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

Electronic Suplimentery Information

for

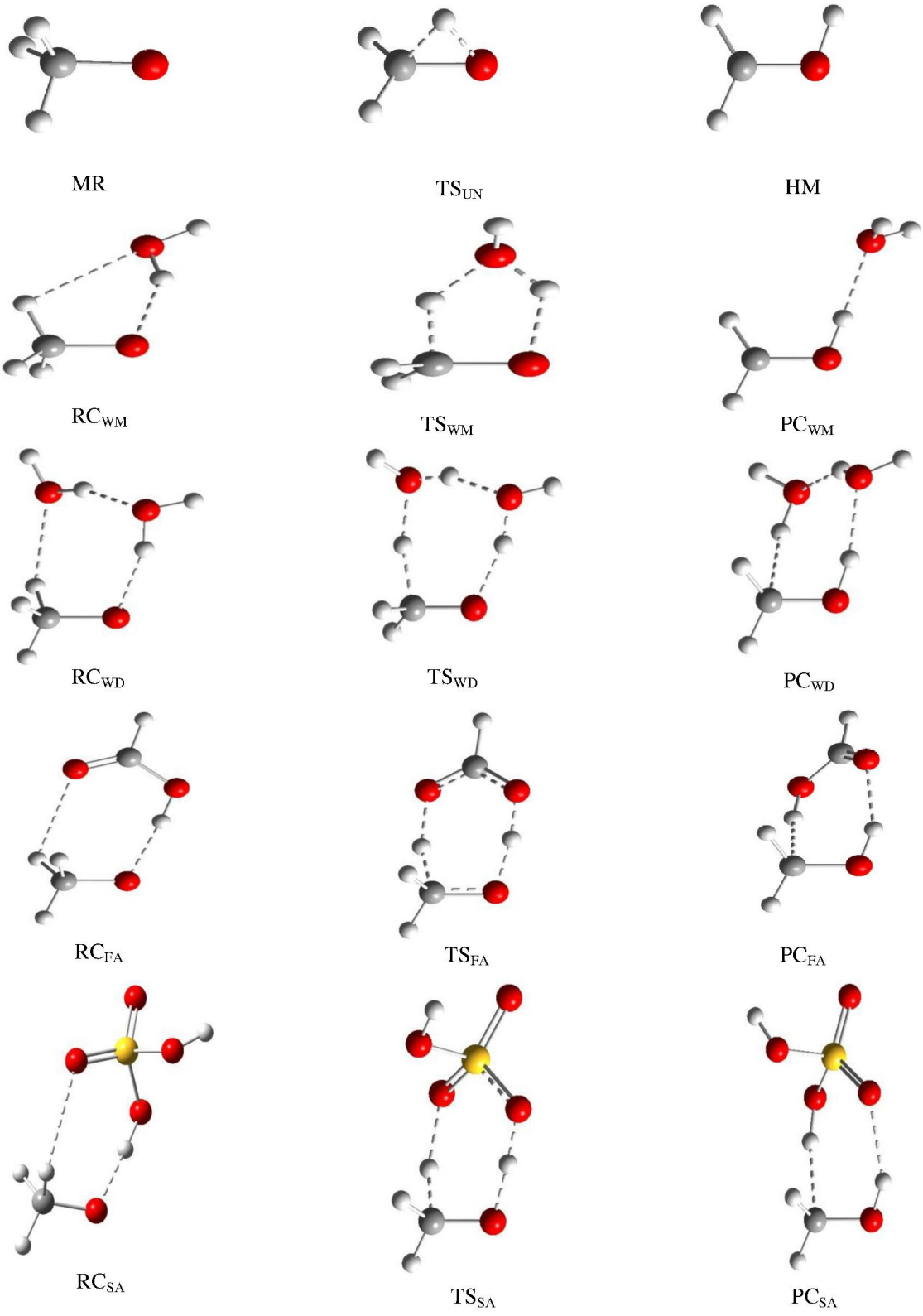
Isomerization of Methoxy Radical in Troposphere: Competition Between Acidic, Neutral and Basic Catalysts

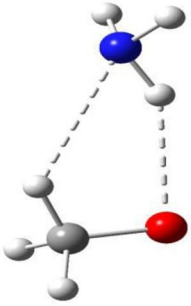
Saptarshi Sarkar,[‡] Subhasish Mallick,[‡] Deepak, Pradeep Kumar[*] and Biman Bandyopadhyay[*]

Department of Chemistry, Malaviya National Institute of Technology Jaipur, Jaipur, 302017,India
[‡]Equal contribution
E-mail: pradeep.chy@mnit.ac.in; biman.chy@mnit.ac.in

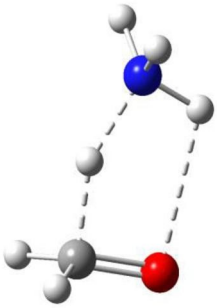
Table of contents

Figure S1: Molecular structures of all the species optimized at MP2/aug-cc-pVTZ level of theory

