TÜBİTAK

Turkish Journal of Physics

Volume 48 | Number 5 Article 2

2024

Temperature-dependent quantum beats between neutral and charged excitons in monolayer MoSe2

İBRAHİM SARPKAYA

TÜBİTAK

Turkish Journal of Physics

http://journals.tubitak.gov.tr/physics/

Research Article

Turk J Phys
(2024) 48: 135 – 141

doi:10.55730/1300-0101.2765

Temperature-dependent quantum beats between neutral and charged excitons in monolayer $MoSe_2$

İbrahim SARPKAYA[1,2*]

[1]National Nanotechnology Research Center (UNAM), Bilkent University, Ankara, Turkiye
[2]Institute of Materials Science and Nanotechnology, Bilkent University, Ankara, Turkiye

Received: 25.07.2024 • **Accepted/Published Online:** 26.09.2024 • **Final Version:** 09.10.2024

Abstract: We studied the interaction between the neutral and charged excitons of monolayer $MoSe_2$ at various temperatures via quantum beat spectroscopy in the time domain. We introduced temperature as an efficient control knob to regulate the relative photoluminescence intensities of the neutral and charged excitons to obtain maximum quantum beat resolution. Furthermore, our quantum beat measurements under different temperatures indicate that the decoherence time of the coupled exciton-trion state slightly decreases from 530 fs at 3.5 K to 420 fs at 63 K with increased temperature due to the low-energy acoustic phonon-induced dephasing.

Key words: Trion, exciton, dephasing time, Michelson interferometer, quantum beats, coherent coupling

1. Introduction

Semiconducting monolayer transition metal dichalcogenides (TMDCs) [1, 2] and their van der Waals heterostructures [3, 4] have attracted tremendous interest during the past decade for their enhanced light-matter interaction.The quasiparticles, such as exciton and trion, formed both in TMDC monolayers [5–7] and heterostructures [8] determine most of the optical, electrical, and optoelectronic properties of the host material platform [6, 9, 10]. It is, therefore, necessary to obtain detailed information about the interaction of these particles with their surroundings and with each other to enable their efficient use in optoelectronic [9, 10], valleytronic [11, 12], and quantum photonic [13] devices. The nature of the interaction, for example, between neutral exciton and charged exciton of the monolayer $MoSe_2$ has been studied in detail by utilizing both linear [14] and nonlinear [15, 16] experimental methods in recent studies. The coherent coupling of intralayer excitons in $MoSe_2$-WSe_2 heterostructure was also explored in another study via multidimensional coherent spectroscopy [17]. The coherent interaction between the two spin species of the interlayer excitons of TMDC heterobilayers has also been shown recently by utilizing quantum beat spectroscopy in linear optical experiments [18]. Although previous work by Shepard et al. [14] shows the presence of coherent interaction between neutral and charged excitons of a monolayer $MoSe_2$, it needs a rather complex device structure and electrical gating. The temperature knob can also be utilized as a natural way to study this interaction in monolayer $MoSe_2$ without the need for complex device structure and electrical gating.

In this work, we introduced temperature as an efficient control knob to regulate the relative photoluminescence (PL) intensities of the exciton and trion of monolayer $MoSe_2$ to obtain maximum quantum beat resolution.We studied the interaction between exciton and trions of a monolayer $MoSe_2$ at various temperatures via quantum beat spectroscopy [19] by using a free space Michelson interferometer. The observed quantum beat pattern indicates the presence of coherent coupling between exciton and trion states. Our temperature-

*Correspondence: sarpkaya@unam.bilkent.edu.tr

dependent quantum beat study shows that the coherence of the coupled state decays within a few hundred femtoseconds. Moreover, the moderate decrease in the dephasing time with increased temperature indicates the important role of the low-energy acoustic phonons in the dephasing of the coupled state.

2. Materials and methods

2.1. Sample fabrication

The monolayer $MoSe_2$ is fabricated by mechanical exfoliation of its bulk crystal (purchased from 2D Semiconductors, USA) onto a Si/SiO_2 substrate using the well-known tape exfoliation technique [20].

