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

First-principles theoretical assessment of catalysis by confinement: NO-O_2 reactions within voids of molecular dimensions in siliceous crystalline frameworks

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Supporting Information

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S1. Calculations of enthalpies and entropies using statistical mechanics treatments

Enthalpies of reactant molecules, intermediates and transition states reflects a sum of their DFT-derived electronic energy (E_0), zero-point vibrational energy (*ZPE*) and at finite temperature vibrational (H_{vib}), translational (H_{trans}) and rotational (H_{rot}) contributions:

$$H = E_0 + ZPE + H_{vib} + H_{trans} + H_{rot} \quad \text{(S-1)}$$

where:

$$ZPE = \sum_i \frac{1}{2} h\nu_i \quad \text{(S-2)}$$

$$H_{vib} = \sum_i \left(\frac{h\nu_i e^{-\frac{h\nu_i}{k_B T}}}{1 - e^{-\frac{h\nu_i}{k_B T}}} \right) \quad \text{(S-3)}$$

$$H_{trans} = \frac{3}{2} k_B T \quad \text{(S-4)}$$

$$H_{rot} = \frac{3}{2} k_B T \quad \text{(S-5)}$$

as reported in [1].

In analogy with enthalpy, the entropy of each molecular system is the result of the sum of the corresponding electronic (S_0), vibrational (S_{vib}), translational (S_{trans}) and rotational (S_{rot}) contributions:

$$S = S_0 + S_{vib} + S_{trans} + S_{rot}. \quad \text{(S-6)}$$

with:

$$S_{vib} = \sum_i \left(\frac{h\nu_i / T \, e^{-\frac{h\nu_i}{k_B T}}}{1 - e^{-\frac{h\nu_i}{k_B T}}} - k_B \ln(1 - e^{\frac{-h\nu_i}{k_B T}}) \right). \quad \text{(S-7)}$$

$$S_{trans} = k \left(\ln \left(\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V \right) + 1 + \frac{3}{2} \right) \quad \text{(S-8)}$$

$$S_{rot} = k\left(\ln\left(\frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\theta_x\theta_y\theta_z}\right)^{1/2}\right)+\frac{3}{2}\right) \quad \text{(S-9)}$$

$$\theta_{x/y/z} = \frac{h^2}{8\pi^2 I_{x/y/z} k_B} \quad \text{(S-10)}$$

as reported in [1]. In the Equations S-1-S-10, h is the plank's constant, ν represents a vibrational frequency, k_B is the Boltzmann Constant, m and V are the mass and the volume occupied by each gaseous species, I_x, I_y, I_z are the moments of inertia about x, y and z axes, respectively, and σ is the rotational symmetry number for gaseous molecules.

The free energy and a given temperature T is given by:

$$G = H - TS \quad \text{(S-11)}$$

S2. Calculation of NO reaction rates

For the reaction network reported in Scheme 1 ($2NO + O_2 \rightarrow 2NO_2$), the overall reaction rate is equal to the rate of step 1.3 of Scheme 1. According to transition state theory formalism [2], the overall rate is given by:

$$r = 2\frac{k_B T}{h} p_{cis-NOO_2NO^{\ddagger}} \quad \text{(S-12)}$$

where p is the partial pressure.

From the equilibrium between the cis-NOO_2NO molecule and the TS of step 1.3, it follows that:

$$K_{eq}^{\ddagger} = exp\left(-\frac{\Delta G^{0,\ddagger}}{RT}\right) = \frac{a_{(cis-NOO_2NO)^{\ddagger}}}{a_{cis-NOO_2NO}} \quad \text{(S-13)}$$

where a is the activity of the species.

If the reference state for Gibbs free energy is ideal gas at P_{ref} = 1 bar, then:

$$a_i = \frac{Px_i}{P_{ref}} \quad \text{(S-14)}$$

From (S-13) and (S-14) we derive that:

$$p_{cis-NOO_2NO^{\ddagger}} = P_{ref} K_{eq}^{\ddagger} a_{cis-NOO_2NO} \quad \text{(S-15)}$$

The combination of (S-15) and (S-12) leads to:

$$r = 2\frac{k_B T}{h} p_{cis-NOO_2NO}^{\ddagger} = 2\frac{k_B T}{h} P_{ref} K_{eq}^{\ddagger} a_{cis-NOO_2NO} \quad \text{(S-16)}$$

S-16 can be expressed in terms of NO and O_2 by considering step 1.1 and step 1.2:

$$r = 2\frac{k_B T}{h} P_{ref} K_{eq}^{\ddagger} K_{eq,1.1} K_{eq,1.2} a_{O2} a_{NO}^2 \quad \text{(S-17)}$$

and by substituting Eq. S-14 for the activities:

$$r = 2\frac{k_B T}{h} P_{ref} K_{eq}^{\ddagger} K_{eq,1.1} K_{eq,1.2} \frac{p_{O_2} p_{NO}^2}{P_{ref}^3} \quad \text{(S-18)}$$

Thus, the reaction rate is given by:

$$r = 2\frac{k_B T}{h} P_{ref}^{-2} exp\left(\frac{\Delta S_{app}}{R}\right) exp\left(-\frac{\Delta H_{app}}{RT}\right) p_{O_2} p_{NO}^2 \quad \text{(S-19)}$$

with:

