Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

On the S_N2 reactions modified in vibrational strong coupling experiments: reaction mechanisms and vibrational mode assignments

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Computational details

All calculations were carried out at the B3LYP/6-31+G(d,p) level[1] with the Gaussian 09 package.[2] Methanol solvent environment was considered via the integral equation formalism variant of the polarizable continuum model (IEF-PCM).[3] The stationary nature of all optimized geometries was verified. Gibbs free energies were obtained via the standard statistical mechanics ideal gas, rigid-rotor and harmonic oscillator models at standard conditions. IRC calculations or relaxed energy scans were performed to verify that the the obtained TS structures were indeed the ones connecting the initial and final species inferred from their imaginary frequency mode.

We also carried out calculations with the OLYP functional[4] which, together with the B3LYP functional, has been widely used for modelling S_N2 reactions.[5] In Table S3 we report the S_N2@Si Gibbs free energies of reaction I calculated with the OLYP functional, where there is a general ~5 kcal/mol overestimation compared with the B3LYP values. Our main interest in this work is not in the absolute values, but rather the reaction profile, and in this sense, both functionals provide very similar results as shown in Figure S2.

Regarding the second step of reaction I dealing with the protonation of the acetylide anion by methanol, the obtained reaction profile is shown in Figure S1 and Table S1. This profile is not unique in the sense that we found other RC conformations very close in energy to the RC shown in the figure, and thus, calculations considering several explicit solvent molecules as well as dynamic effects would be highly desirable. Nevertheless, our main interest herein was to check whether the rate-limiting step had to do with the S_N2@Si reaction or the protonation step, and the static calculations already provide the answer to this question, given that the energy barriers of the S_N2@Si reaction are much larger than those obtained for the protonation step. Moreover, a more realistic description of the solvent would be expected to stabilize the TS, facilitating the protonation.

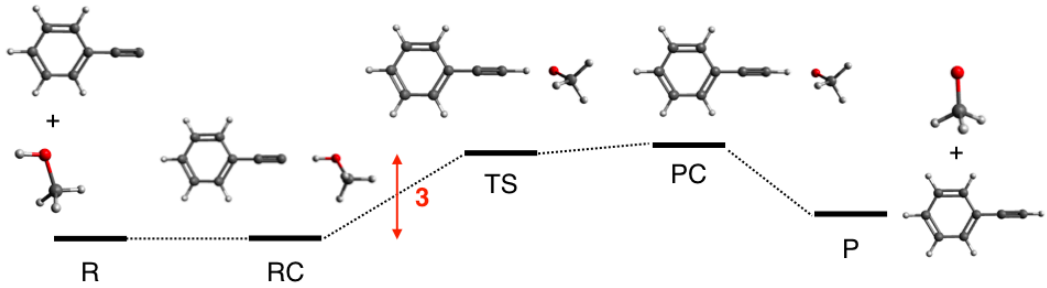

Figure S1. Reaction I protonation step profile. Gibbs free energy barrier (red) in kcal/mol computed at the B3LYP/6-31+G(d,p) level in methanol.

Table S1. Relative potential energies and Gibbs free energies of all the species involved in the protonation step of reaction I including barriers. Calculated at the B3LYP/6-31+G(d,p) level in methanol.

species	E (kcal/mol)	G (kcal/mol)
R	9.2	0.0
RC	0.0	0.0
TS	4.9	2.8
PC	4.8	3.4
P	11.6	0.9
barrier	4.9	2.8

Table S2. Relative potential energies and Gibbs free energies of all the species involved in the S_N2@Si reactions as well as barriers. Calculated at the B3LYP/6-31+G(d,p) level in methanol.

species / barriers	reaction I		reaction II Si-C cleavage		reaction II Si-O cleavage	
	E (kcal/mol)	G (kcal/mol)	E (kcal/mol)	G (kcal/mol)	E (kcal/mol)	G (kcal/mol)
R	0.0	0.0	0.0	0.0	0.0	0.0
TS1	6.8	14.7	7.6	15.6	10.5	19.2
TC	3.0	10.7	4.7	13.1	5.9	15.5
TS2	11.0	17.8	14.6	21.1	16.4	24.5
P	5.0	1.2	8.3	4.5	10.9	5.6
R→TC	6.8	14.7	7.6	15.6	10.5	19.2
TC→R	3.9	4.0	2.9	2.4	4.6	3.7
TC→P	8.1	7.1	9.9	7.9	10.6	9.0

Table S3. Relative potential energies and Gibbs free energies of all the species involved in the S_N2@Si step of reaction I including barriers. Calculated at the OLYP/6-31+G(d,p) level in methanol.

