Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Water adsorption on MoS_2 in realistic atmosphere conditions and impacts on tribology

N. Scott Bobbitt, John F. Curry, Tomas F. Babuska and Michael Chandross

Material, Physical, and Chemical Sciences Center

Sandia National Laboratories, Albuquerque, New Mexico 87123

Supporting Table 1: Relative composition (in percent) of model atmosphere for GCMC simulations.

278 K				
% RH	% H_2O	% N_2	% O_2	% Ar
0	0.000	78.106	20.960	0.934
5	0.043	78.072	20.951	0.934
10	0.086	78.039	20.942	0.934
15	0.129	78.005	20.933	0.933
20	0.171	77.972	20.924	0.933
25	0.214	77.939	20.915	0.932
30	0.257	77.905	20.906	0.932
35	0.300	77.872	20.897	0.932
40	0.343	77.838	20.888	0.931
45	0.386	77.805	20.879	0.931
50	0.429	77.771	20.870	0.930
55	0.472	77.738	20.861	0.930
60	0.514	77.704	20.852	0.930
65	0.557	77.671	20.843	0.929
70	0.600	77.637	20.834	0.929
75	0.643	77.604	20.825	0.928
80	0.686	77.570	20.816	0.928
85	0.729	77.537	20.807	0.928
90	0.772	77.503	20.798	0.927
95	0.814	77.470	20.789	0.927

298 K				
% RH	% H_2O	% N_2	% O_2	% Ar
0	0.000	78.106	20.960	0.934
5	0.157	77.983	20.927	0.933
10	0.314	77.861	20.894	0.931
15	0.471	77.738	20.861	0.930
20	0.628	77.615	20.828	0.929
25	0.786	77.492	20.795	0.927
30	0.943	77.370	20.762	0.926
35	1.100	77.247	20.729	0.924
40	1.257	77.124	20.696	0.923
45	1.414	77.002	20.663	0.921
50	1.571	76.879	20.630	0.920
55	1.728	76.756	20.597	0.918
60	1.885	76.633	20.565	0.917
65	2.042	76.511	20.532	0.915
70	2.199	76.388	20.499	0.914
75	2.357	76.265	20.466	0.912
80	2.514	76.143	20.433	0.911
85	2.671	76.020	20.400	0.909
90	2.828	75.897	20.367	0.908
95	2.985	75.775	20.334	0.907

313 K				
% RH	% H_2O	% N_2	% O_2	% Ar
0	0.000	78.106	20.960	0.934
5	0.366	77.820	20.883	0.931
10	0.733	77.534	20.806	0.928
15	1.099	77.248	20.729	0.924
20	1.465	76.961	20.653	0.921
25	1.832	76.675	20.576	0.917
30	2.198	76.389	20.499	0.914
35	2.564	76.103	20.422	0.910
40	2.931	75.817	20.345	0.907
45	3.297	75.531	20.269	0.904
50	3.663	75.245	20.192	0.900
55	4.030	74.959	20.115	0.897
60	4.396	74.672	20.038	0.893
65	4.762	74.386	19.961	0.890
70	5.129	74.100	19.885	0.887
75	5.495	73.814	19.808	0.883
80	5.861	73.528	19.731	0.880
85	6.228	73.242	19.654	0.876
90	6.594	72.956	19.578	0.873
95	6.960	72.669	19.501	0.869

Supporting Table 2: Percent water and ppm water conversion for 298 K

%water	ppm
0.000	0
0.000	1
0.001	10
0.005	50
0.010	100
0.020	200
0.030	300
0.040	400
0.050	500
0.100	999
0.120	1199
0.157	1571
0.314	3142
0.471	4713
0.628	6284
0.786	7855
0.943	9426
1.100	10997
1.257	12568
1.414	14139
1.571	15710
1.728	17281
1.885	18852
2.042	20423
2.199	21994
2.357	23565
2.514	25136
2.671	26707
2.828	28278
2.985	29849

