Suplimentary Information for Mechanistic insight into N_2O+O(^{1}D,^{3}P) reaction: Role of post-CCSD(T) corrections and non-adiabatic effects.

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Table S1: Optimized geometries in Cartesian coordinates and normal mode frequencies of all species calculate at CCSD(T)/aug-cc-pVTZ level of theory

compound	Cartesian coordinates (Å)				frequency(cm^{-1})		
N_2O	N	0.0000	0.0000	-0.072895	593.2749	593.2773	1286.1339
	N	0.0000	0.0000	-1.205426	2266.8894		
	O	0.0000	0.0000	1.11853			
NO	O	0.0000	0.0000	0.53816	2098.0374		
	N	0.0000	0.0000	-0.61504			
N_2	N	0.0000	0.0000	0.552	2339.6874		
	N	0.0000	0.0000	-0.552			
O_2-S	O	0.0000	0.0000	0.612753	1474.5171		
	O	0.0000	0.0000	-0.612753			
O_2-T	O	0.0000	0.0000	0.6067	1573.4964		
	O	0.0000	0.0000	-0.6067			
RC1	N	-0.607729	0.147332	-0.000046	225.1180	497.7756	516.8776
	N	-1.613986	-0.345403	0.000024	631.4689	1093.3805	2240.5577
	O	0.498196	0.696512	0.000019			
	O	1.445804	-0.5232	0.0000			
RC2	N	-0.187124	0.084234	-0.000676	375.2516	571.4949	624.6608
	O	-1.367057	-0.08934	0.000269	922.5401	1196.3174	1833.0425
	N	0.735207	0.917246	0.00022			
	O	0.887485	-0.786955	0.00013			
RC3	N	0.562181	-0.231175	-0.000124	201.3204	364.7942	463.4955
	N	-0.561965	0.23013	-0.000125	932.6954	1484.4237	1863.4079
	O	1.73901	0.065685	0.000109			
	O	-1.7392	-0.064771	0.000109			
RC	N	0.832985	-0.006389	0.000001	52.2351	123.4813	592.8341
	N	1.084488	-1.109629	-0.000001	654.7804	1373.4294	2796.7141
	O	0.568397	1.155073	-0.000001			
	O	-2.246186	-0.178558	0.0000			
TS1	N	-0.680384	0.224335	-0.003007	-946.2239	152.6449	206.5102
	N	-1.647078	-0.342608	0.001618	656.4398	850.1829	2064.0769
	O	0.618475	0.634038	0.001477			
	O	1.418054	-0.530549	-0.000262			
TS2	N	0.065646	0.083932	0.00004	-646.8003	538.0450	701.3230
	N	-0.640369	1.100567	-0.000014	866.6304	1269.8212	1636.8551
	O	1.276391	-0.09261	-0.000014			
	O	-0.773508	-0.943827	-0.00001			
TS3	N	0.591616	-0.309231	-0.212938	-700.5640	289.9311	448.6233
	N	-0.591632	0.300778	-0.223121	657.8640	1517.1072	1566.1905
	O	1.650127	0.099383	0.189177			
	O	-1.650113	-0.091987	0.192375			
TS1-a	O	-1.697673	-0.356646	-0.000783	-2051.9050	281.7750	293.9385
	N	0.615847	-0.163573	0.00309	681.0669	754.8209	1873.2989
	O	-0.397507	0.646206	-0.000195			
	N	1.778645	-0.167353	-0.001973			
TS1-b	N	0.800445	0.346774	0.000099	-1222.2609	191.7602	364.4188
	N	1.522764	-0.540558	-0.000051	610.1570	768.1695	1921.8375
	O	-0.482501	0.69324	-0.000063			
	O	-1.550307	-0.523678	0.000021			

