Electronic Supplementary Information

Revealing SO_2 and CO_2 Adsorption Features on Forsterite via IR Spectroscopy and Automated Computational Approaches

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Table S1. Miller indices in the Pbnm and standard Pnma notations of the forsterite space group, along with the surface energies at the PBE-D3 level and the fraction that each termination occupies on the crystal equilibrium shape of forsterite obtained with the Wulff construction method.

Miller index (Pbnm)	Miller index (Pnma)	Surface energy (J m^{-2})	Equilibrium shape fraction
(010)	(001)	1.32	**0.198**
(120)	(102)	1.41	**0.331**
(101)	(110)	1.68	**0.153**
(001)	(010)	1.71	**0.155**
(111)	(111)	1.76	**0.115**
(110)	(101)	1.81	**0.000**
(021)	(012)	1.92	**0.047**

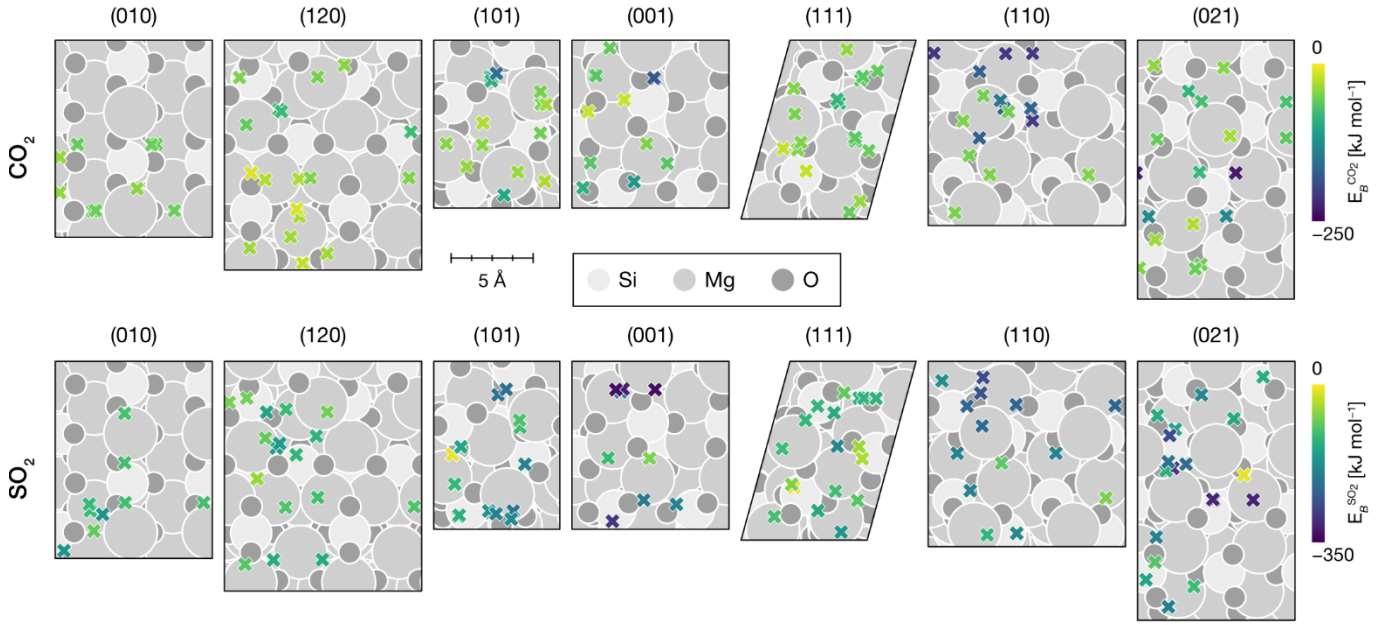


Figure S1. Top view of the surface unit cells depicting the molecular adsorption sites for CO_2 and SO_2. Adsorption sites are denoted as *x* symbols on the surface and correspond to the XY coordinates of the center of mass of the adsorbate in its final, optimal position at the DFT level. Atoms belonging to the surface have been colored in grayscale for readability.