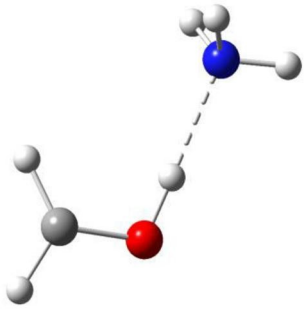




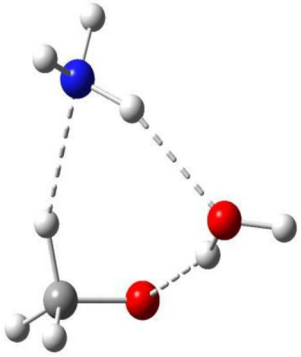
RC_{AM}



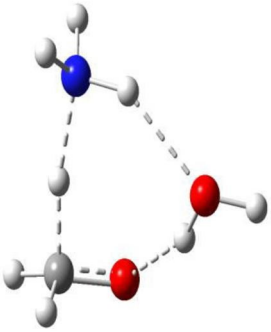
TS_{AM}



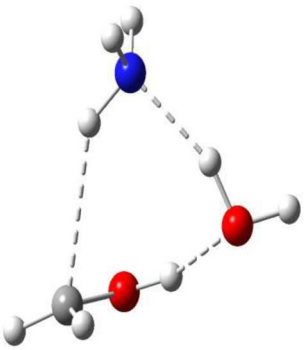
PC_{AM}



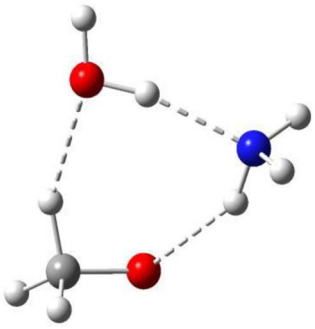
RC_{AW}



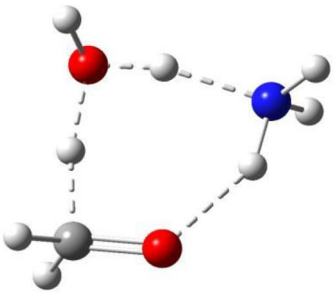
TS_{AW}



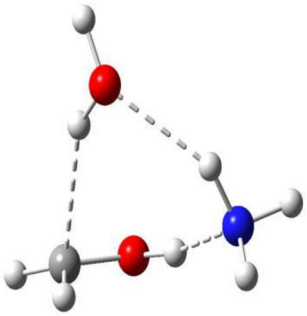
PC_{AW}



RC_{WA}



TS_{WA}



PC_{WA}

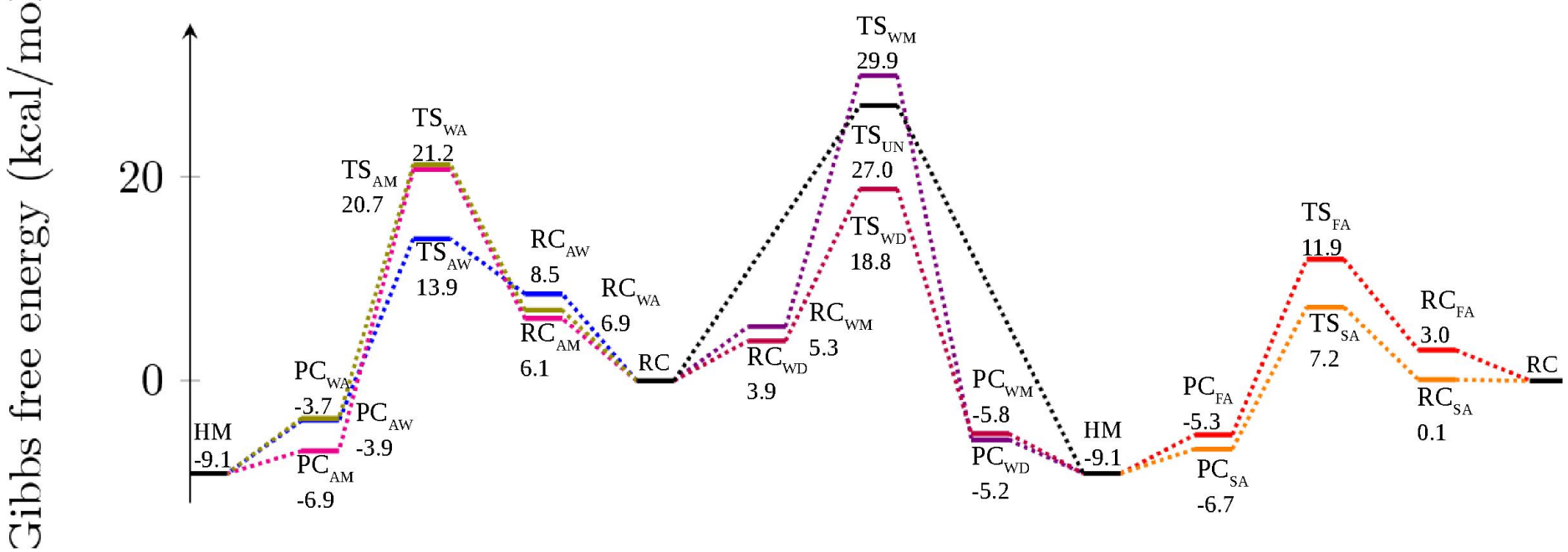


Figure S2: Gibbs free energy profile for isomerization of MR with different catalysts (black: uncatalyzed, magenta: AM, olive: WA, blue: AW, violet: WM, purple: WD, red: FA, orange: SA) calculated at the CCSD(T)/CBS//MP2/aug-cc-pVTZ level of theory

Table S1: Relative ZPE corrected energies (kcal mol^{-1}) of all species with respect to the isolated reactants calculated using two different levels of theory

catalyst	Species		
		MP2/aug-cc-pVTZ	CCSD(T)/CBS//MP2/aug-cc-pVTZ
None	MR	0.0	0.0
	TS	27.4	29.6
	HM	-13.9	-9.2
AM	RC_{AM}	-1.2	-2.2
	TS_{AM}	10.9	12.5
	PC_{AM}	-21.2	-16.3
AW	RC_{AW}	-3.0	-3.6
	TS_{AW}	2.0	1.5
	PC_{AW}	-22.9	-18.1
WA	RC_{WA}	-4.7	-5.0
	TS_{WA}	6.8	8.7
	PC_{WA}	-22.3	-17.5
WM	RC_{WM}	-5.1	-3.4
	TS_{WM}	19.7	21.6
	PC_{WM}	-20.8	-14.2
WD	RC_{WD}	-8.1	-7.1
	TS_{WD}	5.3	6.7
	PC_{WD}	-25.8	-18.7
FA	RC_{FA}	-8.5	-7.3
	TS_{FA}	3.8	2.4
	PC_{FA}	-24.1	-17.3
SA	RC_{SA}	-11.4	-10.3
	TS_{SA}	1.3	-1.3
	PC_{SA}	-25.5	-18.8

Table S2: Comparison with earlier investigations for relative ZPE corrected energies (kcal mol^{-1}) and rate constants (molecule^{-1} cm^3 s^{-1}) for isomerization of MR with different catalysts

Catalysts	Relative ZPE corrected energy (kcal mol^{-1})				Rate constants (molecule^{-1} cm^3 s^{-1})		
	Species	Buszek et al.[a,1]	Kumar et al.[b,2]	This work[c]	Buszek et al.[1]	Kumar et al.[2]	This work
none	MR	0.0	0.0	0.0	-	-	-
	TS	30.2	32.7	29.6			
	HM	-7.7	-8.7	-9.2			
WM	RC_{WM}	-2.0	-5.2	-3.4	1.23×10^{-26}	3.55×10^{-29}	1.4×10^{-28}
	TS_{WM}	25.7	22.9	21.6			
	PC_{WM}	-12.4	-15.4	-14.2			
FA	RC_{FA}	-6.3	-8.8	-7.3	4.19×10^{-16}	3.65×10^{-16}	8.6×10^{-16}
	TS_{FA}	4.2	4.4	2.4			
	PC_{FA}	-15.7	-18.9	-17.3			
SA	RC_{SA}	-9.2	-11.8	-10.3	9.12×10^{-14}	2.80×10^{-13}	5.9×10^{-13}
	TS_{SA}	2.3	1.8	-1.3			
	PC_{SA}	-17.2	-20.3	-18.8			
WD	RC_{WD}	-	-8.4	-7.1	-	2.82×10^{-21}	1.9×10^{-20}
	TS_{WD}	-	7.8	6.7			
	PC_{WD}	-	-20.5	-18.7			

[a] – Calculated at CCSD(T)/aug-cc-pVTZ//QCISD/6-31G(d) level
[b] - Calculated at CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level
[c] - Calculated at CCSD(T)/CBS//MP2/aug-cc-pVTZ level

Table S3: Calculated rate constants (molecule^{-1} cm^3 s^{-1}) in presence of all the catalysts using the results obtained from CCSD(T)/CBS//MP2/aug-cc-pVTZ level of theory