2.2. Low-temperature optical spectroscopy

The microphotoluminescence (μ-PL) setup was used for all low-temperature PL measurements. Samples were mounted on top of an XYZ nanopositioner in the liquid helium-free closed-cycle cryostat and excited with a 532 nm laser diode. The excitation laser was focused onto the sample surface via a microscope objective with a numerical aperture of 0.82. The emitted PL was collected through the same objective and coupled into a fiber after further filtering with a longpass filter with a center wavelength of 550 nm. A spectrograph with a focal length of 0.75 m and a liquid nitrogen-cooled silicon CCD camera was used to disperse and detect the PL emission. A temperature controller (Lake Shore Model 335) was utilized for the temperature-dependent studies. The quantum beat measurements were performed by sending the neutral exciton and trion PL emissions together to the Michelson interferometer using a single-mode fiber. The Michelson interferometer used in this study basically includes one 50/50 beam beamsplitter and retroreflectors in its two arms. Both retroreflectors, one attached to the DC linear travel stage with a step resolution of 5 μm and the other one on another stage with a piezo inertia actuator with a high resolution of 20 nm, are controlled via a custom LabVIEW program. $g^{(1)}(\tau)$ measurements were done by using the piezo stage that can resolve the fringes, and the data collection was done by using a picosecond event timer together with a silicon detector with a time resolution of 50 ps. For the quantum beating interferogram, the decay fit and T_2 values were obtained by using $g^{(1)}(\tau) = I_0(1 + Aexp(-|\tau|/T_2))$.

3. Results

The optical micrograph of a mechanically exfoliated monolayer $MoSe_2$ on a Si/SiO_2 substrate is shown in Figure 1a. Figure 1b shows the schematic of the electronic band structure of the monolayer $MoSe_2$ and the formation basics of the neutral (X^0) and charged (T) excitons. The X^0 is a quasi-particle made up of a strongly Coulomb-bound electron-hole pair, whereas the trion is a quasi-particle formed via the binding of an extra electron or hole to an exciton. The low temperature (T = 3.5 K) PL spectrum of the investigated monolayer $MoSe_2$ is shown in Figure 1c. The observed Lorentzian type of emission peaks at 1.66 eV and 1.63 eV with full-width at half-maximum (fwhm) linewidth values of 6.0 and 6.3 meV belong to the X^0 and T. The energy difference of $\sim$ 30 meV between the X^0 and T PL emission peaks in the time-integrated PL spectrum corresponds to the binding energy of trions in $MoSe_2$ and is similar to the reported values of trion binding energy in the early experimental studies [8, 21].

To study the coherence properties of the exciton-trion coupled state (X^0-T), we next measure the optical decoherence time T_2 of the coupled X^0-T state using a free space Michelson interferometer. The details of the interferometric setup can be found in the methods section and in our previous studies as well [18, 22]. To probe the presence of coupling between X^0 and T, we sent X^0 and T PL emissions in Figure 2a in tandem to the interferometer. The PL interferogram in Figure 2b clearly demonstrates a pronounced quantum beat structure that consists of seven fringes. The decoherence time of the X^0-T coupled state is obtained as $T_2 = 0.42$ ps by fitting the beat pattern using the $g^{(1)}(\tau) = I_0(1 + Aexp(-|\tau|/T_2))$ function. As schematically demonstrated in Figure 2c, the diamond system consisting of two excited states of X^0 and T, including a superposition state

(X^0-T) and shared ground state (0), was used to model the coupling between the X^0 and T [15, 19]. As shown in Figure 2d, the quantum beat period T_{X^0-T} is given by the time difference between the two fringe maxima or minima. The calculated mean value of the quantum beat period by using 7 fringe maxima is given by $T_{X^0-T} = 183 \pm 12$ fs, which gives rise to an energy difference of $\Delta E_{X^0-T} = 2\pi\ \hbar/T_{X^0-T} \sim 22.5 \pm 1.6$ meV. This energy separation corresponds to trion binding energy that is in close agreement with the previously reported values [8, 21]. However, it is slightly lower than the trion binding energy extracted from the PL spectrum in Figure 2a. It is reasonable to have such a difference because inhomogeneous broadening still exists in our time-integrated PL spectrum compared to the homogeneously limited narrow ones [26, 27], which makes the estimation of the true value of this splitting rather difficult. We also note that the PL peak intensities of X^0 and T should be nearly the same to obtain maximum beat resolution. As shown in previous studies, electrostatic gating [14, 23] and temperature [23, 25] can be considered an effective way of bringing those two intensities close to each other. Our PL study under various temperatures in the top panel of Figure 3 shows that starting from 10 K, the PL intensity of X^0 increases relative to the T emission with the increased temperature. Moreover, the fwhm of the inhomogeneously broadened PL spectrum of X^0 moderately increases from 6.0 to 6.9 meV, whereas it changes from 6.3 to 8.6 meV for the T emission once the temperature is increased from 3.5 to 63 K. The observed linewidth broadening is mainly caused by the scattering of both X^0 and T with the low-energy acoustic phonon of the monolayer $MoSe_2$.One can also realize that PL emission energies of both states slightly shift to the low energy side due to the reduction of the band gap at elevated temperatures, as observed in the previous report [25]. Once the sample temperature reached 63 K, the PL peak intensities of X^0 and T were almost the same (Figures 2a and 3a).

