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

Supporting Information

Water-assisted absorption of CO_2 by 3-Amino-1-propanol: A mechanistic insight

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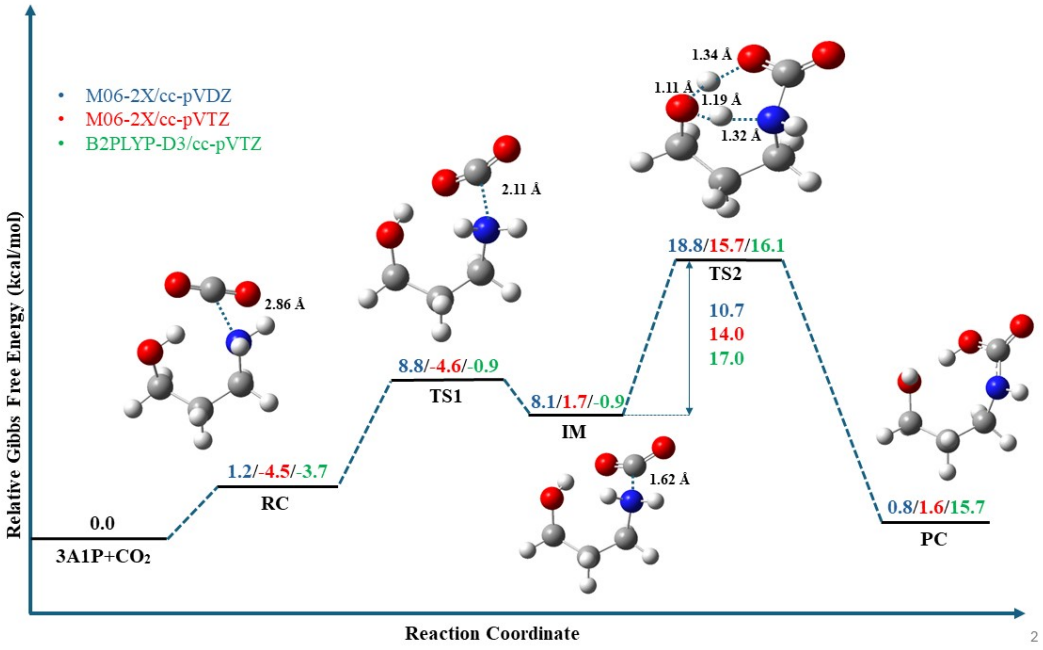


Figure S1: The mechanism and the energy profile diagram for the CO_2 absorption using 3-amino-1-propanol involving two proton transfer in the absence of water molecules at different levels. The optimized geometries obtained at M06-2X/cc-pVDZ are used for the single point energy calculations at M06-2X/cc-pVTZ and B2PLYP-D3/cc-pVTZ levels.