Catalyst	Rate Const.	Temperature (K)								
		213	230	259	280	290	298	300	310	320
WM	k_{eq}	5.8×10^{-22}	3.2×10^{-22}	1.5×10^{-22}	9.3×10^{-23}	7.7×10^{-23}	6.7×10^{-23}	6.5×10^{-23}	5.5×10^{-23}	4.8×10^{-23}
	k_{uni}	2.0×10^{-10}	1.2×10^{-9}	2.9×10^{-8}	2.0×10^{-7}	9.1×10^{-7}	2.1×10^{-6}	2.6×10^{-6}	7.3×10^{-6}	1.9×10^{-5}
	k_f	1.1×10^{-31}	3.9×10^{-31}	4.4×10^{-30}	2.9×10^{-29}	7.0×10^{-29}	1.4×10^{-28}	1.7×10^{-28}	4.0×10^{-28}	9.4×10^{-28}
WD	k_{eq}	1.6×10^{-19}	4.6×10^{-20}	8.2×10^{-21}	3.0×10^{-21}	2.0×10^{-21}	1.4×10^{-21}	1.3×10^{-21}	9.2×10^{-22}	6.5×10^{-22}
	k_{uni}	2.0×10^{-2}	8.9×10^{-2}	9.5×10^{-1}	4.3×10^{0}	8.3×10^{0}	1.4×10^{1}	1.5×10^{1}	2.8×10^{1}	4.8×10^{1}
	k_f	3.1×10^{-21}	4.1×10^{-21}	7.8×10^{-21}	1.3×10^{-20}	1.6×10^{-20}	1.9×10^{-20}	2.0×10^{-20}	2.5×10^{-20}	3.1×10^{-20}
FA	k_{eq}	3.0×10^{-19}	9.0×10^{-20}	1.7×10^{-20}	6.2×10^{-21}	4.1×10^{-21}	3.0×10^{-21}	2.8×10^{-21}	2.0×10^{-21}	1.4×10^{-21}
	k_{uni}	2.7×10^{4}	4.3×10^{4}	9.6×10^{4}	1.7×10^{5}	2.3×10^{5}	2.8×10^{5}	3.0×10^{5}	3.9×10^{5}	5.2×10^{5}
	k_f	8.2×10^{-15}	3.8×10^{-15}	1.6×10^{-15}	1.1×10^{-15}	9.4×10^{-16}	8.6×10^{-16}	8.4×10^{-16}	7.7×10^{-16}	7.2×10^{-16}
SA	k_{eq}	2.8×10^{-16}	5.0×10^{-17}	4.5×10^{-18}	1.1×10^{-18}	6.0×10^{-19}	3.8×10^{-19}	3.5×10^{-19}	2.1×10^{-19}	1.3×10^{-19}
	k_{uni}	2.3×10^{5}	3.3×10^{5}	6.3×10^{5}	1.0×10^{6}	1.3×10^{6}	1.5×10^{6}	1.6×10^{6}	2.0×10^{6}	2.5×10^{6}
	k_f	6.5×10^{-11}	1.7×10^{-11}	2.9×10^{-12}	1.1×10^{-12}	7.7×10^{-13}	5.9×10^{-13}	5.5×10^{-13}	4.1×10^{-13}	3.2×10^{-13}
AM	k_{eq}	3.5×10^{-23}	2.5×10^{-23}	1.7×10^{-23}	1.3×10^{-23}	1.2×10^{-23}	1.1×10^{-23}	1.1×10^{-23}	1.0×10^{-23}	9.4×10^{-24}
	k_{uni}	2.5×10^{-2}	1.2×10^{-1}	1.4×10^{0}	7.1×10^{0}	1.5×10^{1}	2.5×10^{1}	2.9×10^{1}	5.5×10^{1}	1.0×10^{2}
	k_f	8.8×10^{-25}	3.0×10^{-24}	2.3×10^{-23}	9.2×10^{-23}	1.7×10^{-22}	2.8×10^{-22}	3.1×10^{-22}	5.5×10^{-22}	9.5×10^{-22}
AW	k_{eq}	2.6×10^{-24}	1.4×10^{-24}	6.2×10^{-25}	3.9×10^{-25}	3.2×10^{-25}	2.8×10^{-25}	2.7×10^{-25}	2.3×10^{-25}	1.9×10^{-25}
	k_{uni}	2.4×10^{7}	3.6×10^{7}	6.7×10^{7}	1.0×10^{8}	1.2×10^{8}	1.4×10^{8}	1.4×10^{8}	1.7×10^{8}	2.0×10^{8}
	k_f	6.2×10^{-17}	5.0×10^{-17}	4.1×10^{-17}	3.9×10^{-17}	3.8×10^{-17}	3.8×10^{-17}	3.8×10^{-17}	3.8×10^{-17}	3.8×10^{-17}
WA	k_{eq}	1.2×10^{-22}	5.2×10^{-23}	1.6×10^{-23}	8.2×10^{-24}	6.2×10^{-24}	5.0×10^{-24}	4.8×10^{-24}	3.7×10^{-24}	3.0×10^{-24}
	k_{uni}	2.5×10^{-2}	1.2×10^{-1}	1.3×10^{0}	5.9×10^{0}	1.1×10^{1}	1.9×10^{1}	2.1×10^{1}	3.9×10^{1}	6.8×10^{1}
	k_f	3.0×10^{-24}	6.1×10^{-24}	2.1×10^{-23}	4.8×10^{-23}	7.1×10^{-23}	9.5×10^{-23}	1.0×10^{-22}	1.4×10^{-22}	2.0×10^{-22}

Table S4: Concentrations of all the catalysts (in molecule cm^{-3}) within 280K to 320K temperature range at 0 km altitude

catalyst			280	290	298	300	310	320
AM[a]	0.1 ppbv		2.6×10^{9}	2.5×10^{9}	2.5×10^{9}	2.4×10^{9}	2.4×10^{9}	2.3×10^{9}
	10 ppbv		2.6×10^{11}	2.5×10^{11}	2.5×10^{11}	2.4×10^{11}	2.4×10^{11}	2.3×10^{11}
	2900 ppbv		7.6×10^{13}	7.3×10^{13}	7.1×10^{13}	7.1×10^{13}	6.9×10^{13}	6.7×10^{13}
AD	0.1 ppbv		3.9×10^{-4}	3.4×10^{-4}	3.0×10^{-4}	2.9×10^{-4}	2.6×10^{-4}	2.3×10^{-4}
	10 ppbv		3.93	3.38	3.02	2.93	2.57	2.28
	2900 ppbv		3.3×10^{5}	2.8×10^{5}	2.5×10^{5}	2.5×10^{5}	2.2×10^{5}	1.9×10^{5}
AM-WA	20% RH	0.1 ppbv	2.4×10^{6}	3.3×10^{6}	4.2×10^{6}	4.4×10^{6}	5.8×10^{6}	7.3×10^{6}
		10 ppbv	2.4×10^{8}	3.3×10^{8}	4.2×10^{8}	4.4×10^{8}	5.8×10^{8}	7.3×10^{8}
		2900 ppbv	6.9×10^{10}	9.5×10^{10}	1.2×10^{11}	1.3×10^{11}	1.7×10^{11}	2.1×10^{11}
	100% RH	0.1 ppbv	1.2×10^{7}	1.6×10^{7}	2.1×10^{7}	2.2×10^{7}	2.9×10^{7}	3.6×10^{7}
		10 ppbv	1.2×10^{9}	1.6×10^{9}	2.1×10^{9}	2.2×10^{9}	2.9×10^{9}	3.6×10^{9}
		2900 ppbv	3.5×10^{11}	4.8×10^{11}	6.1×10^{11}	6.4×10^{11}	8.4×10^{11}	1.1×10^{12}
WM[b]	20% RH		5.2×10^{16}	9.6×10^{16}	1.5×10^{17}	1.7×10^{17}	2.9×10^{17}	4.1×10^{17}
	40% RH		1.0×10^{17}	1.9×10^{17}	3.1×10^{17}	3.4×10^{17}	5.8×10^{17}	9.4×10^{17}
	60% RH		1.5×10^{17}	2.9×10^{17}	4.5×10^{17}	5.1×10^{17}	8.8×10^{17}	1.4×10^{17}
	80% RH		2.1×10^{17}	3.8×10^{17}	6.2×10^{17}	6.9×10^{17}	1.2×10^{17}	1.9×10^{17}
	100% RH		2.6×10^{17}	4.8×10^{17}	7.7×10^{17}	8.6×10^{17}	1.5×10^{18}	2.3×10^{18}
WD[b]	20% RH		8.2×10^{12}	2.4×10^{13}	5.4×10^{13}	6.5×10^{13}	1.6×10^{14}	3.7×10^{14}
	40% RH		3.3×10^{13}	5.0×10^{13}	2.2×10^{14}	2.6×10^{14}	6.5×10^{14}	1.5×10^{15}
	60% RH		7.4×10^{13}	2.1×10^{14}	4.9×10^{14}	5.8×10^{14}	1.5×10^{15}	3.3×10^{15}