compound	Cartesian coordinates(Å)				frequency(cm^{-1})		
TS2-a	N	0.514467	0.000976	0.000107	-925.0427	269.4177	457.7653
	N	-0.46482	0.667552	-0.000029	582.0238	1170.4971	1895.3758
	O	1.688565	-0.216949	-0.000052			
	O	-1.732005	-0.368012	-0.00001.6			
TS2-b	N	-0.596981	0.372568	0.001035	-880.5666	236.2468	561.8708
	N	0.522223	0.766115	-0.000691	641.5558	1211.2026	1868.8003
	O	-1.453515	-0.456837	-0.000442			
	O	1.518928	-0.539511	0.000141			
MECP-1	O	-0.164612	-1.726339	0.0000	-262.6870	198.6914	616.9825
	N	0	0.685439	0.0000	634.2795	1292.5964	2427.0708
	O	0.866617	-0.138271	0.0000			
	N	-0.802291	1.445544	0.0000			
MECP-2	O	0.894145	1.366037	0.0000	-389.5922	119.7845	622.7858
	O	-0.141514	-1.817167	0.0000	666.3199	1392.6795	2332.5978
	N	-0.86015	-0.102453	0.0000			
	N	0.0000	0.61803	0.0000			

Table S2: Bimolecular rate constant (cm^3 molecule^{-1} sec^{-1}) for N_2O+O(^{1}D) reaction channel proceeds through TS1, TS2 and TS3 within the temperature range of 100K - 500K.

Temp.(K)	$k_{TS1}^{N_2+O_2}$	k_{TS2}^{NO+NO}	k_{TS3}^{NO+NO}	$k_{TS2+TS3}^{NO+NO}$	k_{Total}	k_{NO}/k_{N2+O2}	k_{NO}/k_{Total}
100	5.28×10^{-11}	7.58×10^{-11}	1.02×10^{-11}	8.60×10^{-11}	1.39×10^{-10}	1.63	0.620
120	5.04×10^{-11}	7.21×10^{-11}	9.74×10^{-12}	8.18×10^{-11}	1.32×10^{-10}	1.62	0.619
140	4.91×10^{-11}	6.99×10^{-11}	9.47×10^{-12}	7.93×10^{-11}	1.28×10^{-10}	1.62	0.618
160	4.82×10^{-11}	6.85×10^{-11}	9.29×10^{-12}	7.78×10^{-11}	1.26×10^{-10}	1.61	0.617
180	4.76×10^{-11}	6.75×10^{-11}	9.17×10^{-12}	7.67×10^{-11}	1.24×10^{-10}	1.61	0.617
200	4.72×10^{-11}	6.68×10^{-11}	9.08×10^{-12}	7.59×10^{-11}	1.23×10^{-10}	1.61	0.617
213	4.70×10^{-11}	6.65×10^{-11}	9.03×10^{-12}	7.55×10^{-11}	1.23×10^{-10}	1.61	0.616
216	4.69×10^{-11}	6.64×10^{-11}	9.02×10^{-12}	7.54×10^{-11}	1.22×10^{-10}	1.61	0.616