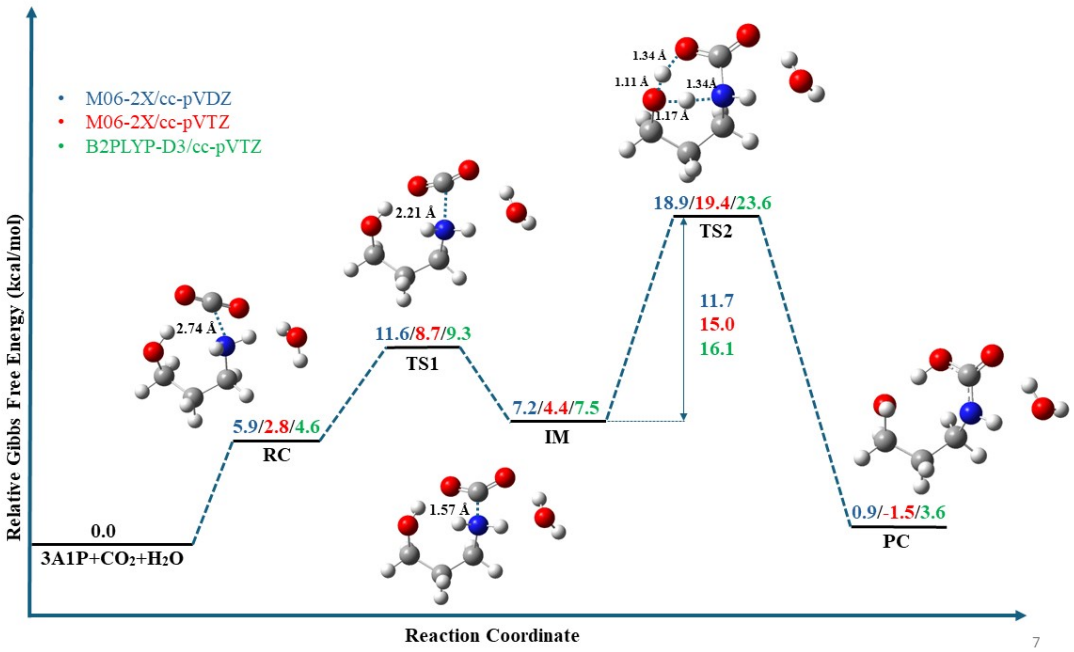


Figure S2: The mechanism and the energy profile diagram for the CO_2 absorption using 3-amino-1-propanol in the presence one water molecule where no water molecule is participating in the proton transfer. The optimized geometries obtained at M06-2X/cc-pVDZ are used for the single point energy calculations at M06-2X/cc-pVTZ and B2PLYP-D3/cc-pVTZ levels.

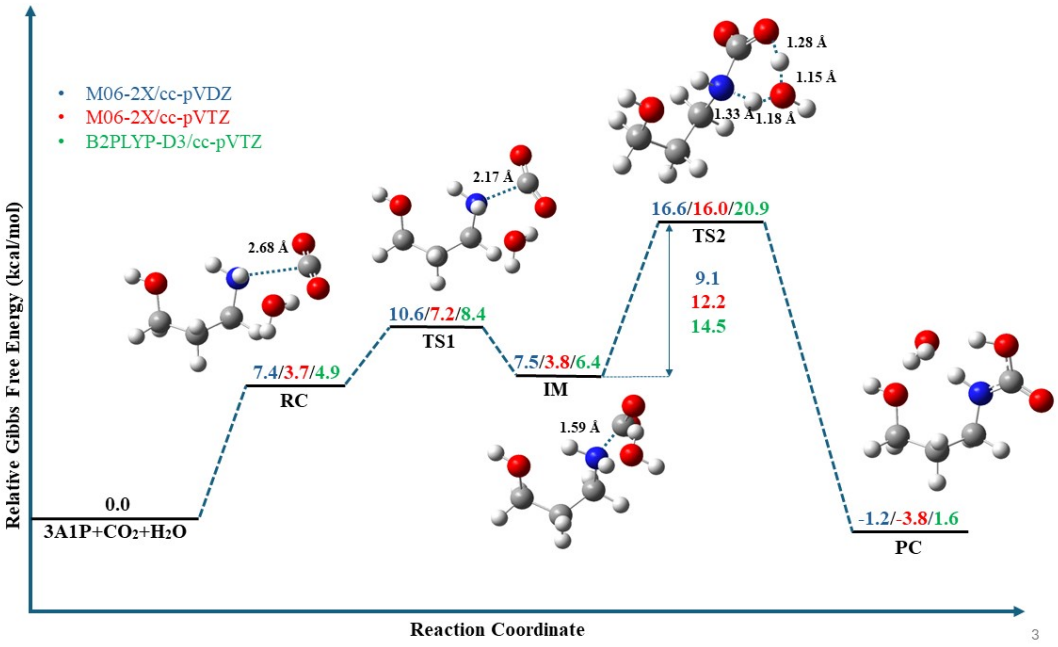


Figure S3: The mechanism and the energy profile diagram for the CO_2 absorption using 3-amino-1-propanol involving two proton transfer in the presence of one water molecule. The optimized geometries obtained at M06-2X/cc-pVDZ are used for the single point energy calculations at M06-2X/cc-pVTZ and B2PLYP-D3/cc-pVTZ levels.

