

Excited Rydberg States in MoSe₂/WSe₂ Heterostructures

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The functional form of Coulomb interactions in the transition metal dichalcogenides and other van der Waals solids is critical to many of their unique properties, e.g. strongly-correlated electron states, superconductivity and emergent ferromagnetism. This paper presents measurements of key excitonic energy levels in MoSe₂/WSe₂ heterostructures. These measurements are obtained from resonance Raman experiments on specific Raman peaks only observed at excited states of the excitons. This data is used to validate a model of the Coulomb potential in these structures which predicts the exciton energies to within ~5 meV. This model is used to determine the effect of heterostructure formation on the single-particle band gaps of the layers and will have a wide applicability in designing the next generation of more complex transition metal dichalcogenide structures.

One of the key reasons for the unique properties of van der Waal's structures is that the reduction of dielectric screening in these 2D systems leads to enhanced Coulomb interactions with functional form quite different from the standard 3D Coulomb potential^{1,2}. This Coulomb potential leads to the renormalisation of the single particle electronic energy and an increase in the band gap^{3,4}; exciton states which follow a non-hydrogenic series⁵ with large oscillator strengths and short radiative lifetimes⁶⁻⁸; and stable multi-particle states such as trions⁹⁻¹². It is critical to the existence of strongly-correlated states leading to optically accessible incompressible electron states, superconductivity^{13,14}, and emergent ferromagnetism¹⁵. It is responsible for the existence of interlayer excitons in transition metal dichalcogenide (TMD) heterostructures and their mutual repulsion leading to a density dependent blue shift of their emission¹⁶. The exchange component of the Coulomb interaction is responsible for mixing of the A and B excitons with implications for spintronics¹⁷.

The importance of quantifying the Coulomb interaction in TMD monolayers has led to a series of experiments aimed at measuring the energy of the bright, zero orbital angular momentum (s), excitonic states in these structures using a variety of techniques including reflectivity^{5,18,19}, photoluminescence excitation^{6,20}, and magneto-PL²¹⁻²³. In addition two-photon absorption measurements have been performed to allow the energy of the one angular momentum (p) states to be determined²⁴. However, despite the wider range of exciting physics, e.g. interlayer excitons, which can be accessed in TMD heterostructures, there are no reliable measurements of the energies of intralayer (single layer) excitons beyond the minimum energy 1s state in such structures. In this paper we discuss the determination of the energy of the (intralayer) A2s and B2s states in a MoSe₂/WSe₂ bilayer heterostructure with accuracies of a few meV in most cases. The method relies on unique Raman peaks only observed at 2s transitions which enable the unequivocal assignment of specific spectral features to these transitions. Additionally, we demonstrate that it is possible to theoretically reproduce these energies to within the errors of the experiments, i.e. 2.5%, using a model whose

parameters can be calibrated with monolayer exciton energies and constrained by separate experiments, and properly takes into account the distance dependent screening.

The results presented here are part of a larger study of high quality hBN encapsulated MoSe₂ and WSe₂ monolayers⁸ and MoSe₂/WSe₂ heterobilayers^{25,26}, with twist angles 2, 6, 20, 57 and 60°, using resonance Raman and reflectivity spectroscopy. All measurements were performed with the samples held at 4 K in the low excitation intensity regime (< 100 μW). The resonance Raman studies were performed with excitation photon energies from 1.6 to 2.27 eV allowing us to probe the MoSe₂ A1s, A2s, B1s and B2s and WSe₂ A1s, A2s and B1s excitonic resonances. The Raman scattering intensity has been calibrated using absolute scattering rates for the silicon peak at 520 cm⁻¹ and corrected for Fabry-Perot effects^{27,28}.

Colour plots of the Raman results for MoSe₂ and WSe₂ monolayer and two MoSe₂/WSe₂ twisted heterostructures, with twist angles of 57 and 20 °, for excitation energies spanning the MoSe₂ A1s and B1s intralayer excitons and the WSe₂ A1s intralayer excitons are presented in Figs 1, 2 and 3 respectively along with representative Raman spectra at key excitation energies.