219	4.69×10^{-11}	6.64×10^{-11}	9.01×10^{-12}	7.54×10^{-11}	1.22×10^{-10}	1.61	0.616
224	4.68×10^{-11}	6.63×10^{-11}	9.00×10^{-12}	7.53×10^{-11}	1.22×10^{-10}	1.61	0.616
235	4.67×10^{-11}	6.60×10^{-11}	8.97×10^{-12}	7.50×10^{-11}	1.22×10^{-10}	1.61	0.616
250	4.65×10^{-11}	6.58×10^{-11}	8.94×10^{-12}	7.47×10^{-11}	1.21×10^{-10}	1.61	0.616
259	4.65×10^{-11}	6.57×10^{-11}	8.92×10^{-12}	7.46×10^{-11}	1.21×10^{-10}	1.61	0.616
265	4.64×10^{-11}	6.56×10^{-11}	8.91×10^{-12}	7.45×10^{-11}	1.21×10^{-10}	1.61	0.616
278	4.63×10^{-11}	6.54×10^{-11}	8.89×10^{-12}	7.43×10^{-11}	1.21×10^{-10}	1.60	0.616
280	4.63×10^{-11}	6.54×10^{-11}	8.88×10^{-12}	7.43×10^{-11}	1.21×10^{-10}	1.60	0.616
290	4.62×10^{-11}	6.53×10^{-11}	8.87×10^{-12}	7.42×10^{-11}	1.20×10^{-10}	1.60	0.616
298	4.62×10^{-11}	6.53×10^{-11}	8.86×10^{-12}	7.41×10^{-11}	1.20×10^{-10}	1.60	0.616
300	4.62×10^{-11}	6.52×10^{-11}	8.86×10^{-12}	7.41×10^{-11}	1.20×10^{-10}	1.60	0.616
310	4.61×10^{-11}	6.52×10^{-11}	8.85×10^{-12}	7.40×10^{-11}	1.20×10^{-10}	1.60	0.616
320	4.61×10^{-11}	6.51×10^{-11}	8.84×10^{-12}	7.39×10^{-11}	1.20×10^{-10}	1.60	0.616
350	4.60×10^{-11}	6.49×10^{-11}	8.81×10^{-12}	7.37×10^{-11}	1.20×10^{-10}	1.60	0.616
370	4.59×10^{-11}	6.48×10^{-11}	8.80×10^{-12}	7.36×10^{-11}	1.20×10^{-10}	1.60	0.616
400	4.58×10^{-11}	6.47×10^{-11}	8.78×10^{-12}	7.34×10^{-11}	1.19×10^{-10}	1.60	0.616
420	4.58×10^{-11}	6.46×10^{-11}	8.77×10^{-12}	7.34×10^{-11}	1.19×10^{-10}	1.60	0.616
440	4.57×10^{-11}	6.45×10^{-11}	8.76×10^{-12}	7.33×10^{-11}	1.19×10^{-10}	1.60	0.616
450	4.57×10^{-11}	6.45×10^{-11}	8.76×10^{-12}	7.33×10^{-11}	1.19×10^{-10}	1.60	0.616
470	4.57×10^{-11}	6.45×10^{-11}	8.75×10^{-12}	7.32×10^{-11}	1.19×10^{-10}	1.60	0.616
500	4.57×10^{-11}	6.44×10^{-11}	8.74×10^{-12}	7.31×10^{-11}	1.19×10^{-10}	1.60	0.616