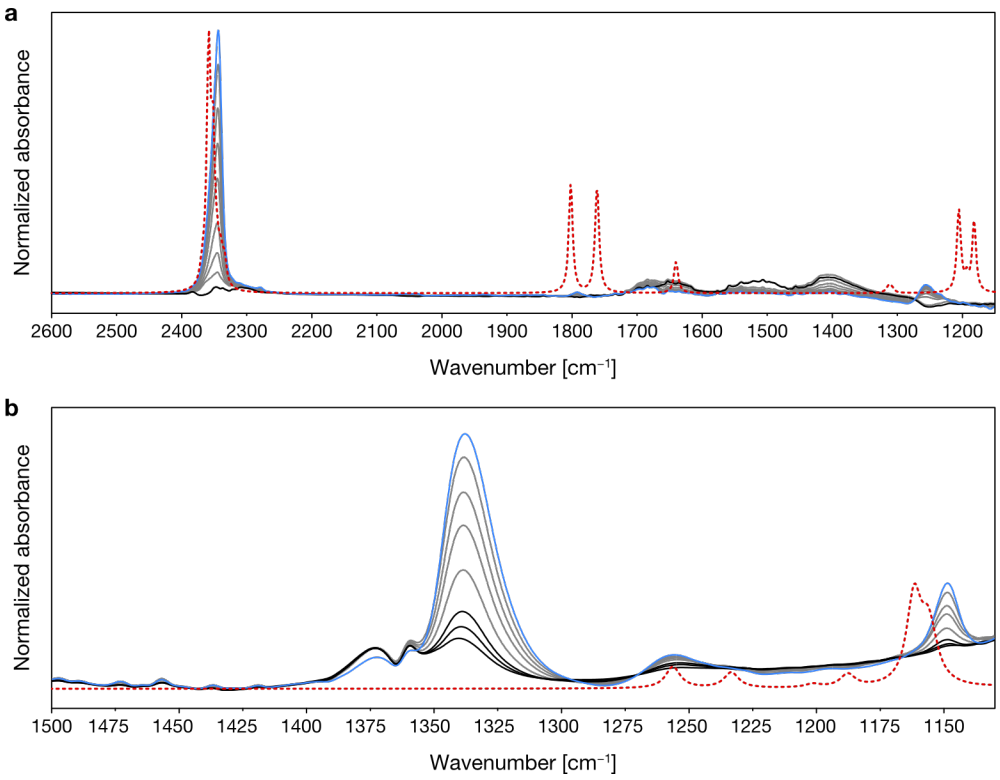
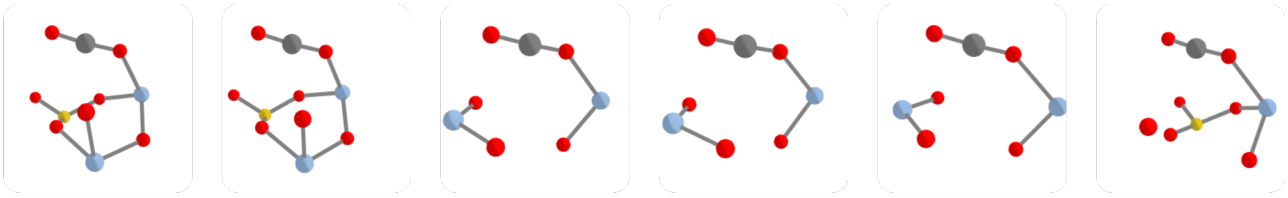


Figure S2. Experimental IR spectra of a) CO_2 and b) SO_2 on crystalline Mg-silicate at progressively increasing temperatures (from blue to black lines); the Boltzmann and Wulff-weighed theoretical total IR spectra are added as dotted red lines for direct comparison.

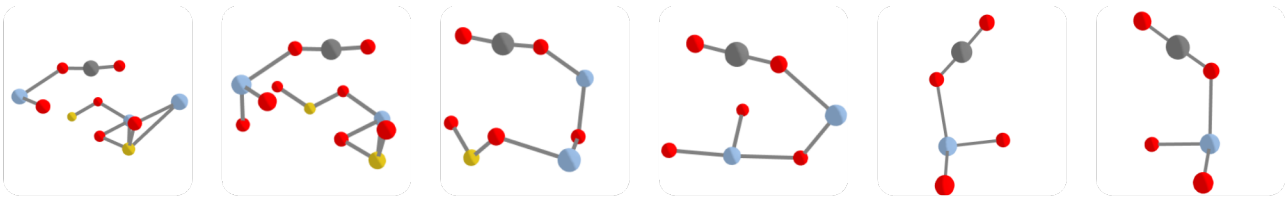
(010)



-60.1		-59.98		-57.64		-57.47		-57.44		-57.01	
2358	1.000	2359	1.000	2371	1.000	2369	1.000	2366	1.000	2359	1.000
1312	0.024	1313	0.023	1324	0.011	1323	0.008	1322	0.007	1312	0.020
606	0.087	606	0.086	606	0.081	599	0.096	599	0.094	606	0.092
579	0.102	580	0.100	586	0.054	577	0.066	578	0.065	591	0.082
195	0.004	195	0.004	151	0.005	149	0.004	149	0.004	193	0.004
113	0.001	119	0.001	107	0.001	129	0.001	130	0.001	104	0.001
96	0.000	97	0.000	92	0.000	106	0.000	115	0.000	93	0.000
60	0.001	65	0.003	49	0.000	76	0.000	75	0.001	58	0.003
0	0.003	28	0.002	38	0.001	46	0.002	49	0.002	20	0.002

Figure S3. Atomic representations of the 6 CO_2 adsorption configurations displaying the lowest adsorption energies on the **(010)** surface of Mg_2SiO_4 in our calculations. Only atoms within a radius of 4 Å from the C center are displayed. Adsorption energies are denoted in purple, in kJ mol^{-1}. The arising spectroscopic features from these adsorptions are displayed under the adsorption energy, where the first column is the wavenumber in cm^{-1}, and the second column is the normalized intensity. Blue, dark yellow, red and gray balls represent Mg, Si, O and C atoms, respectively.