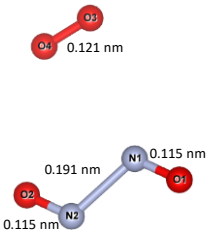
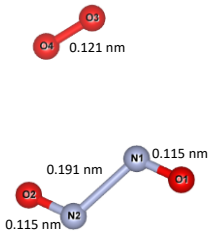
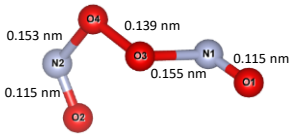
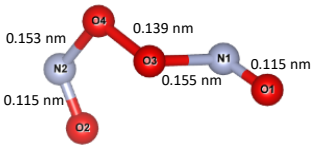
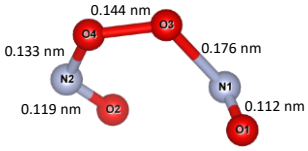
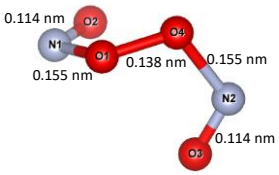
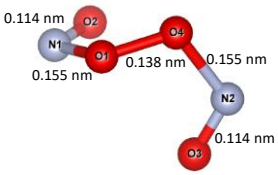
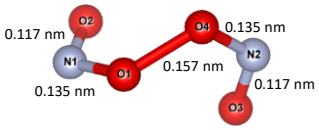
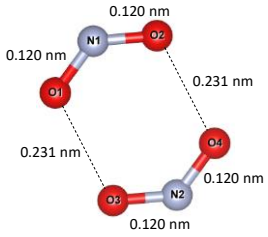
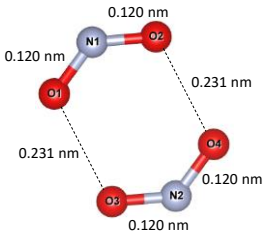
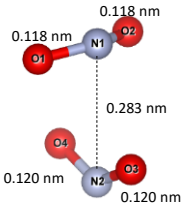
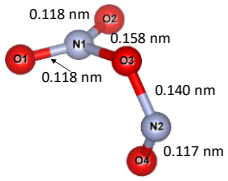
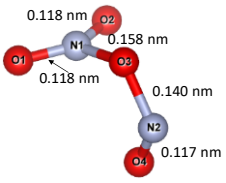
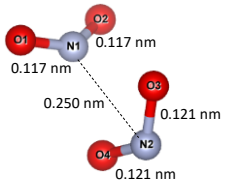
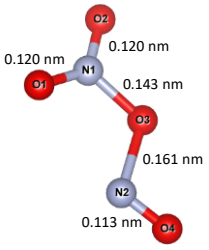
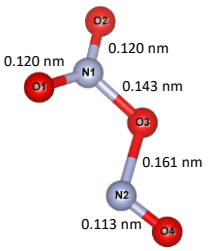
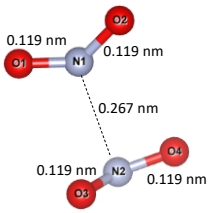
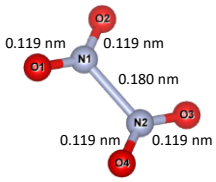
$$\Delta H_{app} = H_{1.1}^{\ddagger} - 2H_{NO} - H_{O_2} \quad \text{(S-20)}$$

$$\Delta S_{app} = S_{1.1}^{\ddagger} - 2S_{NO} - S_{O_2} \quad \text{(S-21)}$$

S-19 is in units of [bar/s]. To express S-19 in terms of concentration per unit of time (e.g., mol/l/s) each pressure terms in S-19 has to be multiplied by RT (in consistent units).

TABLE S-1

Structures of reactants, TS and products of each step of Scheme 1 in gas-phase. Bond length are given at the level of B3LYP/cc-pVTZ.

Step	Reactant	TS	Product
1.2			
	trans-ONNO + O_2		cis-NOO_2NO
1.3			
	cis-NOO_2NO		trans-NOO_2NO
1.4			
	trans-NOO_2NO		ONOONO
1.5			
	ONOONO		cis-$ONONO_2$
1.6			
	cis-$ONONO_2$		trans-$ONONO_2$
1.7			
	trans-$ONONO_2$		O_2NNO_2

S3. Absolute energies and coordinates of atoms for the intermediates and TS along the NO oxidation path in the gas phase

We report below the coordinates of the atoms and the absolute energies (B3LYP-cc-pVTZ – Gaussian 09) of reactant, products and TS molecules of the steps of Scheme and visualized in Table 1 of the manuscript.

Atom coordinates are given in Angstrom (Å) in the format x,y,z for each atom. Absolute energies are given in Hartree (Ha).

trans-ONNO + O_2	-410.26068	Ha	
N	5.931690	6.296436	7.262895
N	4.643581	5.040123	6.609286
O	7.006679	5.887776	7.288564
O	3.568074	5.447015	6.585062
O	4.973692	9.406781	5.454822
O	4.156446	8.533884	5.299806

TS_step_1.2	-410.26065	Ha	
N	6.379691	6.493412	5.377646
N	4.901094	5.346338	4.973118
O	7.340902	5.928527	5.661099
O	3.939705	5.910157	4.688885
O	4.124012	10.234458	5.649985
O	4.256470	9.416215	4.774257

cis-NOO_2NO	-410.27825	Ha	
N	6.287139	8.297443	5.034594
N	3.320878	8.110320	4.031817
O	7.081616	7.735532	5.638772
O	3.728087	7.038569	3.973172
O	4.948077	8.253973	5.805256
O	4.022720	8.982936	5.073415

TS_step_1.3	-410.26075	Ha	
N	6.513164	8.024233	4.459541
N	3.625619	8.161881	4.127512
O	6.832943	7.228998	5.182205
O	4.468004	7.597121	3.500352
O	5.443652	9.161031	5.277401
O	4.030399	8.992606	5.084648

trans-NOO_2NO -410.28088 Ha

N	4.711705	7.471316	6.039622
N	4.540459	4.451374	4.917816
O	5.210738	6.770889	4.744447
O	3.709260	7.069035	6.417632
O	5.396900	4.439616	5.676750
O	4.287972	5.851686	4.291254

TS_step_1.4 -410.27686 Ha

N	4.820914	7.414721	5.949114
N	4.567629	4.501771	4.809982
O	5.219073	6.888736	4.769768
O	3.923315	6.925769	6.517324
O	5.317788	4.431577	5.704385
O	4.347040	5.701151	4.227856

ONOONO -410.29608 Ha

N	5.294968	7.301665	5.958179
N	4.551906	4.401205	4.556860
O	6.228372	6.677438	5.542820
O	4.125787	7.051072	5.952206
O	5.720731	4.653342	4.558934
O	3.619116	5.023723	4.976208

TS_step_1.5 -410.28204 Ha

N	5.834226	6.734206	5.677262
N	4.594535	4.572131	4.335070
O	6.172778	5.857889	6.398338
O	4.783877	7.236188	5.459855
O	5.515511	5.150749	3.822922
O	4.063427	4.758011	5.393308

cis-$ONONO_2$ -410.31241 Ha

N	5.733622	6.314842	5.563278
N	4.563130	4.607886	4.158445
O	6.447318	5.776075	6.336500
O	5.106798	7.317050	5.575780
O	5.615856	5.535741	4.193067
O	3.913764	4.523923	5.125663