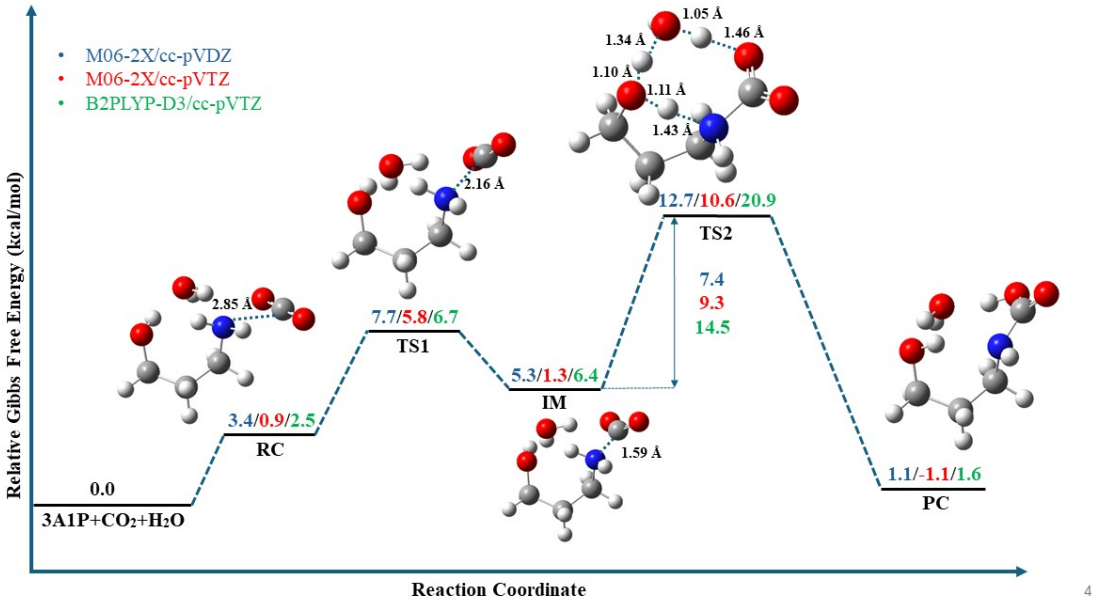


Figure S4: The mechanism and the energy profile diagram for the CO_2 absorption using 3-amino-1-propanol involving three proton transfer in the presence of one water molecule. The optimized geometries obtained at M06-2X/cc-pVDZ are used for the single point energy calculations at M06-2X/cc-pVTZ and B2PLYP-D3/cc-pVTZ levels