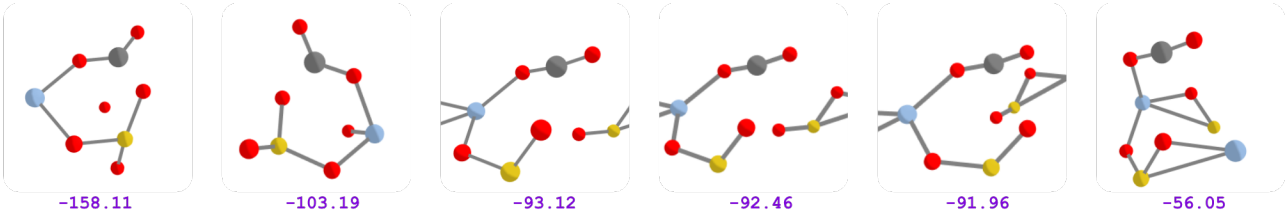
(120)



-81.6		-81.44		-79.25		-61.03		-51.74		-49.38	
2351	1.000	2358	1.000	2367	1.000	2382	1.000	2367	1.000	2371	1.000
1311	0.010	1315	0.014	1321	0.053	1329	0.036	1313	0.022	1316	0.010
587	0.091	590	0.090	604	0.035	608	0.041	621	0.058	624	0.067
564	0.085	565	0.085	546	0.112	594	0.050	612	0.048	606	0.046
189	0.006	194	0.006	181	0.007	170	0.005	199	0.002	212	0.004
143	0.000	140	0.000	138	0.001	97	0.000	88	0.000	91	0.000
108	0.001	113	0.001	85	0.001	66	0.000	68	0.001	78	0.000
60	0.002	73	0.001	59	0.003	55	0.001	26	0.001	34	0.002
55	0.003	65	0.002	36	0.001	8	0.002	18	0.001	34	0.002

Figure S4. Atomic representations of the 6 CO_2 adsorption configurations displaying the lowest adsorption energies on the **(120)** surface of Mg_2SiO_4 in our calculations. Only atoms within a radius of 4 Å from the C center are displayed. Adsorption energies are denoted in purple, in kJ mol^{-1}. The arising spectroscopic features from these adsorptions are displayed under the adsorption energy, where the first column is the wavenumber in cm^{-1}, and the second column is the normalized intensity. Blue, dark yellow, red and gray balls represent Mg, Si, O and C atoms, respectively.

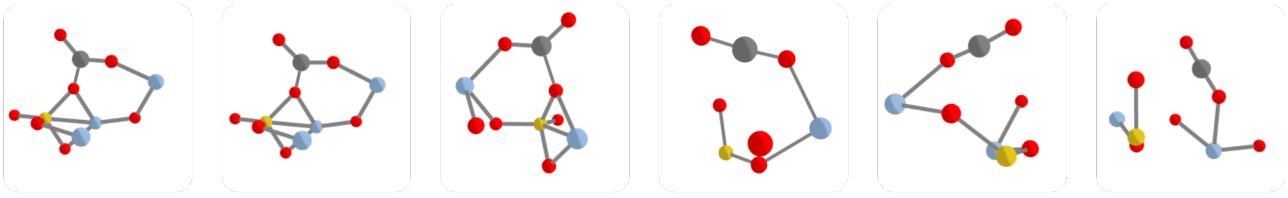
(101)



-158.11		-103.19		-93.12		-92.46		-91.96		-56.05	
1801	1.000	1821	1.000	2352	1.000	2359	1.000	2349	1.000	2321	1.000
1205	0.526	1209	0.517	1309	0.063	1315	0.064	1306	0.067	1284	0.038
764	0.335	741	0.350	564	0.159	575	0.121	562	0.162	584	0.118
720	0.042	729	0.026	550	0.148	548	0.156	542	0.165	572	0.286
457	0.005	441	0.002	193	0.005	197	0.005	189	0.005	225	0.007
331	0.013	324	0.034	151	0.001	154	0.001	162	0.002	136	0.002
244	0.021	220	0.019	125	0.001	113	0.001	138	0.001	120	0.003
139	0.008	135	0.010	63	0.005	72	0.009	79	0.006	63	0.004
64	0.007	35	0.004	54	0.006	52	0.003	63	0.006	41	0.006

Figure S5. Atomic representations of the 6 **CO_2** adsorption configurations displaying the lowest adsorption energies on the **(101)** surface of Mg_2SiO_4 in our calculations. Only atoms within a radius of 4 Å from the C center are displayed. Adsorption energies are denoted in purple, in kJ mol^{-1}. The arising spectroscopic features from these adsorptions are displayed under the adsorption energy, where the first column is the wavenumber in cm^{-1}, and the second column is the normalized intensity. Blue, dark yellow, red and gray balls represent Mg, Si, O and C atoms, respectively.