	80% RH	1.1×10^{14}	3.8×10^{14}	8.7×10^{14}	1.0×10^{15}	2.6×10^{15}	5.9×10^{15}
	100% RH	2.0×10^{14}	5.9×10^{14}	1.4×10^{15}	1.6×10^{15}	4.0×10^{15}	9.2×10^{15}
FA[c]	High	2.6×10^{11}	2.5×10^{11}	2.4×10^{11}	2.4×10^{11}	2.4×10^{11}	2.3×10^{11}
	Average	2.0×10^{10}	1.9×10^{10}	1.9×10^{10}	1.9×10^{10}	1.8×10^{10}	1.8×10^{10}
	Low	2.6×10^{8}	2.5×10^{8}	2.4×10^{8}	2.4×10^{8}	2.4×10^{8}	2.3×10^{8}
SA[d]		3.9×10^{8}	3.8×10^{8}	3.7×10^{8}	3.7×10^{8}	3.6×10^{8}	3.4×10^{8}

[a] – References 3-6, [b] - Reference 7, [c –] Reference 8, [d] - Reference 9

Table S5: Effective rate constants (s^{-1}) for all the catalysts within 280K to 320K temperature range at 0 km altitude using catalyst concentrations given in Table S4

Catalyst	Conc.		280	290	298	300	310	320
AM	0.1 ppbv		2.4×10^{-13}	4.3×10^{-13}	6.8×10^{-13}	7.6×10^{-13}	1.3×10^{-12}	2.2×10^{-12}
	10 ppbv		2.4×10^{-11}	4.3×10^{-11}	6.8×10^{-11}	7.6×10^{-11}	1.3×10^{-10}	2.2×10^{-10}
	2900 ppbv		7.0×10^{-9}	1.5×10^{-8}	2.0×10^{-8}	2.2×10^{-8}	3.8×10^{-8}	6.3×10^{-8}
AW	20% RH	0.1 ppbv	9.3×10^{-11}	1.3×10^{-10}	1.6×10^{-10}	1.7×10^{-10}	2.2×10^{-10}	2.8×10^{-10}
		10 ppbv	9.3×10^{-9}	1.3×10^{-8}	1.6×10^{-8}	1.7×10^{-8}	2.2×10^{-8}	2.8×10^{-8}
		2900 ppbv	2.7×10^{-6}	3.6×10^{-6}	4.6×10^{-6}	4.9×10^{-6}	6.3×10^{-6}	8.0×10^{-6}
	100% RH	0.1 ppbv	4.6×10^{-10}	6.2×10^{-10}	8.0×10^{-10}	8.3×10^{-10}	1.1×10^{-9}	1.4×10^{-9}
		10 ppbv	4.6×10^{-8}	6.2×10^{-8}	8.0×10^{-8}	8.3×10^{-8}	1.1×10^{-7}	1.4×10^{-7}
		2900 ppbv	1.3×10^{-5}	1.8×10^{-5}	2.3×10^{-5}	2.4×10^{-5}	3.2×10^{-5}	4.0×10^{-5}
WA	20% RH	0.1 ppbv	1.2×10^{-16}	2.3×10^{-16}	4.0×10^{-16}	4.5×10^{-16}	8.3×10^{-16}	1.5×10^{-15}
		10 ppbv	1.2×10^{-14}	2.3×10^{-14}	4.0×10^{-14}	4.5×10^{-14}	8.3×10^{-14}	1.5×10^{-13}
		2900 ppbv	3.4×10^{-12}	6.7×10^{-12}	1.2×10^{-11}	1.3×10^{-11}	2.4×10^{-11}	4.3×10^{-11}
	100% RH	0.1 ppbv	5.8×10^{-16}	1.2×10^{-15}	2.0×10^{-15}	2.2×10^{-15}	4.2×10^{-15}	7.3×10^{-15}
		10 ppbv	5.8×10^{-14}	1.2×10^{-13}	2.0×10^{-13}	2.2×10^{-13}	4.2×10^{-13}	7.3×10^{-13}
		2900 ppbv	1.7×10^{-11}	3.4×10^{-11}	5.8×10^{-11}	6.5×10^{-11}	1.2×10^{-10}	2.1×10^{-10}
WM	20% RH		1.5×10^{-12}	6.7×10^{-12}	2.2×10^{-11}	2.9×10^{-11}	1.2×10^{-10}	4.4×10^{-10}
	40% RH		2.9×10^{-12}	1.3×10^{-11}	4.4×10^{-11}	5.8×10^{-11}	2.4×10^{-10}	8.8×10^{-10}

	60% RH	4.4×10^{-12}	2.0×10^{-11}	6.6×10^{-11}	8.7×10^{-11}	3.5×10^{-10}	1.3×10^{-9}
	80% RH	5.9×10^{-12}	2.7×10^{-11}	8.8×10^{-11}	1.2×10^{-10}	4.7×10^{-10}	1.8×10^{-9}
	100% RH	7.4×10^{-12}	3.4×10^{-11}	1.1×10^{-10}	1.5×10^{-10}	5.9×10^{-10}	2.2×10^{-9}
WD	20% RH	1.0×10^{-7}	3.8×10^{-7}	1.1×10^{-6}	1.3×10^{-6}	4.1×10^{-6}	1.2×10^{-5}
	40% RH	4.2×10^{-7}	1.5×10^{-6}	4.2×10^{-6}	5.3×10^{-6}	1.6×10^{-5}	4.6×10^{-5}
	60% RH	9.4×10^{-7}	3.4×10^{-6}	9.5×10^{-6}	1.2×10^{-5}	3.7×10^{-5}	1.0×10^{-4}
	80% RH	1.7×10^{-6}	6.1×10^{-6}	1.7×10^{-5}	2.1×10^{-5}	6.6×10^{-5}	1.8×10^{-4}
	100% RH	2.6×10^{-6}	9.6×10^{-6}	2.6×10^{-5}	3.3×10^{-5}	1.0×10^{-4}	2.9×10^{-4}
FA	High	2.8×10^{-4}	2.4×10^{-4}	2.1×10^{-4}	2.0×10^{-4}	1.8×10^{-4}	1.7×10^{-4}
	Average	2.2×10^{-5}	1.8×10^{-5}	1.6×10^{-5}	1.6×10^{-5}	1.4×10^{-5}	1.3×10^{-5}
	Low	2.8×10^{-7}	2.4×10^{-7}	2.1×10^{-7}	2.0×10^{-7}	1.8×10^{-7}	1.7×10^{-7}
SA		4.4×10^{-4}	2.9×10^{-4}	2.2×10^{-4}	2.0×10^{-4}	1.5×10^{-4}	1.1×10^{-4}