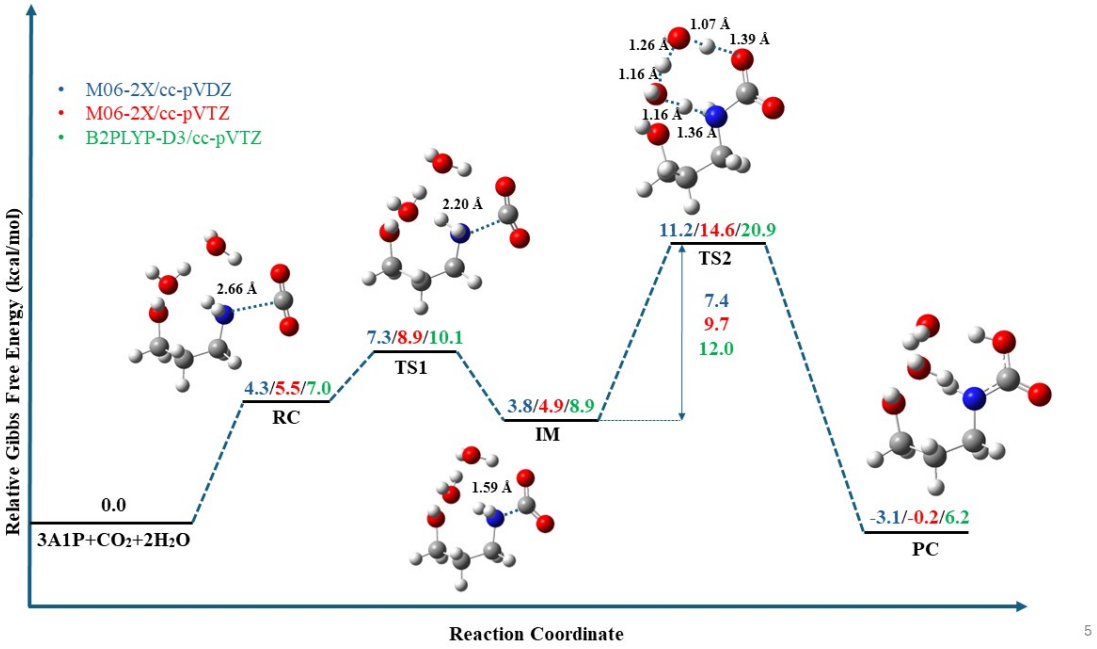
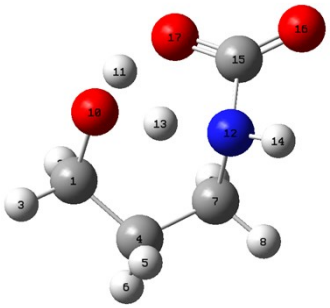
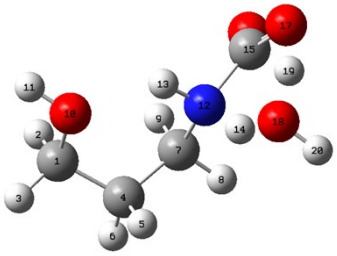
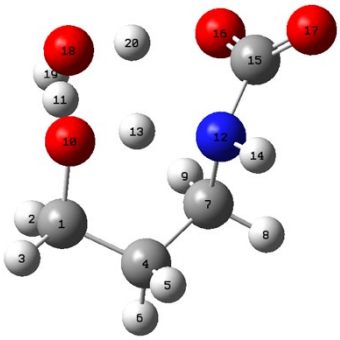
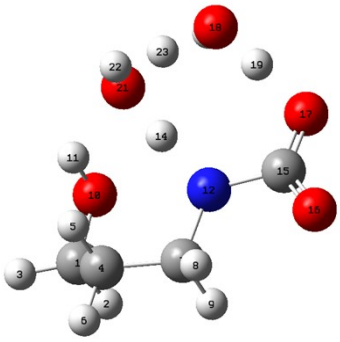


Figure S5: The mechanism and the energy profile diagram for the CO_2 absorption using 3-amino-1-propanol involving three proton transfer in the presence of two water molecules. The optimized geometries obtained at M06-2X/cc-pVDZ are used for the single point energy calculations at M06-2X/cc-pVTZ and B2PLYP-D3/cc-pVTZ levels.

Table S1: Natural bond orbital analysis of the transition states involving the proton transfer

Case	Transition state involving proton transfer	NBO Donor	NBO Acceptor	$\Delta E^{(2)}_{ij}$ (kcal/ mol)	Inference
(i)		LP (N_{12})	σ* ($O_{10}H_{13}$)	139	Leads to large internuclear distance for $O_{10}H_{13}$ indicating less favorable transfer of H_{13} from N_{12}
		LP (O_{17})	σ*(O_{10} H_{11})	123	Leads to the elongation of $O_{10}H_{11}$ bond, indicating favorable transfer of H_{11} towards O_{17}
(ii)		LP (N_{12})	σ* ($O_{18}H_{14}$)	137	Leads to large internuclear distance for $O_{18}H_{14}$ indicating less favorable transfer of H_{14} from N_{12}
		LP (O_{17})	σ* ($O_{18}H_{19}$)	144	Leads to the elongation of $O_{18}H_{19}$ bond, indicating favorable transfer of H_{19} towards O_{17}

(iii)		LP (N_{12})	σ* ($O_{10}H_{13}$)	98	Leads to large internuclear distance for $O_{10}H_{13}$ indicating less favorable transfer of H_{13} from N_{12}
		LP (O_{16})	σ* ($O_{18}H_{20}$)	83	Leads to the elongation of $O_{18}H_{20}$ bond, indicating favorable transfer of H_{20} towards O_{16}
		LP (O_{18})	σ* ($O_{10}H_{11}$)	109	Leads to the elongation of $O_{10}H_{11}$ bond, indicating favorable transfer of H_{11} towards O_{18}