Step 1: S_N2@Si		
species	E (kcal/mol)	G (kcal/mol)
R	0.0	0.0
TS1	11.8	19.9
TC	8.4	15.8
TS2	17.4	23.9
P	6.6	2.7
barrier 1	11.8	19.9
barrier 2	8.9	8.2

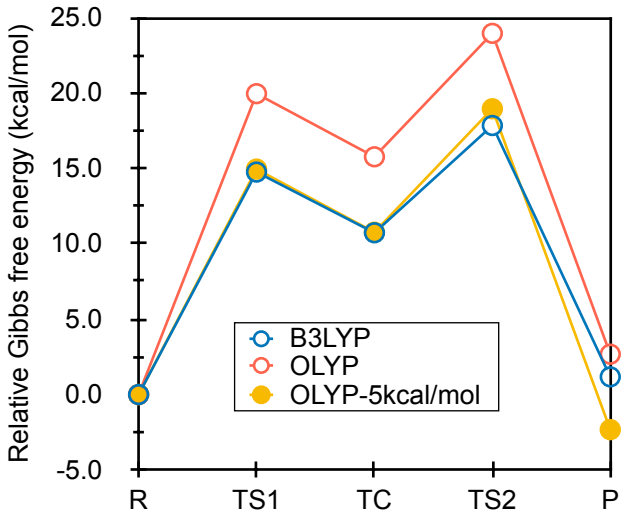

Figure S2. S_N2@Si reaction I profile calculated with the B3LYP and OLYP functionals and the 6-31+G(d,p) basis set in methanol. The values obtained with OLYP shifted by -5kcal/mol are also plotted to show the systematic overestimation obtained with this functional with respect to B3LYP. Lines connecting points are meant to guide the eye.

Rate equations

For the S_N2@Si reaction profile shown in Figure 2a on the main text we have the following elementary steps

$$F^- + R \rightleftharpoons TC \overset{k_2}{\rightarrow} P$$

with k_1 and k_{-1} the forward and backward rate constants of the first step.

The time evolution of each species is given by

$$\begin{cases} \frac{d[F^-]}{dt} = -k_1[F^-] + k_{-1}[TC] \\ \frac{d[TC]}{dt} = k_1[F^-] - (k_{-1} + k_2)[TC] \\ \frac{d[P]}{dt} = k_2[TC] \end{cases}$$

Given that $k_1 \ll k_2 + k_{-1}$, we can apply the steady-state approximation $\frac{d[TC]}{dt} = 0$ and arrive to the first-order rate equation $\frac{d[F^-]}{dt} = -k_{app}[F^-]$, where the apparent rate constant is $k_{app} = \frac{k_1 k_2}{k_{-1} + k_2}$. Since $k_2 \ll k_{-1}$, $k_{app} = \frac{k_1 k_2}{k_{-1}}$ and by integrating we obtain $[F^-] = [F^-]_0 e^{-k_{app}t}$. Note that $k_1 = k_1^{O2}[R]$ since reactant R was in excess in the experiments of reactions I and II, with O2 referring to the second-order rate constant.

In the original experimental papers, the overall rate constant was obtained by determining the quantity $1 - \frac{[P]_t}{[P]_{final}}$ for different times t from the frequency shift of higher order cavity modes due to the change of refractive index.[6,7] Since the reactant R was in excess, this quantity is equivalent to $\frac{[F^-]_t}{[F^-]_{initial}}$, and therefore, the rate constant obtained from the slope of $ln\left(1 - \frac{[P]_t}{[P]_{final}}\right)$ vs t corresponds to k_{app} for reaction I. Similarly, the experimentally determined overall rate constant for reaction II was $k_{app}^{Si-C} + k_{app}^{Si-O}$ since there are two parallel reactions, with $\frac{[P_C]}{[P_O]} = \frac{k_{app}^{Si-C}}{k_{app}^{Si-O}}$.

Table S4. Calculated (B3LYP/6-31+G(d,p) in methanol) and experimental activation enthalpy, entropy and Gibbs free energy at room temperature.