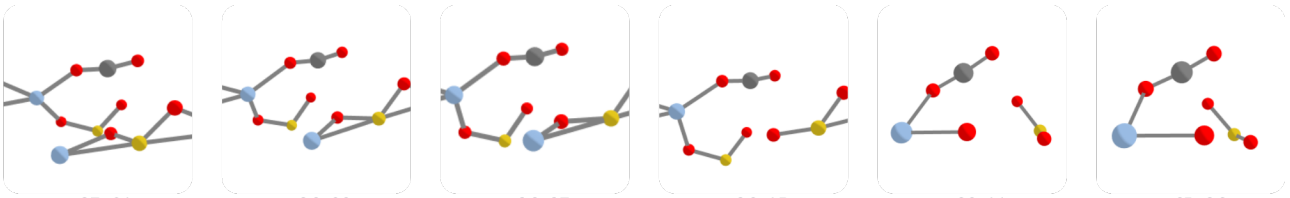
(001)



-182.72		-181.31		-117.83		-92.61		-67.16		-66.97	
1761	1.000	1763	1.000	1856	1.000	2359	1.000	2335	1.000	2361	1.000
1182	0.758	1193	0.782	1209	0.797	1304	0.031	1284	0.049	1312	0.004
788	0.193	791	0.233	735	0.088	611	0.157	595	0.071	614	0.074
753	0.022	749	0.025	715	0.146	565	0.137	546	0.280	582	0.086
459	0.006	460	0.004	435	0.027	225	0.005	217	0.002	176	0.006
367	0.019	369	0.013	314	0.121	123	0.001	128	0.004	134	0.001
276	0.019	263	0.019	219	0.025	114	0.001	93	0.002	89	0.001
67	0.016	74	0.020	120	0.020	46	0.003	52	0.006	63	0.002
48	0.001	59	0.001	40	0.003	29	0.004	39	0.006	22	0.001

Figure S6. Atomic representations of the 6 **CO_2** adsorption configurations displaying the lowest adsorption energies on the **(001)** surface of Mg_2SiO_4 in our calculations. Only atoms within a radius of 4 Å from the C center are displayed. Adsorption energies are denoted in purple, in kJ mol^{-1}. The arising spectroscopic features from these adsorptions are displayed under the adsorption energy, where the first column is the wavenumber in cm^{-1}, and the second column is the normalized intensity. Blue, dark yellow, red and gray balls represent Mg, Si, O and C atoms, respectively.

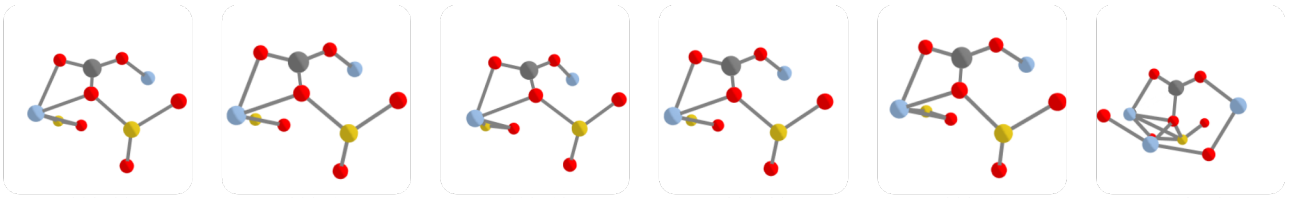
(111)



-87.01		-86.99		-86.87		-86.15		-66.11		-65.86	
2339	1.000	2334	1.000	2345	1.000	2351	1.000	2354	1.000	2351	1.000
1308	0.092	1306	0.081	1311	0.081	1314	0.053	1300	0.031	1298	0.030
576	0.104	578	0.107	572	0.120	567	0.127	608	0.082	602	0.093
527	0.228	523	0.239	538	0.184	550	0.172	593	0.117	583	0.136
188	0.007	194	0.007	194	0.008	187	0.006	214	0.003	212	0.002
175	0.003	184	0.005	168	0.002	164	0.003	110	0.002	112	0.002
123	0.005	130	0.000	127	0.002	125	0.000	97	0.001	101	0.001
68	0.009	82	0.031	74	0.004	76	0.009	55	0.002	62	0.004
61	0.016	71	0.007	50	0.017	50	0.006	39	0.003	38	0.002

Figure S7. Atomic representations of the 6 CO_2 adsorption configurations displaying the lowest adsorption energies on the **(111)** surface of Mg_2SiO_4 in our calculations. Only atoms within a radius of 4 Å from the C center are displayed. Adsorption energies are denoted in purple, in kJ mol^{-1}. The arising spectroscopic features from these adsorptions are displayed under the adsorption energy, where the first column is the wavenumber in cm^{-1}, and the second column is the normalized intensity. Blue, dark yellow, red and gray balls represent Mg, Si, O and C atoms, respectively.