TS_step_1.6 -410.30745 Ha

N	5.584300	6.272060	5.738443
N	4.603748	4.631065	4.133876
O	6.423260	5.778493	6.395259
O	5.081166	7.327620	5.631120
O	5.562825	5.303043	3.811688
O	4.125188	4.763237	5.242346

trans-$ONONO_2$	-410.31648	Ha	
N	6.092453	6.183786	5.631112
N	4.789726	4.347972	4.499636
O	6.763801	5.251997	5.978651
O	6.169196	7.343011	5.917856
O	5.022626	5.928516	4.721573
O	3.948410	4.230929	3.751169

TS_step_1.7	-410.28305	Ha	
N	6.080232	6.167111	5.774881
N	4.596380	4.441428	4.386563
O	7.019623	5.551477	6.167044
O	5.663188	7.261244	5.986022
O	5.673879	4.313110	3.902260
O	3.752910	5.272337	4.283226

O_2NNO_2	-410.33481	Ha	
N	5.973471	5.973471	5.621747
N	4.955260	4.955260	4.544934
O	7.005835	5.457763	5.894929
O	5.457763	7.005835	5.894929
O	3.922907	5.470979	4.271730
O	5.470979	3.922907	4.271730

O_2	-150.38095	Ha	
O	0	0	-0.002910
O	0	0	1.2029090

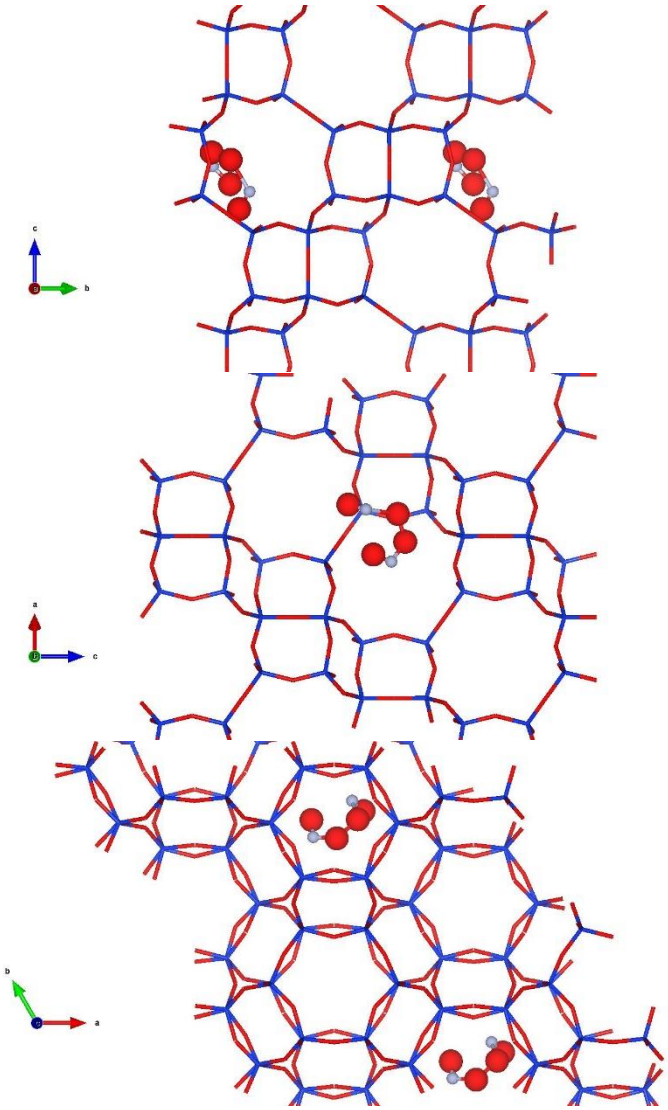
NO	-129.94052	Ha	
N	0	0	-0.001000
O	0	0	1.1449910

NO_2	-205.15595	Ha	
N	-1.809460	0.5707960	-0.000130
O	-2.605780	-0.316150	-0.008880
O	-0.618960	0.6218840	0.0212640

S4. Coordinates of atoms for the TS of the kinetically relevant TS (step 1.3 of Scheme 1) in CHA and SIL

Atom coordinates are given in Angstrom (Å) in the format x,y,z for each atom. For details on the optimized cell parameters and DFT scheme adopted please refer to Section 2 (Methods) of the paper.

TS step 1.3 in CHA (DFT-PBE + Grimme D2 – Quantum Espresso)



