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Intrinsic control of interlayer exciton generation in van der Waals materials via Janus layers

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Abstract

We demonstrate the possibility of engineering the optical properties of transition metal dichalcogenide heterobilayers when one of the constitutive layers has a Janus structure. We investigate different MoS₂@Janus layer combinations using first-principles methods including excitons and exciton-phonon coupling. The direction of the intrinsic electric field from the Janus layer modifies the electronic band alignments and, consequently, the energy separation between dark interlayer exciton states and bright in-plane excitons. We find that in-plane lattice vibrations strongly couple the two states, so that exciton-phonon scattering may be a viable generation mechanism

for interlayer excitons upon light absorption. In particular, in the case of MoS₂@WSSe, the energy separation of the low-lying interlayer exciton from the in-plane exciton is resonant with the transverse optical phonon modes (40 meV). We thus identify this heterobilayer as a prime candidate for efficient generation of charge-separated electron-hole pairs.

Keywords

Interlayer exciton, TMDC, First-principles calculations, Exciton-phonon coupling

The weak dielectric screening of two-dimensional semiconductors allows for the formation of strongly bound electron-hole pairs (excitons) upon light absorption, leading to remarkable optical properties such as discrete excitonic peaks with strong photoluminescence response and layer-dependent exciton modulation¹⁻⁴. In this regard, two-dimensional transition metal dichalcogenides (TMDs) are exemplary since, due to the quasi-2D confinement and weak dielectric screening, they host excitons with binding energies of hundreds of meV⁵⁻⁸. Therefore, this class of materials represents an important testbed for the physics of light-matter interaction⁸⁻¹¹, the realization of advanced optoelectronic and nanophotonic devices¹²⁻¹⁶, as well as valleytronics.^{17,18}

Heterobilayer (HBL) structures with different TMD layers generally host interlayer (IL) excitons (where electron and hole forming the exciton reside in different layers) with a static electric dipole moment. Earlier reports showed that the type-II band alignment of the constituent monolayers causes the IL exciton to be the lowest-energy excitation in the HBL absorption spectrum despite having smaller binding energy than in-plane (intralayer – IP) excitons, where electron and hole reside in the same layer¹⁹⁻²³. These IL excitons have a lifetime almost 100 times longer than the more commonly observed IP ones^{24,25} and are also at the forefront of current research. For example, their ultrafast formation dynamics is investigated^{26,27}, along with their role in valleytronics^{28,29} and charge transfer.

Ovesen *et al.*³⁰ have suggested a scenario for the formation of the IL excitons in HBL

TMDs: the excitation of the IP exciton due to light absorption is followed by the tunneling of holes into a finite-momentum state of the opposite layer which can then relax to the ground state of the IL exciton via phonon-scattering. Therefore, the energy-momentum dependence and exciton energy offsets in bilayer structures are crucial for the formation of IL excitons in HBLs. These excited-state features also strongly depend on structural degrees of freedom such as layer separation and stacking. By these means the engineering of optical transition strengths, energies, and selection rules have been previously demonstrated^{31–35}, notably by the application of external electric fields^{21,36–38}.

However, the electric field does not need to be external: the addition of a so-called “Janus” layer³⁹ can provide a strong intrinsic electric field. Janus monolayers have been experimentally demonstrated in samples with high structural and optical quality.⁴⁰ A first theoretical prediction of the impact of the intrinsic electric field, with a possible reordering of IP and IL excitons, was done recently for Janus-bilayers⁴¹. In this paper, we propose that combining a non-Janus TMD monolayer with a Janus monolayer – thus creating a TMD@JTMD heterostructure – allows for reliable tuning of the relative order of the IP and IL excitons, in turn leading to an efficient pathway for IP-to-IL conversion via exciton-phonon scattering. Experimentally, Trivedi *et al.*⁴² have already shown the controllable room temperature fabrication and optical characterization of TMD@JTMD and JTMD@JTMD HBL crystals. The tuning of the intrinsic net out-of-plane electric dipole moment in these materials, with the large corresponding piezoelectric effect³⁹, is also promising for light-energy/electricity interconversions and valley-contrasting physics^{43–46}.