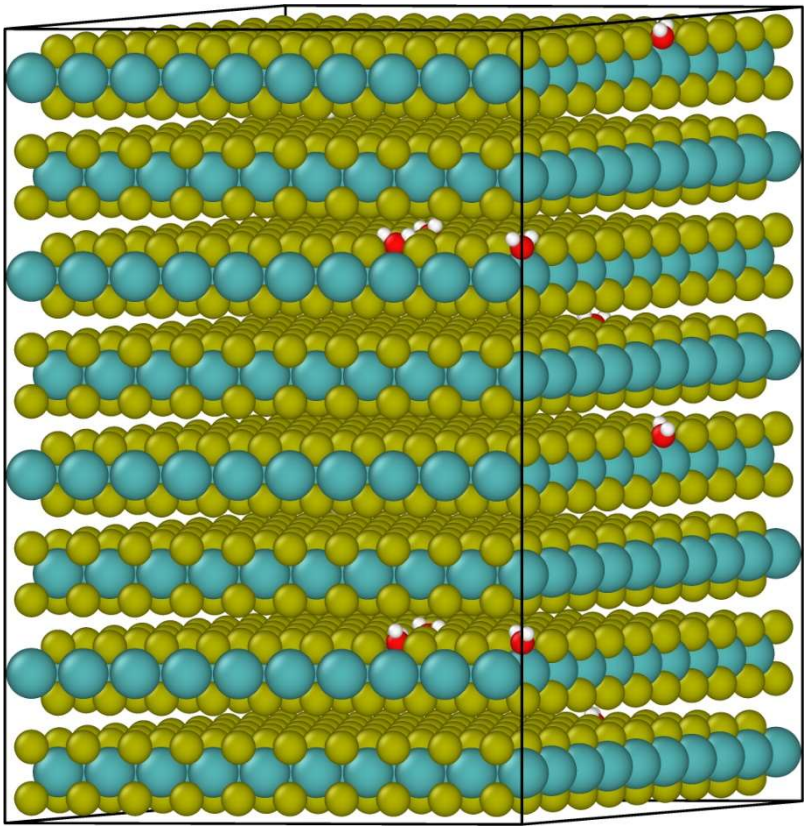
Lennard-Jones Parameters

We used the TIP3P water model (Jorgensen et al. J. Chemical Physics, 1983) for water, TraPPE for oxygen and nitrogen (Zhang et al. *Theoretical Chemistry Accounts* **2006**, *115*, 391-397) and Garcia-Perez for argon (Garcia-Perez et al. *The Journal of Physical Chemistry C* **2008**, *112*, 9976-9979). Mo and S taken from Gu et al *Physical Chemistry Chemical Physics* **2017**, *19*, 3039-3045. Charges for Mo and S were computed with EQeq (Wilmer, Kim, Snurr, J. Phys. Chem. Lett., 2012, *3*, 2506-2511) in RASPA.

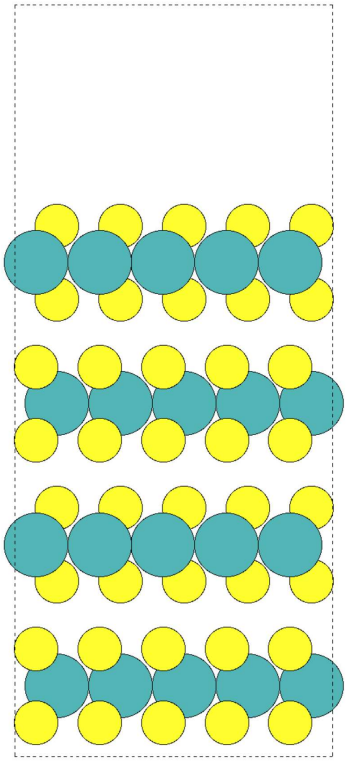
The parameters are given in the table below.

