

**Water adsorption in SAPO-34: Elucidating the role of local heterogeneities  
and defects using dispersion-corrected DFT calculations**

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ELECTRONIC SUPPLEMENTARY INFORMATION

- (1) Snapshots at high water loadings: DFT-D interaction energies**
- (2) Visualisation of selected snapshots**
- (3) Typical CASTEP input files**

## (1) Snapshots at high water loadings: Interaction energies

Interaction energies obtained for individual snapshots for a loading of 30 H<sub>2</sub>O molecules per unit cell.

### a) SAPO-34\_O1

	$E_{int,aver} / \text{kJ mol}^{-1}$	$E_{int,nodisp, aver} / \text{kJ mol}^{-1}$
Snapshot 1	-71.6	-50.6
Snapshot 2	-71.4	-50.5
Snapshot 3	-67.4	-46.1
Snapshot 4	-72.6	-51.6
Snapshot 5	-71.2	-50.5
Average	-70.9 +/- 2.0	-49.9

### b) SAPO-34\_O3

	$E_{int,aver} / \text{kJ mol}^{-1}$	$E_{int,nodisp, aver} / \text{kJ mol}^{-1}$
Snapshot 1	-69.8	-48.9
Snapshot 2	-71.1	-50.6
Snapshot 3	-67.4	-45.9
Snapshot 4	-71.8	-50.6
Snapshot 5	-69.9	-48.6
Average	-70.0 +/- 1.6	-48.9

### c) SAPO-34\_Si\_island

	$E_{int,aver} / \text{kJ mol}^{-1}$	$E_{int,nodisp, aver} / \text{kJ mol}^{-1}$
Snapshot 1	-70.6	-49.3
Snapshot 2	-69.7	-49.0
Snapshot 3	-70.0	-49.2
Snapshot 4	-73.0	-52.0
Snapshot 5	-70.2	-48.8
Average	-70.7 +/- 1.3	-49.7

**d) SAPO-34\_SiAl\_domain**

	$E_{int,aver} / \text{kJ mol}^{-1}$	$E_{int,nodisp, aver} / \text{kJ mol}^{-1}$
Snapshot 1	-68.8	-47.6
Snapshot 2	-70.0	-49.1
Snapshot 3	-71.4	-50.7
Snapshot 4	-68.7	-48.1
Snapshot 5	-68.9	-47.7
Average	-69.6 +/- 1.2	-48.7

**e) SAPO-34\_defect+Si(OH)<sub>4</sub>**

	$E_{int,aver} / \text{kJ mol}^{-1}$	$E_{int,nodisp, aver} / \text{kJ mol}^{-1}$
Snapshot 1	-69.4	-45.8
Snapshot 2	-72.2	-48.8
Snapshot 3	-70.3	-47.3
Snapshot 4	-69.7	-46.8
Snapshot 5	-72.4	-49.1
Average	-70.8 +/- 1.4	-47.6

**f) SAPO-34\_desilicated**

	$E_{int,aver} / \text{kJ mol}^{-1}$	$E_{int,nodisp, aver} / \text{kJ mol}^{-1}$
Snapshot 1	-67.0	-44.3
Snapshot 2	-69.2	-47.1
Snapshot 3	-66.3	-43.7
Snapshot 4	-68.3	-46.5
Snapshot 5	-65.0	-42.2
Average	-67.2 +/- 1.7	-44.8

