease in the optical gap energy will take place at a compression deformation of about 1–2%. Although the research of the strain-induced tunability demonstrated the direct-to-indirect bandgap crossover at $\approx 0.3\%$ which is closer to our case. It should be noted that the behavior of emission in an atomically thin structure under compression is much less studied than for structures under tension, as there are many publications. This is because the compressive strain is more difficult to achieve experimentally. As far as we know, the only experiment was the study of trilayer MoS$_2$, located on a piezoelectric substrate, providing a compression of $\approx 0.2\%$. Neither MLs nor BLs were investigated experimentally under compression.

Among other factors influencing the PL spectra, there is the use of excitation above the bandgap, which increases the population of carriers in the upper valleys. This leads to a quasi-equilibrium carrier distribution instead of a nonequilibrium one in the K valleys with the quasiresonant 532 nm excitation. In a MoS$_2$ ML, such an excitation caused the blueshift of the PL peak by 30 meV relative to its position in the case of the quasiresonant excitation by a 532 nm laser line and suppression of the B exciton line. Similar effects are observed in our structures upon the 405 nm excitation. In addition, Steinhoff et al. demonstrated that the 532 nm excitation is more effective, because it provides a larger number of photoinduced carriers at the same excitation power.

In general, it can lead to a redshift of the emission. The combined action of these effects can explain the $\approx 40$ meV energy difference in our spectra measured in the same structure at different excitation wavelengths. As also shown in the study by Steinhoff et al. at the carrier concentration of $>10^{13} \text{cm}^{-2}$, the influence of strain on the band structure is more pronounced. However, this concentration is markedly higher than in our samples, and we can consider the strain effect alone. In particular, we expect that the strain can change the fine spectrum of excitons, namely, the energy splitting between the bright and dark states, similar to strain-induced tuning of quantum levels in quantum dots.

**4. Time-Resolved Micro-PL Studies**

The primary task of our research was to determine the splitting of dark and bright excitons in unstrained films. The width of the low-temperature line in our ML ($\approx 30 \text{meV}$) does not allow distinguishing the contributions of the dark and bright states, as the separation between them can be small. However, for temperature-dependent TRPL spectroscopy, it does not matter how close they are, as this method deals with the characteristic times of rapidly and slowly decaying components presumably associated with these states. Monitoring the changes in decay times with temperature makes it possible to clearly determine the sign of the splitting and approximately estimate its magnitude.

The time-resolved micro-PL studies of the MoS$_2$ samples on flat and patterned substrates were conducted using an ST-500 Attocube cryostat (Janis) supplied with a three-coordinate piezo-driver, which allows maintaining the position of the laser spot on a sample during long-term series of the measurements with an
However, we can track \( \text{www.pss-rapid.com} \) 0.22 ns, \( \text{fi} \) 15 orders of magnitude higher. Under such conditions, \( \text{cm} \) \( \mu \) 4 meV in MoS, The PL broadens that is markedly less than the intrinsic carrier con-

The vari-

74\[75\] \( \mu \) 0.01 substrate with cw excitation by a 532 nm line. c) The onset part of PL decay a) Temperature variation of the normalized PL spectra (vertically shifted for clarity) measured in a MoS

¼ 2 \( \mu \) 1.8 eV, is still under investigation. The lower-energy trion con-

struction is almost absent at 10

20 K; then it starts to increase,

increase in temperature from 10 to 300 K. Focusing through the cryostat window was done using a 50 \( \times \) Mitutoyo objective (numerical aperture (NA) = 0.42). Therefore, the signal was collected from a spot with a diameter of \( \approx \)4 \( \mu \) m that exceeds the distance between the pyramids. The 405 nm line of a pulsed laser was used for excitation to probe reliably the whole set of exciton transitions. In our TRPL experiments, the chosen average power of excitation was as low as \( \approx \)0.1 \( \mu \) W and a laser spot had a diameter of 3–5 \( \mu \) m; the minimal size corresponds to the average power density of \( \approx \)0.01 \( \mu \) W \( \mu \) m\(^{-2} \). This excludes the changes in spectra under laser exposure, which were observed at a power of 2–3 orders of magnitude higher.\[69\] Under such conditions, the estimated concentration of photoinduced carriers in a ML is \( \leq \text{10}^{10} \text{ cm}^{-2} \) that is markedly less than the intrinsic carrier concentration. Thus, the enhancement of trion formation due to photodoping is negligible. In our measurements, the spectral width of the filter window (10 nm) was chosen to record the predominantly exciton part (For more details, see Experimental Section).