Table S6: Concentrations of all the catalysts (in molecules cm^{-3}) at various altitudes in troposphere

Altitude	T (K)	[WM][a]	[WD][a]	[AM][b]	[FA][c]	[SA][d]	[AM-WM]	[AD]
0 km	298	5.2×10^{17}	1.2×10^{15}	2.5×10^{11}	9.0×10^{10}	3.7×10^{8}	1.4×10^{9}	3.0
5 km	259	2.4×10^{16}	2.7×10^{12}	7.6×10^{9}	2.0×10^{10}	6.0×10^{7}	6.1×10^{6}	4.0×10^{-3}
10 km	230	4.9×10^{15}	2.3×10^{11}	8.5×10^{8}	8.3×10^{9}	8.3×10^{6}	4.2×10^{5}	7.3×10^{-5}
15 km	213	2.0×10^{13}	6.3×10^{6}	1.2×10^{8}	3.2×10^{9}	2.4×10^{5}	5.4×10^{2}	2.1×10^{-6}

[a] – References 7, [b] - Reference 10-12, [c] – References 8 and 13, [d] - Reference 9

Table S7: Absolute energies (in Hartree) of all the species involved in isomerization of MR calculated at the two different levels of theory

species	MP2/aug-cc-pVTZ	CCSD(T)/CBS
MR	-114.843961	-114.9329091109
HM	-114.8663449	-114.9477820086
AM	-56.4605408	-56.5070882913
AW	-247.6665639	-132.8935606102
WA	-132.800219	-132.8935606102
RC_{AM}	-171.3097087	-171.4454992637
RC_{AW}	-247.6512591	-247.8344867717
RC_{WA}	-247.6542078	-247.8369630638
TS_{AM}	-171.2859485	-171.4190139263
TS_{AW}	-247.6403526	-247.8235052945
TS_{WA}	-247.6323819	-247.8115576052
PC_{AM}	-171.3416316	-171.4693385096
PC_{AW}	-247.6847519	-247.8593867851
PC_{WA}	-247.6833917	-247.8579747492
TS_{UN}	-114.7961329	-114.8815135913
MR_{WM}	-114.84396077	-191.3172899055
MR_{WD}	-267.52313693	-267.706694797
MR_{FA}	-304.34423196	-304.5431372354
MR_{SA}	-814.28172138	-814.5862214046
TS_{WM}	-191.14159052	-191.2738167808
TS_{WD}	-267.50181805	-267.6817676209
TS_{FA}	-304.32465040	-304.5229422871
TS_{SA}	-814.26141531	-814.5655541167
PC_{WM}	-191.20605728	-191.3344497798
PC_{WD}	-267.55128696	-267.7267359891
PC_{FA}	-304.36904354	-304.5601492518
PC_{SA}	-814.30415433	-814.6007811311
WM	-76.3289923	-76.273855
WD	-152.6662408	-152.7593796688
FA	-189.4867609	-189.5961416929
SA	-699.4195426	-699.6345763473

Table S8: Optimized geometries in Cartesian coordinates and normal mode frequencies of all species calculated at MP2/aug-cc-pVTZ level of theory

species	Cartesian coordinates (Å)	Vibrational frequencies (cm^{-1})
MR	C -0.59874900 0.00052600 -0.01031100 H -0.89909000 -0.02253500 1.05345300 H -1.01858000 -0.89641400 -0.48584000 H -1.02134100 0.91367500 -0.45062700 O 0.81643800 0.00026500 -0.00689000	802.3959 968.9223 1126.4632 1415.4273 1432.8024 1539.5064 3005.5778 3089.5649 3129.6565
HM	C -0.70158000 0.02971700 -0.05817000 H -1.15175500 0.99174500 0.16449900 H -1.23806100 -0.89751100 0.07297800 O 0.68071200 -0.12438400 0.02477600 H 1.15360200 0.72253900 -0.08666200	433.8851 625.6362 1067.2893 1212.8476 1367.7191 1509.1528 3192.5208 3342.2915 3856.8750
AM	N -0.00001400 0.00007100 -0.11240300 H -0.84258600 0.41732200 0.26235700 H 0.78299500 0.52062400 0.26232500 H 0.05969100 -0.93844300 0.26214100	1036.0525 1668.6736 1668.6867 3504.4346 3651.5437 3651.5633
AW	H 0.58269600 0.05011100 0.00042500 H 1.93463900 0.77175300 0.00077700 N -1.37625500 0.02230400 0.00005000 H -1.62860100 -0.72581900 -0.63421300 H -1.90280500 0.83915100 -0.28327200 H -1.71300800 -0.24354400 0.91720700 O 1.54510800 -0.10597300 -0.00016000	4.7812 168.1711 177.7748 200.3892 456.9858 716.7607 1092.4592 1658.6192 1668.1915 1674.9316 3499.6349 3589.2486 3643.4962 3646.4110 3907.6055
RC_{AM}	C 0.00000000 0.00000000 0.00000000 H 0.00000000 0.00000000 1.09146952 H 1.00863027 0.00000000 -0.41649407 H -0.49932722 -0.92421199 -0.32406502 O -0.78026993 1.01641757 -0.51060446 N -2.06635909 1.19518922 2.39761862 H -3.00372238 0.85895228 2.57958338 H -2.00488224 1.37943939 1.40178320 H -1.98517634 2.08766659 2.86855849	74.0668 94.9091 108.9057 127.4480 149.3097 297.7341 841.3514 984.6935 1064.6198 1124.1518 1415.3202 1436.0154 1534.3633 1668.0309 1681.7070 3001.1754 3090.0892 3140.1627 3486.6382 3625.4488 3645.1634
RC_{AW}	C -1.46032000 0.70493100 0.21829300 H -0.39621900 1.13683600 0.02686400 H -1.53364700 0.70435400 1.31883100 H -2.20433400 1.37343800 -0.23518700 O -1.44489400 -0.56583900 -0.33178800 H 0.02678500 -1.37210600 0.11229000 H 1.29664100 -2.27201400 -0.32325400 N 1.42620000 1.28270200 -0.10185700 H 1.51603000 0.26042400 -0.00615900 H 1.83379200 1.80939300 0.66160000 H 1.69334200 1.64107700 -1.01113700 O 1.01316000 -1.49539900 0.18921200	54.3477 68.6120 120.2669 135.8432 145.0236 156.6947 170.5438 194.0915 223.5393 326.4424 436.6685 560.0862 853.5860 1047.7925 1100.8739 1176.5777 1402.0588 1452.0732 1530.2055 1648.3295 1667.4499 1686.2512 2935.2712 3070.6771 3142.0326 3469.1263 3606.5952 3642.1044 3662.0016 3906.9182
RC_{WA}	C -1.69913000 0.39034400 0.18411600 H -0.78482000 1.01454500 -0.04443000 H -1.81466900 0.44629200 1.27872500 H -2.57178200 0.81240400 -0.32957300 O -1.37879200 -0.90524000 -0.24456100 N 1.53622100 -1.12846400 0.09894300 H 1.98551800 -1.49194300 -0.73593200 H 0.53397000 -1.34072800 0.10969400 H 2.00614400 -1.45034500 0.93912500 H 1.37769600 0.56361300 -0.06078500 H 1.44725200 2.11924700 0.46229400 O 1.03653300 1.51575200 -0.18249100	38.7278 64.1137 95.5402 119.7940 129.5074 157.3975 169.4277 217.4698 227.8059 323.4649 526.4521 782.3047 847.4327 1034.2728 1119.4468 1152.4705 1402.2883 1444.3974 1535.3598 1650.9933 1683.7676 1684.6593 2973.3563 3078.8086 3134.1066 3462.6511 3487.2566 3610.6934 3645.6337 3901.8388
TS_{AM}	C 0.00000000 0.00000000 0.00000000 H 0.00000000 0.00000000 1.36761860 H 1.08383730 0.00000000 -0.20712771 H -0.48373352 -0.96989958 -0.20712771 O -0.66831085 1.08013718 -0.11532866	-1142.1444 103.8584 205.3250 245.9356 461.1817 493.4786 590.3468 1114.9543 1153.1441 1212.0966 1287.8103 1317.2587

