Superposition of intra- and inter-layer excitons in twistronic MoSe$_2$/WSe$_2$ bilayers probed by resonant Raman scattering

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Abstract

Hybridisation of electronic bands of two-dimensional materials, assembled into twistronic heterostructures, enables one to tune their optoelectronic properties by selecting conditions for resonant interlayer hybridisation. Resonant interlayer hybridisation qualitatively modifies the excitons in such heterostructures, transforming these optically active modes into superposition states of interlayer and intralayer excitons. For MoSe$_2$/WSe$_2$ heterostructures, strong hybridization of both single particle and excitonic states can occur via single particle tunnelling. Here we use resonance Raman scattering to provide direct evidence for the hybridisation of excitons in twistronic MoSe$_2$/WSe$_2$ structures, by observing scattering of specific excitons by phonons in both WSe$_2$ and MoSe$_2$. We also demonstrate that resonance Raman scattering spectroscopy opens up a wide range of possibilities for quantifying the layer composition of the superposition states of the exciton and the interlayer hybridisation parameters in heterostructures of two-dimensional materials.

Monolayers of transition-metal dichalcogenides (TMD) are semiconductors with a plethora of appealing optical properties [1–3]. Unlike the bulk compounds, they feature a direct band gap and a strong light–matter interaction involving optical transitions between the K-valleys electrons and holes [4, 5]. Angular momentum, implicit in the conduction and valence band K-valleys states that are dominated by transition metal d-orbitals, determines a valley-selective coupling to the circularly polarised light [6, 7]. At the same time, spin–orbit coupling in transition-metals sets a tight spin-valley locking for the valence band holes, leading to the spin-selectivity of the optical transitions in each valley [2].

In van der Waals heterostructures of TMDs [8], these properties are additionally enriched by the layer-indirect optical transitions [9] across the type-II interface. These excitations are much more sensitive to twist angle than the intralayer excitons. Changing between parallel ($\theta \approx 0^\circ$) and anti-parallel layer ($\theta \approx 60^\circ$) alignment changes the energy of bright interlayer excitons (IXs) by the spin-orbit splitting of carrier in the ‘rotated’ layer (see figure 1). Also, for twist angles near (anti)parallel alignment, a twist-dependent momentum mismatch between K-valleys means that optically active IXs have a finite centre of mass momentum and substantial kinetic energy creating the conditions for valley memory [9], tunability of the lifetime, accumulation of high densities of IX, and even Bose–Einstein condensation [10] at low temperatures.

Interlayer tunnelling of electrons and holes also leads to the hybridisation of the intralayer and IXs (see figure 1). This can lead to strong hybridisation when energies of the two states are resonant [8]. Such resonant conditions naturally occur in homobilayers and few-layer films of TMDs [9, 10]. For some heterostructures, such as highly aligned MoSe$_2$/WSe$_2$ bilayers, strong hybridisation has been observed [11] between the nearly degenerate lowest-energy IX and...
the MoSe$_2$ A exciton, due to the nearly degenerate conduction band edges in the two layers and similar binding energies for the two exciton species. Evidence for the resonance anti-crossing due to the interlayer hybridisation of excitons has also been found in reflectivity spectra of both WSe$_2$/MoS$_2$ and MoSe$_2$/WSe$_2$ bilayers [12], which involved the B exciton in WX$_2$ and a layer-indirect exciton IX with electron on the tungsten and hole on the molybdenum layer. Here, we employ resonance Raman scattering (complemented by reflectivity and photoluminescence spectroscopy, all at 4 K) both to identify the anti-crossing features related to the IX$^\ast$ and B excitons hybridization in WSe$_2$/MoSe$_2$ heterobilayers and to determine the layer composition of the superposition states of these excitons, together with the value of the interlayer coupling.

