Dark interlayer excitons in WS$_2$/tetracene heterostructures

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The vertical stacking of two-dimensional materials into heterostructures gives rise to a plethora of intriguing optoelectronic properties and presents an unprecedented potential for technological concepts. While much progress has been made combining different monolayers of transition metal dichalcogenides (TMDs), little is known about TMD-based heterostructures including organic layers of molecules. Here, we present a joint theory-experiment study on a TMD/tetracene heterostructure demonstrating clear signatures of spatially separated interlayer excitons in low temperature photoluminescence spectra. Here, the Coulomb-bound electrons and holes are localized either in the TMD or in the molecule layer, respectively. In particular, we reveal both in theory and experiment that at cryogenic temperatures, signatures of momentum-dark interlayer excitons emerge. Our findings shed light on the microscopic nature of interlayer excitons in TMD/molecule heterostructures and could have important implications for technological applications of these materials.

A controlled vertical stacking of atomically thin materials into van der Waals heterostructures with tailored properties has recently become feasible$^{1,2}$. In particular, there has been much progress in understanding homo- and heterobilayers of transition metal dichalcogenides (TMDs)$^{3-8}$. The strong Coulomb interaction leads to a variety of bright and dark excitons in these materials$^{9-12}$. Recent experiments have observed signatures of spatially separated interlayer exciton states (cf. Fig. 1)$^{6,13-15}$. So far, interlayer exciton signatures have been mostly demonstrated in TMD homo- and heterobilayers. A recent study showed that interlayer excitons can also be observed in organic/inorganic heterostructures, where a thin crystalline film of organic molecules is stacked on a TMD monolayer$^{16}$. Tetracene (Tc) molecules are of particular interest due to their excellent light-emitting and light-harvesting properties$^{17-19}$ and their similar band gap energies as in TMD materials$^{20}$.

After optical excitation of an intralayer exciton in the TMD layer, efficient charge transfer due to the type-II heterostructure enables the hole to tunnel from the TMD to the organic layer, while still being attracted to the TMD electron (cf. Fig. 2(a)). This spatially separated electron-hole pair is a bright interlayer exciton (also known as charge transfer or hybrid exciton). If the electron stem from a momentum-dark state within the TMD, this leads to formation of a dark interlayer exciton (cf. Fig. 2(a)). For monolayers of TMDs it was shown that momentum-dark excitons can be activated via high-dipole molecules$^{21}$ and phonons$^{22-24}$. Even in TMD homo- and heterobilayers, indirect, phonon-assisted signatures of dark interlayer excitons have been observed$^{15,25}$. However, the nature of interlayer excitons in organic/TMD heterostructures remains unclear.

In this work, we undertake a joint theory-experiment study to uncover the temperature dependent excitonic signatures of a tungsten disulfide (WS$_2$)/Tc heterostructure.

To obtain microscopic insights, we apply a quantum-mechanical approach based on the density matrix formalism. In particular, we solve the Wannier equation allowing us to microscopically resolve the entire intra- and interlayer exciton landscape in these materials including binding energies and wave functions of bright and dark excitons. Solving the generalized Elliott formula we also have microscopic access to their optical signatures. Experimentally, we perform temperature-dependent photoluminescence (PL) measurements on WS$_2$/Tc heterostructures and demonstrate the appearance of interlayer excitons at energies well below the optically excited intralayer exciton. In excellent agreement with theoretical predictions, we show how the intensity of the interlayer exciton resonance increases with decreasing temperature. Furthermore, we demonstrate both in experiment and theory signatures of dark interlayer excitons at temperatures below 100 K. Indirect recombination of dark excitons gives rise to phonon sidebands that are identified as a low-energy shoulder of the interlayer exciton resonance. Overall, our work provides new microscopic insights into the intriguing interlayer exciton landscape and the resulting optical response in technologically promising organic/inorganic heterostructures.