(iv)		LP (N_{12})	σ* ($O_{21}H_{14}$)	125	Leads to large internuclear distance for $O_{21}H_{14}$ indicating non favorable transfer of H_{14} from N_{12}
		LP (O_{17})	σ* ($O_{18}H_{19}$)	103	Leads to the elongation of $O_{18}H_{19}$ bond, indicating favorable transfer of H_{19} towards O_{17}
		LP (O_{18})	σ* ($O_{21}H_{23}$)	145	Leads to the elongation of $O_{21}H_{23}$ bond, indicating favorable transfer of H_{23} towards O_{18}
		σ*($O_{21}H_{14}$)	σ* ($O_{21}H_{23}$)	13	Leads to small internuclear distance for $O_{21}H_{14}$ and $O_{21}H_{23}$ bond elongation, indicating favorable transfer of H_{14} towards O_{21} and favorable transfer of H_{23} from O_{21}
		σ ($O_{18}H_{19}$)	σ* ($O_{21}H_{23}$)	14	Leads to the elongation of $O_{18}H_{19}$ and $O_{21}H_{23}$ bonds indicating favorable transfer of H_{19} from O_{18} and H_{23} from O_{21}

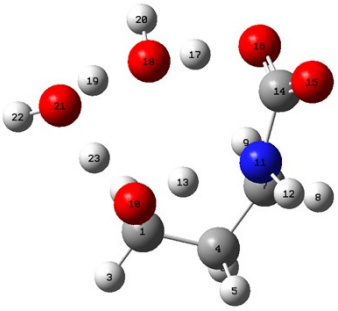
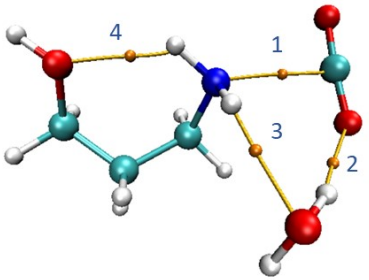
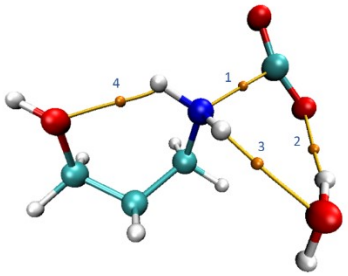
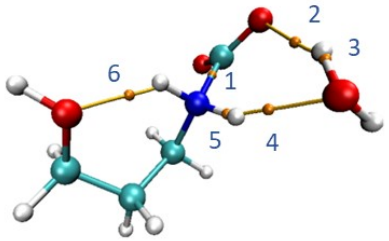
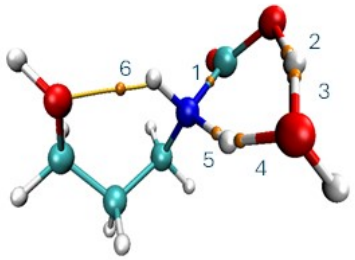
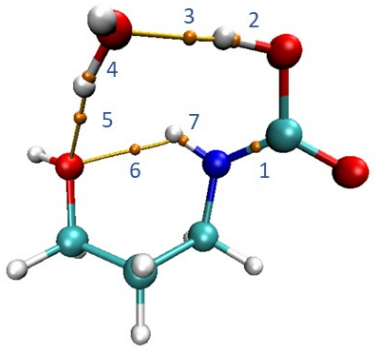
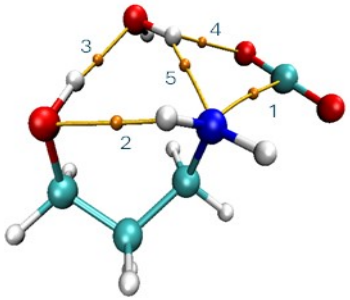
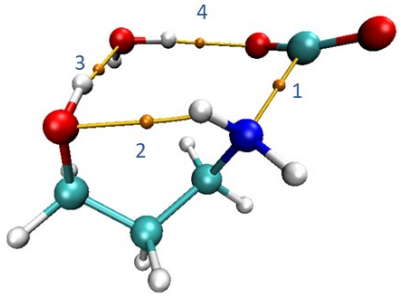
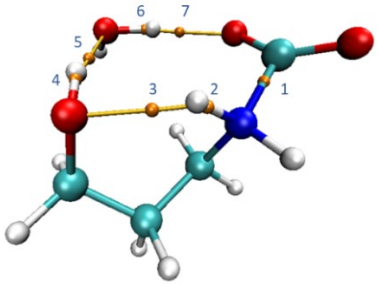
(v)		LP (N_{11})	σ* ($O_{10}H_{13}$)	65	Leads to the elongation of $O_{10}H_{13}$ bond, indicating non favorable transfer of H_{13} from N_{11}
		LP (O_{16})	σ* ($O_{18}H_{17}$)	83	Leads to the elongation of $O_{18}H_{17}$ bond, indicating favorable transfer of H_{17} towards O_{16}
		LP (O_{18})	σ* ($O_{21}H_{19}$)	79	Leads to the elongation of O_{21} H_{19} bond, indicating favorable transfer of H_{19} towards O_{18}
		LP (O_{21})	σ* ($O_{10}H_{23}$)	187	Leads to the elongation of $O_{10}H_{23}$ bond, indicating favorable transfer of H_{23} towards O_{21}
		σ ($O_{21}H_{19}$)	σ* ($O_{10}H_{23}$)	19	Leads to the elongation of $O_{21}H_{19}$ and $O_{10}H_{23}$ bonds resulting in favorable transfer of H_{19} from O_{21} towards O_{18} and H_{23} from O_{10} towards O_{21}