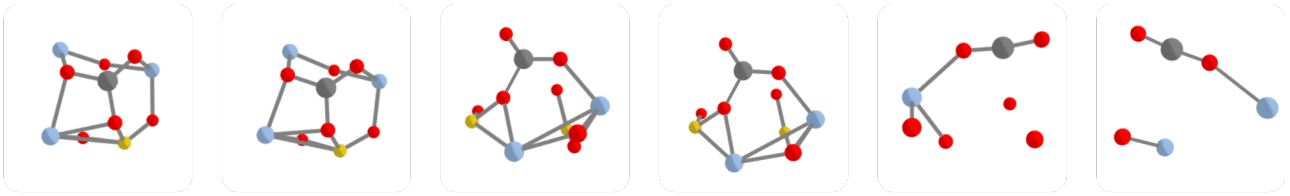
(110)



-209.20		-209.14		-209.12		-208.38		-208.14		-173.42	
1597	1.000	1596	1.000	1599	1.000	1594	1.000	1598	1.000	1648	1.000
1256	0.628	1256	0.622	1257	0.702	1253	0.880	1256	0.905	1253	0.736
816	0.081	816	0.083	815	0.087	816	0.058	816	0.055	813	0.077
741	0.059	741	0.059	741	0.058	741	0.070	741	0.070	760	0.019
512	0.016	512	0.015	512	0.047	512	0.109	512	0.094	516	0.008
398	0.029	398	0.029	398	0.090	398	0.129	398	0.136	407	0.026
269	0.017	269	0.017	269	0.023	270	0.038	271	0.039	230	0.050
206	0.019	206	0.019	208	0.015	207	0.011	207	0.012	166	0.006
173	0.022	173	0.022	173	0.024	170	0.026	176	0.026	115	0.013

Figure S8. Atomic representations of the 6 CO_2 adsorption configurations displaying the lowest adsorption energies on the **(110)** surface of Mg_2SiO_4 in our calculations. Only atoms within a radius of 4 Å from the C center are displayed. Adsorption energies are denoted in purple, in kJ mol^{-1}. The arising spectroscopic features from these adsorptions are displayed under the adsorption energy, where the first column is the wavenumber in cm^{-1}, and the second column is the normalized intensity. Blue, dark yellow, red and gray balls represent Mg, Si, O and C atoms, respectively.

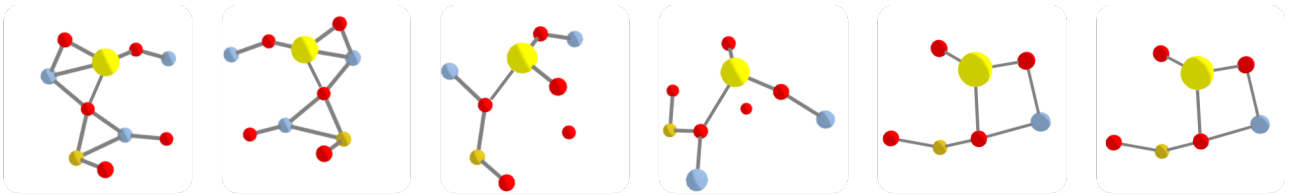
(021)



-232.23		-231.85		-133.86		-133.63		-86.93		-81.56	
1640	1.000	1639	1.000	1770	1.000	1771	1.000	2360	1.000	2375	1.000
1205	0.835	1203	0.841	1200	0.706	1200	0.692	1311	0.058	1322	0.076
832	0.081	833	0.084	766	0.284	765	0.393	584	0.083	595	0.032
778	0.046	778	0.048	723	0.063	725	0.065	563	0.151	540	0.180
520	0.003	521	0.003	454	0.002	453	0.026	202	0.005	175	0.004
426	0.007	427	0.008	347	0.024	345	0.031	146	0.001	115	0.001
283	0.028	280	0.047	225	0.016	224	0.029	117	0.001	80	0.001
247	0.032	242	0.033	184	0.013	183	0.014	70	0.001	46	0.004
172	0.028	172	0.028	77	0.012	75	0.014	52	0.004	11	0.002

Figure S9. Atomic representations of the 6 $\mathbf{CO_2}$ adsorption configurations displaying the lowest adsorption energies on the **(021)** surface of Mg_2SiO_4 in our calculations. Only atoms within a radius of 4 Å from the C center are displayed. Adsorption energies are denoted in purple, in kJ mol^{-1}. The arising spectroscopic features from these adsorptions are displayed under the adsorption energy, where the first column is the wavenumber in cm^{-1}, and the second column is the normalized intensity. Blue, dark yellow, red and gray balls represent Mg, Si, O and C atoms, respectively.

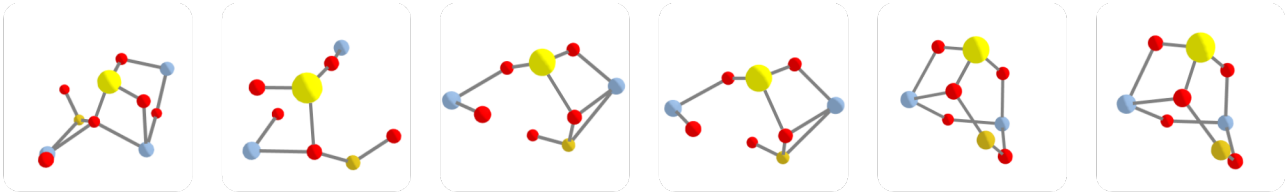
(010)