As previously observed, the Raman spectra of the samples present a large number of distinct Raman peaks^{8,29,30}; 18 in MoSe₂ and 16 in WSe₂. The Raman peaks show clear resonance behaviour with significant enhancements associated with either the incoming or outgoing photons being at the same energy as one of the bright excitonic states in the two materials. The energy of the two conditions for each of the 2s excitons are presented on the figures using a solid line for the incoming resonance and a dashed line for the outgoing resonance. Despite the Raman scattering at the A1s and B1s excitonic resonances being approximately two orders of magnitude stronger than at the A2s and B2s, key phonons which are only observed at these 2s resonances⁸ allow them to be clearly identified. In the case of MoSe₂ the 2s specific peaks are at 480, 530 and 580 cm⁻¹ (see Figs 1 and 2 and reference⁸). We assigned these peaks to two phonon Raman scattering via the 2A₁'(Γ), E'(Γ) + A₁'(Γ) and 2E'(Γ)

phonons respectively⁸. As shown in the colour plots in Figures 1 and 2, the peaks have a clear outgoing resonance with the A2s state and incoming and outgoing resonances with the B2s states. In the case of WSe₂ there is a unique Raman feature which is only observed at the A2s⁸. This feature is a peak with a characteristic dispersion/resonance behaviour. It starts as a single peak at 495 cm⁻¹ at the incoming resonance energy with intensity that drops to zero for energies just above. It reappears when the laser is tuned to approximately half way between the incoming and outgoing resonances. The peak then disperses to lower shift by 2.5 cm⁻¹ with increasing laser energy until excitation energies close to the outgoing resonance at which point its magnitude increases significantly and it splits into three closely spaced peaks; see SI for more details. There are no differences in the behaviour of the 2s specific peaks between heterostructures and monolayers that cannot be explained by a change in the energy or width of the excitonic transitions.

Now that we have identified the key Raman peaks, we can extract their resonance profiles and fit them to obtain the energy and width of the transitions associated with the excitons. The resonance profiles of the peaks associated with the MoSe₂ A2s resonance (480, 530 and 580 cm⁻¹) in the heterostructures were fitted to a Lorentzian lineshape at the outgoing resonance energy. The energy of the phonon was then subtracted to give the energy of the excitonic state. In the case of the MoSe₂ B1s resonance the standard third order perturbation prediction (Shown in Supplementary Section S3) for the Raman scattering was used to fit both incoming and outgoing resonances. For the WSe₂ A2s, the outgoing resonance was fitted using a Lorentzian lineshape; the complexity of this resonance (Shown in Supplementary Section S5) makes fitting both incoming and outgoing resonances with a third order perturbation model impossible and the outgoing resonance fit is simpler. The energies for the various exciton states obtained from these fits and fits to the resonance profiles of the A₁' phonon at the A1s and B1s excitons are summarised in Tables 1 and 2; the linewidths and a brief discussion of them is given in the SI. In Table 3 we present results for the difference in energy between different excitonic states in monolayers of MoSe₂ and WSe₂ from the literature. Where comparison is possible, the results from the current resonance Raman experiments and the literature monolayer results are in agreement to within experimental error.

As presented in Tables 1 and 2, the energies of the intralayer exciton states and the 1s-2s separations are both significantly reduced in the heterostructures. As the binding energy of the excitons scale with the 1s-2s separation³ we can conclude that the binding energy of the excitons is reduced in the heterostructures. This fact combined with the reduction in the absolute energy of the A1s excitons means we can also conclude that the single particle band gaps of the heterostructures must be reduced and by more than the binding energy of the excitons. In addition to the differences between monolayers and heterostructures there are clearly smaller differences in the energies of the various states in the two heterostructures. Whilst it would be tempting to analyse these in terms of twist dependent hybridisation effects, we feel that the possibility of sample to sample variations, independent of twist angle, means it would be premature to do this at this point.

In order to go further in our interpretation of the results we require a theory for the excitonic energies in the heterostructure. Our model is based upon that set out in³¹. We model the MoSe₂ and WSe₂ layers as infinitesimally thin films possessing only in-plane electric polarizabilities κ_{MoSe_2} and κ_{WSe_2} , respectively, separated by an interlayer distance d and embedded in a bulk dielectric medium representing the hBN encapsulation. In the case of a single layer this model leads to the standard Keldysh potential. We then solve the electrostatic problem to obtain an effective interaction between charge carriers within a given TMD layer. This simultaneously includes screening from the layer itself, from the opposite TMD layer, and from the encapsulation (see SI). Once the interaction is known, the intralayer exciton spectra are obtained by solving the corresponding Wannier equations. This requires a number of parameters that are separately constrained by experiments: the electron and hole masses, which we have taken from ARPES³² and magneto-transport experiments^{33,34}; the in- and out-of-plane dielectric constants of hBN, $\epsilon_{\parallel} = 6.9$ and $\epsilon_{\perp} = 3.7^{35,36}$; and the interlayer separation $d = 6.47 \text{ \AA}$, taken as the average interlayer distance in bulk MoSe₂ and WSe₂^{37,38}. The latter value lies at the bottom end of the range of layer step distances measured for MoSe₂ monolayers on WSe₂ by AFM^{39,40}. As a result, the model contains only two free parameters, κ_{MoSe_2} and κ_{WSe_2} , which we have constrained by six pieces of experimental data: the A2s-A1s energies for the two monolayers and the heterostructures reported here, as well as the A4s-A1s and A3s-A1s energies for monolayers reported