114 atoms

Ultrasoft pseudopotential – cut-off energy: 30 Ha

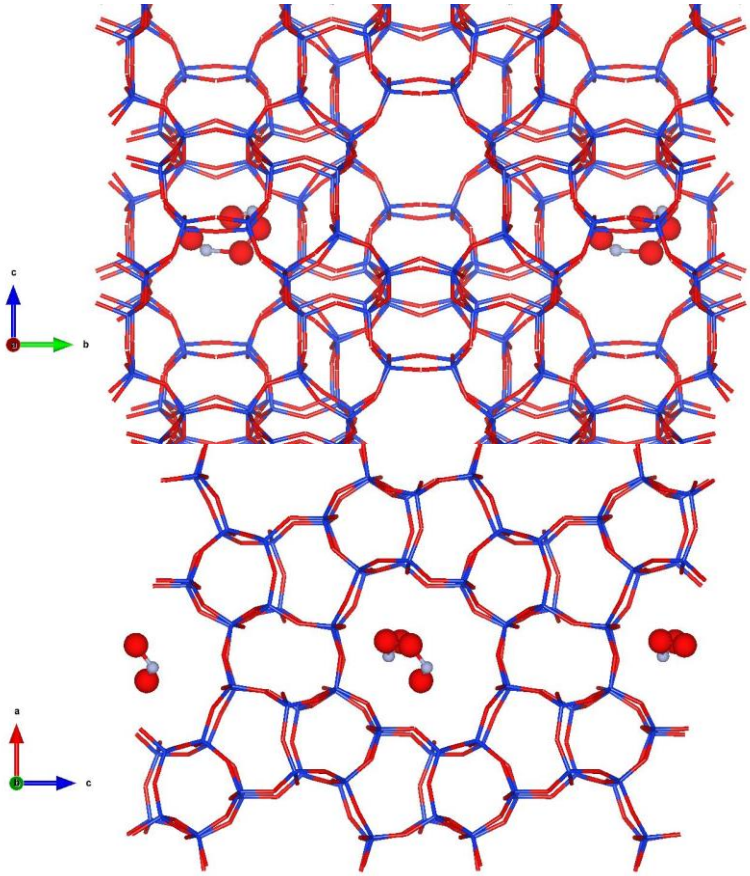
O 11.70852 1.15280 1.83083

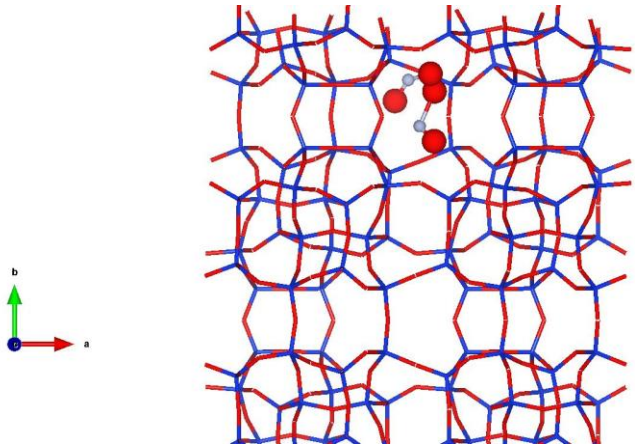
O	4.85581	5.10921	6.76380
O	-1.99671	9.06551	11.69687
O	6.85258	9.56348	1.83083
O	6.85258	1.65064	6.76380
O	-0.00003	5.60709	11.69687
O	1.99669	1.15277	1.83083
O	8.84940	5.10919	6.76380
O	1.99672	9.06549	11.69687
O	-4.85593	10.71625	12.96845
O	8.84931	2.80353	3.10242
O	1.99679	6.75984	8.03550
O	0.00002	2.30556	12.96845
O	6.85261	6.26195	3.10242
O	0.00002	10.21840	8.03550
O	4.85591	10.71628	12.96845
O	4.85588	2.80355	3.10242
O	-1.99680	6.75986	8.03550
O	11.28485	3.72039	2.46664
O	4.43218	7.67683	7.39972
O	-2.42036	11.63309	12.33268
O	4.84082	7.91277	2.46664
O	-2.01183	11.86900	7.39972
O	-2.01177	3.95641	12.33268
O	4.43212	0.23590	2.46664
O	-2.42035	4.19226	7.39972
O	4.43214	8.14860	12.33268
O	9.27300	0.23593	2.46656
O	2.42028	4.19230	7.39965
O	-4.43220	8.14863	12.33260
O	2.42042	3.72042	2.46656
O	-4.43211	7.67688	7.39965
O	2.42043	11.63313	12.33260
O	8.86437	7.91269	2.46656
O	2.01183	11.86892	7.39965
O	2.01177	3.95633	12.33260
O	0.00002	2.87151	1.98273
O	6.85262	6.82779	6.91570
O	0.00003	10.78418	11.84871
O	4.36578	10.43331	1.98273
O	4.36585	2.52065	6.91570
O	-2.48679	6.47698	11.84871
O	-4.36581	10.43327	1.98273
O	9.33933	2.52061	6.91570
O	2.48677	6.47694	11.84871
O	6.85257	8.99751	12.81655
O	6.85257	1.08483	2.95059
O	-0.00003	5.04124	7.88361

O	2.48684	1.43574	12.81655
O	9.33942	5.39208	2.95059
O	2.48676	9.34840	7.88361
O	11.21838	1.43580	12.81655
O	4.36580	5.39213	2.95059
O	-2.48674	9.34845	7.88361
O	-1.78148	3.08574	0.00012
O	5.07114	7.04218	4.93316
O	-1.78158	10.99844	9.86619
O	5.07101	8.78337	0.00012
O	5.07092	0.87064	4.93316
O	-1.78155	4.82694	9.86619
O	3.56307	-0.00006	0.00012
O	10.41574	3.95622	4.93316
O	3.56312	7.91271	9.86619
O	10.14210	0.00005	0.00005
O	3.28946	3.95633	4.93309
O	-3.56312	7.91282	9.86612
O	1.78159	3.08569	0.00005
O	8.63415	7.04213	4.93309
O	1.78167	10.99839	9.86612
O	-5.07110	8.78330	0.00005
O	8.63418	0.87059	4.93309
O	1.78145	4.82688	9.86612
Si	12.15188	2.69861	1.56288
Si	5.29932	6.65496	6.49583
Si	-1.55332	10.61132	11.42893
Si	5.29219	9.17453	1.56288
Si	5.29217	1.26186	6.49583
Si	-1.56042	5.21818	11.42893
Si	3.11372	-0.00410	1.56288
Si	9.96631	3.95222	6.49583
Si	3.11373	7.90860	11.42893
Si	10.59143	-0.00399	1.56283
Si	3.73885	3.95232	6.49579
Si	-3.11377	7.90871	11.42888
Si	1.55343	2.69859	1.56283
Si	8.40598	6.65495	6.49579
Si	1.55342	10.61131	11.42888
Si	8.41293	9.17445	1.56283
Si	8.41295	1.26178	6.49579
Si	1.56035	5.21809	11.42888
Si	-5.29932	9.17047	13.23652
Si	8.40588	1.25776	3.37047
Si	1.55330	5.21405	8.30349
Si	1.56040	2.69447	13.23652
Si	8.41300	6.65082	3.37047

Si	1.56044	10.60722	8.30349
Si	3.73893	11.87316	13.23652
Si	3.73891	3.96047	3.37047
Si	-3.11375	7.91682	8.30349
Si	-3.73889	11.87305	13.23656
Si	9.96632	3.96036	3.37051
Si	3.11378	7.91672	8.30353
Si	5.29921	9.17049	13.23656
Si	5.29922	1.25778	3.37051
Si	-1.55340	5.21408	8.30353
Si	-1.56033	2.69455	13.23656
Si	5.29226	6.65091	3.37051
Si	-1.56037	10.60730	8.30353
O	1.45029	8.49556	2.69418
O	0.12836	7.15480	5.46543
N	-1.02992	7.21893	4.78852
O	-1.11342	8.05876	3.91071
O	1.15996	8.08455	5.10399
N	0.88300	9.00386	3.55086