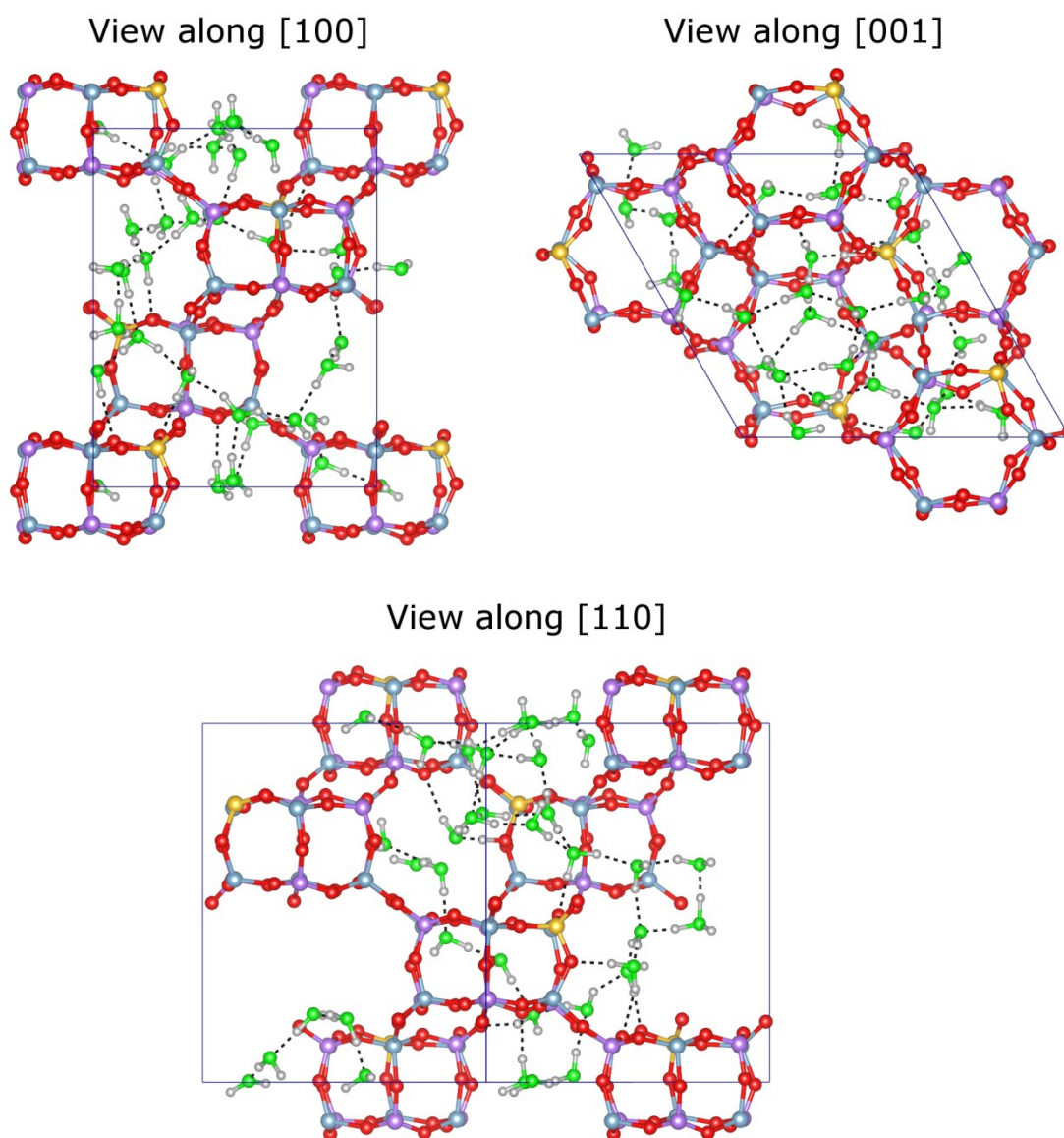
**g) AIPO-34**

	$E_{int,aver} / \text{kJ mol}^{-1}$	$E_{int,nodisp, aver} / \text{kJ mol}^{-1}$
Snapshot 1	-62.8	-41.1
Snapshot 2	-63.4	-42.0
Snapshot 3	-63.7	-42.6
Snapshot 4	-63.8	-42.3
Snapshot 5	-63.7	-42.2
Average	-63.5 +/- 0.4	-42.0