More specifically, we investigate the optoelectronic properties of MoS₂@MoSSe, MoS₂@MoSeS, MoS₂@WSSe, and MoS₂@WSeS (as shown in Fig. 1a-d) using first-principles, many-body perturbation theory techniques including quasiparticle corrections, electron-hole interactions and exciton-phonon coupling^{47–54}. We demonstrate that the direction of the intrinsic electric field polarization of the Janus layer changes both the band alignments and the energy separation of the lowest-energy IL and IP excitonic levels. In addition, we calculate the scat-

tering strength of the IP-to-IL exciton transitions mediated by optical phonons at the zone center, in order to address the generation mechanisms of the charge-separated and long-lived IL excitons as schematically explained in Fig. 1e.

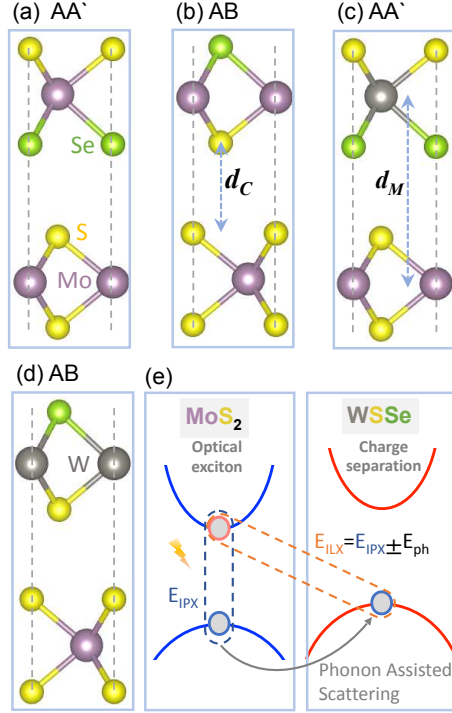


Figure 1: (a) to (d): Schematic representation of the investigated TMD@JTMD heterobilayer structures (only the most stable configurations are reported). The TMD layer (bottom) is always MoS₂. The JTMD layer (top) is either MoSe or WSe, while the TMD@JTMD interface can be either S-S or S-Se. Moreover, the two layers can be stacked in different configurations denoted AA' and AB. (e): Schematic representation of the phonon-assisted IP \rightarrow IL exciton transition in the case of MoS₂@WSe.

The calculated results for the geometric and electronic properties are reported in Table 1. The obtained in-plane lattice parameters are in excellent agreement with the reported values^{55,56} and do not depend on the stacking order. However, the out-of-plane structural parameters d_C (interlayer distance between closest chalcogen layers) and d_M (interlayer distance between metal atom layers) change with the stacking type. These stacking-dependent structural changes do not remarkably affect electronic structures, as seen in the calculated band gaps and exciton energies also reported in Table 1. Among all the considered systems (see Supplementary Information⁵⁷ for more details), the difference in total energies between

Table 1: The calculated lattice constants (a_0), interlayer separation of metal (d_M) and chalcogen (d_C) atoms, total energy with respect to minimum energy stacking (E_{tot}), electronic direct/indirect band gap at PBE (E_{gap}^{DFT}) and G_0W_0 level (E_{gap}^{GW}), inter-layer (IL) and in-plane (IP) exciton energies of the HBLs. Values for the most stable stackings are highlighted in bold.