**Interlayer exciton landscape.** We focus on heterostruc-
turers comprising of a WS$_2$ monolayer and a thin crystalline film of tetracene molecules. The latter attach to the surface of the TMD via van der Waals bonds and form a molecular lattice, as has been shown in previous studies$^{26,27}$. Tetracene molecules tend to form periodic lattices rather than distribute themselves randomly on the surface$^{28-32}$. Motivated by these findings, we describe the tetracene as a quasi two-dimensional structure characterized by a homo-lumo gap. We take into account one state in the conduction and valence band denoted as $l$ (lowest unoccupied molecular orbital) and $h$ (highest occupied molecular orbital). Since the effective mass of Tc is large compared to the TMD$^{33,34}$, the molecular states have a quasi-flat dispersion, cf. Fig. 2.

To describe the TMD/Tc heterostructure on a microscopic level, we use the density matrix formalism$^{35-39}$. For the TMD, we take into account the band structure around the high-symmetry points in the reciprocal space within an effective mass approximation$^{40}$. In particular, we consider the valence band maxima at the $K$ point and conduction band minima at the $\bar{K}, \Lambda$, and $K'$ valley, which are crucial for the formation of momentum-dark exciton states$^{10}$. Depending on the location of electron and hole, we can distinguish bright and dark intralayer $KK, KL, K'K'$ excitons (yellow/orange ovals in Fig. 2) and intralayer molecule excitons $hl$ (black oval in Fig. 2). Furthermore, there are spatially separated interlayer excitons $hK, h', h'K$, $KL$ combining TMD and molecule states (blue ovals in Fig. 2). Here, the first/second letter describes the position of the hole/electron, e.g. the state $hK$ corresponds to the hole located in the $h$ state of the molecule, while the electron can be found in the $K$ valley of the TMD layer, cf. Fig. 2(a).

As excitonic effects are crucial in TMDs$^{37,41-43}$, we project our equations into an excitonic basis with eigen energies $\epsilon_{\mu}$ and wave functions $\varphi_{\mu}$. Note that the index $\mu$ can include both intralayer $\mu=(KK, KL, K'K', hl)$ and interlayer states $\mu=(hK, h'h, h'K', KL)$. The excitonic eigenfunctions and eigenenergies are obtained by solving the Wannier equation$^{35-37}$. The Coulomb matrix element is calculated using an effective 2D Coulomb potential $V_0^k = \frac{e^2}{k r_0 (E)}$ with the dielectric function $\epsilon_{TMD}/\epsilon_{Tc}$, the screening of the surrounding material $\epsilon_{sur}$, the thickness of the layers $d_{TMD}/d_{Tc}$ and the interlayer distance $d_{TMD-Tc}$. Table S1 (c.f Supplementary) summarizes the parameters used in our study. The assumed thickness of the molecular film corresponds to a single layer of molecules in an upright configuration. Note that in experimental setups, the molecular layer might consist of more than one layer, however we assume that the main interaction and charge transfer takes place within the first layer. Molecule-molecule interactions are beyond the scope of this work and could result in some quantitative changes in the optical response.

