Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Tunability in the optical response of defective monolayer WSe_2 by computational analysis

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Formation Energies

Defect formation energies E_f were calculated at the DFT/PBE level using the expression $E_f = \left[E_{defect} + n_i \mu_i \right] - E_{pristine}$, where E_{defect} is the total energy of the WSe_2 supercell with defects; $E_{pristine}$ is the total energy of the pristine WSe_2 supercell; n_i is the number of *i* elements (W or Se) removed from pristine WSe_2 to create the defects; and μ_i is the chemical potential of element *i*. For the SV, DV, WV, T_1, T_2, T_3 defects in 2D WSe_2, $n_i\mu_i = \mu_{Se}, 2\mu_{Se}, \mu_W, 6\mu_{Se}, 10\mu_{Se}, 14\mu_{Se}$, respectively. The chemical potential was calculated by $\mu_W + 2\mu_{Se} = \mu_{WSe_2}$,[1] where μ_W, μ_{Se}, and μ_{WSe_2} are the chemical potentials for W, Se, and WSe_2, respectively. μ_{WSe_2} was calculated as the total energy per primitive cell of pristine WSe_2, μ_W^{Max} is the total energy per atom of a bcc W metal, and μ_{Se}^{Max} the total energy per atom of a grey Se crystal.

At the DFT/PBE level we obtained $\mu_{WSe_2} = -21.67$ eV, $\mu_W^{Max} = -13.02$ eV, $\mu_{Se}^{Max} = -3.50$ eV; $\mu_W^{Min} = \mu_{WSe_2} - 2\mu_{Se}^{Max} = -14.68$ eV, and $\mu_{Se}^{Min} = \left(\mu_{WSe_2} - \mu_M^{Max}\right)/2 = -4.33$ eV. For a W rich environment, $\mu_W = \mu_W^{Max}$ and $\mu_{Se} = \mu_{Se}^{Min}$, and the defect formation energies of 1.85 eV, 3.23 eV, 5.17 eV, 6.91 eV, 11.20 eV, and 15.38 eV, for SV, DV, WV, T_1, T_2, and T_3, respectively, were calculated, while for an Se rich environment, where $\mu_{Se} = \mu_{Se}^{Max}$ and $\mu_W = \mu_W^{Min}$, defect formation energies were 2.68 eV, 4.89 eV, 3.51 eV, 11.88 eV, 19.49 eV, and 26.98 eV, for SV, DV, WV, T_1, T_2, and T_3 defects, respectively. The results for SV, DV, and WV agree with previous DFT calculations.[1]

Reference

1. S. Haldar, H. Vovusha, M. K. Yadav, O. Eriksson, B. Sanyal, *Phys. Rev. B 2015*, **92**, 235408.

Table S1. RPA excitation energies for monolayer WSe_2 with T_1, T_2, and T_3 defects: D_1, D_2, D_3, and D_4 bound excitons (in eV).

	D_1	D_2	D_3	D_4
T_1	1.28	1.00	0.64	
T_2	1.44	0.77	0.11	
T_3	1.26	1.12	0.83	0.10

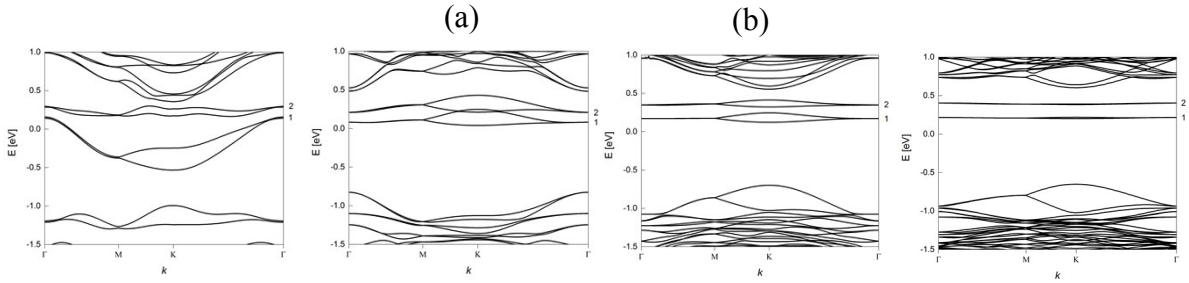


Figure S1. PBE+SOC band structures for monolayer WSe_2 with a SV defect using (a) 2×2×1, (b) 3×3×1, (c) 4×4×1, and (d) 5×5×1 supercells. Defect bands are numerically labelled.