Table S3: Bimolecular rate constant (cm^3 $molecule^{-1}$ sec^{-1}) for $N_2O+O(^3P)$ reaction channel proceeds through MECP-1, TS2-b, TS2-a, and TS1-b within the temperature range of 700K - 4000K.

Temp. (K)	MECP-1	TS2-b	TS2-a	TS1-b
700	9.90×10^{-17}	5.39×10^{-19}	1.10×10^{-20}	4.11×10^{-23}
800	3.65×10^{-16}	5.38×10^{-18}	1.78×10^{-19}	1.50×10^{-21}
900	1.01×10^{-15}	3.28×10^{-17}	1.59×10^{-18}	2.52×10^{-20}
1000	2.31×10^{-15}	1.42×10^{-16}	9.26×10^{-18}	2.46×10^{-19}
1100	4.54×10^{-15}	4.74×10^{-16}	3.97×10^{-17}	1.61×10^{-18}
1200	8.00×10^{-15}	1.31×10^{-15}	1.35×10^{-16}	7.79×10^{-18}
1300	1.30×10^{-14}	3.11×10^{-15}	3.82×10^{-16}	2.99×10^{-17}
1400	1.97×10^{-14}	6.59×10^{-15}	9.41×10^{-16}	9.51×10^{-17}
1500	2.83×10^{-14}	1.27×10^{-14}	2.06×10^{-15}	2.61×10^{-16}
1600	3.90×10^{-14}	2.26×10^{-14}	4.13×10^{-15}	6.36×10^{-16}
1700	5.18×10^{-14}	3.79×10^{-14}	7.64×10^{-15}	1.40×10^{-15}
1800	6.68×10^{-14}	6.00×10^{-14}	1.32×10^{-14}	2.84×10^{-15}
1900	8.40×10^{-14}	9.10×10^{-14}	2.18×10^{-14}	5.35×10^{-15}
2000	1.03×10^{-13}	1.33×10^{-13}	3.41×10^{-14}	9.51×10^{-15}
2100	1.25×10^{-13}	1.87×10^{-13}	5.13×10^{-14}	1.60×10^{-14}
2200	1.48×10^{-13}	2.56×10^{-13}	7.47×10^{-14}	2.59×10^{-14}
2300	1.74×10^{-13}	3.43×10^{-13}	1.05×10^{-13}	4.01×10^{-14}
2400	2.01×10^{-13}	4.48×10^{-13}	1.45×10^{-13}	6.00×10^{-14}
2500	2.30×10^{-13}	5.73×10^{-13}	1.94×10^{-13}	8.72×10^{-14}
2600	2.61×10^{-13}	7.22×10^{-13}	2.55×10^{-13}	1.23×10^{-13}
2700	2.94×10^{-13}	8.95×10^{-13}	3.29×10^{-13}	1.70×10^{-13}
2800	3.28×10^{-13}	1.09×10^{-12}	4.17×10^{-13}	2.30×10^{-13}
2900	3.63×10^{-13}	1.32×10^{-12}	5.20×10^{-13}	3.05×10^{-13}
3000	4.00×10^{-13}	1.58×10^{-12}	6.41×10^{-13}	3.97×10^{-13}
3100	4.38×10^{-13}	1.86×10^{-12}	7.80×10^{-13}	5.08×10^{-13}
3200	4.77×10^{-13}	2.18×10^{-12}	9.39×10^{-13}	6.42×10^{-13}
3300	5.17×10^{-13}	2.53×10^{-12}	1.12×10^{-12}	8.01×10^{-13}
3400	5.58×10^{-13}	2.91×10^{-12}	1.32×10^{-12}	9.86×10^{-13}
3500	6.00×10^{-13}	3.33×10^{-12}	1.54×10^{-12}	1.20×10^{-12}
3600	6.42×10^{-13}	3.78×10^{-12}	1.79×10^{-12}	1.45×10^{-12}
3700	6.86×10^{-13}	4.27×10^{-12}	2.07×10^{-12}	1.73×10^{-12}
3800	7.30×10^{-13}	4.79×10^{-12}	2.36×10^{-12}	2.05×10^{-12}
3900	7.75×10^{-13}	5.35×10^{-12}	2.69×10^{-12}	2.41×10^{-12}
4000	8.20×10^{-13}	5.94×10^{-12}	3.04×10^{-12}	2.81×10^{-12}

Table S4: The value of spin contamination of open shell atoms and molecules.

Species	Spin contamination
O (^{3}P)	0.0
RC	0.0
TS1-a	0.1433
TS1-b	0.0840
TS2-a	0.1331
TS2-b	0.1261

Table S5: Comparison in the frequency of CCSD/aug-cc-pVTZ with CCSD(T)/aug-cc-pVTZ) level of theory.

compound	frequency(cm^{-1}) CCSD/aug-cc-pVTZ			frequency(cm^{-1})CCSD(T)/aug-cc-pVTZ		
RC-1	234.5165	532.8316	564.4742	225.118	497.7756	516.8776
	640.0026	1110.5956	2355.6543	631.4689	1093.3805	2240.5577
TS-1	-988.7137	191.7216	235.7716	-946.2239	152.6449	206.5102
	657.4644	877.1877	2234.9795	656.4398	850.1829	2064.0769