TS step 1.3 in SIL (DFT-PBE + Grimme D2 – Quantum Espresso)





294 atoms

Ultrasoft pseudopotential – cut-off energy: 30 Ha

O	10.146305	1.707832	9.291406
O	7.851830	1.543552	10.552500
O	8.026601	2.878531	8.262478
O	8.206989	0.214372	8.250943
O	6.640166	0.668292	12.794736
O	6.714693	18.572481	10.579000
O	5.197440	1.376826	10.742437
O	5.718926	2.499037	1.349683
O	4.033723	0.630497	0.412895
O	5.919034	-0.004734	2.168893
O	2.318689	2.436186	1.357988
O	1.610837	0.901099	12.412775
O	2.678663	1.777464	10.124218
O	1.455745	18.795619	10.219086
O	4.602552	2.689075	8.566522
O	9.904169	16.689898	9.423407
O	7.548187	16.074888	10.391470
O	8.585861	14.565941	8.476007
O	6.370165	16.930188	12.631018
O	4.937931	16.610175	10.444772
O	6.001304	14.564637	0.669034
O	3.907659	16.052259	-0.024956
O	1.709276	14.565018	-0.012558
O	1.619744	17.071939	12.213409
O	2.418412	16.367417	9.729759
O	4.184802	14.568127	8.915022
Si	8.549531	1.573804	9.078539
Si	6.608089	0.700289	11.173447
Si	5.562289	0.944933	0.904670
Si	2.457972	0.949386	0.709296

Si	1.469768	0.932334	10.796401
Si	4.143877	1.467281	9.516510
Si	8.451071	16.088931	9.033963
Si	6.396746	17.038016	11.006380
Si	5.419736	16.074146	0.560504
Si	2.304746	16.066763	0.210420
Si	1.352211	17.223139	10.606745
Si	3.953118	16.129454	9.249358
O	19.951714	11.393597	2.765106
O	2.191843	11.242698	4.016209
O	2.001866	12.577496	1.730240
O	1.835380	9.914901	1.710701
O	3.394800	10.354959	6.260191
O	3.325149	8.882282	4.039420
O	4.844206	11.070093	4.213128
O	4.302119	12.193308	7.893015
O	5.996409	10.331769	6.962326
O	4.107707	9.695073	8.719728
O	7.725646	12.132984	7.895362
O	8.412855	10.598801	5.865110
O	7.355521	11.484032	3.572099
O	8.556552	9.108670	3.670318
O	5.415924	12.382282	2.028266
O	0.127066	6.984734	2.870366
O	2.480561	6.388260	3.851168
O	1.468645	4.877468	1.919616
O	3.653888	7.234934	6.092903
O	5.092923	6.916466	3.907940
O	4.029650	4.877127	7.217702
O	6.119844	6.376806	6.525839
O	8.312651	4.876304	6.521867
O	8.411571	7.382704	5.668412
O	7.612964	6.673889	3.189195
O	5.847717	4.875482	2.376785
Si	1.488365	11.268717	2.544917
Si	3.431010	10.393978	4.638963
Si	4.466679	10.639544	7.452155
Si	7.574406	10.645844	7.249579
Si	8.558097	10.631941	4.248937
Si	5.886335	11.162394	2.976388
Si	1.587667	6.398010	2.487181
Si	3.634128	7.346393	4.468565
Si	4.606062	6.387879	7.106524
Si	7.724222	6.379755	6.748215
Si	8.675694	7.538076	4.061928
Si	6.077215	6.437089	2.711403
O	10.144459	8.053162	9.304385

O	7.841338	8.196618	10.551617
O	8.038738	6.869263	8.262177
O	8.201593	9.532238	8.250141
O	6.642273	9.082170	12.799350
O	6.711002	10.558277	10.581408
O	5.189958	8.372633	10.753551
O	5.719287	7.249298	1.350546
O	4.034746	9.116695	0.410388
O	5.918332	9.750241	2.173828
O	2.316141	7.316743	1.356865
O	1.609112	8.847517	12.410528
O	2.676818	7.965475	10.123516
O	1.468785	10.340776	10.215796
O	4.605762	7.063493	8.570414
O	9.908201	12.442265	9.419997
O	7.555168	13.053162	10.393837
O	6.375642	12.201854	12.633586
O	4.944291	12.528045	10.446798
O	3.908301	13.071257	-0.021706
O	1.618881	12.055710	12.219507
O	2.422364	12.776982	9.744403
Si	8.547866	8.176216	9.081668
Si	6.604578	9.045478	11.178262
Si	5.561989	8.803322	0.906837
Si	2.458093	8.802219	0.706829
Si	1.470390	8.816743	10.793252
Si	4.143276	8.282960	9.521345
Si	8.453900	13.042750	9.033723
Si	6.400919	12.094066	11.008907
Si	5.421261	13.054426	0.562209
Si	2.305208	13.063814	0.212747
Si	1.356524	11.911050	10.611439
Si	3.955164	13.007944	9.254935
O	19.950309	17.739849	2.758065
O	2.185243	17.899916	4.016009
O	2.007082	16.562029	1.726769
O	1.831769	19.226248	1.714131
O	3.398090	18.780092	6.255336
O	3.322942	0.871850	4.035969
O	4.839833	18.065058	4.203699
O	4.308598	16.942285	7.888280
O	5.999438	18.809381	6.963549
O	4.107627	19.441843	8.715375
O	7.723239	17.001244	7.896646
O	8.413096	18.537354	5.866434
O	7.356103	17.656737	3.571979
O	8.565399	0.642995	3.673207