Supporting Table 3: Lennard-Jones parameters for GCMC simulations

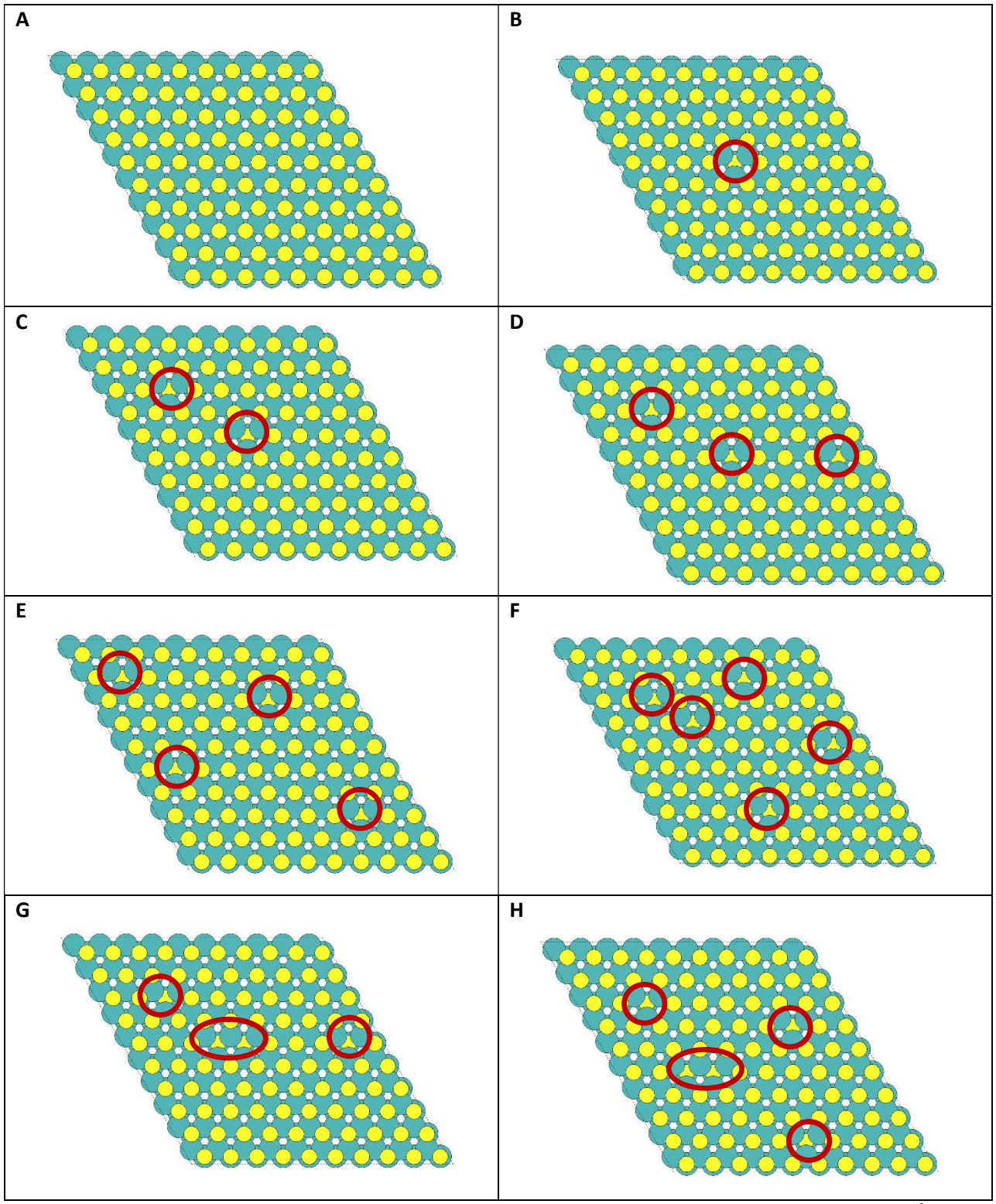
Atom	σ (Å)	ε/kB (K)	q
Mo	2.55	65.308	EQeq
S	3.5	12.685	EQeq
N (center of mass)	0	0	0.964
N (N_2)	3.31	36.0	-0.482
O (center of mass)	0	0	0.226
O (O_2)	3.302	49.0	-0.113
Ar	3.38	124.07	0.0
H (water)	0	0	0.417
O (water)	3.151	76.526	-0.834