HLB	ST	a_0 (Å)	d_M/d_C (Å)	E_{tot} (meV/atom)	E_{gap}^{DFT} dir./ind. (eV)	E_{gap}^{GW} dir./ind. (eV)	IL (eV)	IP (eV)
MoS ₂ @MoSeS	AB	3.22	6.33/3.14	0.14	0.87/0.82	1.85/1.82		
	AA	3.22	7.01/3.75	11.48	0.80/0.90	1.79/1.89		
	AA'	3.22	6.41/3.15	0.00	0.83/0.81	1.80/1.81	1.38	1.82
MoS ₂ @MoSSe	AB	3.23	6.15/3.06	0.00	1.44/0.93	2.44/1.84	1.90	1.83
	AA	3.22	6.79/3.70	9.65	1.35/1.14	2.38/2.08		
	AA'	3.22	6.18/3.10	0.19	1.39/0.94	2.39/1.84		
MoS ₂ @WSeS	AB	3.22	6.35/3.09	0.19	0.55/0.67	1.62/1.71		
	AA	3.22	6.97/3.70	13.79	0.46/0.73	1.55/1.75		
	AA'	3.22	6.37/3.10	0.00	0.51/0.65	1.57/1.69	1.15	1.83
MoS ₂ @WSSe	AB	3.22	6.08/3.00	0.00	1.12/0.82	2.20/1.81	1.78	1.83
	AA	3.22	6.73/3.64	12.61	1.00/1.04	2.11/2.03		
	AA'	3.22	6.12/3.03	0.29	1.06/0.83	2.14/1.82		

the various structures is of the order of a few meV, with the so-called AA-stacked structures clearly being less energetically favored due to the in-line chalcogen-chalcogen interlayer interaction. Therefore, within the the expected computational uncertainties, either the AB or AA' stackings can lead to stable structures depending on the orientation of the Janus layer.

At variance with the stacking order, the polarization direction of the Janus layer (namely S-Mo-S \leftrightarrow S-Metal-Se or S-Mo-S \leftrightarrow Se-Metal-S, with a different interaction at the layers interface) has a notable effect on both structural and electronic properties. In particular, the energy difference between direct and indirect band gaps, as well as the exciton binding energies, change remarkably. For instance, MoS₂@MoSSe(WSSe) HBLs are distinctly indirect band gap materials, whereas MoS₂@MoSeS(WSSe) are direct band gap materials within the limits of thermal fluctuations. The intrinsic dipole moments are caused by the asymmetric charge transfer, in the Janus layer, from the metal atom to the different S and Se atoms. Based on charge transfer analysis, the strengths of the intrinsic dipoles are in agreement with previous results on analogous systems^{58,59}. More quantitative information about charge transfer and polarization-driven band shifts are provided in the Supplementary Information.

The results for quasiparticle band structures (in the G_0W_0 approximation) and the absorption spectra including electron-hole interactions for AA' and AB stacked HBLs are displayed in Fig. 2(a-d) (left: excitonic optical absorption spectrum; right: quasiparticle band structure in the vicinity of the K point of the hexagonal Brillouin zone (BZ); see Supplementary Information⁵⁷ for all the considered materials). The band structures include the projections of the electronic wave functions onto atomic orbitals localized on the constituent layers: the red and blue colors represent electronic states mostly localized on the Janus and on the TMD monolayer, respectively. Electron-hole interactions were included via the solution of the Bethe-Salpeter equation (BSE) from first principles.⁶⁰ In this study we only consider excitons formed by direct electronic transitions at zero momentum.

The investigated structures differ in stacking geometry (AA' vs AB), transition metal in the Janus layer (Mo vs W) and orientation of the Janus layer, controlling the polarization direction (S \leftrightarrow S vs S \leftrightarrow Se interface between the two layers). All the HBLs present some common optoelectronic features, as well as some notable differences. The electronic states around the K points in the quasiparticle band structures are completely confined on one of the two layers. In particular, the four highest valence states comprise two pairs of spin-orbit-split bands, with one pair localised on the TMD layer (blue color) and the other pair on the Janus layer (red color). The same is true for the four lowest conduction states. In addition, the minimum energy transition at the K point always connects a valence state on the Janus layer to a conduction state on the TMD one. As a consequence of the band structure shape, the low-energy region of the excitonic absorption spectra is always dominated by the IP and IL excitons originated from single-particle transitions in the bands around K . Another common excitonic feature is that the low-lying IP states always originate from electronic transition between the TMD valence and conduction bands (blue to blue in the band graph), therefore they are always localised on the TMD layer, as shown in two examples in Fig. 2e-g.