-171.33		-170.02		-113.72		-112.67		-106.36		-106.33	
1080	1.000	1078	1.000	1216	0.882	1218	0.954	1181	1.000	1181	1.000
989	0.484	985	0.438	1044	1.000	1051	1.000	980	0.874	980	0.872
538	0.080	536	0.078	497	0.103	494	0.103	510	0.060	510	0.060
457	0.202	455	0.188	317	0.228	320	0.243	445	0.353	446	0.353
321	0.021	321	0.022	207	0.024	201	0.022	276	0.087	276	0.087
209	0.041	209	0.034	169	0.003	174	0.007	168	0.012	168	0.012
167	0.015	166	0.014	107	0.015	110	0.013	103	0.013	103	0.013
140	0.069	137	0.086	81	0.011	76	0.012	80	0.011	80	0.011
114	0.025	118	0.018	61	0.002	42	0.007	45	0.006	46	0.006

Figure S10. Atomic representations of the 6 $\mathbf{SO_2}$ adsorption configurations displaying the lowest adsorption energies on the **(010)** surface of Mg_2SiO_4 in our calculations. Only atoms within a radius of 4 Å from the S center are displayed. Adsorption energies are denoted in purple, in kJ mol^{-1}. The arising spectroscopic features from these adsorptions are displayed under the adsorption energy, where the first column is the wavenumber in cm^{-1}, and the second column is the normalized intensity. Blue, dark yellow, red and light yellow balls represent Mg, Si, O and S atoms, respectively.

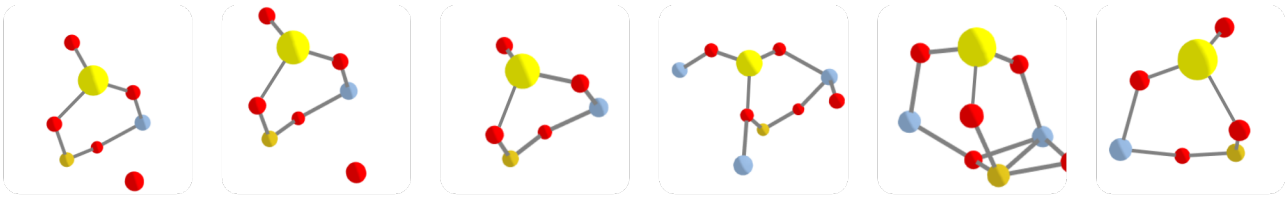
(120)



-162.64		-161.04		-149.10		-148.86		-137.96		-137.91	
1161	1.000	1187	1.000	1138	1.000	1140	1.000	1139	1.000	1138	1.000
1089	0.881	1104	0.493	1031	0.547	1033	0.556	1062	0.405	1060	1.000
599	0.153	527	0.034	578	0.079	576	0.079	582	0.249	582	0.217
461	0.319	417	0.158	479	0.180	473	0.177	463	0.207	463	0.212
280	0.036	258	0.005	336	0.063	335	0.064	364	0.028	364	0.031
264	0.009	209	0.005	209	0.018	207	0.017	236	0.038	233	0.037
172	0.046	154	0.017	174	0.015	172	0.014	221	0.003	220	0.003
139	0.011	129	0.009	147	0.011	156	0.011	165	0.032	165	0.030
89	0.012	107	0.021	86	0.015	89	0.011	120	0.028	118	0.027

Figure S11. Atomic representations of the 6 SO_2 adsorption configurations displaying the lowest adsorption energies on the **(120)** surface of Mg_2SiO_4 in our calculations. Only atoms within a radius of 4 Å from the S center are displayed. Adsorption energies are denoted in purple, in kJ mol^{-1}. The arising spectroscopic features from these adsorptions are displayed under the adsorption energy, where the first column is the wavenumber in cm^{-1}, and the second column is the normalized intensity. Blue, dark yellow, red and light yellow balls represent Mg, Si, O and S atoms, respectively.

(101)



-220.81		-220.75		-219.48		-194.68		-193.44		-180.87	
1256	1.000	1233	0.780	1201	0.769	1153	1.000	1096	1.000	1200	1.000
1011	0.977	1020	1.000	1008	1.000	1081	0.291	1043	0.510	1021	0.980
552	0.080	559	0.231	581	0.268	598	0.048	591	0.163	565	0.203
469	0.411	470	0.480	470	0.402	512	0.183	477	0.309	500	0.474
305	0.018	336	0.028	354	0.018	351	0.022	344	0.003	324	0.025
266	0.012	271	0.023	281	0.007	255	0.005	278	0.013	234	0.030
157	0.019	169	0.011	182	0.013	233	0.019	231	0.011	151	0.009
100	0.013	85	0.013	72	0.021	157	0.007	156	0.009	92	0.027
66	0.012	21	0.001	35	0.004	132	0.018	126	0.020	34	0.001

Figure S12. Atomic representations of the 6 SO_2 adsorption configurations displaying the lowest adsorption energies on the **(101)** surface of Mg_2SiO_4 in our calculations. Only atoms within a radius of 4 Å from the S center are displayed. Adsorption energies are denoted in purple, in kJ mol^{-1}. The arising spectroscopic features from these adsorptions are displayed under the adsorption energy, where the first column is the wavenumber in cm^{-1}, and the second column is the normalized intensity. Blue, dark yellow, red and light yellow balls represent Mg, Si, O and S atoms, respectively.