Let us first consider the MLs placed on the different substrates. The temperature evolution of the spectra in the vicinity of the A exciton in the planar ML is shown in Figure 4a. We observe the redshift of \( \approx \text{50 meV} \) and broadening of the A exciton peak, similar to what was reported for other 2D TMDs.\[25,26,70\]

At low temperatures (LTs), this peak has shoulders at both sides. The nature of the higher-energy shoulder, probably related to excited states of localized excitons, whose band is situated at \( \approx \text{1.8 eV} \), is still under investigation. The lower-energy trion contribution is almost absent at 10–20 K; then it starts to increase, resulting in the broadening of the PL line. We assume that this effect can be associated with the temperature-induced escape of the carriers from weakly localizing sites. The disappearance of the broad peak of localized excitons, LX, is consistent with this assumption. The enhanced concentration of free carriers promotes the formation of trions above 20 K. Remarkably, the neutral exciton line survives up to RT due to giant oscillator strength, whereas the trion dissociates at \( \approx \text{100 K} \), as in other TMD structures with the modest carrier densities of \( \approx \text{10}^{12} \text{ cm}^{-2} \).[72–74]

To confirm the correct assignment of the emission features, we show in Figure 5a the deconvolution of PL spectra measured at different temperatures. The separation between the exciton and trion components perfectly corresponds to the commonly accepted trion binding energy of \( \approx \text{30 meV} \) in MoS.\[42\] The variation of spectra with increasing power is shown in Figure 5b. The intensity of the exciton emission rises linearly, whereas for the trion it increases superlinearly.\[73\] The PL broadens and shifts toward the position of the trion when the photoinduced carrier density is increased with increasing power. In Figure 5c, the A exciton resonance in a reflectivity spectrum perfectly correlates with the main peak in the PL spectrum. The resonance of trions is not pronounced due to their full dissociation at RT. We reject the localized exciton emission as the origin of the dominating peak, because the localized exciton should inevitably quench with increasing temperature via interaction with phonons.\[70,76\]

In the ML on the patterned substrate, the A exciton peak has an average width of 60 meV at 10 K. The quenching of its intensity is not monotonic (Figure 4b). The inset in Figure 4c shows that it is redshifted in energy compared with the planar ML PL. In addition, we observe the suppression of the B exciton line with the nonresonant 405 nm excitation, predicted in the study by Steinhoff et al.\[67\] Strong difference is observed in the decay curves measured in the A peak of these two samples: the slowly decaying component appears in the ML on the patterned substrate, whereas it is absent in the planar ML.

The time resolution of the used system, \( \tau_{\text{b}} \), was about 50 ps; thus, we were unable to resolve the very short radiative time of the A exciton, which is only few ps.\[3,44,45\] However, we can track the peak amplitude immediately after excitation, which gives us information on how the fast component changes with temperature. To take into account the instrumental function, we simulate this sharp peak by two rising (r) and decaying (d) exponents with

Figure 4. a) Temperature variation of the normalized PL spectra (vertically shifted for clarity) measured in a MoS2 ML on a planar SiO2/Si substrate using 405 nm pulsed excitation with a power density of 6 W cm\(^{-2} \). A and T denote the A exciton and trion, LX: localized exciton. b) Temperature dependencies of the energy and intensity of the PL peak recorded in a ML on a patterned Al2O3 substrate with cw excitation by a 532 nm line. c) The onset part of PL decay curves (black lines) in the MLs placed on different substrates measured at 10 K at 6 W cm\(^{-2} \). The color lines present a fitting with decay times as follows: MoS2/SiO2: \( \tau_{2} = 0.22 \text{ ns}, \tau_{3} = 0 \); MoS2/Al2O3: \( \tau_{2} = 0.22 \text{ ns}, \tau_{3} = 3.1 \text{ ns} \). The inset shows a spectrum recorded at 10 K in the patterned sample during this TRPL measurement.
the same amplitude \( A_1 \) and characteristic times \( t_{1,d} \approx t_0/2 \), as
\( A_1 \cdot (\exp(-t/t_1^d) - \exp(-t/t_1^d)) \), where \( t_1^d \) was slightly longer than \( t_1 \).

