Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Stacking-Dependent Optical Properties in Bilayer WSe_2

Kathleen M. McCreary,[1] Madeleine Phillips,[1] Hsun-Jen Chuang,[2] Darshana Wickramaratne,[1] Matthew Rosenberger,[3] C. Stephen Hellberg[1] and Berend T. Jonker[1]

[1]*Naval Research Laboratory*, Washington, DC 20375
[2] *Nova Research, Inc.* Washington, DC 20375
[3] *University of Notre Dame*, Notre Dame IN 46556

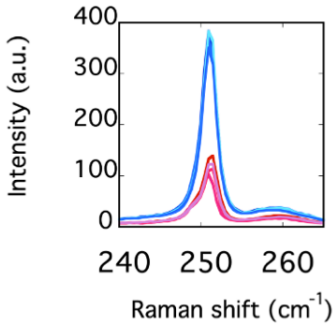


Figure S1. (a) The Raman spectra collected under 532nm excitation from four additional 2H bilayers (blue lines) and four additional 3R bilayers (red lines) confirm the behaviors observed in the main text, figure 2a. Bilayers with 2H stacking consistently exhibit higher intensity of the A_{1g} mode.

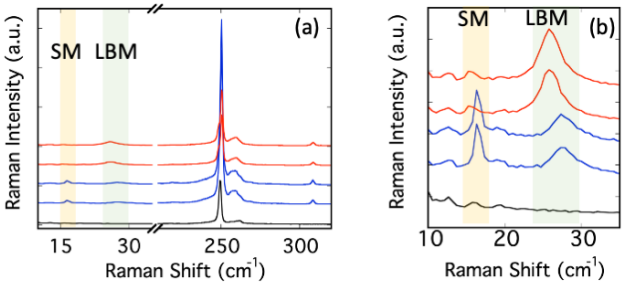


Figure S2. Room temperature ultra-low frequency Raman measurements using 532nm excitation and an Ondax SureBlock ultra narrow-band notch filter. (a) Spectra are acquired from 2H (blue), 3R (red) and monolayer (black). Spectra are offset for clarity. (b) Both shear (SM) and layer-breathing modes (LBM) are evident in 2H bilayers. 3R stacking exhibits only a LBM mode. Monolayer WSe_2 exhibits neither SM or LBM.

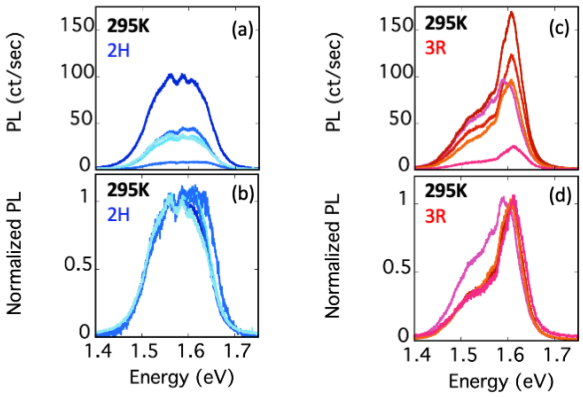


Figure S3. Room temperature photoluminescence from (a) five additional 2H samples and (c) five additional 3R samples. In both stacking orders the overall intensity varies significantly. (b,d) The normalized PL shows a consistent line shape for each stacking order, despite the intensity variations. 532nm excitation and identical parameters are used to probe all samples.