O	5.419515	16.747914	2.025919
O	0.128551	2.770542	2.870165
O	2.483851	3.368540	3.849964
O	3.657118	2.517413	6.090174
O	5.095631	2.835821	3.905974
O	6.119142	3.382563	6.519580
O	8.411290	2.370928	5.667610
O	7.616033	3.074787	3.183999
Si	1.486659	17.868420	2.542409
Si	3.429787	18.744825	4.633887
Si	4.468885	18.497272	7.448784
Si	7.576252	18.489368	7.251184
Si	8.559180	18.506059	4.250963
Si	5.887358	17.970230	2.972095
Si	1.589151	3.356765	2.486800
Si	3.636154	2.407118	4.465796
Si	4.606885	3.366855	7.103856
Si	7.722797	3.373235	6.747332
Si	8.678603	2.214653	4.061547
Si	6.079662	3.313593	2.708534
O	9.919215	17.739248	3.830324
O	12.215435	17.898612	2.572159
O	12.035408	16.564777	4.862502
O	11.859794	19.229097	4.872513
O	13.425594	18.775016	0.329682
O	13.350887	0.871188	2.544957
O	14.869504	18.067646	2.381038
O	14.348680	16.944933	11.775117
O	16.032379	18.814356	12.711603
O	14.146445	19.448704	10.955726
O	17.746169	17.008165	11.764424
O	18.455345	18.540303	0.711122
O	17.387699	17.665263	3.000321
O	18.608249	0.648873	2.903226
O	15.461945	16.753531	4.556291
O	10.159786	2.754694	3.700971
O	12.514685	3.368761	2.729939
O	11.480120	4.878089	4.647007
O	13.694532	2.512097	0.491755
O	15.124840	2.836904	2.678382
O	14.063854	4.878711	12.456287
O	16.157298	3.389765	13.148331
O	18.356063	4.877387	13.135592
O	18.445775	2.369523	0.906877
O	17.646024	3.078840	3.388983
O	15.881500	4.876705	4.208574
Si	11.515868	17.870045	4.045258

Si	13.458133	18.743200	1.950931
Si	14.503912	18.499238	12.219929
Si	17.607868	18.494463	12.414621
Si	18.595791	18.511375	2.327656
Si	15.922264	17.975666	3.607467
Si	11.613585	3.355079	4.088710
Si	13.667168	2.405874	2.116474
Si	14.645101	3.368962	12.563092
Si	17.759991	3.376083	12.911471
Si	18.712346	2.221092	2.514043
Si	16.112061	3.315539	3.872573
O	0.113184	8.053483	10.356103
O	17.871128	8.200670	9.108410
O	18.066021	6.867297	11.394760
O	18.229097	9.530232	11.412073
O	16.669475	9.088730	6.864568
O	16.737382	10.561928	9.085019
O	15.218886	8.373536	8.910348
O	15.761315	7.250020	5.232527
O	14.067967	9.112623	6.161912
O	15.957892	9.748195	4.404951
O	12.338991	7.311888	5.226790
O	11.652083	8.842140	7.259549
O	12.708313	7.957451	9.553563
O	11.511475	10.335340	9.452676
O	14.650558	7.059421	11.094849
O	19.939356	12.459357	10.254674
O	17.587266	13.055288	9.270282
O	18.597075	14.567064	11.202456
O	16.411652	12.208073	7.030072
O	14.974402	12.532760	9.215234
O	16.035929	14.566402	5.906255
O	13.945795	13.066181	6.597356
O	11.752247	14.566181	6.602933
O	11.653988	12.058157	7.451994
O	12.452335	12.772649	9.929506
O	14.214773	14.569331	10.749037
Si	18.576734	8.176095	10.578659
Si	16.632343	9.049852	8.485697
Si	15.597697	8.804085	5.672625
Si	12.490070	8.798086	5.874639
Si	11.507242	8.811146	8.875843
Si	14.178001	8.279410	10.147970
Si	18.478314	13.046281	10.635512
Si	16.431773	12.098179	8.654550
Si	15.459617	13.055489	6.016711
Si	12.341518	13.063373	6.374278

Si	11.390307	11.905212	9.058899
Si	13.987241	13.008145	10.410869
O	9.919917	11.392614	3.821919
O	12.222055	11.246068	2.572139
O	12.027704	12.576693	4.859212
O	11.862903	9.913457	4.875782
O	13.422384	10.362522	0.324827
O	13.352692	8.885211	2.542208
O	14.874198	11.070033	2.371249
O	14.343143	12.193248	11.770482
O	16.029690	10.328439	12.712667
O	14.145743	9.690941	10.951473
O	17.748135	12.128170	11.765226
O	18.455645	10.597416	0.711684
O	17.387779	11.477171	2.999178
O	18.599924	9.104498	2.906315
O	15.460420	12.380397	4.552640
O	10.157599	7.000722	3.700490
O	12.511555	6.390206	2.729117
O	13.691362	7.242618	0.489689
O	15.122332	6.918312	2.677299
O	16.158061	6.371409	13.145081
O	18.447200	7.386014	0.905794
O	17.643336	6.671160	3.382643
Si	11.516771	11.268476	4.042590
Si	13.459497	10.397970	1.945875
Si	14.501966	10.640066	12.216518
Si	17.606243	10.642794	12.415704
Si	18.595350	10.628210	2.328800
Si	15.921883	11.159806	3.602552
Si	11.611820	6.401059	4.088549
Si	13.665283	7.349984	2.114428
Si	14.645001	6.388561	12.561607
Si	17.761234	6.379133	12.911351
Si	18.710099	7.533482	2.513401
Si	16.110316	6.437310	3.869905
O	0.115712	1.705766	10.368059
O	17.882222	1.541787	9.106945
O	18.056332	2.882784	11.394158
O	18.234152	0.218324	11.410689
O	16.667570	0.664279	6.868701
O	16.741093	18.571558	9.087927
O	15.226689	1.379233	8.920940
O	15.759048	2.500983	5.233289
O	14.066723	0.635753	6.159826
O	15.958895	0.000461	4.409385
O	12.342461	2.442445	5.225104

O	11.652704	0.907057	7.256159
O	12.709698	1.786290	9.550895
O	11.496610	18.802339	9.449386
O	14.644720	2.696758	11.097035
O	19.935444	16.674992	10.250923
O	17.580084	16.075369	9.272789
O	16.406235	16.926938	7.033000
O	14.967963	16.608149	9.217682
O	13.945153	16.059842	6.602953
O	11.653788	17.071297	7.457631
O	12.448544	16.373435	9.943147
Si	18.579141	1.575570	10.581207
Si	16.636054	0.698684	8.490070
Si	15.597537	0.946698	5.674631
Si	12.489889	0.954903	5.871690
Si	11.505577	0.939055	8.871530
Si	14.178122	1.473399	10.151681
Si	18.475526	16.087767	10.635392
Si	16.427440	17.036672	8.657459
Si	15.457551	16.076332	6.019279
Si	12.341258	16.069491	6.377026
Si	11.385412	17.230220	9.063172
Si	13.984934	16.131400	10.416526
O	10.785433	3.696258	12.149240
O	10.804401	6.068784	11.458500
N	10.098311	4.416033	11.577189
O	8.922302	5.613806	13.115602
O	10.614402	6.901387	12.607449
N	9.556343	6.610248	13.399128

S5. Coordinates of the atoms and energy of the optimized cis-NOO_2NO intermediate (Scheme 1) using Grimme-D2 and Grimme-D3 approach (VASP[3])

114 atoms - cut-off energy: 30 Ha
Atom coordinates are given in Angstrom (Å) in the format x,y,z for each atom.