The integral intensity of this rapidly decaying contribution is assumed to be \( t_1 \approx A_1 \cdot t_1 \). To model the rest, we used two exponents with middle, \( t_2 \), and slow, \( t_3 \), decay times. We also accounted a background contribution, which was extremely slow at every temperature, by subtracting that as a constant. Thus, the change in the total intensity with temperature is given by the expression \( \text{Sum} = A_1 \cdot t_1 + A_2 \cdot t_2 + A_3 \cdot t_3 \), and the contribution of a particular component is equal to \( A_1 \cdot t_1/\text{Sum} \).

Modeling the decay curves measured at different temperatures in MLs on planar and patterned substrates gives the results shown in Figure 6. In the unstrained ML on SiO\(_2\)/Si, the slow component characterized by time \( t_3 \) is absent. In contrast, it exists in the strained ML on the Al\(_2\)O\(_3\) substrate. For us, this is a weighty argument in favor of assigning the time \( t_3 \) to the momentum-indirect transitions, which can be realized in strained structures. Components with the intermediate decay time \( t_2 \) exist in both samples, although demonstrating different variations with temperature. In previous studies of 2D TMDs, the lifetime of 0.1–0.3 ns was associated with either neutral or charged dark excitons.\(^{[29,77]}\) As the emission of trions is cut by the interference filters, we can regard \( t_2 \) as the characteristic time of spin-forbidden dark exciton states, observed up to RT.

In both MoS\(_2\) MLs under study, the characteristic times \( t_2 \) and \( t_3 \) increase with a temperature rise. At LTs (<100 K), it can be interpreted in terms of an increase in the population of dark states as observed in various nanostructures.\(^{[18,78–81]}\) In the first approximation, the longer characteristic time \( t_2 \) in each doublet, comprising optically allowed and forbidden by spin or momentum states, can be described via their recombination rate at LT\(^{[79]}\):

\[
\tau_{2}^{-1} = (\Gamma_A + \Gamma_B)/2 - [(\Gamma_A - \Gamma_B)/2] \cdot \tanh(\Delta E/(2k_BT))
\]

where \( k_B \) is the Boltzmann constant, \( T \) is temperature, \( \Gamma_A \) and \( \Gamma_B \) are the respective recombination rates of the allowed and forbidden states, and \( \Delta E \) is the energy of acoustic phonons, which matches the dark–bright exciton splitting \( \Delta_{AB} \) (here, it is assumed that thermalization of exciton states is via the interaction with the phonons). When \( k_BT > \Delta E \), the second term in Equation (1) decreases, and the recombination rate tends to the half-sum of \( \Gamma_A \) and \( \Gamma_B \) at LT. Accordingly, \( \tau_2 \) will increase when the bright exciton is the lowest state, possessing a high recombination rate; and decrease when the lowest state is dark. The temperature value corresponding to a threshold change in the populations of states can be used to estimate the splitting of bright and dark excitons, assuming \( \Delta_{AF} = E_A - E_F \approx k_BT \), whereas its sign will be determined either by an increase (“–”) or decrease (“+”) in \( \tau_1 \).

In the unstrained structure, the sharp increase in the time \( t_2 \) at 10–20 K (Figure 6a) corresponds to small value \( \Delta_{AF} \) of \( \approx (1–2) \) meV with the bright exciton being the lowest. There is some uncertainty in determining the absolute value of this splitting due to the relatively small distance between the dark and bright states, but the slope of the temperature dependence of \( t_2 \) undoubtedly indicates their mutual arrangement. An additional argument for confirmation of the above assumption is the dominant contribution of the fast component to the total intensity over the entire temperature range (Figure 6b). A similar picture is also observed for the direct A exciton in a BL on a planar substrate (not shown here).