Raman scattering has a unique ability to determine the nature of the phonons responsible for scattering specific optically active electronic excitations, e.g. excitons. In addition, resonant enhancement of the Raman scattering when the incoming or outgoing photon energies coincide with specific exciton states means that resonance Raman scattering studies (rRs) permit us to access the same information on the exciton energies and linewidths as optical absorption and photoluminescence measurements. By observing the resonance behaviour of phonons due to both the WSe$_2$ and MoSe$_2$ monolayers [13, 14] at hybridised excitons [8] in heterostructures one can directly quantify the exciton’s layer composition. Below, we report the results of such studies performed on several MoSe$_2$/WSe$_2$ heterobilayers. These include sample HS1, where anti-parallel alignment of the 2D crystals (at $\theta = 57^\circ$) promotes the inter-intralayer exciton hybridization, and a reference sample HS2 ($\theta = 20^\circ$), where no interlayer hybridisation is expected due to a large momentum mismatch of the band edges in the two layers (additional samples with $\theta = 6^\circ$ and $\theta = 60^\circ$ are discussed in the supplementary information (SI) (available online at stacks.iop.org/2DM/8/035009/mmedia)). The rRs data in this paper focuses on excitation photon energies from 2.05 to 2.27 eV and is part of a larger dataset containing data for energies from 1.6 to 2.27 eV. This allows us to probe the excitonic resonances A1s, A2s, B1s and B2s in MoSe$_2$ and A1s, A2s and B1s and WSe$_2$ (A1s and B1s are the ground-state excitons in these two spin-orbit-split bands, and A2s and B2s are their first optically active excited states). To remove unwanted, luminescence from the rRs spectra the sample was excited with a linearly polarised excitation Raman scattered light measured for both parallel and crossed polarisations, allowing unpolarised luminescence to be removed (see section 1 for more detail).

In figure 2(a) we present Raman spectra for monolayers of WSe$_2$ and MoSe$_2$ when resonant with their respective A1s excitons along with Raman spectra for HS1 and HS2 measured in resonance with the WSe$_2$ intralayer A1s exciton. As expected, the Raman spectra for HS1 and HS2 are almost identical to the WSe$_2$ monolayer spectra with only minor variations in the relative intensity of different peaks. In figure 2(b) we present Raman spectra for both monolayers and heterostructures taken with an excitation photon energy of 2.161 eV, which is near resonance with the WSe$_2$ B1s exciton. At this excitation energy, in sample HS1, we observe three new peaks at 291, 309 and 354 cm$^{-1}$ which do not appear in the other samples or at other resonances of HS1. In addition, in HS1 there is a peak at 241 cm$^{-1}$, which is anomalously strong ($\sim$3 times greater than in monolayer WSe$_2$ and HS2). The resonance Raman data in figure 3...
Figure 2. Resonant Raman scattering spectra of monolayer WSe$_2$, MoSe$_2$, and their heterostructures (HS). (a) Raman spectra for monolayer WSe$_2$, HS1 (57°) and HS2 (20°) when resonant with the WSe$_2$ A1s exciton and a spectra for a monolayer MoSe$_2$ when resonant with the MoSe$_2$ A1s exciton. To allow for ease of visual comparison each spectra has been normalised to the maximum intensity and offset. The scaling factors shown in each panel are relative to the absolute scattering probability of the WSe$_2$ A1′ peak. In panel (b) the arrows highlight the new peaks at 241, 291, 309 and 354 cm$^{-1}$. Unwanted luminescence was removed by subtraction of parallel and perpendicularly polarised Raman spectra (see section 1 for details).