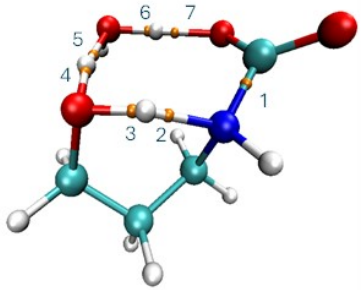
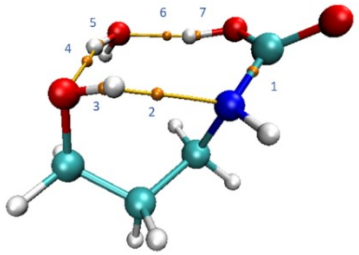
Table S2: The electron density (ρ) and Laplacian of electron density ($\nabla^2(\rho)$) at relevant (3,-1) critical points for various species involved in the proton transfer of different systems.

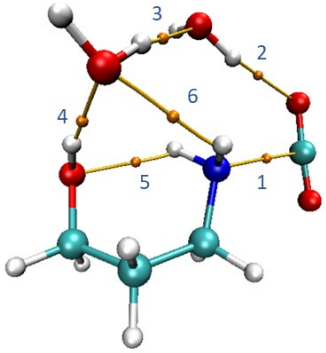
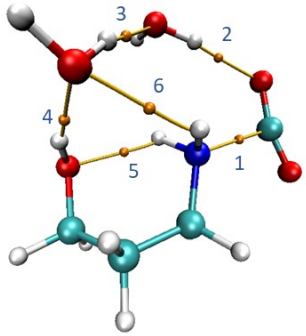
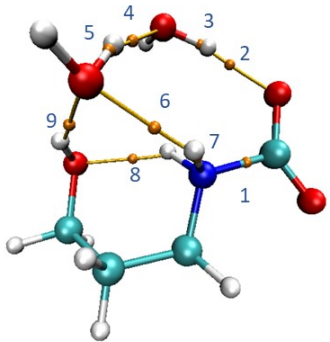
CO_2-3A1P-H_2O involving two proton transfer						
Species	**Figure**	**Critical point**	**Interaction type**	**Electron density (e/a_o^3)**	**Laplacian of electron density (e/a_o^5)**	**Inference**
RC		1	$N\text{---}C_{CO2}$	0.018	0.060	
		2	$H_W\text{---}O_{CO2}$	0.017	0.062	
		3	$H_N\text{---}O_W$	0.017	0.051	
		4	$H_N\text{---}O_{OH}$	0.019	0.061	
TS1		1	$N\text{---}C_{CO2}$	0.055	0.104	Strength of $N\text{---}C_{CO2}$ is slightly increased. However, due to the bending of CO_2 175^0 to 159^0 overall energy is increased w.r.t. RC
		2	$H_W\text{---}O_{CO2}$	0.019	0.068	
		3	$H_N\text{---}O_W$	0.018	0.057	
		4	$H_N\text{---}O_{OH}$	0.019	0.063	