The strain in the ML on the patterned substrate causes pronounced changes (Figure 6c.d). The temperature dependence of the \( t_2 \) value has two distinct kinks near 30–50 K and around 100 K. As the contribution \( A_1 \cdot t_1 \) dominates not up to 100 K, but only up to 50 K, when the \( A_2 \cdot t_2 \) component begins to rise, we accept \( \Delta_{AF} \approx (1–4) \) meV. Although the relative contribution of the \( A_1 \cdot t_1 \) component to the sum intensity rapidly decreases due to the increase in \( A_2 \cdot t_2 \) and \( A_3 \cdot t_3 \) components, its absolute value is stable up to \( \approx 100 \) K, which indicates the neglecting non-radiative process in the temperature range of 10–100 K. The observed increase in \( t_3 \) and \( A_3 \cdot t_3 \) can be associated with a direct–indirect crossover of the bandgaps in MLs, similar to that observed in a multilayer structure.\(^{[83]}\) It means that the energy difference between the transitions K–K and K–A is decreased under compressive strain. At higher temperatures, the momentum-indirect excitons which are out of the light cone can also contribute to the slow radiation.

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*Figure 5.* a) PL spectra of the MoS\(_2\)/SiO\(_2\) ML, measured at the same place at different temperatures during the TRPL studies, shown together with their deconvolution over two Lorentzians. b) Low-temperature PL spectra measured at this place at different excitation powers (\( P_0 = 100 \) nW, excitation: 405 nm, filter window: 10 nm). c) Spectra of differential reflectivity and PL measured at RT in the same MoS\(_2\) ML.
A completely different picture is observed in radiation kinetics of a highly stressed BL on a patterned substrate (Figure 7). This more complex system initially includes both direct and indirect, IX, excitons. With increasing temperature, the slow component in the PL decay curves increases for the A exciton and disappears for IX. The modeling shows that, in contrast to the ML on the same patterned substrate, variation of $t_2$ and $t_3$ for the A exciton transition is opposite with the temperature.
rise: \(t_2\) increases, whereas \(t_3\) decreases. The onset of the \(t_2\) rise occurs at \(\approx 100\) K that corresponds to \(\Delta_{AF} \approx -8\) meV with the lowest bright exciton. At the same time, the \(t_3\) value gradually decreases from 6.3 ns to 4.5 ns starting from 30 to 40 K. For the indirect IX transition, both \(t_2\) and \(t_3\) times decrease. It should be noted that for the reference BL on the planar substrate (not shown here), no variation in \(t_2\) times with temperature was observed (\(\Delta_{AF} = 0\)), which is in good agreement with the predicted degeneracy of the conduction band due to even number of MLs.

As the temperature rises, the contribution of the fast \(A_1\cdot t_1\) component of the A exciton dominates the total radiation intensity up to 175 K, when the combined action of the slower components begins to prevail and the nonradiative recombination is activated. On the contrary, for an indirect IX exciton (Figure 8), a noticeable contribution of the \(A_1\cdot t_1\) component appears at high temperatures, when an approximately twofold decrease in both \(t_2\) and \(t_3\) leads to a decrease in their contributions to the total intensity. In a planar BL, the indirect IX transition also shows a decrease in both \(t_2\) and \(t_3\), starting at 30 K. The much weaker component \(A_1\cdot t_1\) slightly increases at this temperature (\(\Delta_{AF} < 2\) eV). Based on these data, the spin-forbidden state is assigned as the lowest in the indirect exciton series (1.5 eV) in both strained and unstrained BLs.