		ΔH‡ (kcal/mol)	TΔS‡ (kcal/mol)	ΔG‡ (kcal/mol)
reaction I	calculated	10.3	-7.5	17.8
	experimental[6]	9.3	-12.2	21.5
	experimental[8]	7.2	-12.9	20.1
reaction II Si-C cleavage	calculated	13.9	-7.2	21.1
	experimental[7]	8.1	-12.3	20.4
reaction II Si-O cleavage	calculated	15.0	-9.4	24.4
	experimental[7]	5.5	-15.2	20.7

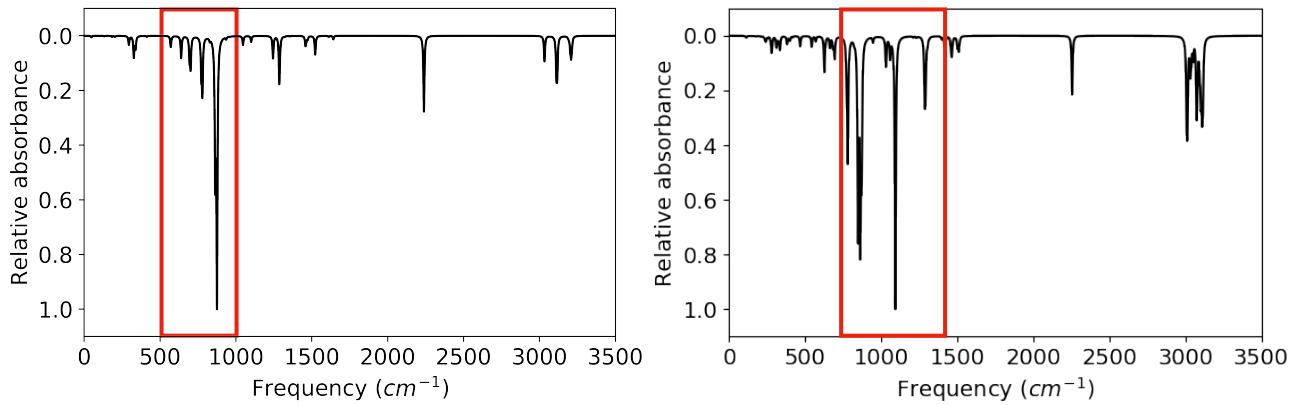

Figure S3. Calculated IR spectrum (HWHH=4 cm^{-1}) of of $\mathbf{R_I}$ (left) and $\mathbf{R_{II}}$ (right) at the B3LYP/6-31+G(d,p) level in methanol. Red rectangle highlights the part of the spectrum shown in the main text.

Table S5. Assignment of the normal modes of R_I with largest displacement between the silicon and sp carbon atoms as well as those responsible for the most intense double peak in the ~860 cm^{-1} region. The absolute value of the relative normalized cartesian displacement between Si-C(sp) along their bond axis is also shown.

mode	label	frequency (cm^{-1})	assignment							ΔΔr Si-C
			Si-C(sp) stretching	Si-C(sp^3) stretching	CH_3 rocking	phenyl CCC bending	phenyl C-H rocking	C(sp^2)-C(sp) stretching	C≡C stretching	
13	1	327	yes		yes	yes				0.17
19	2	582	yes	yes		yes				0.18
21	3	639	yes	yes	yes	yes				0.29
29	4	828	yes		yes	yes				0.28
31	5	863			yes					0.00
32	6	864			yes					0.00
33	7	875	yes		yes					0.16
42	8	1244	yes				yes	yes	yes	0.24
58	9	2239							yes	0.69

Table S6. Assignment of the relevant normal modes of R_{II}. The absolute value of the relative normalized cartesian displacement between Si-C(sp), Si-O and C-O along their bond axis is also shown. Color code assigning IR bands of the VSC experiments: (i) 842cm^{-1} blue, (ii) 1110 cm^{-1} red, (iii) 1250 cm^{-1} green.