by Liu et al.²¹ and Chen et al.²³ (Table 3). Using $\kappa_{\text{WSe}_2} = 30.83 \text{ \AA}$ and $\kappa_{\text{MoSe}_2} = 29.43 \text{ \AA}$, our theory reproduces all six exciton energy splittings to within 2.0%, all values being within twice the experimental error for these energies (Table 2). As shown in Table 2 these also fall within twice the estimated errors of the experimental values. Thus, whilst it is not obvious that the simplification of treating the layers as thin relative to their separation will work there is currently no need for a more complicated model.

It is worthwhile mentioning that further simplifications to the interaction model described above have a significant impact on its accuracy. For instance, treating the encapsulating medium as an isotropic dielectric with average dielectric constant of $\epsilon = \sqrt{\epsilon_{\parallel}\epsilon_{\perp}}$ increases the minimum error to 5%, or four times the experimental error for the six exciton energies. As discussed in the SI, in the limit of large separation between the charges the interaction takes the form of the Keldysh potential with the effective electric polarizability $\kappa = \kappa_{\text{MoSe}_2} + \kappa_{\text{WSe}_2} + \epsilon_{\parallel}d/2\pi$. This coincides with the long-range limit of interlayer interactions studied in³¹, where it was found that this approximation underestimates screening at short distances. Here, we find that this approximation for the intralayer interaction has the opposite shortcoming, severely underestimating the strength of short range interactions by overestimating the screening contribution from the opposite layer, leading to errors of up to 30% when comparing to the measured spectra.

Based upon the agreement between theory and experiment we can now predict the excitonic binding contribution to the shift in the energies of the A1s excitons when forming the bilayers. The theory gives the difference in the binding energies of the A1s excitons in monolayers and the heterostructure are $-8 \pm 0.5 \text{ meV}$ for WSe₂ and $-19 \pm 1 \text{ meV}$ for MoSe₂. The small predicted errors are due to the fact that changes in the model's input parameters cause correlated changes in the monolayer and heterostructure energy predictions. In addition to changes in the excitonic binding energies there are two other contributions to the changes in the exciton energies on formation of the heterostructure; hybridisation of the excitons and changes in the single particle band gaps. Raman scattering has been shown to be sensitive to hybridisation of excitons²⁵ and there is no evidence for strong hybridisation of any of the excitons discussed in this paper. Therefore, we can conclude that the only other

significant contribution to the absolute energies of the excitons is changes in the single particle state energies and therefore we find that the decrease in the single particle band gaps on formation of the heterostructure are 35 ± 2 meV for MoSe₂ and 46 ± 5 meV for WSe₂.

Whilst so far, we have focussed on the A excitons we also have results for the MoSe₂ B 1s and 2s excitons. In the MoSe₂ monolayer, we find a slightly larger 1s-2s separation for the B exciton (Table 2). This is consistent with ab initio predictions⁴¹ of larger effective masses for both the B electron and hole. In the heterobilayer the MoSe₂ 1s-2s separation for the B exciton is 10-20 meV less than for the A excitons. It is not possible to explain this using the current theory without a reduction of the electron or hole masses associated with the B exciton of around 50%. There is no experimental or theoretical reason for believing such a reduction occurs in a heterostructure. Instead, it is likely that some other effect beyond the current theory is occurring. Due to the higher energy of the B excitons there may be more states available for hybridisation which could affect the energy of the 1s and 2s excitons differently. However, hybridisation is likely to be twist angle dependent and the B 1s-2s energy differences measured in the two samples are remarkably similar considering one is near 0° twist and one near 60° twist. Despite our inability to fully explain the B excitons in terms of geometry modifications of the Coulomb interaction it is remarkable that it is possible to explain the energy of the A excitons in the heterostructure and the monolayers using the same set of parameters for the dielectric and band structure properties and the separately constrained interlayer separation distance.