5. Discussion

In this work, we analyze the mutual arrangement of the dark and bright excitons in the MoS\(_2\) ML and BL, which are either not strained or are subjected to compressive strain. The schematic of the possible states is shown in Figure 9, which includes the spin- and momentum-forbidden excitons of different valleys. According to DFT calculations,\(^{10}\) there are two notable exciton series, \(K - K\) and \(\Lambda - K\), for the ML and three, \(K - K\), \(\Lambda - \Gamma\), and \(\Lambda - K\), for BL. Under strain, one should expect changes in energies of these series and in the exciton splitting inside them.

We consider the results of the temperature-dependent TRPL using a simplified model for a system containing dark and bright states, assuming that when the dark exciton is at the top, the values of decay time constants increase with increasing temperature; if it is the lowest, the time is shortened.\(^{79,83}\) The temperature when the states begin to thermalize allows to estimate approximately the dark–bright energy splitting.

![Figure 8](https://www.advancedsciencenews.com/)

**Figure 8.** a,c) Characteristic decay times \(t_2\) and \(t_3\) derived for the A exciton (a) and the indirect IX exciton (c) transitions in the BL on the patterned substrate; b,d) the relative contributions of the fast \(A_1\cdot t_1\) (black squares), middle \(A_1\cdot t_2\) (red diamonds), and slow \(A_1\cdot t_3\) (blue triangles) components to the total radiation for these transitions in the BL. The lines are guides for the eyes.
In addition, we take into account the weights of components with different decay times in the total PL intensity. When the fast component dominates over the whole temperature range, it is a signature of the ground bright state. In the case of MoS$_2$ MLs, this combined approach gives a distinct result: the bright exciton is the lowest and the bright–dark splitting energy does not exceed 2 meV when the strain is absent. This result is in accordance with many theoretical predictions (see references in the study by Durnev et al.$^{[27]}$) and previously reported PL intensity dependencies on temperature.$^{[4,41]}$ The dependences for the K–K exciton in a planar BL, in which no splitting was found, fully agree with the predicted degeneracy of the conduction and valence bands for the structure with even number of MLs.$^{[10,33,34]}$ These findings confirm the validity of our approach.

The feature of 2D TMDs is the very high recombination rate of the bright K–K exciton, which can efficiently recombine even when the dark state is the lowest.$^{[29,43]}$ This makes questionable achieving the full thermal equilibrium in the exciton series. Conditions for that in TMD MLs were analyzed by Zhang et al.$^{[4]}$ They showed that the characteristic time of exciton thermalization is within the timescale of tens of picoseconds that is relevant for our measurements. The rapid radiative decay might result in certain depletion of the exciton population within the radiative cone. However, these exciton states constitute only a relatively small fraction of all excitons for the temperature range of interest and the overall exciton energy distribution should remain largely thermal despite the rapid decay within the radiative cone.

Temperature-dependent nonradiative recombination can also affect the exciton dynamics. To evaluate its impact, we examined the temperature variation of the fast component $A_{1T1}$ of the K–K exciton. In the temperature range of interest to us (10–100 K), where bending and an increase in temperature dependences are observed, the intensity of this component is practically constant in the planar ML and in the BL. This means that the internal quantum efficiency in this temperature range is high enough, and nonradiative channels do not significantly affect our results.

In patterned samples, after 100 K, the $A_{1T1}$ intensity decreases more strongly than in the planar samples. Possibly, providing compressive strain in structures above an Al$_2$O$_3$ pyramid leads to the generation of some additional defects that serve as centers of nonradiative recombination.

Another important factor is the influence of excitons outside the light cone, which need the help of phonons to recombine. It was previously shown that the presence of such states in TMDs can increase the emission time from several ps to 1 ns.$^{[4]}$ However, most of the integral PL intensity in the planar structures is due to the fastest component, the decay time constant of which does not change within the time resolution of $\approx$50 ps in our setup over the entire temperature range. A similar behavior was previously observed in MoS$_2$ MLs by Lagarde et al.$^{[44]}$

It can be assumed that the contribution of the out-of-cone excitons was unreasonably assigned by us to the slowest momentum-indirect component, which increases with temperature. However, it cannot explain the fast times of the dominant component of the emission, which persist up to high temperatures. Additional research is needed to elucidate this inconsistency.