## (2) Visualisation of selected snapshots

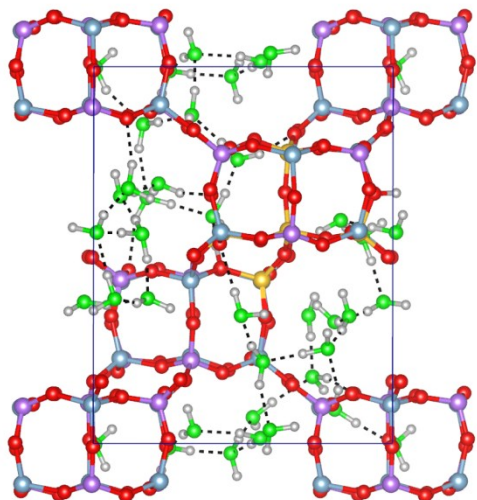
The following figures show selected DFT-D optimised structures of SAPO-34 systems with 30 H<sub>2</sub>O molecules per unit cell. Oxygen atoms of water molecules are shown in green to distinguish them from framework oxygen atoms.

SAPO-34\_O1 + 30 H<sub>2</sub>O (snapshot 4)

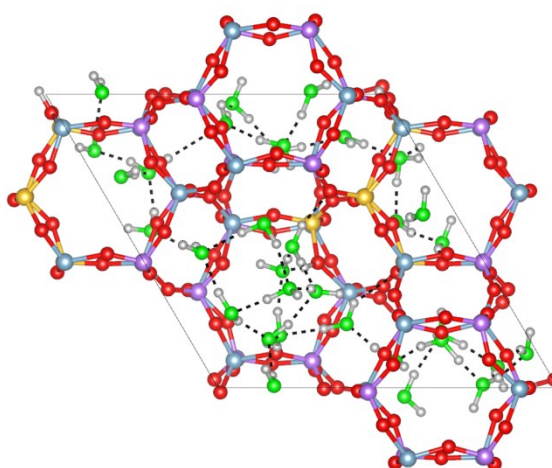


SAPO-34\_Si\_island + 30 H<sub>2</sub>O (snapshot 3)

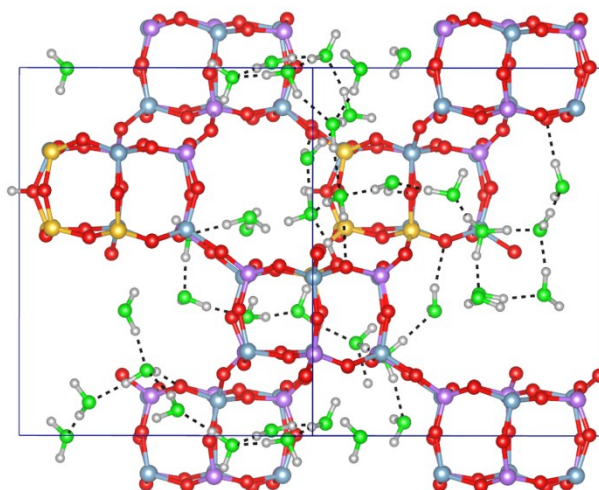
View along [100]



View along [001]

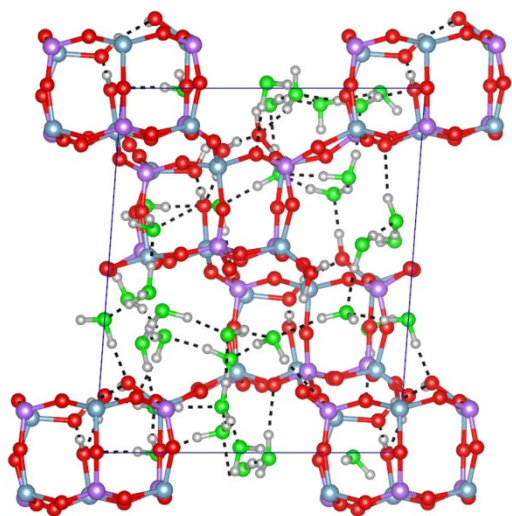


View along [110]