The results presented here are an important advance in underpinning our understanding of the Coulomb potential in the TMDs and other van der Waals structures. They present a method based upon resonance Raman scattering measurements of Raman peaks which are specific to 2s transitions which allows the energy and width of these transitions to be determined with useful precision. These states were not observed in reflectivity measurements of the same heterostructure samples, presented in the supplementary information, due to the lower oscillator strengths and broader linewidths of the 2s excitonic states in the heterostructures. It is likely that the same method could be applied to other heterostructures containing at least one selenide layer and it may be possible to extend the method to the sulphides if 2s specific Raman peaks can be identified for these materials. Based upon these

measurements we have shown that if we treat the screening due to the layers correctly it is possible to use a single set of parameters to predict the binding energies of both monolayer and heterobilayer excitonic states within 2.5%, i.e. to within current experimental errors. The availability of a reliable way to predict the binding energy of excitons in TMD heterostructures will accelerate the interpretation of a wide range of other experiments. For instance, we have used these predictions to determine the change in the single particle bandgaps for the two constituent layers. They will also be important to the quantification of the effect of hybridisation on excitons⁴² and single particle states. This is particularly true for hybridisation effects that do not depend on twist angle, e.g. Förster energy transfer. As the TMD structures being produced increase in complexity we need to be able to quantitatively predict their properties with confidence and accuracy and this work is an important step in this process.