To find out how strain affects the spectrum of the exciton states, we realize compression in the layers under study in an original way—by placing a film on a patterned substrate with pyramids. The results of the TRPL studies of such structures clearly demonstrate that the state ordering in the A exciton series is the same (the bright is the lowest) but the $\Delta_{AF}$ value can increase several times. Importantly, the arrangement of spin-allowed and spin-forbidden states is opposite in the BL for an indirect exciton transition at 1.5 eV, where the spin-forbidden dark exciton is the lowest and the splitting energy is $\approx$3 meV. This excludes, as a significant factor, the temperature change in the lattice parameter of the substrate,$^{[62]}$ which should provide similar effect in a ML and BL. Note that such arrangement with the lowest spin-forbidden state in the indirect transition series was previously proposed for multilayer MoS$_2$ structures.

Figure 9. a–d) Exciton states in unstrained (a,b) and compressively strained (c,d) MLs and BLs. Without strain, the ordering of exciton states is shown in accordance with the study by Ruiz-Tijerina et al.$^{[10]}$ The K–K exciton states are shown for the K+ (allowed states spin-up). The bright and dark states are shown by the red and blue lines; the gray lines mark A–K states with unknown excitons. The vertical arrows indicate radiative transitions.
based on the temperature dependencies of the 1.3 eV radiation.\textsuperscript{[24–30]}

The proposed band structure variation under strain is in good agreement with the TRPL data. In particular, the absence of the slowly decaying PL component (with time \( t_3 \)) in the radiation at the A exciton energy in unstrained MLs indicates that the momentum-indirect transition is impossible here. Its appearance under compression reflects a transformation of the band structure when the \( \Lambda \rightarrow K \) exciton turns out to be very close to the \( K \rightarrow K \) one (compare Figure 8a,c). Analogous to the splitting \( \Delta_{AF} \) of the spin-allowed and spin-forbidden exciton states, this crossover can be characterized as a direct–indirect energy splitting \( \Delta_{fi} \) \((E_0 - E_i \text{ in Figure 3a})\), which is about 4 meV in our samples. In the highly strained BL, which already has the momentum-indirect \( K \rightarrow \Gamma \) transitions at 1.5 eV, the similar transformation is hardly possible for the scheme shown in Figure 9d. It explains the different dependencies of the contributions to the integral intensities shown in Figure 6d and 8d.

We emphasize that some contribution of the trion emission, if any exists, cannot explain the increasing dependencies of the characteristic decay times measured in our samples (see Figure 6). The characteristic decay time of the trions in a TMD ML is close to that of a neutral exciton.\textsuperscript{[84]} When the trion decay time is a bit longer,\textsuperscript{[24]} it rapidly decreases to the exciton value with increasing temperature due to the rapid dissociation of the trion.

Fine structure of the trion states in 2D systems was analyzed in several papers.\textsuperscript{[85–87]} In general, the trions heritage the symmetry properties of the neutral excitons. In the paper by Arora et al.,\textsuperscript{[42]} it was found that the dark trion is \( 2 \pm 3 \) meV above the bright trion in MoS\textsubscript{2}/hBN on sapphire substrate that is consistent rather with our results than with the data of magneto-spectroscopy reported by Robert et al.\textsuperscript{[43]}

It should be noted that we consider the characteristics of the exciton states driven by spin or momentum separately. Such an approximation allows us to outline the variation range of parameters required for a more sophisticated model. Some important data derived from the conducted experiments are shown in Table 1. In addition, we shown in Table 1 the latest literature data on the bright–dark exciton-splitting energy in the hBN-encapsulated MoS\textsubscript{2} ML obtained by magneto-PL spectroscopy.\textsuperscript{[43]}