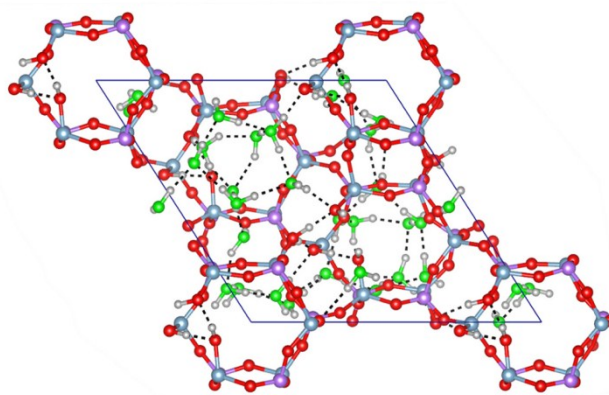


SAPO-34\_desilicated + 30 H<sub>2</sub>O (snapshot 2)

View along [100]



View along [001]



### (3) Typical CASTEP input files

#### \*.param file

```
comment : SAPO-34_O1_opti (including cell relaxation)
task : GeometryOptimization
xc_functional : PBE
sedc_apply: true
sedc_scheme: TS
spin_polarized : false
opt_strategy : Speed
page_wvfns : 0
cut_off_energy : 700.0000000000000000
grid_scale : 2.0000000000000000
fine_grid_scale : 2.0000000000000000
finite_basis_corr : 2
finite_basis_npoints : 3
elec_energy_tol : 1.0000000000000000e-010
max_scf_cycles : 250
fix_occupancy : true
metals_method : dm
mixing_scheme : Pulay
mix_charge_amp : 0.5000000000000000
mix_charge_gmax : 1.5000000000000000
mix_history_length : 20
nextra_bands : 0
geom_energy_tol : 5.0000000000000000e-006
geom_force_tol : 0.0100000000000000
geom_stress_tol : 0.0200000000000000
geom_disp_tol : 5.0000000000000000e-004
geom_max_iter : 1000
geom_method : BFGS
fixed_npw : false
geom_modulus_est : 100.0000000000000000 GPa
calculate ELF : false
calculate_stress : true
popn_calculate : true
calculate_hirshfeld : true
calculate_densdiff : false
popn_bond_cutoff : 3.0000000000000000
pdos_calculate_weights : false
num_dump_cycles : 0
num_backup_iter : 5
write_cif_structure: true
write_cell_structure: true
```

**\*.cell file**

%BLOCK LATTICE\_CART

11.9555244896803	-6.90252528242006	0.000000000000000
0.000000000000000	13.8050505648401	0.000000000000000
0.000000000000000	0.000000000000000	15.1491383582027

%ENDBLOCK LATTICE\_CART

%BLOCK cell\_constraints

1	1	3
0	0	0

%ENDBLOCK cell\_constraints

%BLOCK positions\_frac

H	0.009400893152441	0.361611902007518	0.004985665497903
H	-0.361611902007518	-0.352211008855076	0.671652332164571
H	0.352211008855076	-0.009400893152441	0.338318998831236
O	0.464327171772902	0.211131442763573	0.456314151016584
O	0.229110597118638	0.422582339173060	0.459421212025192
O	0.315662078842782	0.003922377498440	0.503987020351902
O	-0.071527570434649	0.988927005292726	0.989401429019657
O	0.112207589345765	0.536810898337829	0.796632557358482
O	-0.106610273823177	0.752240073247104	0.768337289310215
O	-0.019580905182944	0.338386444144691	0.829115180556433
O	0.606640032830059	0.347033352642810	0.317894954570451
O	-0.217373839970518	0.877728895827369	0.133450863536924
O	0.557296158460006	0.091610232697507	0.117151167080286
O	-0.348466148809293	0.679513957433761	0.167010805167200
O	0.267584501337897	0.671102606051775	0.663624974307154
O	-0.114669949277058	0.798146556125217	0.544511202839707
O	0.115792420759003	0.576641245371058	0.550161909506399
O	0.024858402066615	0.988841176650867	0.497170346643883
O	0.399912439857593	-0.002857536762943	0.007995809618133
O	0.551019429260249	0.115434924528071	0.867463501302560
O	-0.231952349469032	0.913449003910857	0.881822786231570
O	0.684087083964761	0.309464971811532	0.825015517983278
O	0.077138217015639	0.332295590314264	0.346160753680090
O	0.219441714735567	0.465111733056584	0.207155127741646
O	0.434797045418817	0.246198573552324	0.223744755185324
O	0.348751786261864	0.665570052985066	0.176390012396595
O	-0.286506406034049	0.658145330366696	0.670265347949700
O	-0.211131442763573	0.253195729009329	1.122980817683251
O	-0.422582339173060	-0.193471742054422	1.126087878691859
O	-0.003922377498440	0.311739701344342	1.170653687018570
O	-0.988927005292726	-1.060454575727375	1.656068095686324
O	-0.536810898337830	-0.424603308992065	1.463299224025150
O	-0.752240073247104	-0.858850347070281	1.435003955976882
O	-0.338386444144691	-0.357967349327635	1.495781847223099
O	-0.347033352642810	0.259606680187249	0.984561621237117
O	-0.877728895827369	-1.095102735797886	0.800117530203591