mode	label	frequency (cm^{-1})	assignment	ΔΔr Si-C	ΔΔr Si-O	ΔΔr C-O
35	1	467	coupled bendings of Si-O-C-C-C_{sp}-C_{sp}-Si skeleton	0.22	0.04	0.05
36	2	542		0.21	0.14	0.06
38	3	626	Si-C stretching: Si-C(sp) coupled to the three Si-C(sp^3) from $SiMe_3$	0.21	0.09	0.00
45	4	771	Si-O stretching coupled to CH_3 rocking ($SiMe_2$)	0.10	0.37	0.06
51	5	847		0.02	0.18	0.03
52	6	860		0.00	0.09	0.01
53	7	862	CH_3 rocking ($SiMe_3$)	0.01	0.00	0.00
54	8	862		0.00	0.00	0.00
55	9	871	Si-C stretching coupled to CH_3 rocking ($SiMe_3$)	0.08	0.06	0.01
62	10	1058	C-C stretching from CH_2-CH_2 fragment coupled to Si-C(sp) stretching	0.24	0.03	0.05
64	11	1092	C-O stretching	0.02	0.43	0.50
69	12	1285	CH_3 umbrella bending 12, 13, 15: $SiMe_3$ 14, 16: $SiMe_2$	≤0.01		
70	13	1286				
71	14	1289				
72	15	1291				
73	16	1292				

Table S7. Calculated Si-O and C-O stretching frequencies for the products of the S_N2@Si step of reaction II, $\mathbf{P_C}$ and $\mathbf{P_O}$, and the final protonated products of reaction II, $\mathbf{P_{CH}}$ and $\mathbf{P_{OH}}$.

Frequency (cm^{-1})	$\mathbf{P_C}$	$\mathbf{P_{CH}}$	$\mathbf{P_O}$	$\mathbf{P_{OH}}$
Si-O	765	761	-	-
C-O	1074	1094	1130	1043, 1057

Cartesian coordinates

REACTION I: S_N2@Si B3LYP/6-31+G(d,p) in methanol (IEF-PCM)

R_I

6	0.397730	-2.704249	-0.682575
6	0.397934	-2.703992	0.541640
6	0.397818	-2.704640	-2.114090
6	0.398016	-2.705719	-4.926785
6	0.602233	-1.506721	-2.830496
6	0.193420	-3.903082	-2.829604
6	0.194383	-3.898836	-4.224541
6	0.601526	-1.512052	-4.225420
1	0.760109	-0.580885	-2.286528
1	0.035449	-4.828468	-2.284903
1	0.035943	-4.827942	-4.763895
1	0.760029	-0.583356	-4.765463
1	0.398113	-2.706123	-6.012627
14	0.397448	-2.704874	2.393829
6	1.684402	-3.953411	2.986480
1	2.686201	-3.687272	2.631950
1	1.452320	-4.961592	2.626064
1	1.708694	-3.982212	4.082286
6	0.834725	-0.965428	2.983775
1	1.824737	-0.663662	2.624571
1	0.845437	-0.927200	4.079441
1	0.104416	-0.231234	2.626321
6	-1.326610	-3.197707	2.986428
1	-1.362049	-3.210932	4.082228
1	-1.597309	-4.196410	2.626523
1	-2.084208	-2.490689	2.631108

TS1

6	0.781420	0.006117	0.020857
6	-0.446095	0.005365	0.026168
6	2.214677	0.005268	0.010962
6	5.035918	0.002985	-0.015448
6	2.934191	-1.199747	-0.141247
6	2.938740	1.209069	0.149872
6	4.334108	1.204140	0.136466
6	4.329516	-1.197126	-0.153877
1	2.389320	-2.132471	-0.249353
1	2.397455	2.142754	0.267283
1	4.874519	2.140235	0.244351
1	4.866252	-2.134059	-0.272391
1	6.121823	0.002146	-0.026009
14	-2.367557	-0.004452	0.005994
6	-2.634229	-1.880727	0.077833
1	-2.163553	-2.290873	0.979993
1	-2.155060	-2.360099	-0.784847
1	-3.696757	-2.126229	0.081875
9	-4.836234	-0.029041	-0.033431
6	-2.680753	0.997914	1.585039
6	-2.631656	0.872795	-1.654801
1	-2.175871	0.289489	-2.464486
1	-2.139670	1.853203	-1.643405
1	-3.694661	1.004041	-1.860710
1	-3.749163	1.152433	1.742320
1	-2.178667	1.970993	1.518455
1	-2.260442	0.473925	2.452515

TC

6	0.676663	-0.008805	-0.002084
6	-0.556319	-0.012644	-0.001064
6	2.110508	-0.002475	-0.000518