The four HBLs however differ remarkably with respect to the nature of the quasiparticle band gap, which is direct at K for the AA' stackings with S-Se interface (Fig. 2(a) and

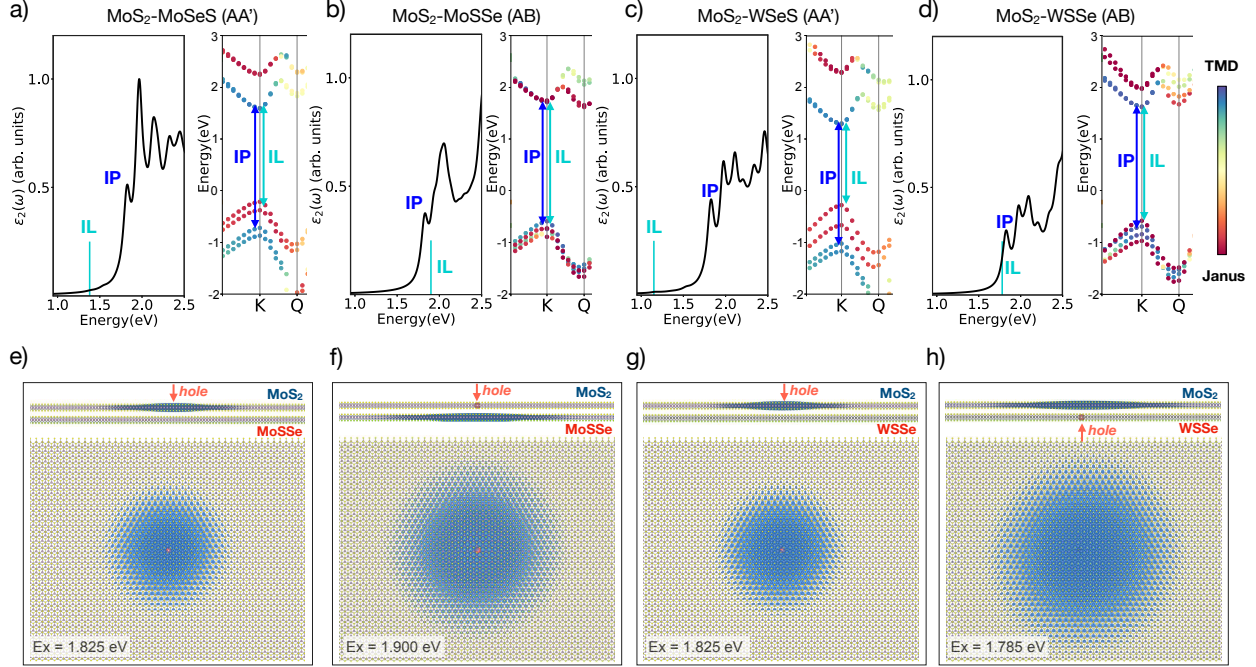


Figure 2: Excitonic properties of TMD@JTMD HBLs. Top panels (a to d): optical absorption spectra and quasiparticle band structures (zoomed-in to the vicinity of the K point in the BZ, see the Supplementary Information for the full band structures) of the investigated systems. The absorption spectrum is given by the imaginary part of the excitonic macroscopic dielectric function ε_2 , which is the plotted quantity on the left panels. The band color (right panels) represents the projections of the electronic wave function onto its atomic orbitals components localized either in the JTMD or in the TMD layers (blue: mostly TMD state, red: mostly Janus state). The calculations are performed on the stacking configurations with minimal energy and are: (a) MoS₂@MoSeS in AA' stacking, (b) MoS₂@MoSSe in AB stacking, (c) MoS₂@WSeS in AA' stacking and (d) MoS₂@WSSe in AB stacking. The most important single-particle transitions forming the IL (Janus \leftrightarrow MoS₂), IP (MoS₂ \leftrightarrow MoS₂) excitons are labeled in the band plots, while the energy of the resulting exciton states is emphasized in the absorption plots. Bottom panels (e to h): Wave-function intensity plot in real space for excitons corresponding to (e) IP in MoS₂@MoSSe, (f) IL in MoS₂@MoSSe, (g) IP in MoS₂@WSSe, and (h) IL in MoS₂@WSSe. The plot is obtained by fixing the hole in a position consistent with its band orbital character and plotting the resulting electron distribution.