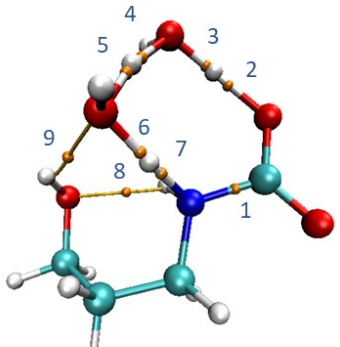
IM		1	$N---C_{CO2}$	0.198	-0.262	Strength of $N---C_{CO2}$ increased Strength of H_w---O_{CO2} increased Strength of O_W----H_N increased Strength of H_N---O_{OH} increased Overall energy is decreased w.r.t. TS1
		2	H_w---O_{CO2}	0.033	0.114	
		3	O_W----H_W	0.326	-2.242	
		4	H_N---O_W	0.032	0.105	
		5	H_N---N	0.312	-1.515	
		6	$O_{OH}---H_N$	0.029	0.103	
TS2		1	$N---C_{CO2}$	0.255	-0.587	Strength of $N---C_{CO2}$ increased Strength of H_w---O_{CO2} increased Strength of O_W----H_W decreased Strength of H_N---O_W increased Strength of H_N---N decreased Strength of $O_{OH}---H_N$ decreased Overall energy is increased w.r.t. IM
		2	H_w---O_{CO2}	0.136	-0.103	
		3	O_W----H_W	0.130	-0.447	
		4	H_N---O_W	0.178	-0.332	
		5	H_N---N	0.140	-0.219	
		6	$O_{OH}---H_N$	0.027	0.093	

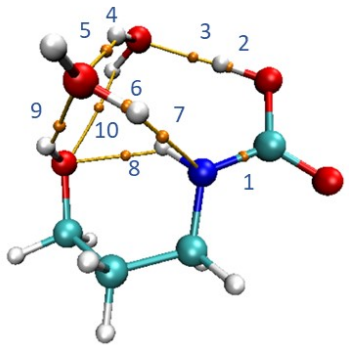
PC		1	N---C_{CO2}	0.321	-1.056	Strong N---C_{CO2} interaction leading to N- C bond formation Additional bond formations: H_{CO2}---O_{CO2} and H_W---O_W Overall energy is decreased w.r.t. TS2
		2	H_{CO2}---O_{CO2}	0.314	-2.118	
		3	O_W---H_{CO2}	0.043	0.146	
		4	H_W---O_W	0.326	-2.283	
		5	H_W----O_{OH}	0.031	0.121	
		6	H_N---O_{OH}	0.020	0.068	
		7	H_N---N	0.330	-1.55	
CO_2-3A1P-H_2O involving three proton transfer						
Species	**Figure**	**Critical point**	**Interaction type**	**Electron density (a.u.)**	**Laplacian**	**Inference**
RC		1	N---C_{CO2}	0.012	0.044	
		2	H_N---O_{OH}	0.017	0.055	
		3	H_{OH}---O_W	0.034	0.124	
		4	H_W---O_{CO2}	0.010	0.043	
		5	H_W---N	0.032	0.099	

TS1		1	N---C_{CO2}	0.057	0.104	Strength of N---C_{CO2} slightly increased Strength of H_W---O_{CO2} sllightly increased Strong H_W---N interaction disappeared. In addition, due to the bending of CO_2 from 178^0 to 158^0 overall energy is increased w.r.t. RC
		2	H_N---O_{OH}	0.019	0.059	
		3	H_{OH}---O_W	0.037	0.138	
		4	H_W---O_{CO2}	0.023	0.093	
IM		1	N---C_{CO2}	0.196	-0.251	Strength of N---C_{CO2} increased Strength of H_N---O_{OH} slightly increased Strength of H_W---O_{CO2} slightly increased Overall energy is decreased w.r.t. TS1
		2	H_N---N	0.313	-1.525	
		3	H_N---O_{OH}	0.030	0.094	
		4	H_{OH}---O_{OH}	0.321	-2.203	
		5	H_{OH}---O_W	0.043	0.150	
		6	H_W---O_w	0.318	-2.249	
		7	H_W---O_{CO2}	0.038	0.141	