6	4.940387	0.010986	0.003427
6	2.844329	-1.181277	-0.263311
6	2.832415	1.183381	0.263734
6	4.228085	1.187022	0.265324
6	4.239988	-1.171706	-0.260609
1	2.307198	-2.102269	-0.469097
1	2.285932	2.099265	0.467704
1	4.761118	2.111127	0.471616
1	4.782381	-2.090658	-0.465505
1	6.026419	0.016107	0.005075
14	-2.593160	-0.005387	-0.000647
6	-2.609889	-1.919415	0.145166
1	-2.090341	-2.232807	1.059841
1	-2.062590	-2.367669	-0.693813
1	-3.622653	-2.333951	0.161924
9	-4.449371	0.002308	-0.000444
6	-2.594661	1.080994	1.581990
6	-2.596448	0.825543	-1.730901
1	-2.089589	0.180488	-2.460146
1	-2.033844	1.767179	-1.701570
1	-3.607287	1.033874	-2.095009
1	-3.604417	1.331728	1.921418
1	-2.045445	2.013683	1.400924
1	-2.071838	0.563423	2.396553

TS2

6	1.014721	0.002178	0.067525
6	-0.233535	-0.003182	0.112772
6	2.447646	0.006451	0.013030
6	5.287941	0.015218	-0.096107
6	3.191806	-1.196068	0.087387
6	3.176496	1.213582	-0.117495
6	4.571244	1.215640	-0.171155
6	4.586529	-1.189564	0.033544
1	2.658295	-2.136863	0.187832
1	2.631053	2.151055	-0.176533
1	5.101327	2.159291	-0.271917
1	5.128584	-2.129913	0.093039
1	6.373276	0.018552	-0.137986
14	-3.205801	0.012831	0.022863
6	-3.016251	-1.861982	-0.028004
1	-3.569927	-2.311746	0.805549
1	-1.970532	-2.164571	0.035689
1	-3.444359	-2.254384	-0.958761
9	-4.913090	0.105465	-0.028179
6	-2.902173	0.852676	1.686324
6	-2.805169	0.951513	-1.566001
1	-2.034529	0.438741	-2.145773
1	-2.434357	1.957724	-1.343547
1	-3.710633	1.045098	-2.177718
1	-3.850817	0.969244	2.224147
1	-2.456664	1.843142	1.548900
1	-2.213510	0.267918	2.300555

REACTION II: S_N2@Si B3LYP/6-31+G(d,p) in methanol (IEF-PCM)

R_{II}

6	0.042500	-1.969382	0.013020
6	0.404352	-2.411485	1.093206
6	-0.399236	-1.461580	-1.286726
14	0.953281	-3.065714	2.734299
6	1.983044	-4.622542	2.444220
1	2.866937	-4.403772	1.834927
1	1.398090	-5.393238	1.930173

1	2.324394	-5.037546	3.399976
6	1.989414	-1.737389	3.588847
1	2.872688	-1.481305	2.993393
1	2.331930	-2.092474	4.568030
1	1.407661	-0.822225	3.745025
6	-0.579437	-3.470439	3.761554
1	-0.288159	-3.862511	4.743218
1	-1.199126	-4.225669	3.265578
1	-1.194598	-2.578131	3.922007
6	-0.887463	-2.580728	-2.221261
1	0.422114	-0.924651	-1.777320
1	-1.212912	-0.738870	-1.147710
8	-1.303788	-1.990499	-3.445562
1	-1.718506	-3.117876	-1.745162
1	-0.072894	-3.297694	-2.390382
14	-1.916227	-2.857873	-4.765315
6	-0.597421	-4.055842	-5.393871
1	0.318764	-3.533859	-5.690420
1	-0.962040	-4.618713	-6.260851
1	-0.333861	-4.784453	-4.618440
6	-3.435013	-3.839990	-4.218829
1	-3.165581	-4.582739	-3.459034
1	-3.873410	-4.382543	-5.064290
1	-4.209397	-3.191076	-3.795624
6	-2.349322	-1.514803	-6.058916
6	-2.909482	-2.185459	-7.334369
1	-3.163047	-1.419654	-8.080933
1	-3.822237	-2.757993	-7.132347
1	-2.182494	-2.863036	-7.796931
6	-1.086265	-0.705564	-6.429084
1	-0.305903	-1.339197	-6.866089
1	-0.659825	-0.198802	-5.556725
1	-1.336601	0.064830	-7.172463
6	-3.413291	-0.550795	-5.488143
1	-3.656968	0.223687	-6.229463
1	-3.058003	-0.044793	-4.583979
1	-4.346306	-1.069602	-5.239740