Figure 3. Comparison of Raman intensity plots between monolayer and heterostructures. Resonance Raman spectra for (a) monolayer WSe$_2$, (b) HS1 (57°), and (c), HS2 (20°) are presented for excitation energies from 2.05 to 2.25 eV. The data is plotted using a logarithmic scale for the intensity in order to highlight weak features. Arrows included along the top of panels (b) and (c) indicate the position of the new peaks in HS1 (241, 291, 309 and 354 cm$^{-1}$), two defect activated peaks in HS2 106 and 124 cm$^{-1}$, along with the Si Raman peak at 520 cm$^{-1}$. The peak at 37 cm$^{-1}$ in HS1 is attributed to a moiré zone-folded acoustic phonon like those reported in homobilayers [20, 21]. In each colour map the white lines indicate the incoming (solid) and outgoing (dashed) resonance conditions for each excitonic state. For monolayer WSe$_2$ and HS2 the resonance behaviour is explained in terms of a single resonance with the WSe$_2$ B1s intralayer exciton. Whereas in HS1 two resonances are required to explain the resonance Raman data. These are attributed to the hybridised excitons formed from the WSe$_2$ B1s intralayer exciton and interlayer exciton IX$^*$ and are labelled as hX$^+$ and hX$^-$. Also demonstrates the unique behaviour of these new Raman peaks. For monolayer WSe$_2$ (figure 3(a)) all of the Raman peaks appear to have a broad resonance centred at $\sim$2.180 eV. Likewise in HS2 (figure 3(c)) all the peaks demonstrate a broad resonance centred at $\sim$2.170 eV. In contrast in HS1 (figure 3(b)) the WSe$_2$ peaks at 257, 261 and 396 cm$^{-1}$ have a resonance centred at $\sim$2.18, whereas the new peaks at 241, 291, 309 and 354 cm$^{-1}$ have a resonance which peaks at a lower energy $\sim$2.15 eV and is narrower. As a result in HS1 it is clear that the four new peaks have a common resonance behaviour which is different from the other peaks observed in HS1 or the other samples. Based upon Raman spectra reported for few layer WSe$_2$ and MoSe$_2$ [15, 16], along with spectra for heterobilayers containing either MoSe$_2$ or WSe$_2$ layers [17–20] we assign the peaks at 309 and 354 cm$^{-1}$ to the WSe$_2$ and MoSe$_2$ A$_2''$($\Gamma$) phonons. Based upon the assignment of a MoSe$_2$ phonon we also assign the peak at 291 cm$^{-1}$ to the MoSe$_2$ E($\Gamma$) phonon and the peak at 241 cm$^{-1}$ to the MoSe$_2$ A$_1'$($\Gamma$). Both of which are observed at the same shift in the monolayer and heterostructure samples when resonantly exciting the MoSe$_2$ A1s and B1s excitons.

Whilst the observation of three MoSe$_2$ phonons at energies far from MoSe$_2$ resonances and near a predominantly WSe$_2$ B1s resonance is quite unexpected, it can be explained if the rRs probes an exciton which is a superposition of two excitons which involves electron/hole states in both the WSe$_2$ and MoSe$_2$ layers. We can also discard the possibility that these new peaks are hybridised phonon modes [17] as they are not observed at any of the other resonances. While the observed Raman scattering...
at MoSe$_2$ A1s and B1s and WS$_2$ A1s resonances are only weakly perturbed by the other layer in the heterostructures, the WS$_2$ B1s state is significantly hybridised with an exciton involving electrons in the MoSe$_2$ layer which excites MoSe$_2$ phonons, leading to the observation of peaks in the Raman spectra due to three of the four zone-centre MoSe$_2$ phonons. The fourth zone-centre phonon, the E$^\prime$(Γ), is not observed in any spectra as it is forbidden by an in-plane symmetry which is likely inherited by the heterostructure [16, 23].

With clear evidence for exciton hybridisation, we now determine the composition of the hybrid states. Without any MoSe$_2$ intralayer exciton near the WS$_2$ B1s energy (see SI), the only other option is its hybridisation with an IX. The energy of the fundamental IX, in which the electron is in MoSe$_2$ and the hole in WS$_2$, is known [14, 24] to have an energy of $\sim$1.33 eV, and so we can discount it as the hybridised IX. However, a higher-energy IX (IX$^*$) which involves an electron in the WS$_2$ layer and a hole in MoSe$_2$ layer (see figure 1(a)) may have sufficient energy to hybridise resonantly with the B1s in WS$_2$ via spin-conserving interlayer tunnelling of a hole. Using a combination of measured transition energies for HS1, experimental lattice and band structure parameters [25–29], and theoretical predictions for monolayer dielectric constants, interlayer band alignment and exciton binding energies [1, 30–33] (see section 1), we conclude that the energy difference $E_{\text{B1s}} - E_{\text{IX}}^*$ between the WS$_2$ B1s exciton and IX$^*$ is in the range from $-17$ to 233 meV for a twist angle of 57°, suggesting that hybridisation of these two states is possible.