Solving the Wannier equation, we obtain the binding energies of the entire exciton landscape including bright and dark intra- and interlayer excitons, as illustrated in Figure 2(b). For WS$_2$/Tc heterostructures on a Si/SiO$_2$ substrate, we find an exciton binding energy of 196 meV for the intralayer exciton within the WS$_2$. Furthermore, we find binding energies of 243 meV and 272 meV for the two bright $hK$ and KI interlayer exciton states, respectively. The dark interlayer state has a larger binding energy of 328 (272) meV reflecting the larger effective mass at the $\Lambda$ ($K'$) point. The binding energies are slightly lower then for intralayer excitons in the WS$_2$ monolayer due to the larger dielectric screening within a heterostructure. The energies are in a similar range as values reported for TMD/TMD heterostructures$^{6,7,44}$. While the large effective masses and smaller dielectric screening in the molecular film lead to heavier excitons and hence enlarged binding energies, the relatively large thickness of the molecular layer compared to the TMD monolayer reduces the exciton binding energy. Note that the energies discussed so far are pure binding energies $E_0^{b}$. For the absolute spectral position $E_\mu$ of excitons (shown in Fig. 2(b)), one needs to take into account the band gap energy $E_\mu$ with $E_\mu = E_0^b - E_\mu$. Note that we shifted the whole exciton landscape to match the experimentally measured A exciton resonance at 2.0 eV. Overall, we find that the interlayer $h'K$ exciton is the energetically lowest state, followed by $E_{hK}$ and $E_{h'h}$, cf. Fig. 2(b) and Table S1. The interlayer Kl exciton is located 1.1 eV above the bright KK exciton and thus has no influence on PL spectra and will be neglected in the following. Moreover, we do not consider the intralayer molecule state $hl$ (located at 2.56 eV), since our focus lies on optical excitation resonant to the energetically lower intralayer TMD exciton.

**Interlayer excitons in photoluminescence.** After determining the exciton landscape in WS$_2$/Tc heterostructures, we focus now on their optical response in PL spectra. The important (fixed) input parameters (effective masses, band gap energies) are shown in Table S1 obtained from DFT calculations for the electronic bandstructure$^{33,40}$. We exploit the equation of motion for the photon-assisted polarization to obtain the PL intensity $I_{PL}$ for intra- and interlayer excitons resulting in the Elliott formula$^{22}$

$$I_{PL}(\omega) \propto \sum_{\mu=KK, K'K'} \left| M_{\mu} \right|^2 \frac{1}{(E_\mu - \omega)^2 + \left(\gamma_\mu + \Gamma_\mu\right)^2},$$

where the position of the resonances is given by the energy $E_\mu$, the resonance width by the radiative ($\gamma_\mu$) and the non-radiative phonon-assisted ($\Gamma_\mu$) dephasing, and finally the os-
Figure 3. Optical signature of interlayer excitons. (a) Calculated photoluminescence spectrum of a WS\(_2\)/Tc heterostructure on a Si-SiO\(_2\) illustrating the growing intensity of the hK interlayer exciton resonance for reduced temperatures. For comparison, the calculated PL for a WS\(_2\) monolayer at 200 K is shown with the dashed line exhibiting only the intralayer exciton resonance. (b) The intensity ratio between the hK interlayer (iX) and KK intralayer excitons (X\(_0\)), plotted on a log scale.

cillator strength by the exciton-photon matrix element \(M_\mu = \delta_{Q,0} \sum_q \varphi^\mu_q M^\mu_q \hat{U}_\mu\). The latter is determined by the exciton wave function \(\varphi^\mu_q\), the momentum-dependent optical matrix element\(^{27}\) \(M^\mu_q\) and the transformation matrix \(\hat{U}_\mu\) which includes the tunneling. The Kronecker-delta ensures that only bright excitons within the light cone with \(Q = 0\) are optically active\(^{22}\). The appearing exciton occupation \(N_\mu\) is crucial in determining the spectral weight of different transitions in the PL spectrum. In this study, we assume thermalized Boltzmann distributions, since we discuss the stationary PL only\(^{22,38}\). More details on the origin of Eq. 1 can be found in the supplementary.