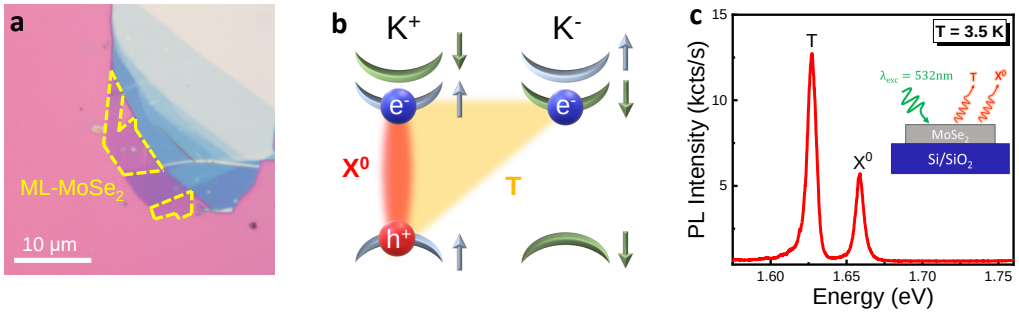

Figure 1. (a) Optical microscope image of the monolayer $MoSe_2$. The regions enclosed by the yellow dashed lines show the monolayer part of the $MoSe_2$. (b) Schematic of the electronic band structure of the monolayer $MoSe_2$. The lowest energy exciton (electron-hole pair) and negatively charged trion (electron bound to exciton) states are shown by X^0 and T in the figure. (c) Photoluminescence (PL) spectrum of the monolayer $MoSe_2$ at 3.5 K. The observed peaks around 1.66 eV and 1.63 eV correspond to X^0 and T emissions, respectively. The CW laser diode with an energy of 2.33 eV was used as an excitation source. The pump power of the excitation laser was 40 μW. The inset shows the schematic of the sample structure.