	N -0.33321728 0.53855234 2.60417051 H -0.97436006 0.00123915 3.17486044 H -0.82069646 1.32642581 2.18062230 H 0.43376322 0.87248411 3.17486044	1499.9369 1584.4674 1659.8105 1661.3455 2922.0367 2991.4996 3450.5275 3604.7015 3651.1594
TS_{AW}	C -1.51595700 0.14518300 0.34404500 H -0.34368600 1.11500300 0.17613800 H -1.39908600 -0.04312600 1.42285000 H -2.42728800 0.69328700 0.07510300 O -1.06520100 -0.74151900 -0.49135700 H 0.38909200 -1.17163100 -0.06935200 H 1.80468100 -1.90132200 -0.11354900 N 0.77895400 1.51073500 -0.10146100 H 1.32741700 0.63072400 -0.05021100 H 1.13111400 2.20808500 0.54289200 H 0.78468200 1.87167400 -1.04879000 O 1.36221800 -1.11459800 0.20521700	-1128.6348 74.7148 136.5373 167.4760 185.9102 209.8887 267.8842 308.1244 463.7405 490.7352 607.5625 614.3086 793.2418 1105.9255 1170.1750 1212.2251 1306.7469 1311.3303 1439.3966 1555.9201 1649.0112 1669.4377 1683.8921 2963.2236 3058.2403 3360.8936 3414.2150 3585.1414 3652.9300 3902.8916
TS_{WA}	C 0.00000000 0.00000000 0.00000000 H 0.00000000 0.00000000 1.35691221 H 1.08614384 0.00000000 -0.18709088 H -0.47265126 -0.98502981 -0.14663847 O -0.67181580 1.06087367 -0.23948774 N -1.98868130 1.95207021 2.04172885 H -2.96421623 1.72032445 2.18031858 H -1.75019697 1.79511290 1.05158053 H -1.87835304 2.93790241 2.24270223 H -0.92724419 0.93455901 2.57632520 H 0.58018497 0.55832106 3.04294259 O -0.21349479 0.17192117 2.65134505	-1056.5016 48.1835 177.9252 217.9275 262.8361 318.3402 345.8346 403.5939 528.0945 535.2544 594.3111 695.1827 1065.0838 1144.3645 1205.4556 1217.3169 1267.3987 1388.0945 1505.0835 1577.6927 1643.2944 1686.7201 1710.0323 2359.9414 2934.9067 3013.6348 3275.2467 3568.4586 3646.5412 3826.7487
PC_{AM}	C 0.00000000 0.00000000 0.00000000 H 0.00000000 0.00000000 3.74485999 H 0.11463529 0.00000000 -1.07044288 H -0.88285408 -0.42406954 0.45748514 O 0.63921983 1.01074028 0.63834545 N -0.13247687 0.92441115 3.35288803 H -1.09754108 1.18259228 3.51850100 H 0.37588857 0.99433744 1.58491507 H 0.44042356 1.55971313 3.89515127	33.0481 91.9831 161.6703 222.8421 295.4226 325.2906 579.8902 897.4853 1113.0448 1136.9760 1244.3082 1495.0207 1511.2722 1668.2273 1668.4252 3170.9216 3318.0219 3427.4725 3499.8740 3641.4292 3643.1923
PC_{AW}	C 1.56121300 -0.75357700 0.34360600 H -0.71211500 -1.35689200 -0.03282100 H 1.26085700 -0.64257500 1.38601900 H 2.36826400 -1.43209500 0.09276800 O 1.45436600 0.33116000 -0.49386500 H 0.68548500 0.93798300 -0.22163200 H -1.20825400 2.24633200 0.01074400 N -1.67954500 -1.02735700 -0.12301000 H -1.31200700 0.57450500 0.10425400 H -2.27914400 -1.41909700 0.59694300 H -2.04665400 -1.21300100 -1.05176400 O -0.75022800 1.42106500 0.23323100	60.2705 98.3891 109.5448 117.5278 228.4804 237.8190 247.8494 263.3083 291.5676 357.3674 554.1692 685.1896 765.1669 952.2063 1134.4084 1137.9767 1245.1464 1477.8297 1508.7858 1643.1938 1672.2327 1681.0888 3168.6347 3313.3881 3362.5241 3467.7440 3508.6145 3603.3403 3643.0155 3896.3783
PC_{WA}	C 1.57303700 -0.46528600 0.32514200 H -0.21528700 -1.44653300 0.04381400 H 1.28149800 -0.44934400 1.37881000 H 2.48260100 -0.98919600 0.05152400 O 1.28573000 0.62200400 -0.45535100 N -1.16504800 1.35322900 0.13867000 H -1.56374100 1.91103200 -0.61091000 H 0.37721500 1.06316500 -0.18778000 H -1.34180900 1.78272000 1.04175300 H -1.47686000 0.37046000 0.10323200 H -1.45132500 -2.01604500 -0.81574400 O -1.20762700 -1.48539700 -0.03543000	77.6659 88.7860 119.5142 146.1343 157.9226 171.1920 248.9685 263.9658 334.0151 353.6542 457.5602 514.5687 748.8079 996.5571 1140.9368 1151.0499 1261.3526 1506.4770 1529.4779 1639.5308 1665.0784 1684.7545 3140.7383 3225.1209 3296.7395 3466.8170 3605.8664 3646.2227 3662.2869 3900.9854