According to the results presented in the study by Han et al.,\textsuperscript{[20]} the encapsulated ML should undergo tensile strain, whose absolute magnitude \( |\epsilon| \) is almost the same as in our structures under compression. It is noteworthy that in the MoS\textsubscript{2}/hBN the magnitude of \( \Delta_{AF} \approx 14 \) meV is of the same order as in our samples, but the sign of \( \Delta_{AF} \) is opposite, that is, the dark exciton is the lowest. Assuming a linear dependence of \( \Delta_{AF} \) on the \( |\epsilon| \) value, we can conclude that deformation of the opposite sign can give a similar effect in terms of the magnitude of its impact but will shift the exciton levels in opposite directions. This phenomenon arises likely due to the complex nature of the spin–orbit coupling, the two components of which, associated with chalcogen and metal orbitals, almost cancel each other in unstrained 2D MoS\textsubscript{2},\textsuperscript{[88]} while strain can disturb this delicate balance. We believe that the possible dependence of the dark–bright exciton splitting on strain can explain the huge dispersion of the data on the fine exciton spectrum in 2D MoS\textsubscript{2}, published in literature.\textsuperscript{[4,41–43]}

It can also be noted that the characteristic lifetimes for dark excitons are not as long as in quantum dots or in epitaxial 2D GaN/AlN systems,\textsuperscript{[48,83]} where they can approach tens and hundreds of ns at LTs. This fact, which is probably associated with the different energy splitting between the dark and bright excitons, along with the strong oscillator strength in the TMDs, requires a comprehensive study along with the dependence of the fine spectrum of the exciton states on strain.

6. Conclusion

We carried out time-resolved micro-PL measurements in atomically thin MoS\textsubscript{2} films transferred to different substrates, which create different strains inside them. The main results of this work are the elucidation of the fine exciton spectrum and the discovery of its dependence on strain. The change of fast, intermediate, and slow decaying components with temperature, their characteristic times, and contributions to the total radiation makes it possible to estimate the spin-allowed–forbidden splitting \( \Delta_{AF} \) and assume the existence of transitions indirect in momenta near the A exciton energy due to the strain-induced modification of the band structure. Our findings clearly show that the bright exciton in the A exciton series (1.9 eV) is the lowest in both the unstrained ML and BL, and the splitting energy does not exceed 2 meV. The splitting is almost equal to zero in the unstrained BL due to constraints associated with the symmetry of an even number of MLs. It is also shown that the bright–dark exciton splitting value increases several times with increasing compressive strain. On the contrary, the dark exciton is the lowest in the indirect exciton series (1.5 eV) in BLs. Such an arrangement in the BL leads to an additional decrease in the light emission intensity for this indirect transition in the system with two competing channels of recombination. We have determined the decay time constants characteristic of the emission of spin- and momentum-forbidden states; at LTs, they are in the range (0.2–0.4) ns and (6–7) ns, respectively. The observed trends in variation of the fine exciton spectrum upon strain allow us to suggest that the sign of splitting could be opposite with tensile deformation. We underline that we have used a simplified approach, taking into account only the basic channels of recombination. To refine the results obtained, it is necessary to consider other...
factors, for example, nonradiative recombination and the contribution of excitons which occur out of the light cone. We hope that our results will stimulate studies using angular-resolved PL spectroscopy and magneto-PL of structures under different strains. This work demonstrates that the effect of strain must be taken into account to obtain the desired optical properties in atomically thin TMD nanostructures.

7. Methods

Sample Preparation: Atomically thin MoS$_2$ flakes were mechanically exfoliated from the bulk crystal (production of HQ Graphene) and transferred by dry viscoelastic stamping using a commercial HQ Graphene 2D transfer system at the Ioffe Institute and homemade one at TU Ilmenau. To form planar structures, the flakes were positioned on a SiO$_2$/Si substrate or a Si$_3$N$_4$/Si one. The surface roughness of both MoS$_2$/SiO$_2$ and substrate was around 0.3 nm. We emphasize that this level of substrate roughness was optimal for our study. Atomically thin layers lay freely, without tight contact with the substrate. As a result, the strains in our planar samples were close to zero. Sapphire substrates with pyramids on their surface were used to create stress in the flakes suspended from the tops of the pyramids. To realize the adhesion between the flakes and the substrate, the MoS$_2$ flakes attached to the Gel-Pak PF X4 polymer film came into contact with the substrate, whereas the glass holder was tilted at a small angle of 1–2° with respect to the substrate. When full contact was achieved between the flake and the substrate, the holder was moved a few micrometers in the $x$-direction and then slowly lifted in the $z$-direction. This procedure made it possible to obtain a uniform film of a suitable size—more than 10 $\mu$m$^2$ for ML and BL regions. Based on the dependencies reported by Amani et al., we concluded from the optical characterization that internal quantum yield in our structures was not less than 1%.