(c)), while indirect from Γ to K for the AB stackings with S-S interface (Fig. 2(b) and (d); see Supplementary Information for the full band structures). Another important difference is due to the effect of the intrinsic electric field arising from the Janus monolayer, which shifts the TMD bands with respect to the Janus ones in both valence and conduction states. The direction of the shift depends on the direction of the field, i.e., on the orientation of the

Janus layer. More specifically, in the HBLs with S/Se interface the TMD bands are shifted *away* from the Janus ones, leading to a substantial energy separation. When the Janus dipole orientation is reversed, instead, the TMD bands are shifted *closer* to the Janus ones becoming almost degenerate with them. These changes at the quasiparticle level determine the most important optical feature for charge transfer efficiency: the energy difference – and thus likelihood of transition – between the IL and IP excitonic states, which varies considerably between the systems. We emphasize that although optical excitation of the IL states is not explicitly forbidden by selection rules, their oscillation strength is always negligible (approximately 7 order of magnitudes smaller than bright states) and thus they do not play any role in the optical absorption spectra shown in Fig. 2(a-e). Intriguingly, the localization of the IL excitons changes depending on the stacking and JTMD layer types. In MoS₂@MoSSe, the exciton is formed by electronic transitions from the TMD layer to the JTMD one (blue to red in the band graph), while in all other cases the hole is on the JTMD layer and the electron on the TMD one (red to blue in the band graph). This difference in spatial localization can be seen in Fig. 2f-g. Based on these figures, we also emphasise that in all cases the degree of layer segregation of the electron density either on the same layer as the hole (IP) or on the opposite one (IL) is very high, being around 99.9% of the total calculated value. A detailed numerical breakdown of this fact is presented in the Supplementary Information.

MoS₂@MoSeS (AA' stacking, S-Se interface). The geometry of this system is represented in Fig. 1(a), the quasiparticle/BSE results in Fig. 2(a). This HBL is a direct gap material with a gap of 1.80 eV. The indirect band gap sits 0.01 eV above. Note that at the DFT-PBE level this energy ordering is reversed as seen in Table 1, which shows that the quasiparticle correction to the Kohn-Sham energies is not just a rigid shift of the bands owing to the k -dependence of the GW self-energy. The ordering of the bands at the K point indicates a type-II character for this HBL at the quasiparticle level, as previously observed for MoS₂@WS₂ and MoSe₂@WSe₂ HBLs.^{19,20,22,23} The energy of the IL exciton which forms via the transitions

from the valence band maximum (VBM) to conduction band minimum (CBM) is 1.38 eV. The energy difference between the lowest energy IL and the first in-plane exciton, IP, is 0.44 eV, which is too large for a one-phonon scattering process to enable the direct transitions from the optically excited IP to the IL state.