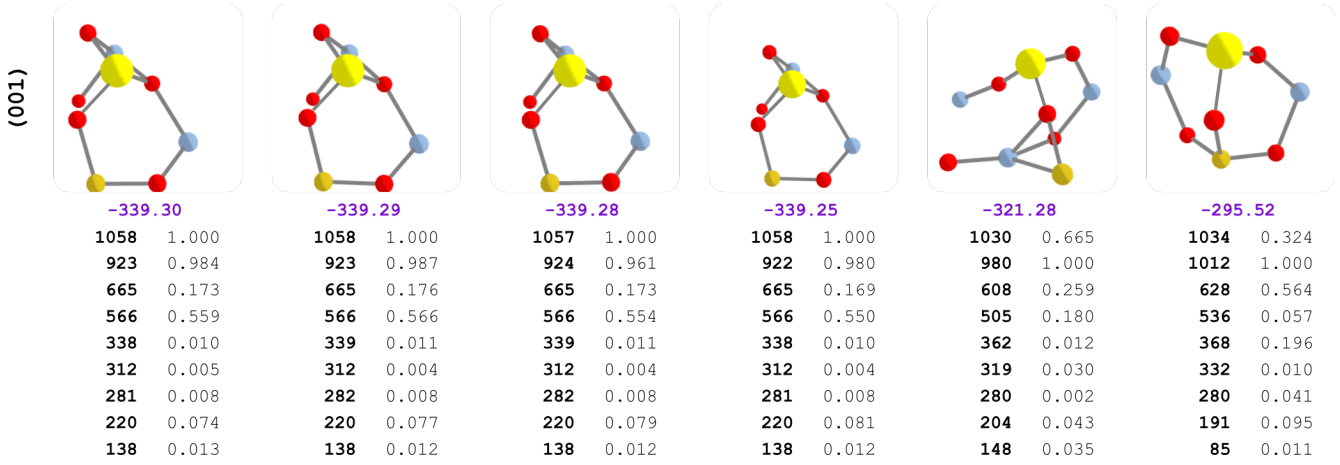


Figure S13. Atomic representations of the 6 SO_2 adsorption configurations displaying the lowest adsorption energies on the **(001)** surface of Mg_2SiO_4 in our calculations. Only atoms within a radius of 4 Å from the S center are displayed. Adsorption energies are denoted in purple, in kJ mol^{-1}. The arising spectroscopic features from these adsorptions are displayed under the adsorption energy, where the first column is the wavenumber in cm^{-1}, and the second column is the normalized intensity. Blue, dark yellow, red and light yellow balls represent Mg, Si, O and S atoms, respectively.

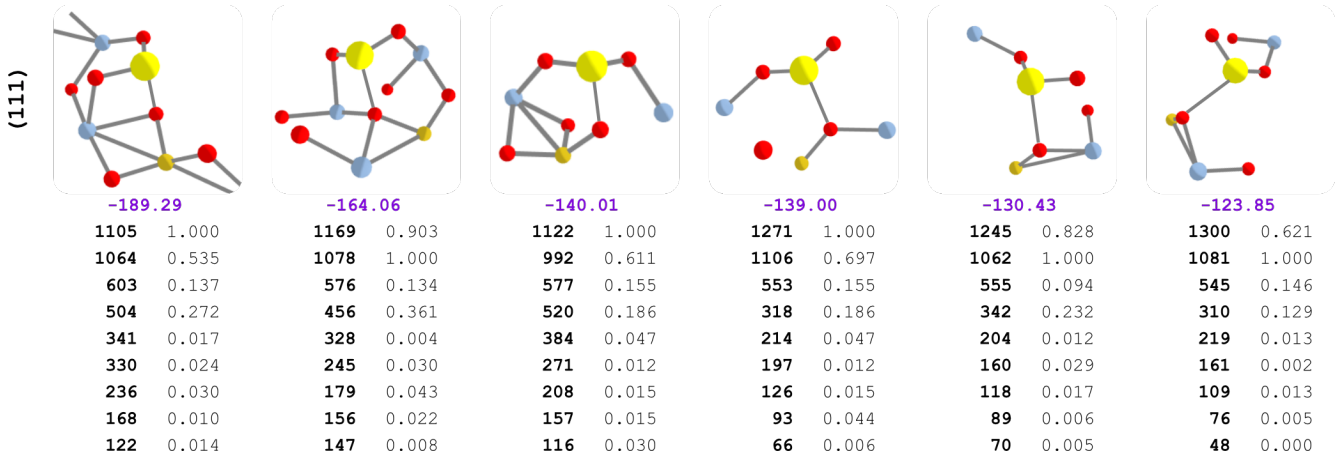
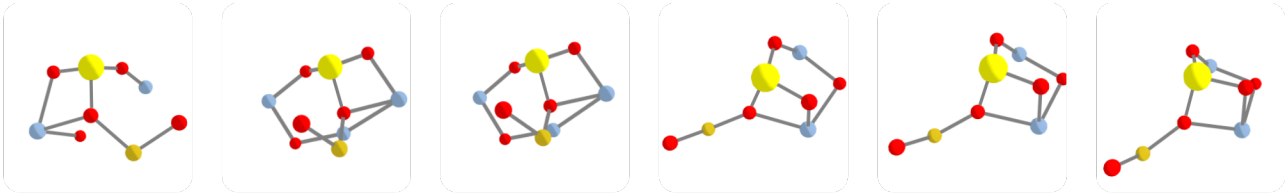