O	-0.091610232697507	0.465685925762499	0.783817833746953
O	-0.679513957433761	-1.027980106243052	0.833677471833867
O	-0.671102606051775	-0.403518104713878	1.330291640973822
O	-0.798146556125217	-0.912816505402275	1.211177869506374
O	-0.576641245371058	-0.460848824612055	1.216828576173066
O	-0.988841176650867	-0.963982774584251	1.163837013310551
O	0.002857536762943	0.402769976620536	0.674662476284800
O	-0.115434924528071	0.435584504732178	1.534130167969227
O	-0.913449003910857	-1.145401353379891	1.548489452898236
O	-0.309464971811532	0.374622112153228	1.491682184649945
O	-0.332295590314264	-0.255157373298625	1.012827420346757
O	-0.465111733056584	-0.245670018321017	0.873821794408313
O	-0.246198573552324	0.188598471866493	0.890411421851991
O	-0.665570052985066	-0.316818266723202	0.843056679063262
O	-0.658145330366696	-0.944651736400745	1.336932014616368
O	-0.253195729009329	-0.464327171772902	0.789647484349917
O	0.193471742054422	-0.229110597118638	0.792754545358524
O	-0.311739701344342	-0.315662078842782	0.837320353685235
O	1.060454575727375	0.071527570434649	1.322734762352990
O	0.424603308992065	-0.112207589345765	1.129965890691816
O	0.858850347070281	0.106610273823177	1.101670622643548
O	0.357967349327635	0.019580905182944	1.162448513889765
O	-0.259606680187249	-0.606640032830059	0.651228287903784
O	1.095102735797886	0.217373839970518	0.466784196870258
O	-0.465685925762499	-0.557296158460006	0.450484500413619
O	1.027980106243053	0.348466148809293	0.500344138500533
O	0.403518104713878	-0.267584501337897	0.996958307640487
O	0.912816505402275	0.114669949277058	0.877844536173040
O	0.460848824612055	-0.115792420759003	0.883495242839731
O	0.963982774584251	-0.024858402066615	0.830503679977216
O	-0.402769976620536	-0.399912439857593	0.341329142951466
O	-0.435584504732178	-0.551019429260249	1.200796834635893
O	1.145401353379891	0.231952349469032	1.215156119564902
O	-0.374622112153228	-0.684087083964761	1.158348851316611
O	0.255157373298625	-0.077138217015639	0.679494087013423
O	0.245670018321017	-0.219441714735567	0.540488461074978
O	-0.188598471866493	-0.434797045418817	0.557078088518657
O	0.316818266723202	-0.348751786261864	0.509723345729928
O	0.944651736400746	0.286506406034049	1.003598681283034
Al	0.333039405421623	0.560372234743437	0.440077513024831
Al	-0.004623095333817	0.890611726463268	0.765271010774867
Al	-0.340321130370054	0.231272758143320	0.096776998923156
Al	0.007574619662869	0.440188876177873	0.564250316938522
Al	0.665950683337393	0.773210699822171	0.900971362420237
Al	0.333190057400229	0.107012646501225	0.227984510861082
Al	-0.560372234743437	-0.227332829321813	1.106744179691497
Al	-0.890611726463268	-0.895234821797084	1.431937677441533
Al	-0.231272758143320	-0.571593888513374	0.763443665589823
Al	-0.440188876177873	-0.432614256515003	1.230916983605188
Al	-0.773210699822171	-0.107260016484778	1.567638029086904