TS1 Si-C cleavage

6	0.076752	-1.991540	-0.064628
6	0.408392	-2.432364	1.029670
6	-0.330031	-1.483158	-1.379902
6	-0.919362	-2.580278	-2.278973
1	0.527438	-1.032576	-1.896362
1	-1.079367	-0.689098	-1.265396
8	-1.301623	-1.995898	-3.520480
1	-1.787695	-3.033451	-1.782243
1	-0.169683	-3.367940	-2.434510
14	-1.965241	-2.856087	-4.817143
6	-0.704901	-4.115787	-5.446278
1	0.224623	-3.635001	-5.769881
1	-1.106399	-4.682206	-6.294449
1	-0.454119	-4.837538	-4.660211
6	-3.515253	-3.770237	-4.239881
1	-3.264688	-4.516455	-3.477023
1	-3.988402	-4.301755	-5.073556
1	-4.255902	-3.086531	-3.811050
6	-2.362822	-1.517561	-6.127844
6	-2.953633	-2.186736	-7.390079
1	-3.187682	-1.423414	-8.145615
1	-3.883016	-2.726579	-7.174120
1	-2.252291	-2.893894	-7.847955
6	-1.076484	-0.755617	-6.517594
1	-0.319342	-1.420771	-6.948680
1	-0.629167	-0.249531	-5.655388
1	-1.305997	0.010944	-7.271707

6	-3.389896	-0.510334	-5.564288
1	-3.613285	0.260913	-6.315410
1	-3.010983	-0.003036	-4.670457
1	-4.337790	-0.993819	-5.301357
1	-0.639926	-1.406266	3.681881
1	0.660867	-1.756885	4.851129
6	0.434096	-1.599450	3.795977
1	0.962865	-0.705687	3.441783
1	-1.234327	-4.332047	2.712165
14	0.936378	-3.103577	2.752244
9	1.598277	-3.962480	4.919557
6	-0.183578	-4.636311	2.798094
1	-0.046557	-5.201145	3.721131
1	0.035710	-5.284597	1.940445
6	2.784855	-3.349907	2.397346
1	3.221798	-2.417160	2.019792
1	3.319542	-3.664790	3.294477
1	2.916812	-4.108572	1.615456

TC Si-C cleavage

6	0.069337	-2.020550	0.001458
6	0.407462	-2.471639	1.094829
6	-0.343702	-1.499469	-1.310165
6	-0.909524	-2.592580	-2.227539
1	0.504135	-1.025070	-1.822633
1	-1.109432	-0.720709	-1.192575
8	-1.301032	-2.001658	-3.465696
1	-1.771069	-3.069383	-1.740964
1	-0.145107	-3.364328	-2.391834
14	-1.929273	-2.864020	-4.776745
6	-0.629274	-4.079850	-5.412672
1	0.288073	-3.568638	-5.724272
1	-1.008748	-4.647442	-6.270173
1	-0.362629	-4.803263	-4.633359
6	-3.457147	-3.830424	-4.224944
1	-3.191289	-4.578041	-3.468656
1	-3.907528	-4.365370	-5.069002
1	-4.221078	-3.173838	-3.794500
6	-2.356527	-1.523009	-6.075972
6	-2.916194	-2.193917	-7.351328
1	-3.167841	-1.428746	-8.099355
1	-3.830037	-2.765003	-7.149808
1	-2.189661	-2.873244	-7.812072
6	-1.090787	-0.717721	-6.445373
1	-0.310605	-1.354434	-6.878343
1	-0.665516	-0.209698	-5.573223
1	-1.337118	0.051243	-7.191741
6	-3.418650	-0.554565	-5.509364
1	-3.657713	0.220332	-6.251911
1	-3.064106	-0.049128	-4.604571
1	-4.354175	-1.069835	-5.262933
1	-0.582162	-1.328917	3.595632
1	0.714687	-1.490208	4.801857
6	0.491453	-1.514522	3.730822
1	1.015413	-0.682377	3.243845
1	-1.318406	-4.185581	2.648669
14	0.975294	-3.178737	2.902906
9	1.500399	-3.832037	4.578754
6	-0.310920	-4.600164	2.781545
1	-0.314945	-5.249233	3.662586
1	-0.107615	-5.215663	1.895626
6	2.767628	-3.446731	2.267903
1	3.190731	-2.493927	1.924144
1	3.430744	-3.866543	3.030463
1	2.763417	-4.117567	1.399368