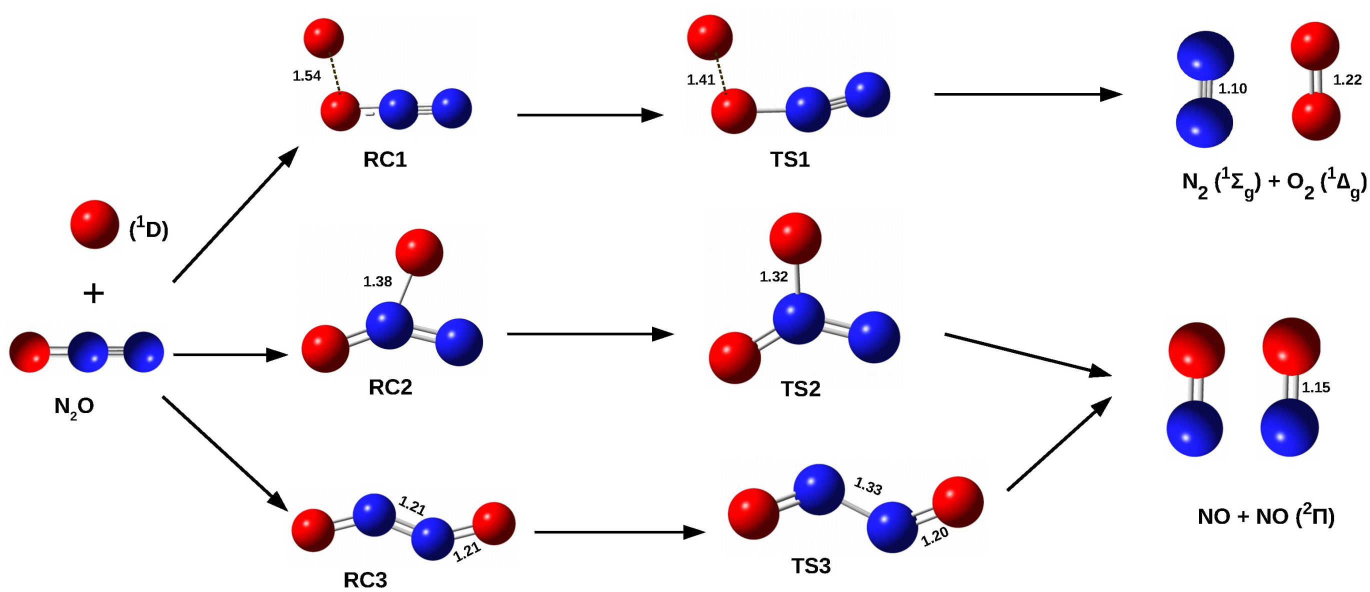

Figure S1: Reaction scheme for N_2O+O(^{1}D) reaction at CCSD(T)/aug-cc-pVTZ level of theory. The bond lengths are in Å.