MoS₂@MoSSe (AB stacking, S-S interface). The geometry of this system is represented in Fig. 1(b) and the quasiparticle/BSE results are shown in Fig. 2(b). Contrary to the previous case, here we have an indirect gap semiconductor at both the DFT-PBE (0.93 eV) and G₀W₀ (1.84 eV), respectively. Because of the direction of the intrinsic electric field, the TMD and Janus bands overlap at the CBM and have very similar band energies at the VBM. This leads to a situation where the electron-hole interaction strength of the IL and IP excitons become the determining factor for the energy ordering of these excitons in the absorption spectrum. In MoS₂@WS₂ and MoSe₂@WSe₂ HBLs it has been shown that the binding energies¹ of IL excitons are approximately 100 meV lower than the ones of IP excitons²². The case of the MoS₂@MoSSe HBL, here, is similar: the IP exciton (1.83 eV) has approximately 70 meV higher binding energy than the first IL exciton (1.90 eV) as reported in Table 1. Due to this, the IP exciton automatically becomes the lowest energy exciton in the absorption spectrum as shown in Fig. 1(b). The spatial distribution of the excitonic wave functions for this system is shown in Fig. 2e and f for the IP and IL states, respectively. The energy separation between the IP and the IL exciton is around 70 meV. This is not ideal because the charge-separated state is not energetically favored, and even a thermal population of the IL exciton would be very tiny.

MoS₂@WSeS (AA' stacking, S-Se interface). The geometry of this system is represented in Fig. 1(c) and the quasiparticle/BSE results are shown in Fig. 2(c). Similar to the Mo case, this is a direct band gap material with a quasiparticle gap of 1.57 eV (see Table1). Again, orbital projections indicate the type-II character of the electronic bands in this HBL. The SOC splitting of the Janus bands, shown in red, is more pronounced than in the Mo

¹Here, the binding energy of an IP (IL) exciton is defined as the difference between the exciton energy and the lowest-energy single-particle IP (IL) transition.

case due to the presence of the heavier W atoms. Here the energy difference between the IL exciton (1.15 eV) and the lowest-energy IP exciton (1.83 eV) is 0.65 eV, even larger than in the Mo case with the same stacking and Janus orientation, due to the more substantial SOC. This again rules out efficient IL exciton generation from the IP states via first-order phonon-assisted conversion processes, with incoherent exciton scattering (i.e., relaxation dynamics^{30,61}) likely being the most important mechanism.

MoS₂@WSSe (AB stacking, S-S interface). The geometry of this system is represented in Fig. 1(d) and the quasiparticle/BSE results are shown in Fig. 2(d). This HBL has an indirect quasiparticle band gap of 1.81 eV. At the VBM, the TMD bands (blue) are squeezed in between SOC-split Janus bands (red). Compared to the previous W-based HBL, the opposite intrinsic dipole moment from the Janus layer shifts the bands of the MoS₂ layer so that the bands localized on the two layers are energetically very close to each other just as in the case of the Mo-based system with the same geometry. We estimated the effective electric field generated by the WSSe layer on the MoS₂ layer as 0.07 V/Å (see Supplementary Information⁵⁷ for more details), that is consistent with values calculated by Xu *et al.* for MoS₂@MoSSe and MoS₂@MoSeS heterobilayers as 0.08 and 0.07 V/Å, respectively.⁶² The lowest-lying IL state (1.78 eV) is just 40 meV below the IP exciton as shown in Fig. 2(d), while the real-space excitonic wavefunctions are represented in Fig. 2g-h. We will see in the following that this small energy difference will drastically improve the efficiency of the exciton-phonon scattering channel between the two excitonic states and, hence, the charge carrier separation efficiency of this HBL.

We now focus on MoS₂@WSSe (AB stacking), the HBL where the lowest-bound intralayer and interlayer excitons have a very small energy separation (40 meV), lower than the maximum phonon energy (56 meV). This means that phonon-mediated charge separation, i.e., excitonic intralayer-interlayer (IP-IL) scattering might be very efficient, due to two concurring mechanisms. First, the exciton relaxation dynamics suggests that after the higher-energy intralayer exciton is photoexcited, incoherent scatterings mediated by low-