Additional information, supporting the hybridisation of the B1s and IX$^*$ excitons to form our hybridised upper (hX$^*_+$) and lower (hX$^*_-$) excitons, comes from the fine structure of the rRs profiles of the Raman peaks measured in HS1, HS2 and the WS$_2$ monolayer (see figure 4 and SI). Analysis of these profiles using standard third order perturbation theory allows the energies of the excitonic states to be determined. The resonance behaviours of the monolayer and HS2 peaks are dominated by a single (figure 4(a)) at 2.156 ± 0.003 eV and 2.161 ± 0.006 eV respectively; the energies and errors were obtained from fitting (see SI). However, HS1 has clear evidence for two hybridised excitonic states in the same energy range, at 2.102 ± 0.001 eV and 2.168 ± 0.001 eV (figure 4(a)). In HS1 the peaks also observed in WS$_2$ monolayer show two peaks in the rRs profiles, one centred on the energy of each hybridised states (figure 4(a)). However, the hybridisation specific peaks at 291, 309 and 354 cm$^{-1}$ show a single narrower resonance between the two energies (figure 4(b)). This behaviour occurs because for these phonons scattering between the two hybridised excitons is stronger than scattering within each exciton band [34].

As observed in both the resonance Raman and reflectivity spectra (see figure 5), the lower energy hybridised state has a significantly lower oscillator strength $I_-$ than the upper's $I_+$, by a factor of $I_+/I_- \approx 11$ (see SI for more info). As the oscillator strength of the non-hybridised IX is negligible compared to the intralayer exciton, the oscillator strength ratio is a direct measurement of the intralayer exciton component of the two hybridised states (for details, see section 2).
see section 1 and the SI). Let \( \varepsilon_{B1s} \) and \( \varepsilon_{IX} \) be the energies of the non-hybridised B and IXs, respectively. The hybridised exciton energies are given by

\[
\varepsilon_{\pm} = \left( \frac{\varepsilon_{B1s} + \varepsilon_{IX}}{2} \right) \pm \sqrt{T^2 + \left( \frac{\varepsilon_{B1s} - \varepsilon_{IX}}{2} \right)^2},
\]

where \( \varepsilon_{B1s} \) and \( \varepsilon_{IX} \) are the corresponding exciton Bohr radii, \( m_e \) is the mass of the electron shared by both excitons, \( m_{B1s} \) the total mass of the WSe\(_2\) B1s exciton, and \( \Delta K = 0.066 \) is the mismatch in wavevector between the MoSe\(_2\) K’ and WSe\(_2\) K valleys for a 57° twist angle.

The ratio between the intralayer exciton components of the hybridised states takes the simple form

\[
I_{+}/I_{-} = \left( \frac{|\varepsilon_{B1s}|}{|\varepsilon_{IX}|} \right)^2 = \left( \frac{\varepsilon_+ + \varepsilon_{B1s} - \varepsilon_{IX}}{2} \right) / \left( \varepsilon_+ + \varepsilon_{B1s} + \varepsilon_{IX} / 2 \right),
\]

which depends indirectly on \( T \). Then, fixing \( \varepsilon_{\pm} \) to their corresponding experimental values, 2.102 eV and 2.168 eV, and requiring an oscillator strength ratio of \( I_+/I_- = 11 \) we obtain \( T = 15 \) meV and the energies of the non-hybridised B and IXs as 2.156 eV (in agreement with the monolayer B1s exciton) and 2.110 eV, respectively. This, together with experimental values for the masses [28, 29] and Bohr radii obtained from our own solutions to the excitons’ Wannier equations (see SI) give the valence-band tunnel coupling as \( t_r \approx 11 \) meV. The above process is shown in figures 6(a) and (b).