Evaluating Eq. (1) numerically, we investigate optical signatures of intra- and interlayer excitons in the WS\(_2\)/Tc heterostructure. The PL spectrum at large temperature (>200 K) exhibits a pronounced resonance at 2 eV stemming from the bright intralayer KK exciton, cf. Fig. 3(a). As the temperature decreases we observe the emergence of a second peak at around 1.71 eV that corresponds to the expected position of the interlayer exciton. Further lowering the temperature increases the ratio between the inter- and intralayer exciton peaks (cf. Fig 3 (b)) until at low temperatures (<150 K) the intralayer contributions becomes negligible and the PL spectrum is entirely dominated by interlayer excitons. The lower the temperature, the higher the occupation of the energetically lower-lying interlayer states leading to a more intense PL resonance of interlayer excitons. Therefore, the temperature acts as an externally accessible knob allowing the relative visibility of interlayer excitons to be tuned. Figure 3 (b) shows the temperature-dependent intensity ratio of inter- and intralayer excitons on a logarithmic scale, which resembles the Boltzmann distribution. The interlayer exciton in the TMD/Tc system is visible at higher temperatures than in TMD/TMD heterostructures\(^{7,13-15,44}\). This leads to a higher occupation \(N_\mu\) in equilibrium and thus to the stronger contribution of interlayer excitons, cf. Eq. (1). Note that we have neglected temperature-induced spectral shifts, linewidth changes and possible modifications in the molecular layer, since they are not expected to have an impact on the qualitative temperature trend of PL intensity ratios.

**Dark interlayer excitons.** So far, we have focused on direct emission from bright interlayer exciton states (hK) neglecting lower lying momentum-dark interlayer states (hΛ, hK'). While they cannot emit light directly, we know from TMD monolayers that dark intralayer excitons show pronounced signatures via phonon-assisted indirect emission resulting in phonon sidebands\(^{22}\). To account for these indirect emission channels, we exploit a generalized Elliott formula\(^{22}\)

\[
I_{PL}^\nu(\omega) \propto \sum_{Q,\alpha \pm} \Theta^\nu(\omega) |D_{Q\alpha}^\nu|^2 \Gamma_\mu N_\mu \eta_\alpha^\pm
\]

with \(\Theta^\nu(\omega) = \frac{|M^\nu|^2}{(E_\mu - \omega)^2 + (\Gamma_\mu)^2}\). We take into account all interlayer exciton states \(\nu = (KK, KL, KK', hK, h\Lambda, hK')\). The position of resonances is determined by the energy of the corresponding exciton \(E_\mu\) plus/minus the energy of the absorbed/emitted phonon \(\gamma\Omega\). In contrast to bright excitons, dark states cannot decay radiatively\(^{46}\) hence the width of the peak is only determined by non-radiative dephasing \(\Gamma_\mu\).\(^{22,38,46}\) The oscillator strength of phonon-assisted indirect emission scales with the exciton-phonon scattering element \(|D_{Q\alpha}^\nu|^2 = \sum_q \varphi^\mu_q g_{Q\alpha}^\nu \varphi^\nu_{-Q\alpha}\) where \(g_{Q\alpha}^\nu\) is the electron-phonon coupling element\(^{22,38}\).

Evaluating Eqs. (1) and (2), we calculate the temperature-dependent PL including direct emission from bright states and indirect phonon-assisted emission from dark excitons in a TMD/Tc heterostructure, cf. Fig. 4(a). We find that at room temperature the PL is dominated by the bright KK exciton X\(_0\), while the bright interlayer exciton (hK) located approximately 300 meV below X\(_0\) becomes dominant in the intermediate temperature range of 100-200 K. At even lower temperatures new resonances at lower energies appear and become more dominant. Located 375 and 395 meV below X\(_0\), they can be assigned to phonon-assisted emission from dark interlayer hΛ and hK' excitons, respectively.
Figure 4. **Dark interlayer excitons.** (a) Calculated temperature-dependent PL of WS2/Tc heterostructure exhibiting signatures from intra- and interlayer excitons. Note that the origin of the energy axis has been shifted to the position of the bright KK exciton (E_{X0}). (b) Zoom-in into the contributions of the phonon-assisted indirect PL from bright interlayer exciton hK and momentum-dark hK' and hΛ states. (c) For comparison, we also show the low-temperature PL for MoSe2 exhibiting no phonon sidebands.