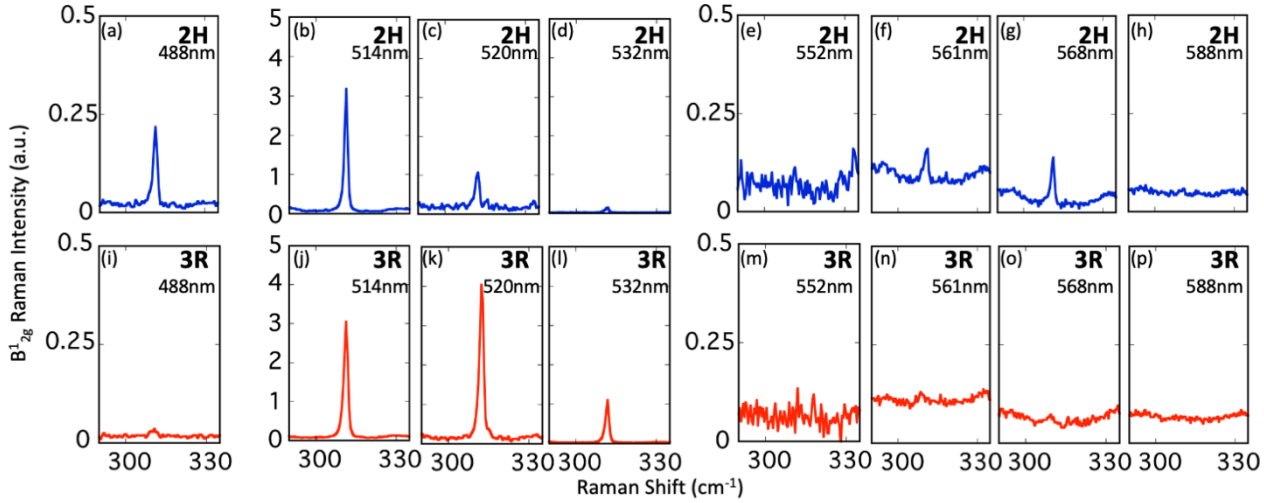


Figure S4. Low-temperature (4K) excitation-dependent Raman of the B^1_{2g} Raman mode in WSe_2 bilayers for (a-h) 2H and (i-p) 3R stacking orientation. All spectra are normalized to Si Raman intensity at 523 cm^{-1} and excitation wavelength is indicated in the upper right corner.

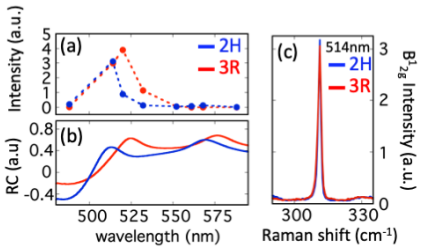
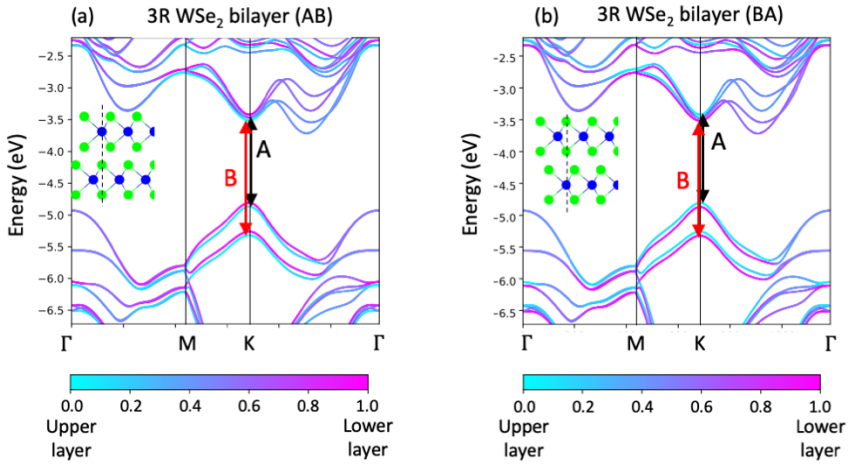


Figure S5. (a) Low-temperature (4K) excitation-dependent Raman intensity of the B^1_{2g} mode and (b) reflectance contrast, RC, plotted as a function of wavelength. The RC is the same data presented in Fig 5b of the main text, replotted here for clarity. (c) The B^1_{2g} mode of 2H (blue) and 3R (red) WSe_2 is nearly indistinguishable for 514 nm excitation.