Grimme-D2:

Si	0.00479764	3.11608618	1.562879887
Si	9.141562251	7.684485305	6.495829506
Si	4.573128113	12.25289598	11.42892913
Si	10.58910655	10.59383393	1.562879887
Si	6.020704746	1.457070303	6.495829506
Si	1.452297515	6.025434802	11.42892913
Si	3.111352634	13.70039026	1.562879887

Si	12.24812434	4.563630214	6.495829506
Si	7.67976175	9.132063981	11.42892913
Si	10.58912556	13.70051727	1.562829877
Si	6.020722554	4.563745676	6.495789501
Si	1.452325732	9.132190995	11.42887913
Si	3.111461421	3.116063091	1.562829877
Si	12.24821625	7.684473769	6.495789501
Si	7.6798621	12.25288443	11.42887913
Si	0.004675597	10.59374154	1.562829877
Si	9.141438317	1.45697793	6.495789501
Si	4.573015319	6.025330877	11.42887913
Si	13.70037785	10.58914584	13.23651898
Si	9.132047375	1.452336034	3.370469743
Si	4.56363282	6.020665875	8.303489368
Si	3.116052735	3.111305717	13.23651898
Si	12.25285178	7.679704842	3.370469743
Si	7.684520739	12.24816171	8.303489368
Si	10.59390131	0.004818667	13.23651898
Si	6.025487967	4.573156499	3.370469743
Si	1.457028056	9.141555624	8.303489368
Si	3.11601837	0.004691653	13.23655899
Si	12.25283398	4.573029469	3.370509748
Si	7.684499829	9.141440147	8.303529359
Si	10.59379406	10.58916893	13.23655899
Si	6.025399161	1.452359139	3.370509748
Si	1.456950383	6.020700517	8.303529359
Si	13.7004937	3.111398105	13.23655899
Si	9.132163979	7.679808767	3.370509748
Si	4.563757167	12.24825409	8.303529359
O	12.37408844	1.331138678	1.830829867
O	7.805613175	5.899607086	6.763799481
O	3.237264398	10.46794848	11.6968691
O	12.37405681	11.04295466	1.830829867
O	7.805576854	1.905994756	6.763799481
O	3.237224671	6.474509342	11.6968691
O	2.662241865	1.331104036	1.830829867
O	11.79919133	5.899583996	6.763799481
O	7.230682542	10.46792539	11.6968691
O	1.331099714	12.3740587	12.96844902
O	10.46792801	3.237237358	3.102419757
O	5.899584997	7.805590289	8.035499383
O	1.331135584	2.662231177	12.96844902
O	10.46794772	7.23067648	3.102419757
O	5.899615537	11.79919108	8.035499383
O	11.04295629	12.37409334	12.96844902
O	6.474509848	3.237260447	3.102419757
O	1.906006845	7.805613378	8.035499383

O	13.43281714	4.295936001	2.466639805
O	8.864399186	8.86443905	7.399719431
O	4.296007323	13.43273427	12.33267905
O	9.409259169	9.136879085	2.466639805
O	4.84073998	1.5115E-05	7.399719431
O	0.272464363	4.568468408	12.33267905
O	4.56831658	0.272393841	2.466639805
O	5.24324E-05	4.840804503	7.399719431
O	9.136735701	9.409192091	12.33267905
O	9.409213528	0.272428483	2.466559809
O	4.840705162	4.840850697	7.399649439
O	0.27241371	9.409226732	12.33259906
O	4.568405132	4.295970642	2.466559809
O	0.000138744	8.864496797	7.399649439
O	9.136820038	13.43278044	12.33259906
O	13.43276268	9.136786713	2.466559809
O	8.864353477	13.70504727	7.399649439
O	4.295957859	4.568376036	12.33259906
O	1.65788694	3.315733888	1.982729849
O	10.79464558	7.884052193	6.915699477
O	6.226278749	12.4524975	11.8487091
O	10.38945355	12.04734776	1.982729849
O	5.821147516	2.910595688	6.915699477
O	1.252696057	7.478971724	11.8487091
O	1.657841115	12.04730157	1.982729849
O	10.79460404	2.91054951	6.915699477
O	6.226232573	7.478925529	11.8487091
O	12.04728389	10.38942884	12.81654902
O	7.478896313	1.252653684	2.950589781
O	2.910531046	5.821122092	7.883609392
O	3.31576463	1.657849631	12.81654902
O	12.45253789	6.226237204	2.950589781
O	7.884060647	10.79460169	7.883609392
O	12.04733859	1.657918899	12.81654902
O	7.47894713	6.226294934	2.950589781
O	2.910589901	10.79465942	7.883609392
O	7.28116E-05	3.563105361	0.000120002
O	9.136943818	8.131608411	4.933159623
O	4.568371952	12.69990363	9.866189252
O	10.14209027	10.1421613	0.000120002
O	5.573583821	1.005328406	4.933159623
O	1.005285031	5.573669784	9.866189252
O	3.563035093	13.70505525	0.000120002
O	12.69986371	4.568249022	4.933159623
O	8.131524632	9.136809802	9.866189252
O	10.14212809	5.77308E-05	4.99963E-05
O	5.573647763	4.568376036	4.933089617

O	1.005348677	9.136936816	9.866119246
O	3.563113681	3.56304763	4.99963E-05
O	12.69992469	8.13155068	4.933089617
O	8.131592803	12.69984588	9.866119246
O	13.70506515	10.14208046	4.99963E-05
O	9.136814676	1.005270659	4.933089617
O	4.568250127	5.573600517	9.866119246
O	7.621617344	10.7770202	4.131660314
O	4.075424424	8.653980772	5.615982922
O	3.124199499	8.384999021	3.44155668
O	5.364383241	8.821044524	4.980487154
N	2.727984003	8.327244973	4.548003774
N	6.4970437	10.63149672	4.611429706