Besides providing direct experimental evidence for the hybridisation of layer-direct and -indirect excitons, resonant Raman scattering analysis of intra-layer phonons provides a method for a non-invasive measurement of the interlayer tunnelling for the spin and valley matching states in the crystallographically aligned layers. Obtaining quantitative information on the interlayer hybridisation constants for the states in heterostructures of two-dimensional semiconductors opens new opportunities for the intelligent design of heterostructures for optoelectronics applications in the areas of quantum technologies. The hybridised layer-direct and -indirect excitons represent a two-level system, which is tunable by an externally applied vertical displacement field [8], and where the superposition of two modes can be operated as an optical qubit. Placing such bilayers inside an optical cavity with a localised photon mode close to the hybridised exciton pair [10, 36–38] may additionally open ways towards making a three-level quantum-optical bit for ultrafast information processing.

1. Methods

1.1. Experimental methods

MoSe\(_2\)/WSe\(_2\) heterobilayers and constituent monolayers were fabricated via mechanical exfoliation and encapsulated in hexagonal boron nitride, using dry stamp transfer [39] on oxide coated silicon substrates. For heterobilayer samples twist angles were determined using optical microscope images and have an uncertainty of \( \pm 1^\circ \) with the crystal axes of the monolayers determined through second harmonic generation prior to stacking [40]. For all measurements, the samples were held at 4 K in a liquid helium flow cryostat. For the Resonance Raman measurements two laser sources were used a Coherent Mira 900 (1.6–1.76 eV) and Coherent CR 599 dye
laser (1.74–2.27 eV), utilising DCM, Rhodamine 6G and Rhodamine 110 laser dyes. The Raman scattered light was coupled into a Princeton Instruments Tri-vista triple spectrometer equipped with a liquid nitrogen cooled CCD. The samples were excited using a horizontally polarised laser, and the Raman scattered light measured for both parallel and perpendicular linear polarisations. Unwanted luminescence, from the sample, was eliminated by subtraction of the parallel and perpendicular polarised spectra. This allows for removal of unwanted luminescence with negligible effect on the measured Raman intensity due to the strong linear polarisation of the Raman and unpolarised nature of the luminescence signal. Frequency calibration of the Raman spectra was accomplished using the silicon peak at 520 cm$^{-1}$ as an internal reference. Comparison of the Raman intensity across multiple different samples was achieved via an absolute normalisation. This involved normalisation to the Silicon Raman intensity, correction for thin film interference effects and use of the absolute Raman cross-section for the silicon peak. Reflectivity spectra were obtained using a Fianium super continuum source and Ocean Optics HR 4000 USB spectrometer, and measured relative to the Silicon substrate. For both Raman and reflectivity measurements the incident power was kept below 100 µW to ensure minimal photo-doping or laser heating of the sample. All optical measurements were performed using a back-scattering geometry with a ×50 Olympus objective resulting in a laser spot diameter of ∼3 µm on the sample.

For more information on experimental methods and data analysis see supporting information.

1.2. Theoretical model

1.2.1. Estimation of the WSe$_2$ B1s and interlayer exciton IX$^*$ detuning in anti-parallel stacked WSe$_2$/MoSe$_2$

To approximate the IX$^*$ energy we solved the Wannier equation for a MoSe$_2$ hole and a WSe$_2$ electron with effective masses extracted from the earlier publications [25–29] and using the long-range interlayer electron–hole interaction derived in Danovich et al [41]. The layer-indirect gap between MoSe$_2$ valence-band and WSe$_2$ conduction-band edges (see figure 3(a)), was estimated from the $ab$ initio DFT data reported in Gong et al [33, 42] and experimental and DFT spin-orbit splitting energies for the MoSe$_2$ valence band and WSe$_2$ conduction band, respectively [1, 29]. Combining this with the exciton binding energy gives a total energy of $2.039 \pm 0.111$ eV for the momentum-indirect IX$^*$ state, and we estimate an additional kinetic energy of $\approx 17$ meV for the bright (momentum-direct) IX$^*$ due to momentum mismatch determined by the interlayer twist angle. Contrasting this with the measured WSe$_2$ B1s energy of 2.164 ± 0.001 eV we conclude that the detuning between the two excitons is between $-17$ and 233 meV.