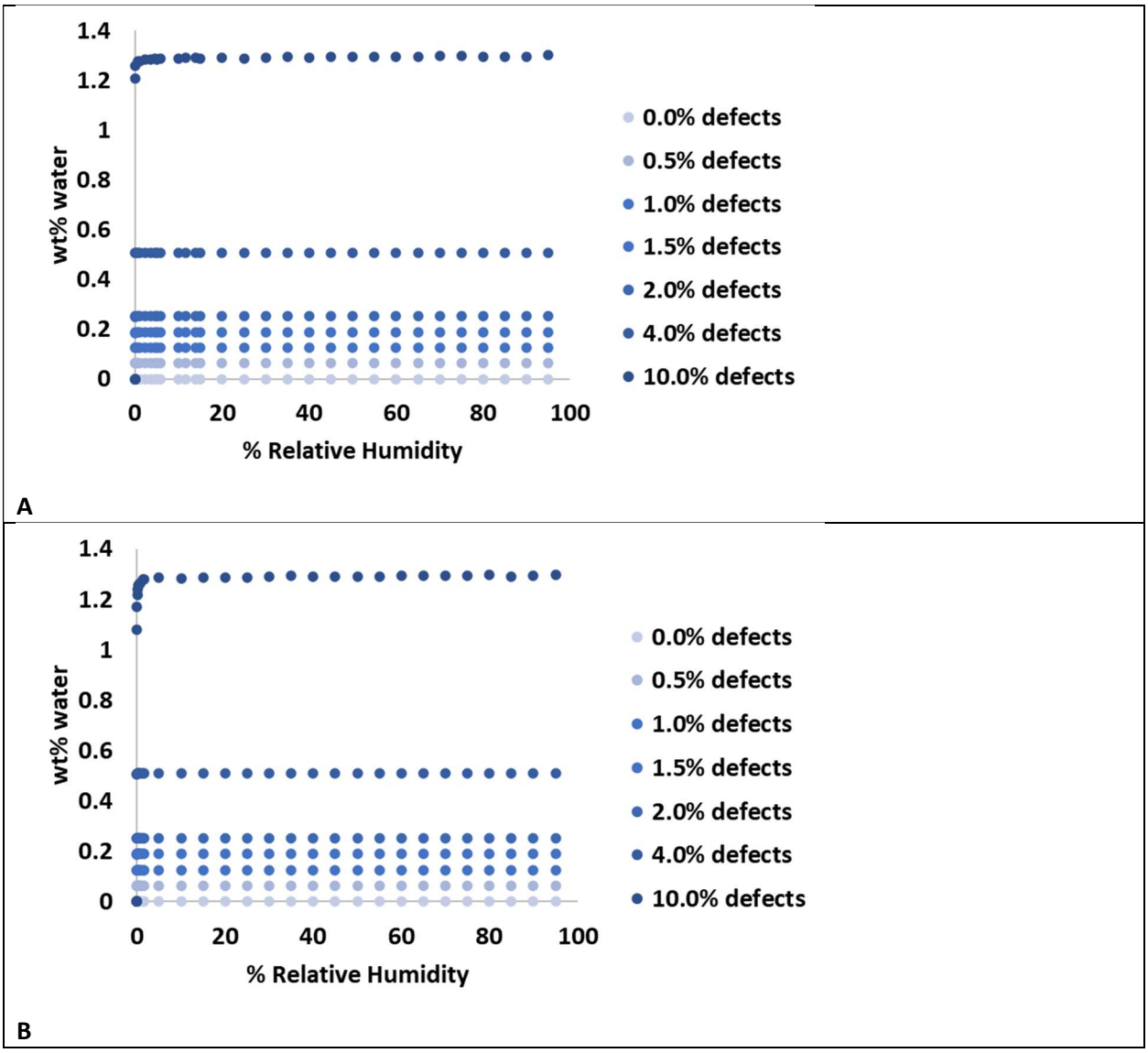
Supporting Figure 1: Visualization of water adsorbed on MoS2 with 1% S vacancies at 298 K and 95% relative humidity. Colors: red O, white H, teal Mo, yellow S