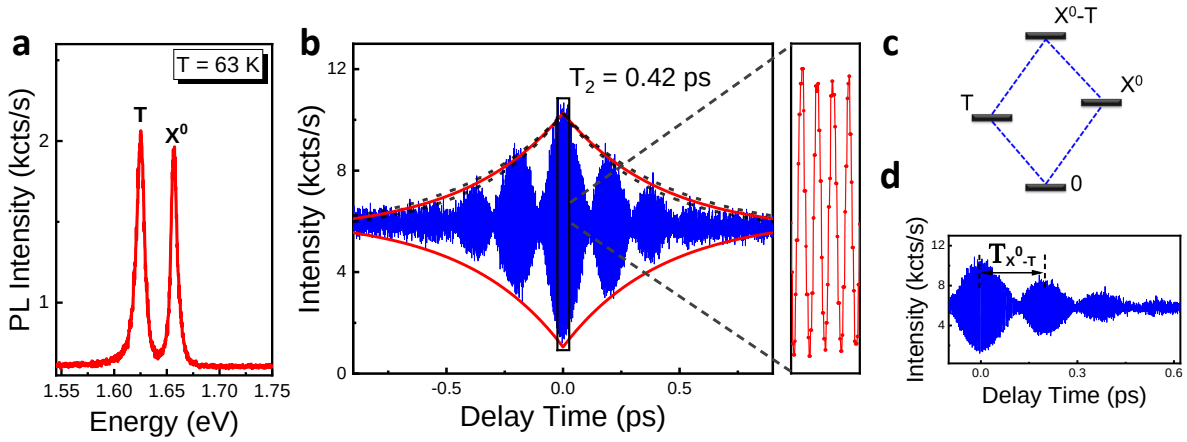

Figure 2. Quantum beat study of neutral and charged excitons of a monolayer $MoSe_2$. (a) The PL spectra of the X^0 and T. The CW laser diode with an energy of 2.33 eV was used as an excitation source. The power of the laser was 40 μW. (b) The PL interferogram was obtained by coupling both the X^0 and T PL emissions in tandem to the interferometer. The red solid line shows the exponential fit of the beat envelope that results in T_2 = 0.42 ps for coupled state X^0-T. The $g^{(1)}(\tau) = I_0(1 + Aexp(-|\tau|/T_2))$ function was used for fitting. The dashed lines show the error interval when fitting the interferogram via the aforementioned expression, which is given by $\pm$0.04 ps (c) The diamond system consisting of two excited states of X^0 and T, including a superposition state (X^0-T) and shared ground state (0) can be used to model the coupling between the X^0 and T states. (d) As shown by the two vertical dashed lines, the beat period (T_{X^0-T}) is given by the difference between the two fringe maximums. All data are taken at 63 K.

In order to shed more light on the dephasing mechanism of the coupled X^0-T state, we also conducted quantum beat measurements at various temperatures, as shown in Figure 3. We used constant laser pump power during these measurements. As shown in Figure 3a, the trion emission is much stronger than the neutral exciton PL emission at 3.5 K. Starting from 10 K, the PL emission intensity of X^0 increases relative to the intensity of the T emission once the temperature is increased. Around 63 K, the peak intensity of these two emissions is almost equal to each other. The same temperature dependence of intensity ratio was also observed in one of the previous studies [23], and the decrease in the PL intensity of the trion emission at elevated temperatures was attributed to the dissociation of the trion state due to thermal fluctuations. Although the observed behavior of the intensity ratio was explained very well with the mass action model in that study, recent studies [24, 25] combining both time-integrated and time-resolved PL argue that it is rather caused by the exploration of highly efficient nonradiative recombination channels by both trions and excitons with the increased temperature. Considering the nearly 30 meV binding energy of trions, it is less likely that trions are dissociated at about 60 K in our case as well. Similar to the second scenario, we can attribute the PL intensity decay of both trions and neutral excitons with increasing temperature to the exploration of nonradiative recombination centers by mobile trions and excitons. We also note that the initial increase in the intensity ratio can be attributed to the more efficient localization of heavy and charged trions in disorder-induced localization potentials compared to the excitons. Once the temperature is further increased, the number of both free trions and excitons increases. Due to the presence of nonradiative recombination centers and the lower probability of trion formation from

free excitons in higher temperatures, the intensity ratio decreases when the temperature increases. Figure 3b shows the corresponding quantum beat spectroscopy measurements at each individual temperature value. It can be clearly seen that the beat resolution is decreased when the PL peak intensity ratio (I_T/I_{X^0}) of these two states deviates from unity. We also note that the quantum beat dephasing time of the coupled state moderately decreases with increased temperature due to the increased contribution of dephasing caused by the intrinsic short-range deformation potential interaction of excitons and trions with the low-energy acoustic phonons of the $MoSe_2$ monolayer [21, 28]. The deformation potential interaction of excitons and trions with the low-energy acoustic phonons of $MoSe_2$ in this temperature range is rather limited possibly because of the localization of these quasiparticles in the disorder-induced shallow localization potentials. Once the temperature is increased, some of them can escape the potential barrier and interact much more strongly with the phonons, and a shortening of dephasing time can be observed.