1.2.2. Estimation of the interlayer valence-band hopping energy from the resonance Raman spectrum

Hybridization between the intralayer WSe$_2$ B1s and interlayer IX$^*$ excitons can be modelled by a 4 × 4 Hamiltonian with one basis state corresponding to WSe$_2$ B1s, and three representing the valley-mismatched IXs formed by holes at the three equivalent K valleys of MoSe$_2$, each bound to an electron at the nearest K valley of WSe$_2$. The intralayer–IX hybridization term is related to the interlayer valence-band hopping energy $t_v$ as described in the main text, following [8]. Diagonalizing the Hamiltonian gives two bright states $\psi_{-}$ and $\psi_{+}$ at energies $\varepsilon_{-}$ and $\varepsilon_{+}$ with oscillator strengths deriving from their WSe$_2$ B1s exciton components, and two dark states formed solely by IXs, which we shall ignore henceforth. We computed the oscillator strength ratio of the two bright states as the modulus squared of the ratio of their WSe$_2$ B1s components for a range of values of $t_v$, fixing the energies $\varepsilon_{-}$ and

![Figure 6. Twist angle dependent hybridisation of the WSe$_2$ B1s and IX$^*$ excitons. (a) Calculated optical absorption spectrum of hybridized excitons (normalized) for a 57$^\circ$ heterostructure, as a function of the hole tunnelling energy $t_v$. The bare WSe$_2$ B1s and IX$^*$ energies corresponding to each value of $t_v$ are shown with solid lines. (b) Absorption intensity ratio between the higher and lower energy absorption lines. The experimentally measured value is shown in purple and the range of $t_v$ consistent with this measurement is highlighted in yellow. This places the detuning between WSe$_2$ B1s and IX$^*$ at 46.9 ± 0.4 meV. See section 1 for calculation details.](image-url)
\( \varepsilon^+ \) at the experimental values for the hybridised exciton resonances, as determined by the rRS data in figure 3(b). Comparing the theoretical oscillator strength ratios to that measured by resonance Raman gives a hopping strength \( t_h \approx 11 \text{ meV} \). The available data on the interlayer tunnel coupling for electrons are between 26 and 43 meV \([11, 12]\), comparable with our obtained value.

**Data availability statement**

The data that support the findings of this study are openly available at the following URL/DOI: 10.5258/SOTON.D1314.

**Author contributions**

The experiments were conceived by D C S, L P M and X X. Samples were fabricated by P R. The experimental measurements were performed by J V and L P M. Theoretical calculations were performed by D R T and V F. Data analysis and interpretation was carried out by L P M, D C S, J V, D R T and V F. The paper was written by D C S, L P M, D R T and V F. All authors discussed the results and commented on the manuscript.

**Conflict of interests**

The authors declare no competing financial interests.

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**References**

[1] Kormányos A, Burkard G, Gmitra M, Fabian J, Zólyomi V, Drummond N D and Fal’ko V 2015 K P theory for two-dimensional transition metal dichalcogenide semiconductors 2D Mater. 2 022001

[2] Choi W, Choudhary N, Han G H, Park J, Akinswande D and Lee Y H 2017 Recent development of two-dimensional transition metal dichalcogenides and their applications Mater. Today 20 116–30

[3] Manzeli S, Ovchinnikov D, Pasquier D, Yazyev O V and Kis A 2017 2D transition metal dichalcogenides Nat. Rev. Mater. 2 17033

[4] Mak K F, Lee C, Hone J, Shan J and Heinz T F 2010 Atomically thin MoS\(_2\): a new direct-gap semiconductor Phys. Rev. Lett. 105 2–5