Figure S14. Atomic representations of the 6 SO_2 adsorption configurations displaying the lowest adsorption energies on the **(111)** surface of Mg_2SiO_4 in our calculations. Only atoms within a radius of 4 Å from the S center are displayed. Adsorption energies are denoted in purple, in kJ mol^{-1}. The arising spectroscopic features from these adsorptions are displayed under the adsorption energy, where the first column is the wavenumber in cm^{-1}, and the second column is the normalized intensity. Blue, dark yellow, red and light yellow balls represent Mg, Si, O and S atoms, respectively.

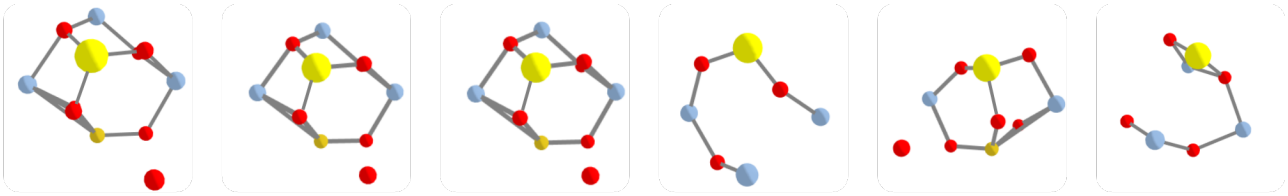
(110)



-268.62		-258.59		-258.58		-238.68		-238.36		-238.27	
1097	1.000	1036	1.000	1034	1.000	1075	1.000	1071	1.000	1073	1.000
1008	0.673	1002	0.577	1001	0.444	1021	0.830	1018	0.844	1017	0.880
571	0.203	604	0.263	603	0.223	604	0.267	603	0.267	604	0.318
484	0.118	526	0.096	525	0.112	489	0.298	489	0.298	488	0.291
349	0.015	406	0.017	405	0.017	356	0.019	356	0.019	357	0.016
260	0.007	303	0.020	300	0.019	297	0.044	301	0.044	300	0.045
228	0.015	224	0.047	224	0.028	254	0.003	257	0.003	255	0.002
164	0.019	165	0.017	164	0.022	177	0.049	175	0.049	174	0.041
149	0.042	116	0.009	117	0.011	111	0.041	108	0.041	108	0.036

Figure S15. Atomic representations of the 6 $\mathbf{SO_2}$ adsorption configurations displaying the lowest adsorption energies on the **(110)** surface of Mg_2SiO_4 in our calculations. Only atoms within a radius of 4 Å from the S center are displayed. Adsorption energies are denoted in purple, in kJ mol^{-1}. The arising spectroscopic features from these adsorptions are displayed under the adsorption energy, where the first column is the wavenumber in cm^{-1}, and the second column is the normalized intensity. Blue, dark yellow, red and light yellow balls represent Mg, Si, O and S atoms, respectively.

(021)



-316.10		-316.08		-315.91		-294.51		-270.94		-226.57	
1153	0.747	1153	0.747	1147	0.766	1040	0.404	1075	1.000	1039	0.285
828	1.000	829	1.000	825	1.000	940	1.000	1022	0.484	947	1.000
605	0.282	605	0.282	608	0.282	491	0.048	596	0.213	576	0.044
537	0.185	537	0.186	543	0.184	309	0.014	530	0.166	307	0.009
363	0.023	363	0.023	367	0.026	254	0.030	411	0.031	222	0.082
295	0.005	295	0.005	293	0.003	136	0.008	281	0.011	190	0.026
273	0.026	274	0.025	277	0.027	127	0.028	238	0.017	141	0.049
237	0.027	236	0.028	232	0.028	96	0.002	160	0.017	114	0.069
157	0.024	157	0.024	153	0.024	39	0.015	138	0.012	85	0.006

Figure S16. Atomic representations of the 6 $\mathbf{SO_2}$ adsorption configurations displaying the lowest adsorption energies on the **(021)** surface of Mg_2SiO_4 in our calculations. Only atoms within a radius of 4 Å from the S center are displayed. Adsorption energies are denoted in purple, in kJ mol^{-1}. The arising spectroscopic features from these adsorptions are displayed under the adsorption energy, where the first column is the wavenumber in cm^{-1}, and the second column is the normalized intensity. Blue, dark yellow, red and light yellow balls represent Mg, Si, O and S atoms, respectively.