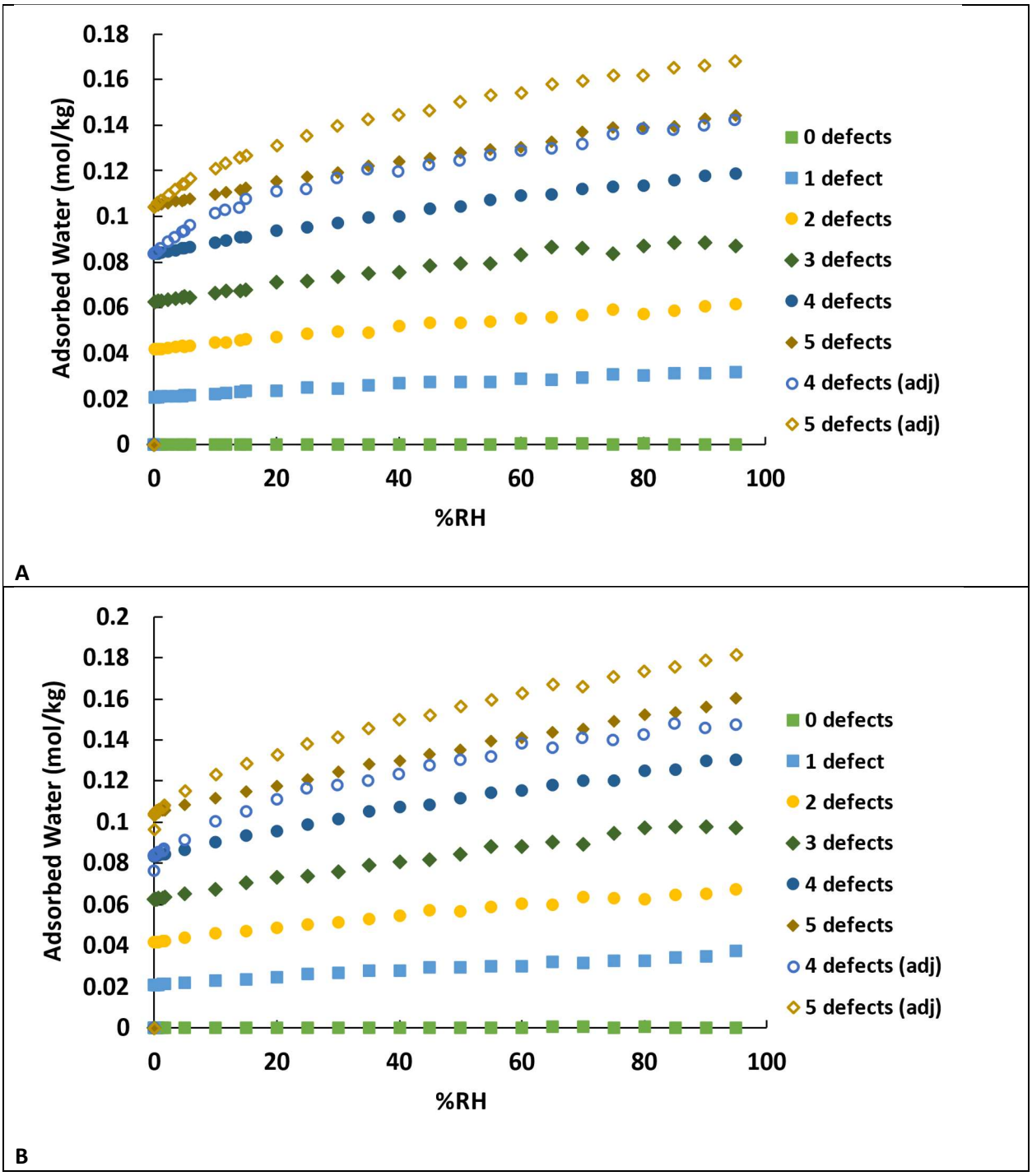
Supporting Figure 2: Visualization of MoS_2 structure used for layer separation calculations. The system is periodic in all directions. Colors: yellow S, teal Mo