To better understand these phonon sidebands, we zoom into the low-energy contributions from bright and dark interlayer excitons at 77 K, cf. Fig. 4(b). We find that the energetically lowest dark hK' interlayer exciton (blue-shaded) has the largest PL contribution. It consists of two peaks at -375 and -395 meV stemming from indirect light emission driven by acoustic and optical K phonons, respectively. Note that these peaks appear at the location E_{K'} ± ΩA/O, i.e. they are shifted by the phonon energy. We find that the dark hΛ interlayer exciton has a smaller contribution (green-shaded) reflecting its smaller occupation compared to hK'. By increasing the temperature, the occupation of dark interlayer exciton states decreases, reducing their weight in PL spectra. Already at 100 K, the phonon-assisted peaks can only be seen as a low-energy shoulder from the bright hK interlayer exciton.

A crucial condition for the appearance of dark interlayer excitons is the exciton landscape in WS2 monolayers, where momentum-dark KΛ and KK' excitons lie below the bright KK states. In contrast, in MoSe2 the bright exciton is the energetically lowest state.5-11,38 Here, the low-temperature PL spectrum is qualitatively different exhibiting only one peak at -346 meV stemming from the bright hK interlayer exciton, cf. Fig. 4(c). There are no signatures from dark interlayer excitons.

**Theory-experiment comparison**

To experimentally verify the theoretically predicted low temperature PL interlayer exciton signatures, we fabricated a high quality WS2/Tc heterostructure and collected its PL spectra over a broad temperature range (100-245K). To prepare the heterostructure, a monolayer of WS2 was exfoliated onto a silicon dioxide wafer (oxide thickness of 90nm) from bulk WS2. A 20nm layer of tetracene was then thermally evaporated onto the monolayer. Further information on sample preparation is included in the SI. We selectively excited WS2 with 2.14 eV light to prevent the signal from interlayer excitons to become masked by Tc emission. Figure 5(a) shows the measured temperature dependent PL of the heterostructure. At 245K, the bright interlayer hK exciton emits at 1.71eV and its intensity significantly grows with decreasing temperature. This reflects the increasing occupation of the hK excitonic state which is in excellent agreement with our calculations, Fig. 5(b). In the inset of Fig. 5(b), we compare the experimental (red crosses) and theoretical (green curve) evolution of the interlayer exciton peak intensity as a function of temperature. We normalize the intensity from the the interlayer exciton to the value at 100 K. We find a good quantitative agreement between our theoretical model and experimental data, with a significant PL from the hK exciton in the temperature range of 100-150 K.

At around 100 K, we also begin to see the emergence of an additional signature appearing as a low-energy shoulder (marked with an arrow) at approx. 1.63 eV. This signature also appears in the theoretically calculated PL spectrum, cf. Fig 5(b), and can be ascribed to a phonon sideband stemming from the indirect, phonon-assisted recombination of the dark hK' interlayer exciton states. The sideband is red-shifted with respect to the position of the hK' resonance at 1.65 eV, reflecting the emission of an acoustic phonon.38 At low temperatures, the occupation of the energetically lower hK' exciton significantly increases relative to the higher, bright exciton. This compensates the lower efficiency of the phonon-assisted indirect recombination process. Already at temperatures above 150 K, this phonon sideband vanishes and is hardly visible in both the theory and experiment. Furthermore, we have performed lifetime measurements at 102 K and 245 K, cf. the SI. Upon cooling to 102 K, the heterostructure’s lifetime is considerably enhanced. The increase of the non-radiative component of the lifetime provides further evidence that at low temperature we indeed access dark interlayer excitonic states.

Note that our measurement was only able to resolve the indirect light emission from dark interlayer excitons assisted by acoustic phonons. Signal from the optical K phonons, as predicted in Fig. 4(b) are masked by the broadness and higher intensity of the acoustic phonon sideband. While we have the means to microscopically estimate the radiative and phonon-induced broadening of the exciton peaks, broadening mechanisms in TMD-molecule heterostructures are currently not well understood, and our model underestimates the observed experimental broadening. Therefore, to better compare to experiment we extract values for the broadening from the experimental data and use a phenomenological model7 to describe the temperature dependence in Fig. 5(b). Taking the broader linewidths into account, we also see just one phonon-sideband at approx. 1.63 eV, as observed in the experiment.