TS	C -0.62808200 0.00000100 0.00676700 H -1.15105300 0.93424600 -0.17166900 H -1.15105200 -0.93423400 -0.17172800 O 0.74219000 0.00000400 -0.08415100 H 0.13307500 -0.00005100 0.97600400	-2108.1221 844.6455 1031.7460 1149.5383 1191.3855 1502.6439 2602.6083 3112.3675 3229.7230
MR_{WM}	C -1.30475900 -0.49602600 -0.01136000 H -0.60397000 -1.18715700 -0.48279900 H -2.30556400 -0.56428800 -0.43841000 H -1.36523700 -0.77137600 1.05099900 O -0.82477600 0.79838800 -0.00810000 H 1.11902900 0.40769400 0.01747500 H 2.64645100 0.35504600 -0.00353100 O 1.86700600 -0.20635900 -0.00134600	69.9095 96.5984 113.9642 179.4596 350.2688 437.0240 935.9952 1025.5283 1123.5392 1411.2713 1435.1920 1535.8440 1642.0936 3004.8808 3097.0467 3149.0056 3727.8958 3915.5858
MR_{WD}	C 1.62468400 -0.64678000 0.27844000 H 0.80434100 -1.28659500 -0.08065300 H 1.42984000 -0.49034800 1.34255700 H 2.58459400 -1.13286400 0.10832200 O 1.49561300 0.53531000 -0.41963900 H -1.42329200 2.15335800 -0.32818000 H -0.16305400 1.33676600 -0.00879600 H -1.59719600 -0.35578100 -0.01384200 H -2.36514400 -1.67758200 0.12026400 O -1.09899600 1.44528700 0.23506200 O -1.52389100 -1.31388100 -0.16671200	49.1017 65.6727 66.6667 120.7245 155.1269 197.3499 199.9369 211.0277 357.2039 397.2183 574.0497 656.6707 843.5776 1042.3798 1178.9727 1394.6224 1455.0533 1529.9077 1646.3266 1665.9121 2986.3907 3081.9598 3148.8682 3617.9921 3659.8581 3900.1893 3909.3785
MR_{FA}	C -2.05269900 0.52499300 0.07621500 H -1.30612500 1.25913100 -0.22875500 H -2.15141700 0.60648800 1.16871800 H -3.03159600 0.69421200 -0.37085500 O -1.60489300 -0.76489500 -0.13457200 C 1.72230500 0.11520900 0.02060800 O 1.15345900 -1.08901600 0.05926100 H 0.17689100 -0.96995600 -0.01075400 O 1.13705800 1.17197700 -0.07866200 H 2.80961600 0.02439000 0.09249400	40.3170 86.4580 125.6243 155.2585 180.6970 209.6524 672.2190 807.7323 937.8172 1042.9286 1079.5520 1142.6640 1202.5510 1375.1448 1410.0677 1430.1417 1441.4301 1525.8871 1771.4689 2998.9995 3100.0066 3109.3138 3161.6177 3426.1857
MR_{SA}	C -2.91502300 0.49635900 0.01189800 H -2.52273500 1.06814700 -0.83034600 H -2.49442500 0.96503200 0.91326800 H -4.00203600 0.51053800 0.06450500 O -2.41519000 -0.79099600 0.02324600 O 0.13133800 -0.98998600 -0.78600400 H -0.81361200 -0.94252500 -0.47222100 O 0.07653000 1.25209200 0.22819100 S 0.95185200 0.14922700 -0.07178100 O 1.28321800 -0.50293900 1.35704400 H 2.05436500 -1.07981500 1.24132900 O 2.17897200 0.29593300 -0.80240500	21.7927 47.5046 105.8865 108.4937 137.4555 224.7016 267.1392 376.4545 424.1798 507.4708 536.6131 546.5106 767.1543 827.4224 903.2702 911.0901 1035.7410 1151.8127 1162.4900 1212.7792 1324.3341 1391.2265 1437.2317 1456.8997 1528.8446 3002.8137 3100.7217 3168.1656 3229.8462 3767.1996
TS_{WM}	C 1.00642200 -0.51599700 0.00883500 H -0.36302600 -0.76968100 0.01503500 H 1.34091800 -1.02690800 0.92363700 H 1.27316300 -1.03372300 -0.92503400 O 0.82880100 0.74863600 0.01074700 H -0.86044600 0.68366500 -0.08740400 H -1.98731900 -0.05773800 0.73927800 O -1.50902800 -0.08609000 -0.10056300	-1381.2761 188.7210 373.6247 402.1024 553.3765 617.1818 821.9900 1138.1143 1197.4839 1211.1802 1375.3100 1519.3544 1597.7765 1713.9734 2960.7275 3041.2434 3088.2784 3817.0573
TS_{WD}	C -1.55256500 0.22596700 0.17721600 H -0.47499800 1.00329200 -0.01628900 H -1.63239200 0.40005800 1.26337600 H -2.31945700 0.73810200 -0.41813800 O -1.09268400 -0.89316700 -0.24163100 H 1.88993200 -1.54072100 -0.45468700 H 0.46406800 -1.17192500 0.08211700 H 1.24485300 0.56314400 -0.08966300	-1075.7766 71.2262 186.2543 314.6233 318.9303 349.1730 387.4418 470.8772 539.1420 582.0361 599.9233 907.2542 1072.7153 1136.1818 1198.7408 1241.9055 1352.1661 1508.8484 1586.5513 1647.0529 1694.1074 2876.3894 2947.9467 3052.1656

	H 1.06023700 2.00315000 0.55113300 O 1.44432800 -0.98474900 0.19103900 O 0.78374900 1.45905400 -0.19705200	3101.5656 3831.9969 3884.0190
TS_{FA}	C -1.68623300 0.46958300 0.22640100 H -0.55892700 0.99039400 -0.05668200 H -1.53230700 0.57599400 1.31217500 H -2.49543300 1.07422600 -0.18414200 O -1.45604300 -0.68345600 -0.30857500 C 1.49574500 0.08099600 0.00845300 O 0.95889600 -1.09191700 0.15079800 H -0.07725600 -1.04247300 0.01964900 O 0.89980400 1.15480600 -0.16203400 H 2.58559800 0.06291800 0.05836600	-1581.0941 111.5960 228.2984 261.0540 389.4417 415.6065 544.6929 760.9463 1013.5993 1067.4046 1162.5465 1198.6602 1242.5259 1294.9177 1317.4490 1406.1732 1476.9912 1541.1681 1595.5030 1743.4637 2359.8199 2975.1113 3133.1158 3138.3702
TS_{SA}	C -2.45064700 0.56566800 -0.02088900 H -1.45748400 0.75811700 -0.73397900 H -2.05096700 1.18477600 0.79683400 H -3.35894800 0.92801800 -0.49388500 O -2.32441800 -0.72309200 0.09701700 O -0.00858200 -1.07553100 0.62329800 H -1.13567300 -0.95267400 0.45368800 O 0.03647100 0.65050800 -1.12804800 S 0.84493900 -0.05219800 -0.12073200 O 2.11018500 -0.61056500 -0.50457000 O 1.10443900 1.09809900 0.97502000 H 1.84317100 0.80757000 1.53265400	-1703.5797 35.0188 114.6252 211.4644 219.0340 337.9861 378.8078 409.2606 452.8162 479.6697 548.1197 562.8545 675.8058 818.4387 900.9640 1002.4573 1074.7410 1151.5177 1196.6273 1220.2323 1253.6144 1324.6264 1365.2764 1403.8972 1519.7100 1602.4591 1743.6568 2993.2428 3186.3530 3765.2460
PC_{WM}	C -1.59415400 0.45307600 0.04992900 H -2.64766700 0.26233200 -0.05784000 H -1.16483300 1.39388500 -0.26039500 O -0.81717200 -0.66197900 0.00115000 H 2.47549200 -0.24985900 -0.63922700 H 0.11494800 -0.38947000 -0.01261100 H 2.32438100 0.13715500 0.82899200 O 1.87499800 0.17791600 -0.02096100	64.1035 80.9239 154.5240 185.1505 236.9218 288.9752 584.6835 774.3066 1116.4078 1233.4945 1436.2419 1508.4694 1629.4883 3183.9586 3330.1810 3666.6407 3813.7576 3935.3650
PC_{WD}	C 1.57705900 -0.50874000 0.41031800 H -0.42010300 -1.41399300 -0.12484000 H 1.20837100 -0.31400300 1.40934700 H 2.47485900 -1.08806700 0.26955800 O 1.37197700 0.43312500 -0.53918500 H -1.58365000 2.01796500 -0.26057200 H 0.58319300 0.95783100 -0.28814900 H -1.44393400 0.52445100 0.10630300 H -1.76365800 -1.97822200 0.34870600 O -1.05563400 1.40641200 0.26007200 O -1.38102300 -1.29622700 -0.21117000	78.4354 105.7851 142.1018 200.4226 216.0428 228.7773 274.0925 281.0657 320.8114 398.4614 550.5696 699.1170 760.9075 899.9195 1140.4513 1251.0869 1478.5869 1510.4094 1632.4822 1651.6078 3159.2826 3306.6386 3489.5276 3602.5402 3669.1636 3894.8141 3898.1470
PC_{FA}	C -1.80071700 0.52367500 0.35427600 H 0.15726000 1.11478300 -0.12074100 H -1.42981500 0.44454200 1.36936100 H -2.66444500 1.13247800 0.14467300 O -1.67689400 -0.55392400 -0.45510700 C 1.60816700 -0.09698200 0.00879100 O 0.94522100 -1.08890300 0.24342900 H -0.86378900 -1.02434400 -0.19047500 O 1.13891400 1.12750100 -0.20431400 H 2.69816500 -0.10500200 -0.05328400	92.1393 132.5318 158.0052 177.8394 210.0715 335.1436 671.4281 745.0239 801.0968 830.7942 1075.8084 1116.4975 1198.0583 1248.4473 1359.6488 1420.7062 1439.6606 1509.5197 1756.5087 3132.0642 3152.8849 3308.5377 3430.4857 3603.3954
PC_{SA}	C 2.51087500 0.68096200 0.05019800 H 0.79598300 0.57627600 1.02245500 H 2.00434500 1.18830400 -0.76302600 H 3.31553100 1.17262700 0.57240000 O 2.65419900 -0.66088600 -0.02898800	39.5454 92.0279 133.9790 157.3991 193.4639 273.6392 339.8196 382.3827 424.2778 503.4366 536.7415 547.1142 657.9004 732.0890 831.6837