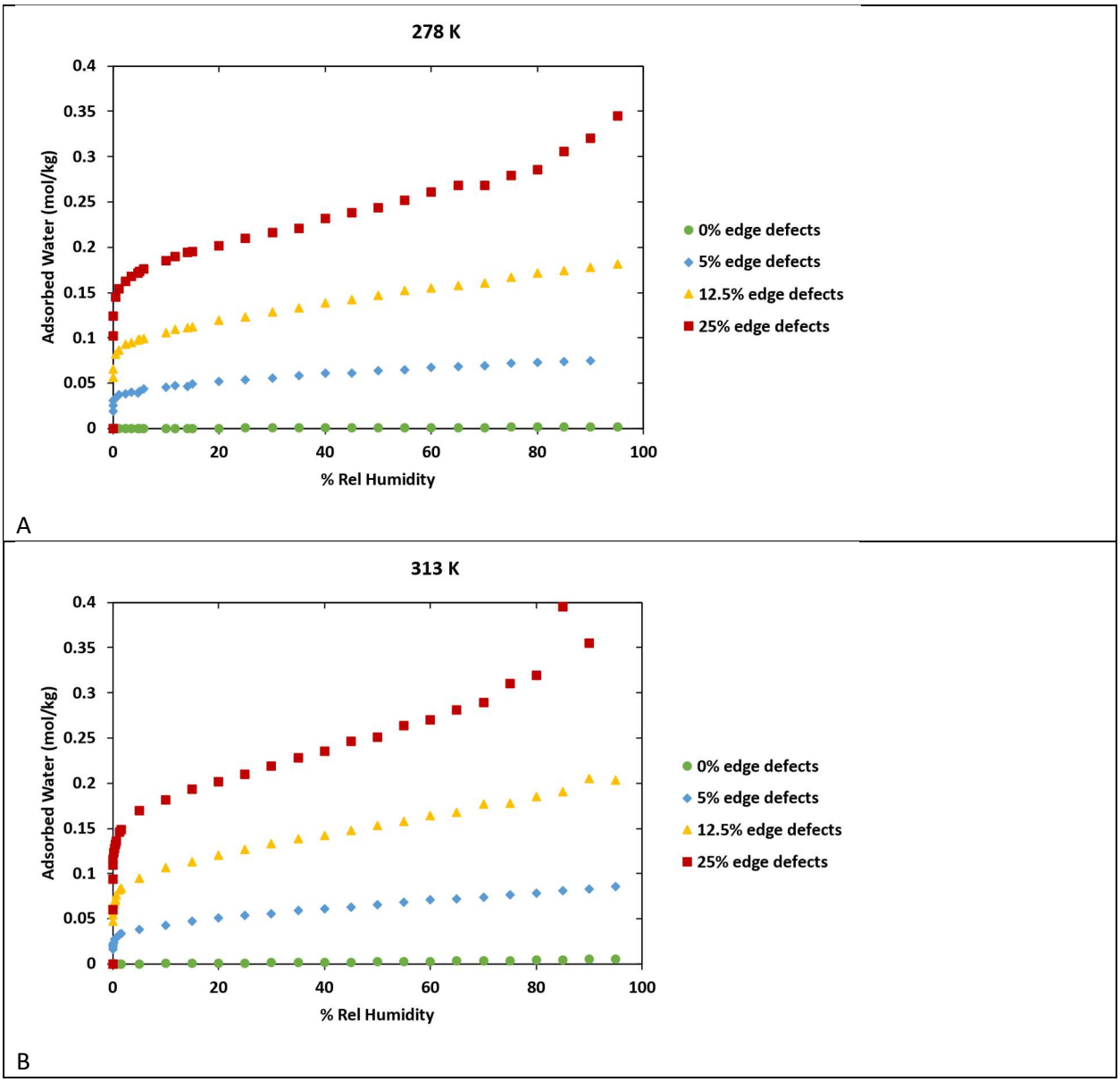
Supporting Figure 3: Top-down view of MoS_2 surfaces with defects. Each structure contains three layers of MoS_2 and 20 Å of vacuum space above the surface. Defects are only on the top basal surface. A) 0 defects, B) 1 defect, C) 2 defects, D) 3 defects, E) 4 defects (none adjacent), F) 5 defects (none adjacent), G) 4 defects (2 adjacent), H) 5 defects (2 adjacent). Colors: yellow S, teal Mo



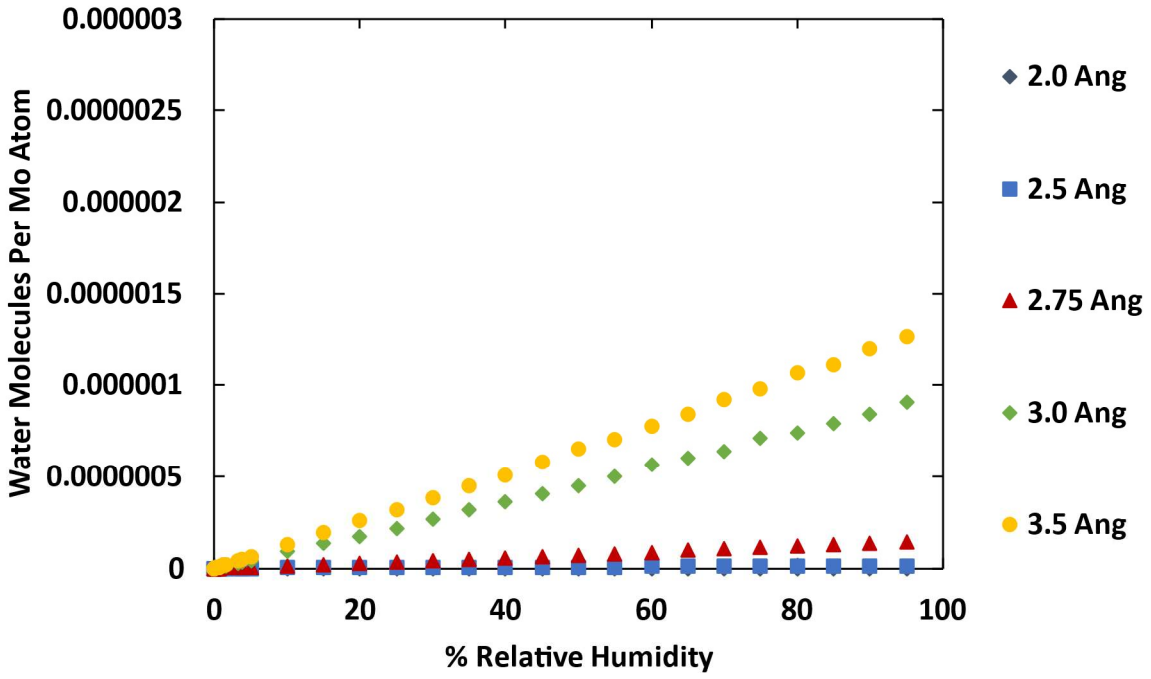
Supporting Figure 4: Adsorption isotherms for bulk MoS_2 with various defect densities at A) 278 K and B) 313 K