While we obtain an excellent qualitative agreement between theory and experiment, some quantitative discrepancies
do exist. These differences may stem from molecule-molecule interactions within the molecular film, which have been neglected in this work. In particular, there is an increasing PL signal at higher energies above the hK resonance in the experiment, while in theory the PL is strongly suppressed in this spectral region. This could be traced back to a particularly broad intralayer exciton resonance in the experiment that is expected to occur at about 2 eV (see supplementary). Interestingly, the peak position of the hK interlayer exciton does not spectrally shift in the experiment. This suggests that the temperature-dependent Varshni energy shifts, arising from the thermal expansion of the crystal lattice\textsuperscript{47}, are negligible for interlayer excitons, justifying the omission of such effects in our theory. The strongly suppressed Varshni shift could be explained by the involvement of the molecular lattice, which is expected to be less susceptible to thermal expansion.

In conclusion, we have presented a joint theory-experiment study on the optical response of bright and dark interlayer excitons in a TMD/tetracene heterostructure. We find both in experiment and theory a clear signature of the bright interlayer exciton in photoluminescence spectra and show how the relative intensity of this resonance can be boosted by variation in temperature. Furthermore, we show the appearance of an additional low-energy PL signature at temperatures around 100 K stemming from indirect phonon-assisted emission from dark interlayer exciton states. Our work provides new insights into the microscopic nature of interlayer excitons in TMD/molecule heterostructures and could guide future studies in the growing research field of technologically promising organic/inorganic heterostructures.

Acknowledgments: This project has received funding from Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) through SFB 1083 and the European Union’s Horizon 2020 research and innovation program under grant agreement No 881603 (Graphene Flagship). The experimental work at Purdue was supported by the US Department of Energy, Office of Basic Energy Science, through award DE-SC0016356 (optical spectroscopy) and DE-SC0022082 (sample fabrication).

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Supplementary Information: Dark interlayer excitons in WS$_2$/tetracene heterostructures

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I. PREPARATION OF TUNGSTEN DISULFIDE/TETRACENE HETEROSTRUCTURE

A. Tungsten disulfide preparation

The silicon dioxide wafer (oxide thickness of 90 nm) was cleaned in a sonication bath. The wafers were first sonicated in acetone, then isopropyl alcohol and finally deionized water for five minutes each. Bulk WS$_2$ crystals (purchased from Graphene Supermarket) were then exfoliated onto the cleaned wafer using Scotch Magic Tape. Before lifting off the tape from the wafer, the bulk crystal taped to the silicon wafer was annealed on a hot plate at 100°C for two minutes [1]. The monolayer of WS$_2$ was found on the substrate using an Olympus Fluorescence Microscope. Optical images of the monolayer shown in Figure S1a. A mercury lamp was used to excite the monolayer which is shown in red in Figure S1a(ii). The room temperature PL spectra (447nm excitation) of the monolayer, heterostructure and pure tetracene used in this study is shown in Figure S1b. The single, narrow KK exciton peak at 2.0 eV is indicative that the WS$_2$ flake is a monolayer. The inset in Figure S1b is an enlargement of the spectra between 1.4-2.0 eV.

B. Tetracene Evaporation

Tetracene (98% ACROS Organics) was then thermally evaporated onto the sample using a LC Technology thermal evaporator with an INFICON (SQC-310) deposition controller. The tetracene was deposited at a rate of 0.5Å/s under a vacuum of $< 2 \times 10^{-6}$ mbar. The tetracene height was measured using a Veeco Dimension 3100 Atomic Force Microscope (AFM). The AFM image in Figure S2 shows two profiles which were used to determine a tetracene thickness of $\sim$ 20 nm.