[5] Splendiani A, Sun L, Zhang Y, Li T, Kim J, Chini C-Y, Galli G and Wang F 2010 Emerging photoemission evidence in monolayer MoS\(_2\) Nano Lett. 10 1271–5

[6] Yao W, Xiao D and Niu Q 2008 Valley-dependent optoelectronics from inversion symmetry breaking Phys. Rev. B 77 1–7

[7] Cao T et al 2012 Valley-selective circular dichroism of monolayer molybdenum disulphide Nat. Commun. 3 887

[8] Ruiz-Tijerina D A and Fal’ko V I 2019 Interlayer hybridization and moiré superlattice minibands for electrons and excitons in heterobilayers of transition-metal dichalcogenides Phys. Rev. B 99 30–2

[9] Shimazaki Y, Schwartz I, Watanabe K, Taniguchi T, Kroner M and Imamoglu A 2020 Strongly correlated electrons and hybrid excitons in a moiré heterostructure Nature 580 472–7

[10] Król M et al 2020 Exciton-polaritons in multilayer WSe\(_2\) in a planar microcavity 2D Mater. 7 015006

[11] Alexeev E M et al 2019 Resonantly hybridized excitons in moiré superlattices in van der Waals heterostructures Nature 567 81–6

[12] Hsu W T, Lin B-H, Lu L-S, Lee M-H, Chu M-W, Li L-J, Yao W, Chang W-H and Shih C-K 2019 Tailoring excitonic states of van der Waals bilayers through stacking configuration, band alignment, and valley spin Sci. Adv. 5 1–7

[13] McDonnell L P, Viner J S, Rivera P, Xu X and Smith D C 2020 Observation of intravalley phonon scattering of 2s excitons in MoSe\(_2\) and WSe\(_2\) monolayers 2D Mater. 7 045008

[14] Seyler K L, Rivera P, Yu H, Wilson N P, Ray E L, Mandrus D G, Yan J, Yao W and Xu X 2019 Signatures of moiré-trapped valley excitons in MoSe\(_2\)/WSe\(_2\) heterobilayers Nature 567 66–70

[15] Terrones H et al 2014 New first order Raman-active modes in few layered transition metal dichalcogenides Sci. Rep. 4 4215

[16] Soubale B, Bruchhausen A E, Fainstein A, Nagajewski K and Faugeras C 2016 Resonance effects in the Raman scattering of monolayer and few-layer MoSe\(_2\) Phys. Rev. B 93 1–9

[17] Chiu M H, Li M-Y, Zhang W, Hsu W-T, Chang W-H, Terrones M, Terrones H and Li L-J 2014 Spectroscopic signatures for interlayer coupling in MoS\(_2\)/WSe\(_2\) van der Waals stacking ACS Nano 8 9649–56

[18] Wang K et al 2016 Interlayer coupling in twisted WSe\(_2\)/WSe\(_2\) bilayer heterostructures revealed by optical spectroscopy ACS Nano 10 6612–22

[19] Nayak P K et al 2017 Probing evolution of twist-angle-dependent interlayer excitons in MoSe\(_2\)/WSe\(_2\) van der Waals heterostructures ACS Nano 11 4041–50