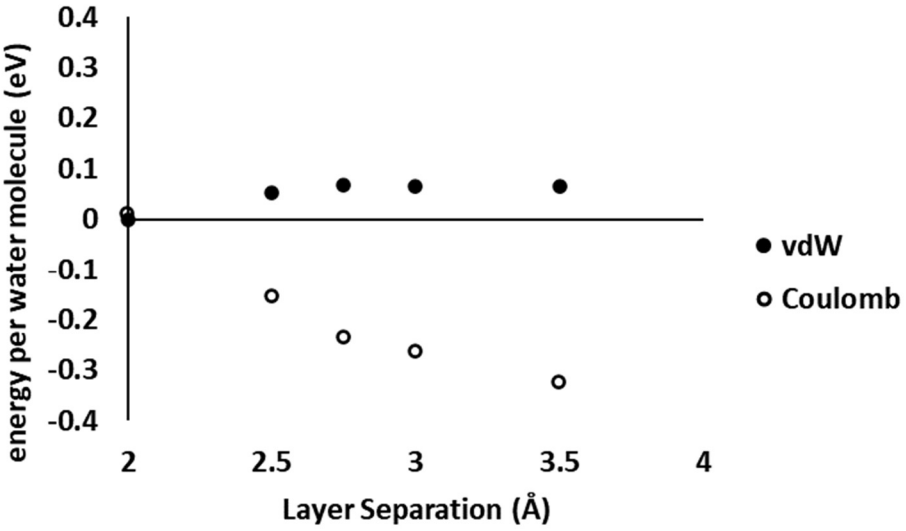
Supporting Figure 5: Adsorption isotherms for water on MoS_2 surfaces with defects. A) 278 K, B) 313 K



Supporting Figure 6: Adsorption isotherms for water on MoS_2 with edge defects. A) 278 K, B) 313 K



Supporting Figure 7: Water adsorption isotherms for MoS2 with no defects at 298 K. Separation values are the distance the layers are moved from the crystallographic minimum. Amount of water uptake is normalized by the number of Mo atoms in the system.



Supporting Figure 8: Energy decomposition of adsorbate-adsorbate interactions as a function of layer separation (separation beyond minimum). Energy is in eV per water molecule.

MoS_2 Unit Cell Coordinates

CIF file generated by openbabel 2.3.90, see http://openbabel.sf.net

data_I

_chemical_name_common ''

_cell_length_a 3.14754

_cell_length_b 3.14754

_cell_length_c 12.0721

_cell_angle_alpha 90

_cell_angle_beta 90

_cell_angle_gamma 120

_space_group_name_H-M_alt 'P 1'

_space_group_name_Hall 'P 1'

loop_

_symmetry_equiv_pos_as_xyz

x,y,z

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_occupancy

Mo1 Mo 0.00000 0.00000 0.12984 1.000

Mo2 Mo 0.66660 0.33320 0.62980 1.000

S1 S 0.66660 0.33325 0.25964 1.000

S2 S 0.66660 0.33325 0.00000 1.000

S3 S 0.00005 0.99995 0.49996 1.000

S4 S 0.00005 0.99995 0.75964 1.000