Micro-Raman and cw Micro-PL measurements: Micro-Raman measurements were carried out using a Horiba Jobin Yvon T64000 spectrometer with 1800 g mm$^{-1}$ diffraction grating. At RT, the laser beam ($\lambda = 532$ nm) incident normally to the surface was focused by Olympus MPLN 100$\times$ (NA = 0.9) objective into a spot with a diameter of less than 1 $\mu$m. To suppress the Rayleigh scattering and obtain information from the low-frequency ($5–50$ cm$^{-1}$) range, a set of BraggGrate optical filters was used. Micro-PL measurements at cw excitation were carried out on the same spectrometer using a 600 $\mu$m$^{-1}$ grating. For low-temperature measurements, a Linkam THMS600 temperature-controlled microscope stage and a long-working-distance Leica PL FLUOTAR 50$\times$ (NA = 0.55) objective were used. To avoid laser-induced modification of the MoS$_2$ films, the laser power was limited to 400 $\mu$W.

Micro-PL Measurements with Temporal Resolution (micro-TRPL): The micro-PL spectra and PL decay curves of MoS$_2$ samples were measured at temperatures ranging from 8–10 K to 300 K using the ST-500-Attocube cryostat (Janis) supplied with a temperature controller. The sample was adjusted with an accuracy of about $\approx 20$ nm, using a three-coordinate piezodriver located directly in the cold zone of the cryostat. This provided mechanical stability and vibration isolation during prolonged temperature-dependent measurements. PL excitation was conducted by focusing laser radiation on a sample with a minimum spot size of the order of 3–5 $\mu$m. Focusing was achieved by introducing laser radiation into an objective (Mitutoyo plan apochromat with 50$\times$ magnification, NA = 0.42, and focal length: 4 mm), which was also used to collect PL radiation. The PL radiation transmitted through the objective was focused by a triplet achromatic lens in the plane of the mirror with a calibrated aperture (Pinhole) with a diameter of 200 $\mu$m. Due to the magnification of the objective, this aperture corresponded to a resolution of $\approx 4$ $\mu$m. The PL radiation passed through the aperture was collected and focused onto the entrance slit of an SP-2500 spectrometer (Princeton Instruments) with a grating 600 g mm$^{-1}$ using two triplet achromatic lenses. For additional blocking of laser radiation scattered on the sample surface and/or optical elements, a bandpass interference filter was used. A cooled PyLoN CCD (Princeton Instruments) was used as a PL detector in the spectrometer. To measure the micro-TRPL spectra in this work, we used a picosecond pulsed semiconductor laser PILAS 405 nm (Advanced Laser Systems) with the average excitation power of 100 nW measured before the cryostat window. A single-photon avalanche photodiode (SPAD) PDM 100 (Micro Photon Devices) with time resolution of $\approx 40–50$ ps was chosen as a detector for TR measuring. The time-correlated single-photon counting system SPC-130 (Becker & Hickl) was used. To isolate a chosen excitonic line from emission of the background and other excitonic lines, we used long-pass and short-pass tunable interference optical filters.

Acknowledgements

This work was supported by the Russian Science Foundation (project #19-12-00273). Samples’ fabrication was partly funded by DAAD under grant 57435564, Carl Zeiss Foundation under contract P2018-01-002 and the Free State of Thuringia, the European Union and the European Social Fund by the Thüringer Aufbau Bank under contract 2018 FCR 0088. The authors are grateful to M. Glazov, A. Rodina, and M. Nestoklon for fruitful discussions and to B. Borodin and L. Kotova for the help in characterization of samples.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

bilayers, bright allowed excitons, dark forbidden excitons, excitons, molybdenum disulfide, monolayers, photoluminescence
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