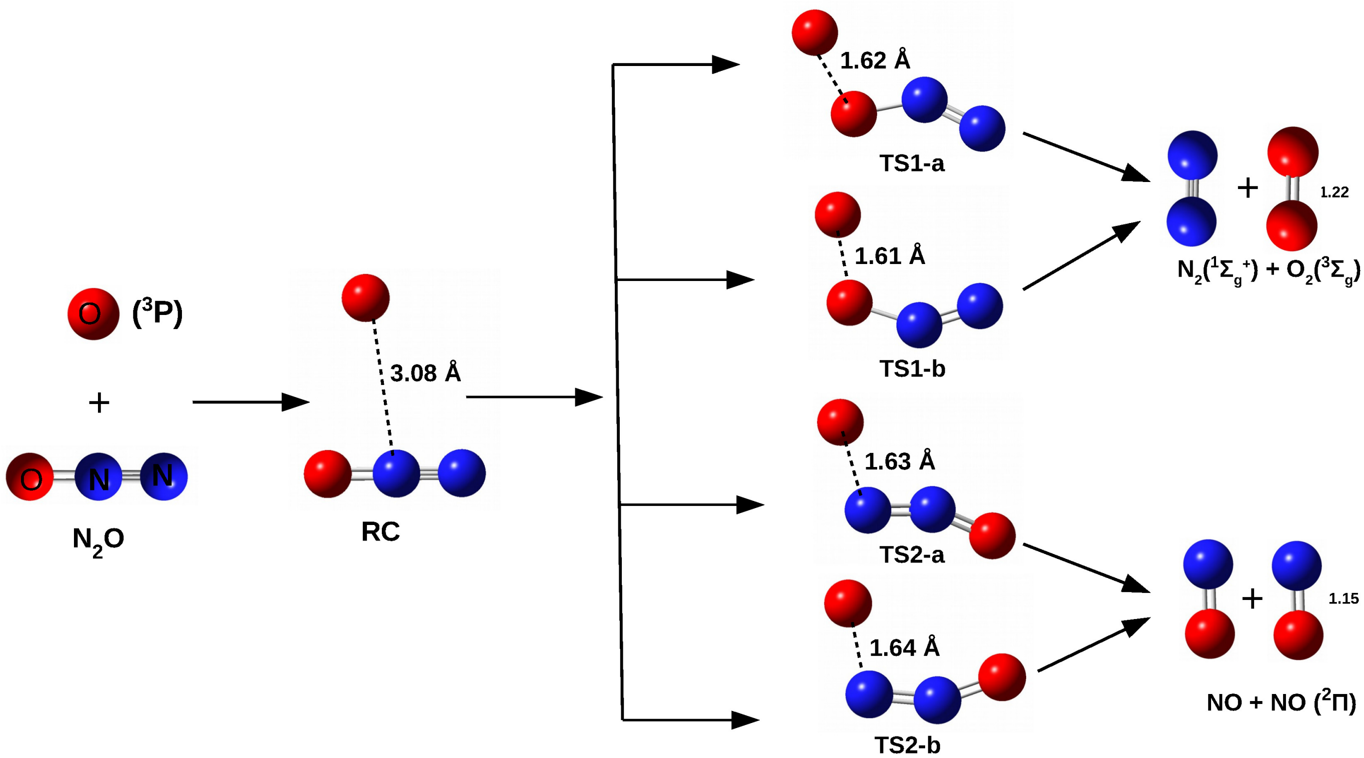

Figure S2: Reaction scheme for N_2O+O(^{3}P) reaction at CCSD(T)/aug-cc-pVTZ level of theory. The bond lengths are in Å

1 Formal derivation of $\triangle$E.

Rate expression for N_2 and NO production paths

$$k_{N_2} = A_1 e^{(-\beta E_1)} \tag{1}$$

$$k_{NO} = A_2 e^{(-\beta E_2)} \tag{2}$$

Rate of N_2 relative to the total reaction= $\frac{k_{N_2}}{k_{N_2}+k_{NO}}$

$$= [1 + \frac{k_{NO}}{k_{N_2}}]^{-1} \tag{3}$$

Putting the value in equation (3) from (1) and (2)

$$= [1+\frac{A_2 e^{(-\beta E_2)}}{A_1 e^{(-\beta E_1)}}]^{-1}$$

$$= [1-\frac{A_2}{A_1} e^{-\beta(E_1-E_2)} + (\frac{A_2}{A_1})^2 e^{-2\beta(E_1-E_2)} - (\frac{A_2}{A_1})^3 e^{-3\beta(E_1-E_2)} + (\frac{A_2}{A_1})^4 e^{-4\beta(E_1-E_2)}]$$

(Neglect higher order term)

$$= [1-\frac{A_2}{A_1} e^{-\beta(\Delta E)}]$$