Al	-0.107012646501225	0.226177410899004	0.894651177527749
Al	0.227332829321813	-0.333039405421623	0.773410846358164
Al	0.895234821797084	0.004623095333817	1.098604344108199
Al	0.571593888513374	0.340321130370054	0.430110332256489
Al	0.432614256515003	-0.007574619662869	0.897583650271855
Al	0.107260016484777	-0.665950683337393	1.234304695753570
Al	-0.226177410899004	-0.333190057400229	0.561317844194415
Si	-0.234154743985973	0.657728874245963	0.777016875598720
Si	-0.657728874245963	-0.891883618231937	1.443683542265388
Si	0.891883618231937	0.234154743985973	1.110350208932054
P	0.236116482445369	0.669755148638883	0.566409850013761
P	-0.107203597464283	0.996590780565982	0.895320781654570
P	0.558532339781856	0.339423827498928	0.225696172205492
P	0.107816719689173	0.330044625916336	0.442600155364228
P	0.436320275870833	-0.000422029905173	0.103442276035612
P	-0.669755148638884	-0.433638666193514	1.233076516680428
P	-0.996590780565982	-1.103794378030265	1.561987448321237
P	-0.339423827498928	0.219108512282928	0.892362838872158
P	-0.330044625916336	-0.222227906227163	1.109266822030895
P	0.000422029905173	0.436742305776005	0.770108942702279
P	0.433638666193514	-0.236116482445369	0.899743183347094
P	1.103794378030265	0.107203597464283	1.228654114987903
P	-0.219108512282928	-0.558532339781856	0.559029505538824
P	0.222227906227163	-0.107816719689173	0.775933488697562
P	-0.436742305776006	-0.436320275870833	0.436775609368945

%ENDBLOCK positions\_frac

FIX\_COM : false

%BLOCK species\_mass

AMU

H	2.00000000
O	15.99899960
Al	26.98200035
Si	28.08499908
P	30.97400093

%ENDBLOCK species\_mass

```

%BLOCK species_pot
H 1|0.8|3.675|7.35|11.025|10UU(qc=6.4)[]
O 2|1.3|16.537|18.375|20.212|20UU:21UU(qc=7.5)[]
Al 2|2|3.675|5.512|7.717|30UU:31UU:32LGG[]
Si 2|1.8|3.675|5.512|7.35|30UU:31UU:32LGG[]
P 2|1.8|3.675|5.512|6.982|30UU:31UU:32LGG[]
%ENDBLOCK species_pot

```

```

%BLOCK species_lcao_states
H 1
O 2
Al 2
Si 2
P 2

```

```

%ENDBLOCK species_lcao_states

```

```

%BLOCK symmetry_ops

```

```

# Symm. op. 1 E
1.0000000000000000 0.0000000000000000 0.0000000000000000
0.0000000000000000 1.0000000000000000 0.0000000000000000
0.0000000000000000 -0.0000000000000000 1.0000000000000000
0.0000000000000000 0.0000000000000000 0.0000000000000000
# Symm. op. 2 3_2
-0.5000000000000000 0.866025403784438 -0.0000000000000000
-0.866025403784439 -0.5000000000000000 -0.0000000000000000
0.0000000000000000 -0.0000000000000000 1.0000000000000000
0.0000000000000000 0.0000000000000000 0.6666666666666671
# Symm. op. 3 3_1
-0.5000000000000000 -0.866025403784438 -0.0000000000000000
0.866025403784439 -0.5000000000000000 0.0000000000000000
0.0000000000000000 0.0000000000000000 1.0000000000000000
0.0000000000000000 0.0000000000000000 0.333333333333329

```

```

%ENDBLOCK symmetry_ops

```

```

kpoint_mp_grid: 1 1 1

```