(c)	A_{upper} (eV)	A_{lower} (eV)	B_{upper} (eV)	B_{lower} (eV)
3R (AB)	1.399	1.387	1.809	1.798
3R (BA)	1.387	1.399	1.798	1.809

Figure S6. DFT band structures for 3R bilayers are shown for (a) AB and (b) BA ordering. All bands are aligned to the vacuum level. Insets show the side view of a schematic of each stacking. AB (BA) refers to a stacking geometry where W (Se) in the top layer is aligned with Se (W) in the bottom layer. The two stackings are related by a z → -z mirror operation. Black (red) arrows indicate the origin in the band structure of the A (B) excitons. (See figure S7 for a more detailed schematic.) For each stacking there are two A excitons, one associated with the upper layer and one with the lower layer. Likewise there are two B excitons in each bilayer. (c) The table compares the band gaps associated with the A and B excitons in each stacking. The average values of upper and lower A and B exciton transitions are quoted in the main manuscript.

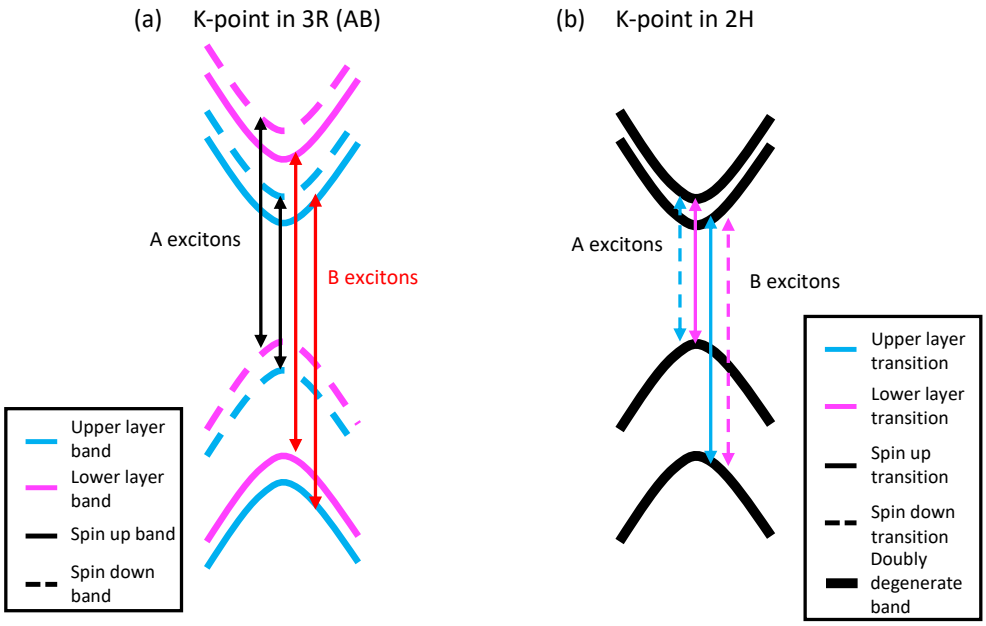


Figure S7. (a) A schematic of the bands at K in the AB-stacked 3R bilayer, showing that the conduction and valence bands involved in a given A or B exciton transition must match in layer and spin. Blue (magenta) bands correspond to states localized in the upper (lower) layer. Solid (dashed) bands correspond to spin up (down) states. Each band in the 3R bilayer is layer and spin polarized. (b) A schematic of the bands at K in the 2H bilayer. Blue (magenta) arrows correspond to transitions in the upper (lower) layer, and solid (dashed) arrows correspond to transitions with spin up (down) carriers. Each band is doubly degenerate, with contributions from both layers and both spin species. However, A and B transitions are always between spin-and layer-matched states. All transitions occur at the K point, but arrows are offset for clarity. The holes involved in the A exciton are located in the upper valence band, while the holes involved in the B excitons are located in the lower valence band.