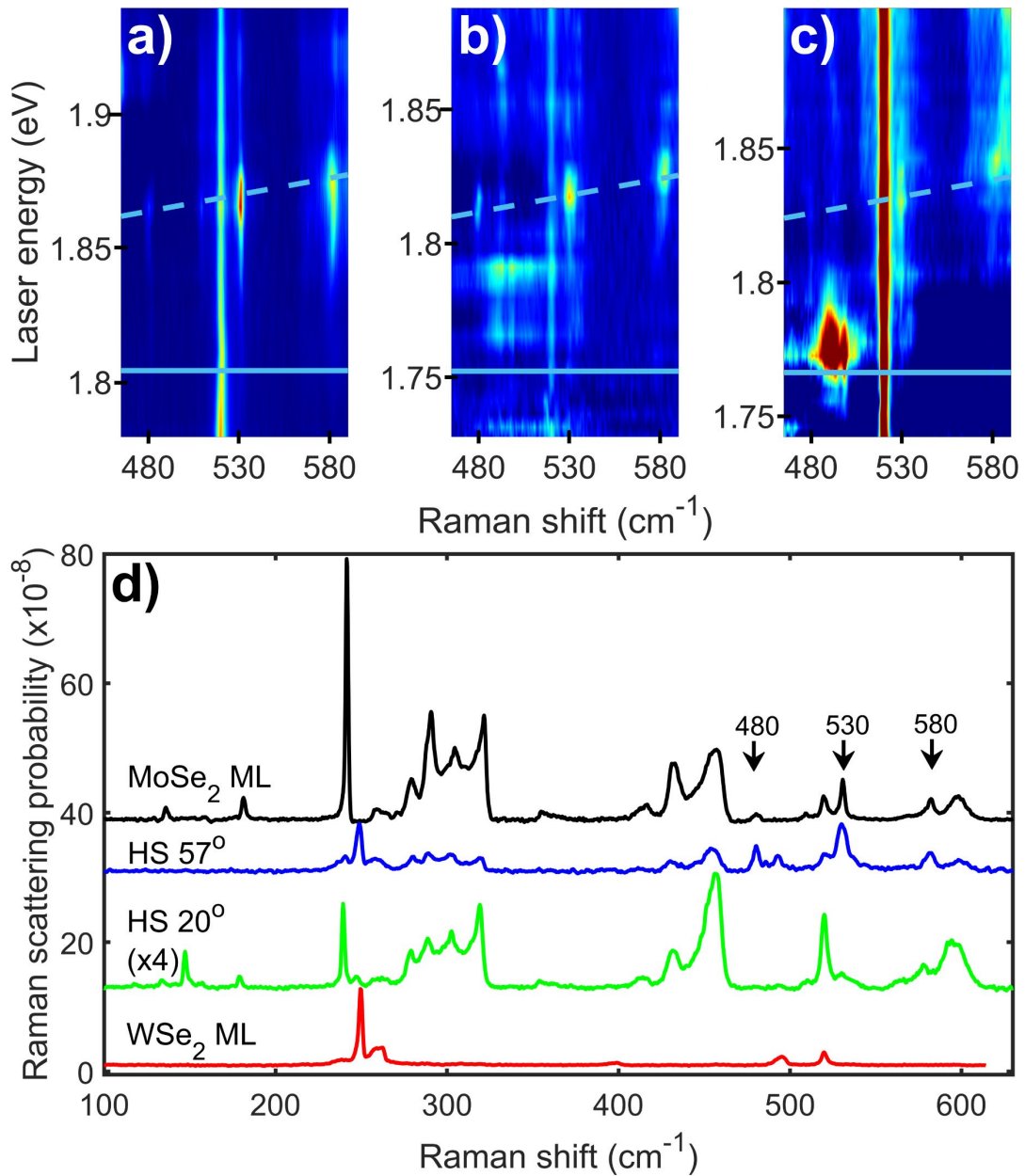


Figure 1: (a)-(c) Resonance Raman colour maps of a MoSe₂ (ML) (a) and two MoSe₂/WSe₂ heterostructures with twist angles of 57° (b) and 20° (c). The three key Raman peaks, that are only observed at the 2s resonances of MoSe₂ have their frequencies marked at 480, 530 and 580 cm⁻¹. The colour maps are presented with a logarithmic scale for the intensity to enhance the weaker peaks. The light blue lines represent the energies of the incoming (solid) and outgoing (dashed) resonances with the MoSe₂ intralayer A₂s exciton (See S3 in the supplementary information for additional discussion of incoming/outgoing resonances). The energy of the exciton was determined by fitting the resonance behaviour of key Raman peaks and is presented in Table 1. (d) Raman spectra for the MoSe₂ (ML) and two MoSe₂/WSe₂ heterostructures plus a WSe₂ monolayer at the outgoing resonance energy of the A₂s exciton, showing the key Raman peaks with their frequencies marked by arrows.