[20] Mouri S, Zhang W, Kozawa D, Mijauchy Y, Eda G and Matsuda K 2017 Thermal dissociation of inter-layer
excitons in MoS$_2$/MoSe$_2$ hetero-bilayers Nanoscale 9 6674–9
[21] Lin M L et al 2018 Moiré phonons in twisted bilayer MoS$_2$ ACS Nano 12 8770–80
[22] McDonnell L P et al 2020 Experimental realisation of dual periodicity moiré superlattice in a MoSe$_2$/WSe$_2$ heterobilayer (https://arxiv.org/abs/2009.07676)
[23] Zhao W, Ghorannevis Z and Kumar A K 2013 Lattice dynamics in mono-and few-layer sheets of WS$_2$ and WSe$_2$ Nanoscale 5 9677–83
[24] Rivera P et al 2017 Determination of band offsets, hybridization, and exciton binding in 2D semiconductor heterostructures Sci. Adv. 3 e1601832
[25] Wilson J A and Yoffe A D 1969 The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties Adv. Phys. 18 193–335
[26] Hicks W T 1964 Semiconducting behavior of substituted tungsten diselenide and its analogues J. Electrochem. Soc. 111 1058
[27] Al-Hilli A A and Evans B L 1972 The preparation and properties of transition metal dichalcogenide single crystals J. Cryst. Growth 15 95–101
[28] Gustafsson M V, Yankowitz M, Forsythe C, Rhodes D, Watanabe K, Taniguchi T, Hone J, Zhu X and Dean C R 2018 Ambipolar Landau levels and strong band-selective carrier interactions in monolayer WSe$_2$ Nat. Mater. 17 411–5
[29] Nguyen P V et al 2019 Visualizing electrostatic gating effects in two-dimensional heterostructures Nature 572 220–3
[30] Kumar A and Ahluwalia P K 2012 Tunable dielectric response of transition metals dichalcogenides MX$_2$ (M = Mo, W; X = S, Se, Te): effect of quantum confinement Physica B 407 6627–34
[31] Berkelbach T C, Hybertsen M S and Reichman D R 2013 Theory of neutral and charged excitons in monolayer transition metal dichalcogenides Phys. Rev. B 88 1–6
[32] Kang J, Tongay S, Zhou J, Li J and Wu J 2013 Band offsets and heterostructures of two-dimensional semiconductors Appl. Phys. Lett. 102 012111
[33] Gong C, Zhang H, Wang W, Colombo L, Wallace R M and Cho K 2013 Band alignment of two-dimensional transition metal dichalcogenides: application in tunnel field effect transistors Appl. Phys. Lett. 103 055313
[34] McDonnell L P, Huang C-C, Cui Q, Hewak D W and Smith D C 2018 Probing excitons, trions and dark excitons in monolayer WS$_2$ using resonance Raman spectroscopy Nano Lett. 18 7651–64
[35] de Luca M, Cartron X, Martín-Sánchez J, López-Suárez M, Trotta R, Rurali R and Zardo I 2020 New insights in the lattice dynamics of monolayers, bilayers, and trilayers of WSe$_2$ and unambiguous determination of few-layer-flakes’ thickness 2D Mater. 7 025004
[36] Dufferwiel S et al 2015 Exciton-polaritons in van der Waals heterostructures embedded in tunable microcavities Nat. Commun. 6 8579
[37] Flatten L C, He Z, Coles D M, Trichet A A P, Powell A W, Taylor R A, Warner J H and Smith I M 2016 Room-temperature exciton-polaritons with two-dimensional WS$_2$ Sci. Rep. 6 1–7
[38] Han X, Wang K, Xing X, Wang M and Lu P 2018 Rabi splitting in a plasmonic nanocavity coupled to a WS$_2$ monolayer at room temperature ACS Photonics 5 3970–6
[39] Castellanos-Gomez A, Buscema M, Molenaar R, Singh V, Janssen L, Van Der Zant H S J and Steele G A 2014 Deterministic transfer of two-dimensional materials by all-dry viscoelastic stamping 2D Mater. 1 011002
[40] Rivera P, Seyler K L, Yu H, Schaibley J R, Yan J, Mandrus D G, Yao W and Xu X 2016 Valley-polarized exciton dynamics in a 2D semiconductor heterostructure Science 351 688–91
[41] Danovich M, Ruiz-Tijerina D A, Hunt R J, Szymieszewski M, Drummond N D and Fal’ko V I 2018 Localized interlayer complexes in heterobilayer transition metal dichalcogenides Phys. Rev. B 97 1–18
[42] Xu K et al 2018 The role of Anderson’s rule in determining electronic, optical and transport properties of transition metal dichalcogenide heterostructures Phys. Chem. Chem. Phys. 20 30351–64