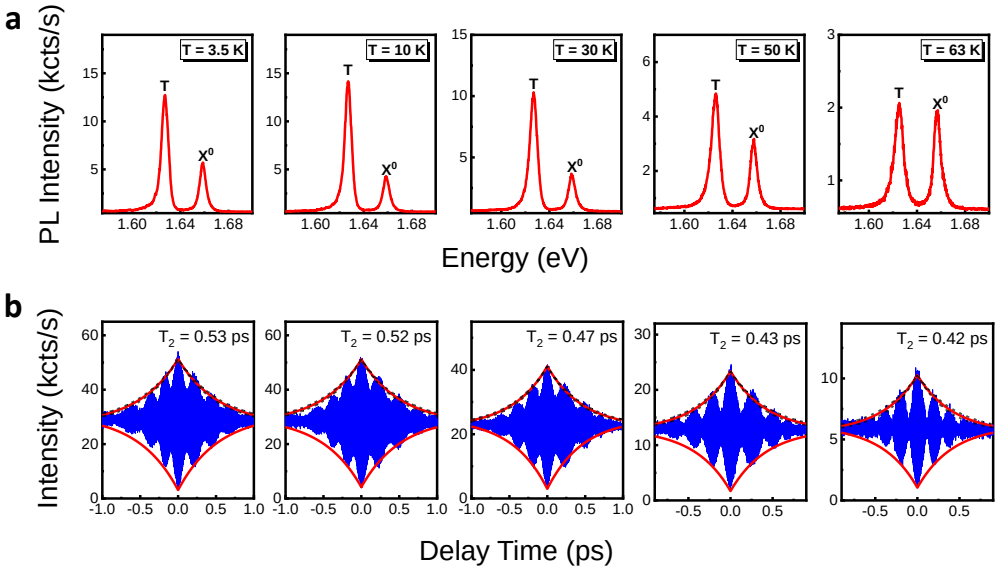

Figure 3. Temperature-dependent quantum beat interferometry of X^0 and T of monolayer $MoSe_2$.(a) Time-integrated PL spectra of the X^0 and T emissions at different temperature values. (b) Corresponding quantum beat interferograms are obtained by sending both the X^0 and T PL in tandem into the Michelson interferometer. The red solid lines show the exponential fits of the beat envelopes that result in corresponding T_2 values of the X^0-T coupled state at the corresponding temperatures. The fits are obtained via the $g^{(1)}(\tau) = I_0(1 + Aexp(-|\tau|/T_2))$ expression. The dashed lines show the error interval when fitting the beat interferogram via the aforementioned expression, which is given by ± 0.04 ps, ± 0.04 ps, ± 0.03 ps, ± 0.04 ps, and ± 0.05 ps, from 3.5 K to 63 K, respectively.

4. Conclusion

In conclusion, we have studied the nature of the interaction between exciton and trion states of a monolayer $MoSe_2$ at various temperatures via quantum beat spectroscopy by using a Michelson interferometer. The observed quantum beat signals indicate the existence of coherent interaction between the exciton and trion states of $MoSe_2$. Our quantum beat measurements under various temperatures also show that the decoherence time T_2 of the coupled state slightly decreases from 530 fs to 420 fs with increased temperature due to the low-energy acoustic phonon-induced dephasing.

Acknowledgment

We acknowledge financial support from The Scientific and Technological Research Council of Türkiye (TÜBİTAK) under project numbers 121F138 and 118C402. I would also like to thank Mehmet Atıf Durmuş for his help with some part of the data analysis.

References

[1] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, "Atomically Thin MoS_2: A New Direct-Gap Semiconductor," *Phys. Rev. Lett.* **105** (2010) 136805.

[2] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim et al.,"Emerging Photoluminescence in Monolayer MoS_2," *Nano Lett.* **10** (2010) 1271–1275.

[3] A. K. Geim and I. V. Grigorieva,"Van der waals heterostructures," *Nature* **499** (2013) 419–425.

[4] P. Ajayan, P. Kim, and K. Banerjee,"Two-dimensional van der Waals materials," *Physics Today* **69** (2016) 38–44.

[5] G. Wang, A. Chernikov, M. M. Glazov, T. F. Heinz, X. Marie et al., "Colloquium: Excitons in atomically thin transition metal dichalcogenides," *Rev. Mod. Phys.* **90** (2018) 021001.

[6] T. Mueller and E. Malic, "Exciton physics and device application of two-dimensional transition metal dichalcogenide semiconductors," *npj 2D Mater Appl* **2** (2018) 29.

[7] I. Sarpkaya,"Optical properties of semiconducting transition metal dichalcogenide materials,"in Synthesis, Modeling, and Characterization of 2D Materials, and Their Heterostructures, *Elsevier* (2020) 57-75.

[8] P. Rivera, H. Yu, K. L. Seyler, N. P. Wilson, W. Yao et al., "Interlayer valley excitons in heterobilayers of transition metal dichalcogenides," *Nature Nanotech* **13** (2018) 1004–1015.

[9] K. F. Mak and J. Shan, "Photonics and optoelectronics of 2d semiconductor transition metal dichalco-genides," *Nature Photon* **10** (2016) 216–226.

[10] Y. Liu, A. Elbanna, W. Gao, J. Pan, Z. Shen et al., "Interlayer excitons in transition metal dichalcogenide semiconductors for 2d optoelectronics," *Advanced Materials* **34** (2022) 2107138.