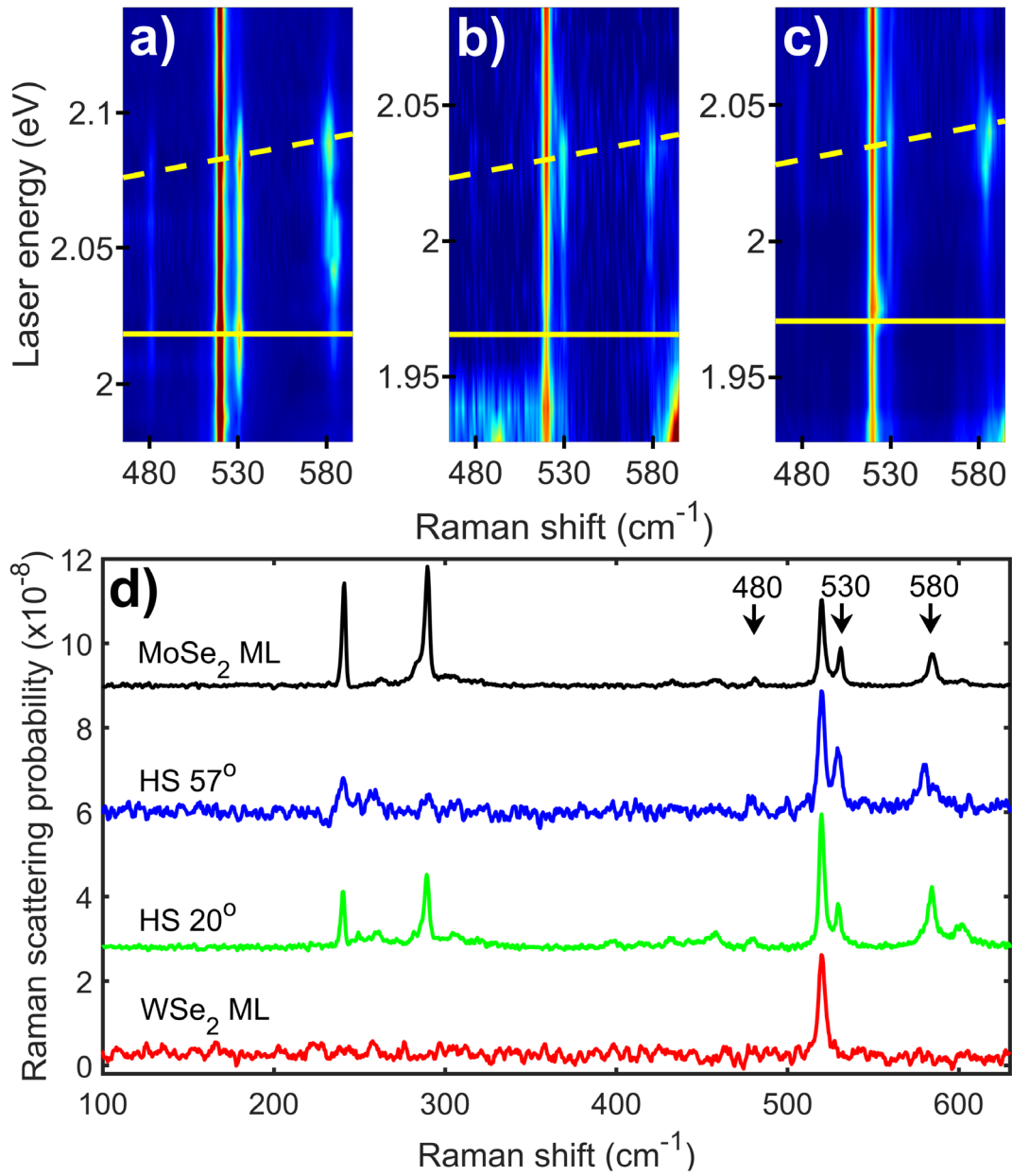


Figure 2: (a)-(c) Resonance Raman colour maps of a MoSe₂ monolayer (ML) (a) and two MoSe₂/WSe₂ heterostructures with twist angles of 57° (b) and 20° (c) across the MoSe₂ B_{2s} intralayer exciton resonance. The three key Raman peaks, that are only observed at the 2s resonances of MoSe₂ have their frequencies marked at 480, 530 and 580 cm⁻¹. The plots are presented with a logarithmic scale for intensity to enhance the weaker peaks. The yellow lines represent the energies of the incoming (solid) and outgoing (dashed) resonances with the MoSe₂ intralayer B_{2s} exciton. The energy of the exciton was determined by fitting the resonance behaviour of the key Raman peaks and is presented in Table 1. (d) Raman spectra for the MoSe₂ monolayer (ML) and two MoSe₂/WSe₂ heterostructures plus a WSe₂ monolayer at the outgoing resonance of the MoSe₂ B_{2s} exciton, showing the key Raman peaks with their frequencies marked by arrows.