II. LOW TEMPERATURE PHOTOLUMINESCENCE MEASUREMENTS

To measure the low temperature spectra of the heterostructure, the sample was cooled using a Montana Instrument Cryostation s50 (temperature stability $< 10$ mK). The steady state PL spectra were collected using a home-built confocal micro-PL set up as
described in previous publications [2]. The sample was excited using a PHAROS Light Conversion Ltd. Laser (repetition rate of 750 kHz) whose output was directed into an optical parametric amplifier (OPA, TOPAS-Twins, Light Conversion Ltd) to create 580 nm (2.1377 eV) light. This wavelength was chosen to selectively excite the WS2 and minimise tetracene emission, as shown in the inset of Figure S1b, when using 447 nm excitation, Tc emission overpowers that of the charge transfer (CT) exciton in the heterostructure, as no CT peak is present at 1.7eV. The 580nm light (fluence of 112 µJcm$^{-2}$) was focused using a 40x numerical aperture (NA) 0.6 objective. The sample emission was collected using the same objective and later dispersed and detected using an Andor Technology monochromator and thermoelectric-cooled charge-coupled device. The lifetime measurements included in Figure S3 were collected using a single photon avalanche diode (Pico-Quant, PDM series) and a single photon counting module (Pico-Quant) with a time resolution of $\sim$ 100 ps.

**III. THEORETICAL MODEL**

**A. Elliot Formula**

In this section we aim to outline the origin of the excitonic Elliot formula in a TMD/Tc heterostructure within our density matrix formalism. The PL intensity can be described using the time evolution of the photon number, $I_{PL}(\omega_q) = \omega_q \frac{\partial}{\partial t} n_q \propto S^Q_{\omega_q}$.
with the number of emitted photons \( n_q = \langle c_q^\dagger c_q \rangle \) and the photon-assisted polarization \( S_{Q}^\mu = \sum_q \varphi_q^\mu S_{q}^{vc} \) with \( S_{k_1 k_2}^q(t) = \langle c_q^\dagger a_{k_1}^q a_{k_2}^q \rangle \) [3]. This microscopic quantity describes optically induced transitions from an initial state \((v, k_1)\) to a final state \((c, k_2)\) under annihilation (creation) of a photon \( c_q^{(1)} \). Here, \( k_1 \) is the electronic momentum and \( \lambda = v, c \) the band index denoting valence or conduction band, respectively.

Next, we exploit the Heisenberg equation of motion \( i\hbar \dot{S}_Q^\mu(t) = [H, S_Q^\mu(t)] \) [4] to obtain the temporal evolution of the photon-assisted polarization. The Hamilton operator \( H = H_0 + H_{\text{photon}} + H_{\text{phonon}} + H_{\text{tunnel}} \) includes the interaction-free part for excitons, photons and phonons \( H_0 \), the exciton-phonon interaction \( H_{\text{photon}} \) including the optical matrix element \( M_Q^{\mu \sigma} \), and the exciton-phonon coupling \( H_{\text{phonon}} \).

The crucial contribution to the Hamilton operator in this work is the tunneling part \( H_{\text{tunnel}} = \sum_{Q, i} T_{ij}^Q \sum_{\alpha} \varphi_{ij}^{\alpha} X_Q^{\dagger \alpha} X_{Q'} \) describing the charge transfer between the layers. The appearing tunneling matrix element \( T_{ij}^Q = \sum_{\alpha} \varphi_{ij}^{\alpha} \varphi_{ij}^{\beta} \) is determined by the overlap of Bloch waves \( \Psi_q \) with a tunneling potential \( V_{\text{tunnel}} \), i.e. \( t_{ij}^{Q} = \langle \Psi_q | V_{\text{tunnel}} | \Psi_j \rangle \). We separate the potential into an in-plane disorder part and out-of-plane part, which is only non-zero between the layers [5]. Then, we can write \( t_{ij}^{Q} = V_{\text{in}}(\{k_j - k_i\}) \sum_{\alpha} \langle u^i \rangle_{SC} \) with \( u^i \) the lattice periodic parts of the Bloch waves integrated over a unit cell. This integral determines the tunneling strength and we assume a typical value of 0.01 known from TMD/TMD heterostructures [5]. The remaining in-plane disorder potential can be estimated via a disorder potential with correlation length in the order of the exciton Bohr radius.