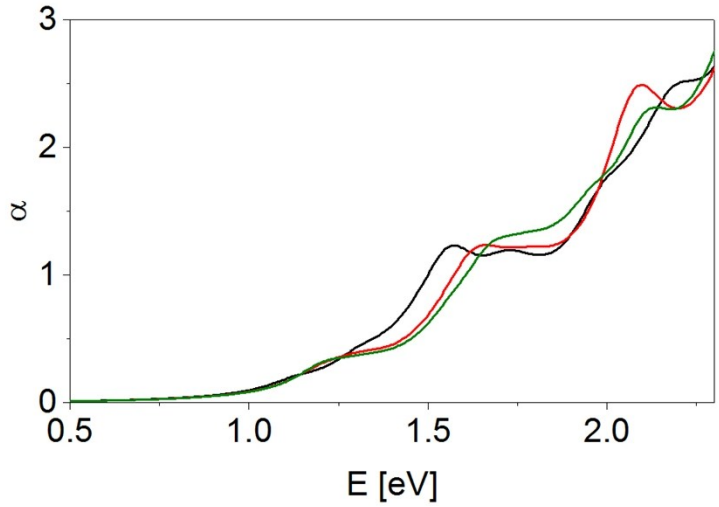


Figure S2. Convergence of the absorption spectrum of monolayer WSe_2 with a SV defect with respect to *k*-point sampling. Black, red, and green are for 3×3×1, 4×4×1, and 5×5×1 *k* samplings, respectively.

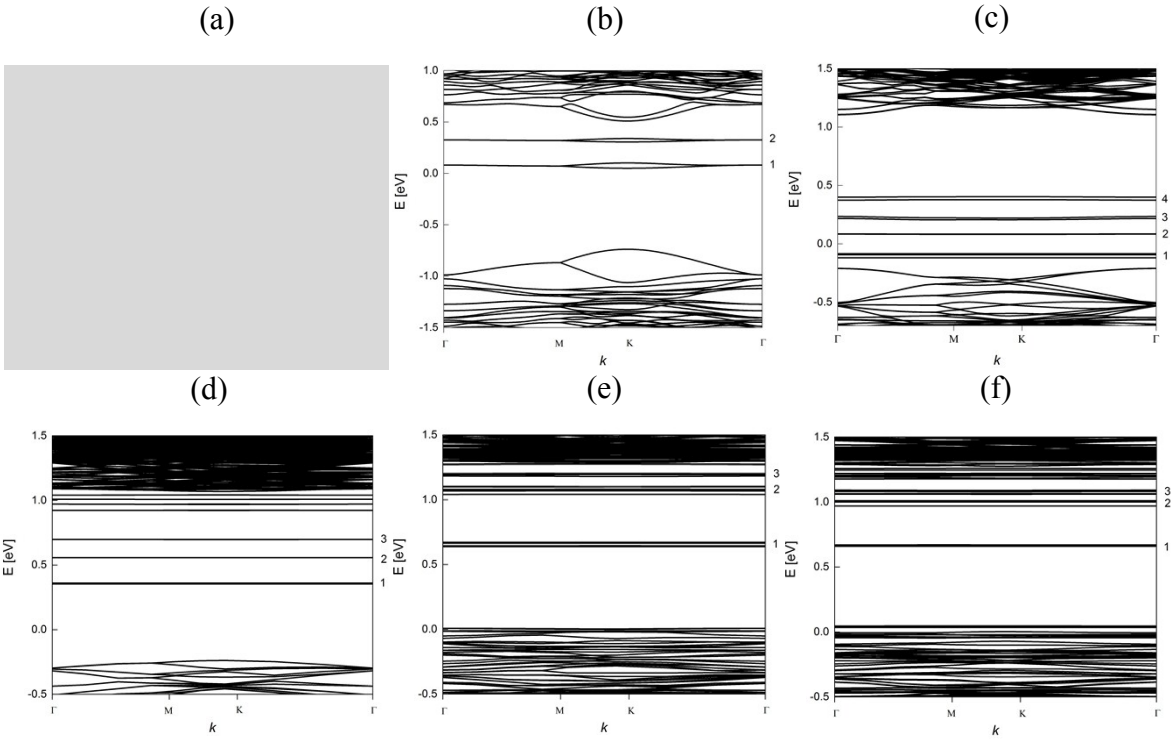
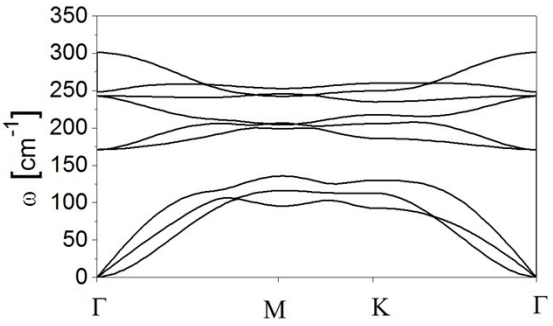
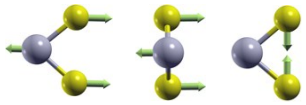


Figure S3. PBE+SOC band structures for monolayer WSe_2 with (a) SV, (b) DV, (c) WV, (d) T_1, (e) T_2, and (f) T_3 defects. Bound defect bands are numerically labelled.

(a)



(b)



E′(1)1 E′(2)1 A_1'

Figure S4. Phonons in pristine 2D WSe_2: (a) phonon dispersion, and (b) phonon eigenvectors for 1st order Raman active modes E′ and A_1'.