TS2 Si-C cleavage

6	-0.036275	-1.948248	-0.168540
6	0.314166	-2.403259	0.937192
6	-0.460433	-1.429469	-1.483107
6	-0.991051	-2.532024	-2.409024
1	0.371493	-0.927536	-1.998015
1	-1.250964	-0.672918	-1.373520
8	-1.399196	-1.953636	-3.651663
1	-1.840065	-3.036549	-1.928073
1	-0.204039	-3.280752	-2.574063
14	-1.970904	-2.841831	-4.969016
6	-0.610859	-3.998097	-5.592334
1	0.286807	-3.446127	-5.891583
1	-0.954433	-4.579611	-6.455699
1	-0.321794	-4.711127	-4.811431
6	-3.460271	-3.879195	-4.439357
1	-3.170380	-4.612946	-3.678300
1	-3.872785	-4.435062	-5.289281
1	-4.260457	-3.259233	-4.020525
6	-2.443780	-1.522617	-6.275240
6	-2.963057	-2.217162	-7.554911
1	-3.239868	-1.463850	-8.306161
1	-3.853851	-2.826074	-7.361038
1	-2.204507	-2.865743	-8.008364
6	-1.210011	-0.664746	-6.634231
1	-0.400861	-1.268273	-7.061620
1	-0.812425	-0.140843	-5.758408
1	-1.482096	0.094305	-7.381867
6	-3.551293	-0.600222	-5.718975
1	-3.816320	0.164329	-6.463506
1	-3.227231	-0.081105	-4.810549
1	-4.466185	-1.155273	-5.481470
1	0.380625	-0.939425	3.214364
1	0.079351	-1.537872	4.866102
6	0.795076	-1.524982	4.034196
1	1.708109	-1.035848	4.396988
1	-0.838761	-4.501655	4.273295
14	1.196116	-3.301521	3.535019
9	1.739301	-3.832554	5.081840
6	-0.234590	-4.520550	3.357472
1	0.161978	-5.538062	3.247839
1	-0.869066	-4.297636	2.500426
6	2.804051	-3.649015	2.607259
1	3.593747	-2.987923	2.986754
1	3.118021	-4.681341	2.807631
1	2.707927	-3.502928	1.532175

TS1 Si-O cleavage

6	0.322975	-2.027202	0.217837
6	0.697782	-2.499308	1.281404
6	-0.135546	-1.489607	-1.063919
14	1.275324	-3.204014	2.889218
6	1.862226	-4.975384	2.592637
1	2.689399	-5.002185	1.874650
1	1.051814	-5.599557	2.200174
1	2.212134	-5.424088	3.529943
6	2.697125	-2.139792	3.534678
1	3.534767	-2.129111	2.828522
1	3.064478	-2.532282	4.490367
1	2.374943	-1.104926	3.695002
6	-0.166054	-3.185143	4.110671
1	0.146118	-3.600022	5.076479
1	-1.005348	-3.784083	3.740175
1	-0.526325	-2.164537	4.280955
6	-0.891612	-2.530252	-1.914236
1	0.722526	-1.122183	-1.640954

1	-0.793326	-0.628024	-0.892836
8	-1.276342	-1.932641	-3.129521
1	-1.764219	-2.887368	-1.345171
1	-0.233236	-3.396930	-2.081033
14	-2.146425	-2.823279	-4.362708
6	-0.907751	-4.216889	-4.721038
1	-1.054260	-4.610533	-5.726869
1	-1.047880	-5.044624	-4.014576
1	0.122480	-3.855770	-4.610191
6	-3.727409	-3.272750	-3.412610
1	-3.994372	-2.473370	-2.709996
1	-3.577514	-4.190614	-2.830445
1	-4.552728	-3.447469	-4.102761
6	-2.314054	-1.435580	-5.713630
6	-1.643337	-1.895962	-7.026139
1	-1.764211	-1.125132	-7.803137
1	-2.096410	-2.826557	-7.376505
1	-0.565982	-2.060729	-6.896721
6	-1.650617	-0.112832	-5.269703
1	-0.579402	-0.232666	-5.077654
1	-2.102743	0.289014	-4.357194
1	-1.768012	0.640327	-6.063833
6	-3.806512	-1.155335	-5.995707
1	-3.905484	-0.387070	-6.778306
1	-4.325854	-0.780134	-5.104651
1	-4.309732	-2.065508	-6.331301
9	-3.408864	-4.262274	-6.061331