Grimme-D3:

Si	0.00479764	3.11608618	1.562879887
Si	9.141562251	7.684485305	6.495829506
Si	4.573128113	12.25289598	11.42892913
Si	10.58910655	10.59383393	1.562879887
Si	6.020704746	1.457070303	6.495829506
Si	1.452297515	6.025434802	11.42892913
Si	3.111352634	13.70039026	1.562879887
Si	12.24812434	4.563630214	6.495829506
Si	7.67976175	9.132063981	11.42892913
Si	10.58912556	13.70051727	1.562829877
Si	6.020722554	4.563745676	6.495789501
Si	1.452325732	9.132190995	11.42887913
Si	3.111461421	3.116063091	1.562829877
Si	12.24821625	7.684473769	6.495789501
Si	7.6798621	12.25288443	11.42887913
Si	0.004675597	10.59374154	1.562829877
Si	9.141438317	1.45697793	6.495789501
Si	4.573015319	6.025330877	11.42887913
Si	13.70037785	10.58914584	13.23651898
Si	9.132047375	1.452336034	3.370469743
Si	4.56363282	6.020665875	8.303489368
Si	3.116052735	3.111305717	13.23651898
Si	12.25285178	7.679704842	3.370469743
Si	7.684520739	12.24816171	8.303489368
Si	10.59390131	0.004818667	13.23651898
Si	6.025487967	4.573156499	3.370469743
Si	1.457028056	9.141555624	8.303489368
Si	3.11601837	0.004691653	13.23655899
Si	12.25283398	4.573029469	3.370509748
Si	7.684499829	9.141440147	8.303529359
Si	10.59379406	10.58916893	13.23655899

Si	6.025399161	1.452359139	3.370509748
Si	1.456950383	6.020700517	8.303529359
Si	13.7004937	3.111398105	13.23655899
Si	9.132163979	7.679808767	3.370509748
Si	4.563757167	12.24825409	8.303529359
O	12.37408844	1.331138678	1.830829867
O	7.805613175	5.899607086	6.763799481
O	3.237264398	10.46794848	11.6968691
O	12.37405681	11.04295466	1.830829867
O	7.805576854	1.905994756	6.763799481
O	3.237224671	6.474509342	11.6968691
O	2.662241865	1.331104036	1.830829867
O	11.79919133	5.899583996	6.763799481
O	7.230682542	10.46792539	11.6968691
O	1.331099714	12.3740587	12.96844902
O	10.46792801	3.237237358	3.102419757
O	5.899584997	7.805590289	8.035499383
O	1.331135584	2.662231177	12.96844902
O	10.46794772	7.23067648	3.102419757
O	5.899615537	11.79919108	8.035499383
O	11.04295629	12.37409334	12.96844902
O	6.474509848	3.237260447	3.102419757
O	1.906006845	7.805613378	8.035499383
O	13.43281714	4.295936001	2.466639805
O	8.864399186	8.86443905	7.399719431
O	4.296007323	13.43273427	12.33267905
O	9.409259169	9.136879085	2.466639805
O	4.84073998	1.5115E-05	7.399719431
O	0.272464363	4.568468408	12.33267905
O	4.56831658	0.272393841	2.466639805
O	5.24324E-05	4.840804503	7.399719431
O	9.136735701	9.409192091	12.33267905
O	9.409213528	0.272428483	2.466559809
O	4.840705162	4.840850697	7.399649439
O	0.27241371	9.409226732	12.33259906
O	4.568405132	4.295970642	2.466559809
O	0.000138744	8.864496797	7.399649439
O	9.136820038	13.43278044	12.33259906
O	13.43276268	9.136786713	2.466559809
O	8.864353477	13.70504727	7.399649439
O	4.295957859	4.568376036	12.33259906
O	1.65788694	3.315733888	1.982729849
O	10.79464558	7.884052193	6.915699477
O	6.226278749	12.4524975	11.8487091
O	10.38945355	12.04734776	1.982729849
O	5.821147516	2.910595688	6.915699477
O	1.252696057	7.478971724	11.8487091

O	1.657841115	12.04730157	1.982729849
O	10.79460404	2.91054951	6.915699477
O	6.226232573	7.478925529	11.8487091
O	12.04728389	10.38942884	12.81654902
O	7.478896313	1.252653684	2.950589781
O	2.910531046	5.821122092	7.883609392
O	3.31576463	1.657849631	12.81654902
O	12.45253789	6.226237204	2.950589781
O	7.884060647	10.79460169	7.883609392
O	12.04733859	1.657918899	12.81654902
O	7.47894713	6.226294934	2.950589781
O	2.910589901	10.79465942	7.883609392
O	7.28116E-05	3.563105361	0.000120002
O	9.136943818	8.131608411	4.933159623
O	4.568371952	12.69990363	9.866189252
O	10.14209027	10.1421613	0.000120002
O	5.573583821	1.005328406	4.933159623
O	1.005285031	5.573669784	9.866189252
O	3.563035093	13.70505525	0.000120002
O	12.69986371	4.568249022	4.933159623
O	8.131524632	9.136809802	9.866189252
O	10.14212809	5.77308E-05	4.99963E-05
O	5.573647763	4.568376036	4.933089617
O	1.005348677	9.136936816	9.866119246
O	3.563113681	3.56304763	4.99963E-05
O	12.69992469	8.13155068	4.933089617
O	8.131592803	12.69984588	9.866119246
O	13.70506515	10.14208046	4.99963E-05
O	9.136814676	1.005270659	4.933089617
O	4.568250127	5.573600517	9.866119246
O	7.621939038	10.77605221	4.133194755
O	4.075676932	8.655261852	5.613994548
O	3.124258867	8.383950855	3.440733547
O	5.362398676	8.820114624	4.977046728
N	2.728004684	8.327647103	4.546924715
N	6.497082741	10.63133936	4.611077794

	Grimme-D2 (eV)	**Grimme-D3 (eV)**
CHA-NOO_2NO	-897.574	-896.539
CHA	-861.107	-859.993
NO	-12.280	-12.280
O_2	-9.869	-9.869
CHA-NOO_2NO – (CHA+2NO+O_2)	-2.037	-2.117

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