[11] K. F. Mak, D. Xiao, and J. Shan, "Light–valley interactions in 2d semiconductors," *Nature Photon* **12** (2018) 451–460.

[12] A. Ciarrocchi, D. Unuchek, A. Avsar, K. Watanabe, T. Taniguchi, and A. Kis, "Polarization switching and electrical control of interlayer excitons in two-dimensional van der waals heterostructures," *Nature Photon* **13** (2019) 131–136.

[13] M. Turunen, M. Brotons-Gisbert, Y. Dai, Y. Wang, E. Scerri et al., "Quantum photonics with layered 2d materials,"*Nat Rev Phys* **4** (2022) 219–236.

[14] G. D. Shepard, J. V. Ardelean, O. A. Ajayi, D. Rhodes, X. Zhu et al., "Trion-species-resolved quantum beats in $mose_2$," *ACS Nano* **11** (2017) 11550–11558.

[15] K. Hao, L. Xu, P. Nagler, A. Singh, K. Tran et al., "Coherent and incoherent coupling dynamics between neutral and charged excitons in monolayer $mose_2$," *Nano Lett.* **16** (2016) 5109–5113.

[16] T. Jakubczyk, V. Delmonte, M. Koperski, K. Nogajewski, C. Faugeras et al., "Radiatively limited dephasing and exciton dynamics in $mose_2$ monolayers revealed with four-wave mixing microscopy," *Nano Lett.* **16** (2016) 5333–5339.

[17] T. L. Purz, E. W. Martin, P. Rivera, W. G. Holtzmann, X. Xu, and S. T. Cundiff, "Coherent exciton- exciton interactions and exciton dynamics in a $mose_2/wse_2$ heterostructure," *Phys. Rev. B* **104** (2021) L241302.

[18] M. A. Durmuş, I. Sarpkaya, "Quantum beats between spin-singlet and spin-triplet interlayer exciton transitions in wse_2–$mose_2$ heterobilayers," *Nano Lett.* **24** (2024) 5767–5773.

[19] J. Erland and I. Balslev, "Theory of quantum beat and polarization interference in four-wave mixing," *Phys. Rev. A* **48** (1993) R1765(R).

[20] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. E. Jiang, Y. Zhang et al., "Electric Field Effect in Atomically Thin Carbon Films," *Science* **306** (2004) 666-669.

[21] S. Shree, M. Semina, C. Robert, B. Han, T. Amand et al., "Observation of exciton-phonon coupling in $MoSe_2$ monolayers," *Phys. Rev. B* **98** (2018) 035302.

[22] M. A. Durmuş, K. Demiralay, M. M. Khan, Ş. E. Atalay, and I. Sarpkaya, "Prolonged dephasing time of ensemble of moiré-trapped interlayer excitons in wse_2-$mose_2$ heterobilayers," *npj 2D Mater Appl* **7** (2023) 65.

[23] J. S. Ross, S. Wu, H. Yu, N. J. Ghimire, A. M. Jones et al., "Electrical control of neutral and charged excitons in a monolayer semiconductor," *Nat Commun* **4** (2013) 1474.

[24] C. Robert, D. Lagarde, F. Cadiz, G. Wang, B. Lassagne et al., "Exciton radiative lifetime in transition metal dichalcogenide monolayers," *Phys. Rev. B* **93** (2016) 205423.

[25] T. Godde, D. Schmidt, J. Schmutzler, M. Aßmann, J. Debus et al., "Exciton and trion dynamics in atomically thin $mose_2$ and wse_2: Effect of localization," *Phys. Rev. B* **94** (2016) 165301.

[26] F. Cadiz, E. Courtade, C. Robert, G. Wang, Y. Shen et al., "Excitonic linewidth approaching the homogeneous limit in mos_2-based van der waals heterostructures," *Phys. Rev. X* **7** (2017) 021026.

[27] O. A. Ajayi, J. V. Ardelean, G. D. Shepard, J. Wang, A. Antony et al., "Approaching the intrinsic photoluminescence linewidth in transition metal dichalcogenide monolayers," *2D Materials* **4** (2017) 031011.

[28] P. Dey, J. Paul, Z. Wang, C. Stevens, C. Liu et al., "Optical coherence in atomic-monolayer transition-metal dichalcogenides limited by electron-phonon interactions,"*Phys. Rev. Lett.* **116** (2016) 127402.