TC Si-O cleavage

6	-0.022054	-1.834013	-0.098298
6	0.348287	-2.263464	0.985543
6	-0.472782	-1.347666	-1.402766
14	0.911058	-2.889449	2.628671
6	1.652496	-4.612652	2.400355
1	2.509679	-4.586375	1.718416
1	0.913512	-5.309504	1.989539
1	1.996500	-5.011407	3.362151
6	2.213433	-1.702361	3.312260
1	3.077578	-1.635925	2.641930
1	2.569104	-2.046509	4.290748
1	1.802425	-0.694343	3.436763
6	-0.577232	-2.966388	3.791079
1	-0.273617	-3.335825	4.777866
1	-1.348945	-3.638915	3.400352
1	-1.026214	-1.975758	3.923748
6	-0.978575	-2.472896	-2.338976
1	0.346846	-0.816547	-1.903703
1	-1.282269	-0.618789	-1.266440
8	-1.412944	-1.920420	-3.538832
1	-1.782646	-3.018105	-1.810992
1	-0.153231	-3.195343	-2.478584
14	-1.869390	-2.969493	-5.001488
6	-0.082792	-3.665669	-5.189223
1	0.660521	-3.166917	-4.558647
1	0.231826	-3.569687	-6.235353
1	-0.062393	-4.738831	-4.957610
6	-3.254238	-3.897557	-4.037638
1	-2.916135	-4.910255	-3.777645
1	-4.136749	-4.019497	-4.675702
1	-3.558445	-3.398709	-3.111608
6	-2.353719	-1.344971	-6.003716
6	-2.839925	-1.617941	-7.442069
1	-3.086756	-0.665794	-7.939283
1	-3.735882	-2.246649	-7.461633
1	-2.077086	-2.121598	-8.044381
6	-1.131756	-0.402425	-6.099552

1	-0.301687	-0.868989	-6.645900
1	-0.765839	-0.120946	-5.108790
1	-1.399753	0.518853	-6.641713
6	-3.486616	-0.595929	-5.264594
1	-3.753882	0.326223	-5.805680
1	-3.186713	-0.320883	-4.249828
1	-4.397228	-1.205082	-5.194544
9	-2.295232	-4.093923	-6.419008

TS2 Si-O cleavage

6	-0.006773	-1.763501	0.552970
6	0.404617	-2.358860	1.541639
6	-0.502322	-1.118461	-0.660834
14	1.035737	-3.231306	3.036614
6	1.084280	-5.089497	2.689392
1	1.742824	-5.315654	1.843321
1	0.085576	-5.473357	2.453033
1	1.458202	-5.633778	3.564921
6	2.776114	-2.601094	3.424550
1	3.459374	-2.789547	2.588898
1	3.178106	-3.105774	4.311273
1	2.771260	-1.523182	3.621493
6	-0.120157	-2.874365	4.490032
1	0.233315	-3.382534	5.395219
1	-1.137227	-3.224241	4.280701
1	-0.168299	-1.800302	4.701641
6	-0.901913	-2.126812	-1.802365
1	0.262505	-0.438815	-1.060265
1	-1.380747	-0.502070	-0.426414
8	-1.340108	-1.506382	-2.928857
1	-1.655010	-2.814079	-1.337962
1	0.003567	-2.767564	-1.959564
14	-1.961940	-3.291731	-5.104172
6	-0.122661	-3.623740	-4.866367
1	0.391289	-3.577170	-5.834109
1	0.025622	-4.632135	-4.461420
1	0.320837	-2.896987	-4.185038
6	-3.154164	-3.919932	-3.786719
1	-3.210787	-3.232743	-2.942081
1	-2.826145	-4.901989	-3.424932
1	-4.153423	-4.044930	-4.221183
6	-2.437778	-1.636916	-5.982363
6	-2.935286	-1.904907	-7.421265
1	-3.202409	-0.951727	-7.901140
1	-3.823968	-2.545453	-7.438990
1	-2.169939	-2.384919	-8.041044
6	-1.208154	-0.705002	-6.049321
1	-0.400876	-1.140156	-6.651816
1	-0.823827	-0.508886	-5.044829
1	-1.485571	0.251355	-6.518246
6	-3.561105	-0.927188	-5.195271
1	-3.809913	0.031140	-5.676061
1	-3.242688	-0.735927	-4.167077
1	-4.480170	-1.526111	-5.169352
9	-2.277331	-4.457154	-6.308608

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