In a last step, we project into a new basis where the tunneling part of the Hamiltonian is included in an effective single-particle Hamiltonian, i.e. \( H_0 + H_{\text{tunnel}} = \sum_{i,j} \epsilon_{ij} x_{ij}^\dagger X_j + \sum_{q,ij} T_{ij}^{Q} \sum_{\alpha} \varphi_{ij}^{\alpha} X_Q^{\dagger \alpha} X_{Q} \) is determined by the overlap of Bloch waves \( \Psi_q \) with a tunneling potential \( V_{\text{tunnel}} \), i.e. \( t_{ij}^{Q} = \langle \Psi_q | V_{\text{tunnel}} | \Psi_j \rangle \). We separate the potential into an in-plane disorder part and out-of-plane part, which is only non-zero between the layers [5]. Then, we can write \( t_{ij}^{Q} = V_{\text{in}}(\{k_j - k_i\}) \sum_{\alpha} \langle u_j \rangle_{SC} \) with \( u_j \) the lattice periodic parts of the Bloch waves integrated over a unit cell. This integral determines the tunneling strength and we assume a typical value of 0.01 known from TMD/TMD heterostructures [5]. The remaining in-plane disorder potential can be estimated via a disorder potential with correlation length in the order of the exciton Bohr radius.

To calculate the appearing matrix elements in the Hamilton operator, we apply a nearest-neighbor tight-binding approach [4, 6, 7] which includes fixed (not adjustable) input parameters (effective masses, band gap energies, cf. Table S1) from DFT calculations for the electronic bandstructure [8, 9].

| \( E_{\mu}^g \) | KK | hK | hK' | h\Lambda | Kl | hl |
|---|---|---|---|---|---|---|
| 2.18 | 1.95 | 1.92 | 1.98 | 3.4 | 3.0 |
| 196 | 243 | 272 | 328 | 272 | 440 |
| 2.00 | 1.71 | 1.64 | 1.65 | 3.12 | 2.56 |

| screening parameters | \( \epsilon_{\text{TD}} \) | \( \epsilon_{\text{C}} \) | \( \epsilon_{\text{M}} \) | \( d_{\text{TD}} \) | \( d_{\text{C}} \) | \( d_{\text{M}} \) |
|---|---|---|---|---|---|---|
| 13.61 | 3.69 | 2.45 | 0.61 | 1.1 | 0.3 |

| electronic masses | \( m_K^\mu \) | \( m_h^\mu \) | \( m_K^{\mu \sigma} \) | \( m_h^{\mu \sigma} \) | \( m_K^h \) | \( m_h^h \) |
|---|---|---|---|---|---|---|
| 0.27 | 0.64 | 0.36 | 0.36 | 3.0 | 6.7 |

Table S1. **Energy Landscape and screening parameters.** Electronic band gap energies \( E_{\mu}^g \) (in eV, from [2, 8]), calculated exciton binding energies \( E_{\mu}^b \) (in meV) and spectral position \( E_{\mu} \) (eV) for intra- and interlayer excitons, screening parameters for dielectric environment \( \epsilon \) (from [10, 11]) and thickness \( d \) (in nm, from [10, 12]) and electronic masses (in \( m_{\text{ref}} \), from [8, 13]). All values refer to a WS\(_2\)/Tc heterostructure on an SiO\(_2\) substrate.

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