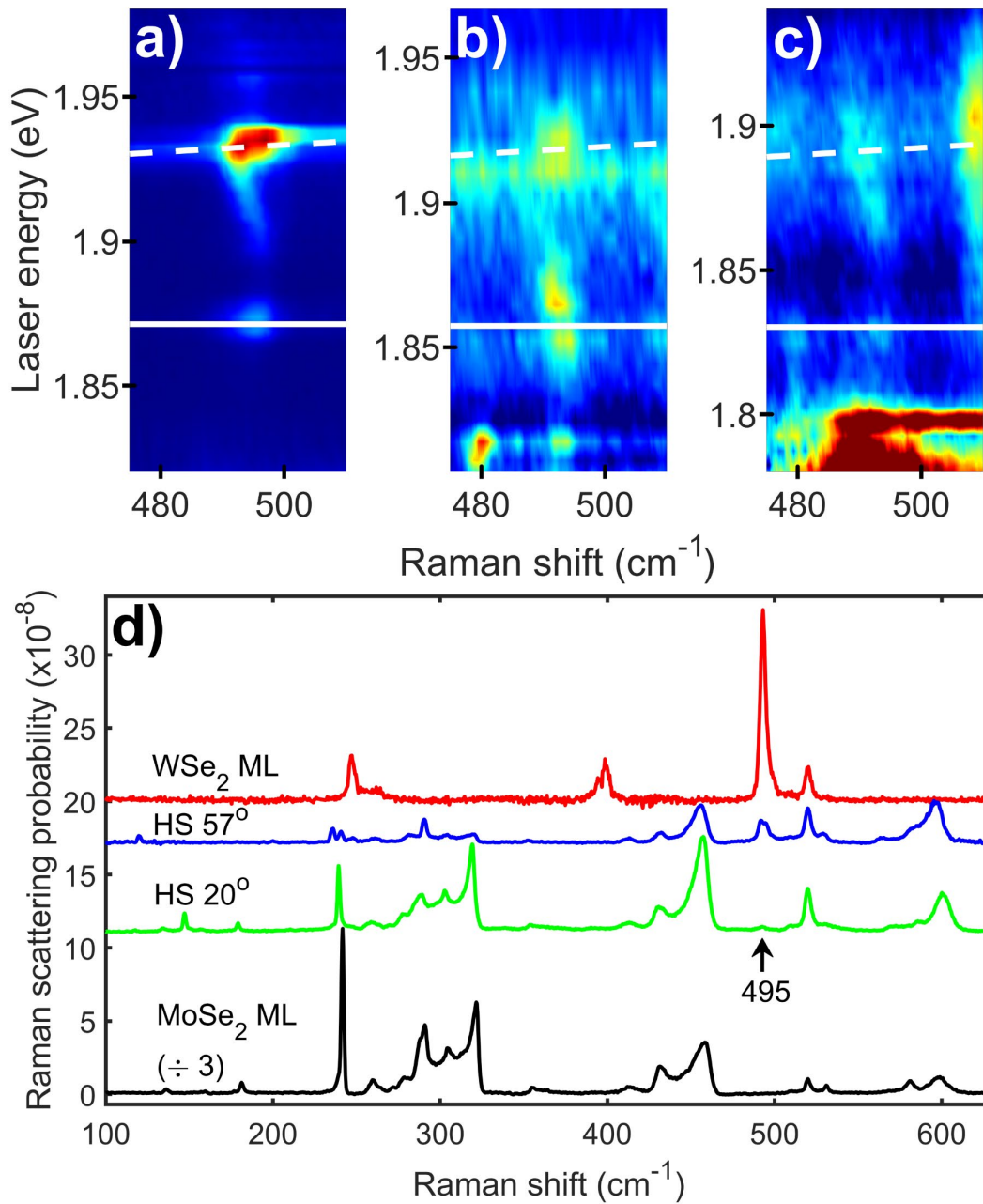


Figure 3: (a)-(c) Resonance Raman colour maps of a WSe₂ monolayer (ML) (a) and two MoSe₂/WSe₂ heterostructures with twist angles of 57° (b) and 20° (c) for excitation energies near the WSe₂ A_{2s} intralayer exciton resonance. The key A_{2s} specific Raman peak is at around 495 cm⁻¹. The plots are presented with a logarithmic scale for intensity to enhance the weaker peaks. The white lines represent the energies of the incoming (solid) and outgoing (dashed) resonances with the WSe₂ intralayer A_{2s} exciton. The energy of the exciton was determined by fitting the resonance behaviour of the key Raman peak and is presented in Table 1. (d) Raman spectra for the WSe₂ monolayer (ML) and two MoSe₂/WSe₂ heterostructures plus a MoSe₂ monolayer at the outgoing resonance of the WSe₂ A_{2s} exciton. The frequency of the associated 495 cm⁻¹ Raman peak is marked with an arrow.

		Measured Exciton Energy in Sample (eV)			
Material	Exciton	MoSe ₂ ML	WSe ₂ ML	HS (57°)	HS (20°)
MoSe ₂	A1s	1.648 ± 0.001	---	1.620 ± 0.001	1.623 ± 0.001
MoSe ₂	A2s	1.803 ± 0.002	---	1.754 ± 0.001	1.765 ± 0.002
MoSe ₂	B1s	1.858 ± 0.001	---	1.839 ± 0.001	1.849 ± 0.001
MoSe ₂	B2s	2.016 ± 0.001	---	1.961 ± 0.016	1.969 ± 0.004
WSe ₂	A1s	---	1.740 ± 0.001	1.728 ± 0.002	1.718 ± 0.002
WSe ₂	A2s	---	1.871 ± 0.001	1.857 ± 0.003	1.835 ± 0.004
WSe ₂	B1s	---	2.166 ± 0.001	2.161 ± 0.007	2.164 ± 0.001

Table 1: Energies of the various excitonic transitions obtained by fitting from the Raman results for hBN encapsulated vdW MoSe₂/WSe₂ heterostructure samples (HS) with twist angles of 57 and 20 ° and their constituent monolayers (ML).