momentum acoustic phonons will quickly transfer the carriers to the lower-energy interlayer state (the description of out-of-equilibrium carrier dynamics is beyond the scope of this paper). Second, direct intralayer-interlayer scatterings mediated by optical phonons at vanishing momenta will also be permitted and may play an important role. We quantitatively analyze the latter mechanism by computing *ab initio* the exciton-phonon coupling matrix elements \mathcal{G} at zero exciton and phonon momenta for this system.^{54,63–65} Here we assume that excitons can be approximately described as well-defined quasiparticle excitations with bosonic character.⁶⁶ In particular, the values of $|\mathcal{G}_{\alpha\beta}^{\mu}|$ represent the coupling strengths of the transition between excitonic states $\alpha \rightarrow \beta$ via absorption/emission of phonon mode μ . More details about this calculation are found in the Supplementary Information. The calculated values for the IL-IP scattering are displayed in Fig. 3a, showing that out of the 10 distinct optical phonon modes present in these material, all those with atoms oscillating in the layer plane may couple the two excitons and represent possible scattering channels. These are doubly degenerate modes with E symmetry (the point group of the system being C_{3v}). The coupling is instead forbidden for the out-of-plane phonons. This confirms that an IP exciton localised on one layer may transfer its carriers to the lower-lying IL one with the help of ionic oscillations in that layer. In the case of MoS₂@WSSe, the coupling strengths vary between 0.5 and 2 meV. A scheme of the oscillation patterns⁶⁷ is provided in Fig. 3b.

The other factor affecting scattering probabilities is energy conservation. We define the resonance offset energy (ROE) as $\Delta E_{\alpha,\beta}^{\mu} = |E_{\alpha} - E_{\mu} - E_{\beta}|$ (E_{μ} being the phonon energy). The closer $\Delta E_{\alpha,\beta}^{\mu}$ is to zero, the more likely the transition is to happen. Here we consider only the phonon emission case, since it is the dominant contribution with respect to phonon absorption. The ROE values are shown with a color scale in Fig. 3a. For MoS₂@WSSe, the energy of the fourth E phonon mode is exactly resonant (within 0.22 meV) with the excitonic transition at 40.4 meV. This phonon mode corresponds to ionic oscillation of the Janus layer only. In addition, strongly coupled E modes three and five (mostly the TMD layer moving) are both just 5 meV from the resonance. Therefore, our calculations predict

that the Janus-enhanced IP-IL excitonic scattering mediated by optical phonons will be a particularly efficient process for the W-based HBL. This mechanism then represents an important contribution to the total scattering rate for IL excitons, which is given by⁶⁴ $R_{IL} \propto \sum_{\alpha\mu q} |\mathcal{G}_{\alpha,IL}^{\mu}(q)|^2 F_{\alpha}^{\mu}(q) \delta(\Delta E_{\alpha,\beta}^{\mu})$ (phonon emission case; here F is a temperature-dependent occupation factor accounting for both phononic and excitonic populations).