	O -0.00815200 -0.88037600 -0.87131600 H 1.89834900 -1.01135400 -0.52986700 O -0.13946700 0.34517800 1.27339300 S -0.90767100 -0.14699700 -0.01339500 O -1.17521900 1.21807300 -0.80726200 H -1.95173400 1.64346200 -0.40954500 O -2.15698500 -0.68488000 0.43676200	851.1883 901.8792 1106.0538 1161.4534 1207.9206 1254.4039 1271.2194 1407.9641 1454.8035 1508.6361 3147.9997 3237.1761 3304.7289 3686.2906 3759.2855
WM	H 0.00000000 -0.75816200 0.47292300 H 0.00000000 0.75816200 0.47292300 O 0.00000000 0.00000000 -0.11823100	1628.4005 3821.6010 3947.4441
WD	H 1.74591300 -0.76713300 0.34149800 H 1.74787800 0.75456700 0.36668600 H -0.55933700 0.00122200 -0.04931800 H -1.91356400 0.01432900 -0.75056500 O 1.38502100 0.00190000 -0.11053300 O -1.51263200 -0.00227300 0.12199500	126.0108 146.5765 155.1927 184.4065 360.5296 630.2755 1629.4157 1650.2010 3718.8151 3814.0244 3915.2013 3935.2878
FA	C 0.00000000 0.42239200 0.00000000 H -0.37677400 1.44769500 0.00000000 O 1.16341800 0.10815400 0.00000000 O -1.03499400 -0.43952800 0.00000000 H -0.65061600 -1.33105500 0.00000000	625.9522 674.7722 1058.5575 1130.1310 1301.3232 1408.9059 1794.0380 3125.3065 3741.3578
SA	H 1.68390300 -0.01480300 1.10770300 O 0.65948600 1.08434700 -0.82706100 O 1.03476900 -0.68787400 0.84848100 S 0.00005800 0.00006400 -0.15924300 O -1.03529300 0.68717400 0.84851600 H -1.68450600 0.01382500 1.10679800 O -0.65900400 -1.08365300 -0.82826200	242.8958 328.1320 367.2603 431.4837 485.9993 531.5543 542.2237 821.4432 873.6608 1155.1241 1170.0433 1219.2879 1469.2375 3760.6034 3764.8107

References:

1. Buszek, R. J.; Sinha, A.; Francisco, J. S. The isomerization of methoxy radical: intramolecular hydrogen atom transfer mediated through acid catalysis. J. Am. Chem. Soc. 2011, 133, 2013–2015.

2. Kumar, P.; Biswas, P.; Bandyopadhyay, B. Isomerization of the methoxy radical revisited: the impact of water dimers. Phys. Chem. Chem. Phys. 2016, 18, 27728–27732.

3. Atmospheric Chemistry and Global Change, ed. Brasseur, G. P.; Orlando, J. J.; Tyndall, G. S. Oxford University Press, 1999.

4. Aneja, V. P.; Nelson, D. R.; Roelle, P. A.; Walker, J. T.; Battye, W. Agricultural ammonia emissions and ammonium concentrations associated with aerosols and precipitation in the southeast United States. J. Geophys. Res. 2003, 108 .

5. Warner, J.; Wei, Z.; Strow, L.; Dickerson, R.; Nowak, J. The global tropospheric ammonia distribution as seen in the 13 year AIRS measurement record. Atmos. Chem. Phys Discuss. 2015, 15 .

6. Hiranuma, N.; Brooks, S. D.; Thornton, D. C.; Auvermann, B. W. Atmospheric ammonia mixing ratios at an open-air cattle feeding facility. J. Air Waste Manage. Assoc. 2010, 60, 210–218.

7. J. M. Anglada, G. J. Hoffman, L. V. Slipchenko, M. M. Costa, M. F. Ruiz-López and J. S. Francisco, J. Phys. Chem. A, 2013, 117, 10381.

8. Razavi, A.; Karagulian, F.; Clarisse, L.; Hurtmans, D.; Coheur, P.-F.; Cler-baux, C.; Müller, J.-F.; Stavrakou, T. Atmos. Chem. Phys. 2011, 11, 857–872.

9. R. P. Turco, P. Hamill, O. B. Toon, R. C. Whitten and C. S. Kiang, J. Atmos. Sci., 1979, 36, 699.

10. Nowak, J. B.; Neuman, J. A.; Bahreini, R.; Brock, C. A.; Middlebrook, A. M.; Wollny, A. G.; Holloway, J. S.; Peischl, J.; Ryerson, T. B.; Fehsenfeld, F. C. J. Geophys. Res., 2010, 115.

11. Oelhaf, H.; Leupolt, A.; Fischer, H. Appl. Opt., 1983, 22, 647.

12. Höpfner, M.; Volkamer, R.; Grabowski, U.; Orphal, M. G. J.; Stiller, G.; von Clarmann, T.; Wetzel, G. Atmos. Chem. Phys. Discuss., 2016, 16, 14357.

13. M. W. Shephard, A. Goldman, S. A. Clough and E. J. Mlawer, J. Quant. Spectrosc. Radiat. Transfer., 2003, 82, 383-390.