		Energy differences for Exciton States (meV)						
Material	Exciton	MoSe ₂ ML		WSe ₂ ML		Heterostructures		
		Experiment	Theory	Experiment	Theory	(57°)	(20°)	Theory
MoSe ₂	A1s-A2s	155 ± 3	152.3	---	---	134 ± 2	142 ± 3	138.2
MoSe ₂	B1s-B2s	158 ± 2	---	---	---	122 ± 17	120 ± 3	---
MoSe ₂	A1s-B1s	210 ± 2	---	---	---	219 ± 2	226 ± 2	---
WSe ₂	A1s-A2s	---	---	131 ± 1	130.2	129 ± 4	117 ± 4	122.4
WSe ₂	A1s-B1s	---	---	426 ± 2	---	433 ± 8	446 ± 3	---

Table 2: Energy separations between key excitonic transitions within each sample determined from the results in Table 1 plus predictions for these energies from the model described in the main body of the paper. The agreement between experiment and theory is to within twice the error estimates in all cases.

		Energy differences for Exciton States (meV)		
Material	Exciton	Literature Experimental Values		Theory
MoSe ₂ ML	A1s-A2s	151 ¹⁹ ;	150 ⁴³	152.3
WSe ₂ ML	A1s-A2s	131 ²³ ;	131 ²¹ , 130 ¹⁸	130.2
WSe ₂ ML	A1s-A3s	157 ²³ ;	152 ²¹ , 152 ¹⁸	151.0
WSe ₂ ML	A1s-A4s	161 ²³ ;	161 ²¹	157.9

Table 3: Comparison of the difference in energy between different excitonic states in MoSe₂ and WSe₂ monolayers predicted using the theory discussed in the main body of the paper with previously published experimental values. There is excellent agreement which is within the experimental errors where these are available.

Methods

Monolayers of WSe₂ and MoSe₂ were mechanically exfoliated from bulk crystals and then stacked with layers of hexagonal boron nitride using dry transfer methods⁴⁴ onto a 290 nm SiO₂ coated Si wafer. All spectra in this paper were taken at 4 K (unless specified otherwise) with the samples in an Oxford Instruments High Resolution liquid helium flow Microstat. This was mounted on a 3-axis translation stage which allowed accurate positioning of the < 3 μm laser spot from the 50x Olympus 0.5 NA microscope objective on the samples. For the Raman spectra a CW Ti:Sapphire laser, provided excitation energies from 1.24 to 1.77 eV, and a dye laser using DCM, Rhodamine 6G and Rhodamine 110 laser dyes provided excitation energies from 1.74 to 2.25 eV. Reflectivity spectra were taken using a Fianium Supercontinuum laser. An Ocean optics HR4000 was used for the reflectivity spectra and a Princeton Instruments Tri-Vista triple spectrometer equipped with a liquid nitrogen cooled CCD was used for the Raman spectra. For each chosen wavelength, Raman spectra were taken with the spectrometer having both parallel linear polarization and crossed linear polarization to the laser. The Raman peaks were observed to have strongly co-linear polarization. The spectra were then subtracted, eliminating any non-Raman features such as photoluminescence - which can be observed when exciting just above the excitons. The constant 520 cm⁻¹ peak from the Si substrate was used as an internal reference which allowed us to calibrate the Raman shift of the TMD peaks to within 0.5 cm⁻¹. The intensities of the Raman peaks were also converted to absolute scattering probability using the Si peak intensity as a reference²⁸ with corrections for Fabry-Perot effects modelled using the reflectivity spectra as were performed in our previous paper⁸. The laser power incident on the sample was kept below 100 μW to avoid photo-doping and laser heating effects^{45,46}.

Supporting Information

The supplementary information contains reflectivity measurements on all 4 sample areas presented in the main body of the paper as well as more detailed discussion of the analysis of the resonance Raman data. Additional analysis of the $A_1'(\Gamma)$ and $2s$ associated Raman peaks in the monolayers and a discussion of the linewidths of the excitonic states is also included. Further details on the exciton energy modelling calculations are also included.

Data Availability

The data presented in this paper is openly available from the University of Southampton Repository with the DOI: <https://doi.org/10.5258/SOTON/D1747>

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. Data analysis and interpretation was carried out by J.V, D.C.S and L.P.M. The theoretical calculations were performed by D.A.R. The paper was written by D.C.S and J.V. All authors discussed the results and commented on the manuscript.

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Competing financial interests

The authors declare no competing financial interests.

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