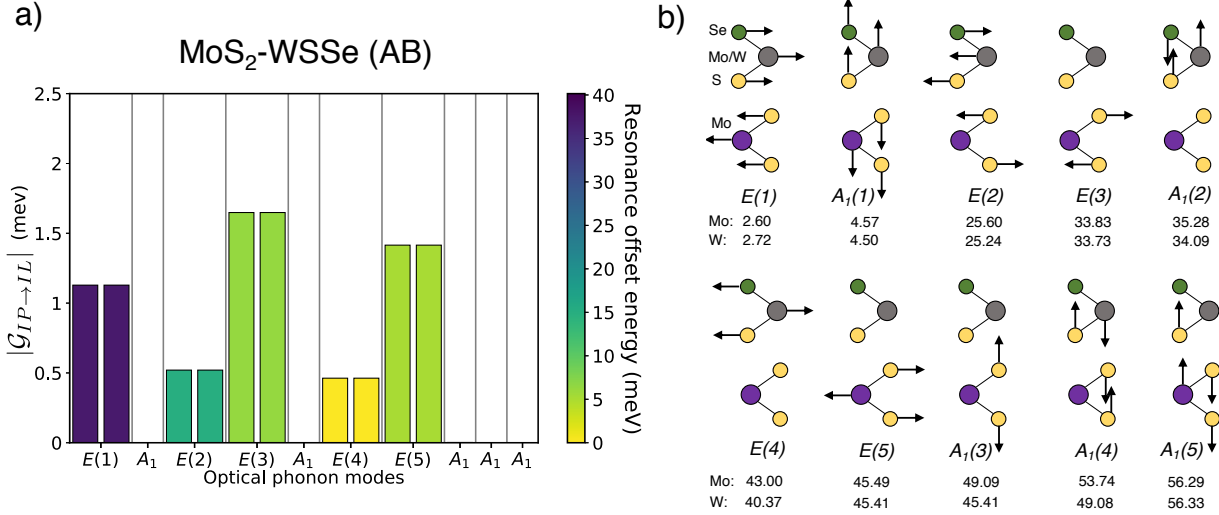


Figure 3: (a) Exciton-phonon coupling strengths, $|\mathcal{G}|$ (see explicit expression in Supplementary Information) for the intralayer (IP) to interlayer (IL) exciton scattering per phonon mode in MoS₂@WSSe (AB stacking, see Fig. 2[d]). The height of the bars is the coupling strength, while the color represents how close to resonance the transition is (see text). (b) Oscillation patterns of the zone-center optical phonon modes for MoS₂@MoSSe (AB stacking) and MoS₂@WSSe (AB stacking). These two systems have the same modes, with variations only in their energies. The gray balls represent the Mo/W atom in the Janus layer, while S, Se and the Mo atom in the TMD layer are represented with orange, green and purple balls respectively. The arrow lengths are not scaled by the ionic masses, but they are set to zero for oscillations one order of magnitude weaker than the rest. The phonon energies associated with each mode are reported, in meV, for both systems.

We have shown that the intrinsic net out-of-plane electric dipole moment of a Janus-type TMD layer has a strong influence on the optoelectronic properties of heterobilayer systems in which it is used. In particular, our first-principles analysis on MoS₂@MoSSe, MoS₂@MoSeS, MoS₂@WSSe, and MoS₂@WSeS demonstrates that the polarization direction of the Janus layer can be used to tune the dynamics of excitons – most notably by altering the energy separation between interlayer and in-plane excitonic states – without the use of external

fields. Surprisingly, for MoS₂@WSSe the calculated energy difference is exactly resonant with in-plane optical phonon modes. Moreover, the calculated zero-momentum exciton-phonon couplings point to efficient excitonic scattering between in-plane to interlayer states mediated by optical phonons, again with MoS₂@WSSe being the prime candidate for this mechanism. It is important to note, however, that this system also has an indirect band gap: hence, new low-lying dark excitonic states at finite momentum may be important, introducing an additional possible pathway for exciton dynamics which could be detrimental to the intra- to interlayer conversion rate. This opens a relevant future avenue of investigation theoretically, experimentally, and from a materials design perspective. Theoretically, the next step is computing the exciton-phonon couplings at finite momenta and simulating the excitonic relaxation dynamics in order to compare the transition rates of the various competing mechanisms. Experimentally, these quantities can be measured by photoluminescence and time-resolved, pump-and-probe studies. In materials design, it would be important to target excited-state properties both microscopically and at the excitonic level, rather than just optical properties at the single-particle level (e.g., band alignment studies) in order to obtain candidate systems more effectively.

In conclusion, our results clearly support the use of Janus materials in layer engineering to boost the generation rate of long-lived interlayer excitons in heterobilayer TMD crystals. These excitons are obtained by phonon-assisted conversion of optically excited intralayer states.

Supporting Information Available

The Supplementary Information file includes the following sections: Methods^{47–53,60,68–74}, Considered Heterobilayer Structures and Corresponding Electronic/Optical Properties, Lattice constants comparison, Effect of different vDW functionals on the geometric and the electronic structure of the most promising heterobilayer cases, Analysis of exciton localization

in reciprocal space, Exciton-phonon coupling matrix element, Bader charge analysis, Effect of orientation of the Janus layer on the band structure, Phonon modes analysis, Quantum ESPRESSO input files used in the ground state calculations.

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