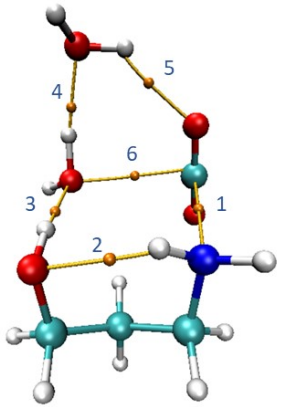
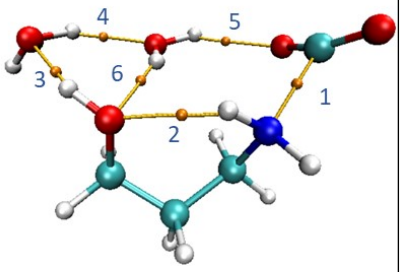
TS2		1	N---C_{CO2}	0.256	-0.607	Strength of N---C_{CO2} slightly increased Strength of H_N---N decreased Strength of H_N---O_{OH} increased Strength of H_{OH}---O_{OH} decreased Strength of H_{OH}---O_W increased Strength of H_W---O_W decreased Strength of H_W---O_{CO2} slightly increased Overall energy is increased w.r.t. IM
		2	H_N---N	0.110	-0.035	
		3	H_N---O_{OH}	0.218	-0.681	
		4	H_{OH}---O_{OH}	0.222	-0.794	
		5	H_{OH}---O_W	0.114	0.016	
		6	H_W---O_w	0.255	-1.351	
		7	H_W---O_{CO2}	0.083	0.127	
PC		1	N---C_{CO2}	0.307	-0.946	Strongest N---C_{CO2} interaction leading to N- C bond formation Additional bond formations: H_{OH}---O_{OH} , H_{CO2}---O_{CO2} and H_{OH}---O_{OH} Overall energy is decreased w.r.t. TS2
		2	H_{OH}---N	0.0232	0.068	
		3	H_{OH}---O_{OH}	0.337	-2.249	
		4	H_W---O_{OH}	0.041	0.139	
		5	H_{OH}---O_W	0.316	-2.206	
		6	H_{CO2}---O_w	0.054	0.166	
		7	H_{CO2}---O_{CO2}	0.300	-1.987	

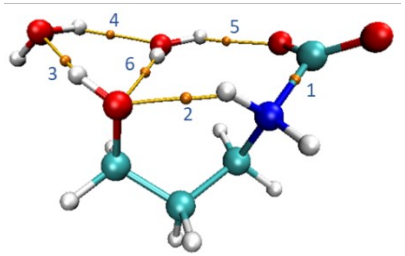
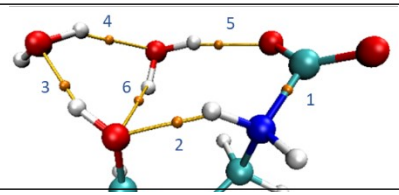
CO_2-3A1P-2H_2O involving three proton transfer						
Species	**Figure**	**Critical point**	**Interaction type**	**Electron density (a.u.)**	**Laplacian**	**Inference**
RC		1	$N---C_{CO2}$	0.019	0.063	
		2	$H_{W1}---O_{CO2}$	0.015	0.056	
		3	$H_{W2}---O_{W1}$	0.034	0.128	
		4	$H_{OH}---O_{W2}$	0.035	0.128	
		5	H_N---O_{OH}	0.019	0.058	
		6	$O_{W2}---H_N$	0.011	0.045	
TS1		1	$N---C_{CO2}$	0.052	0.104	Strength of $N---C_{CO2}$ is slightly increased. However, due to the bending of CO_2 175^0 to 160^0 overall energy is increased w.r.t. RC
		2	$H_{W1}---O_{CO2}$	0.023	0.089	
		3	$H_{W2}---O_{W1}$	0.036	0.135	
		4	$H_{OH}---O_{W2}$	0.035	0.128	
		5	H_N---O_{OH}	0.019	0.060	
		6	$O_{W2}---H_N$	0.012	0.045	
IM		1	$N---C_{CO2}$	0.201	-0.278	Strength of $N---C_{CO2}$ increased Strength of $H_{W1}---O_{CO2}$ slightly

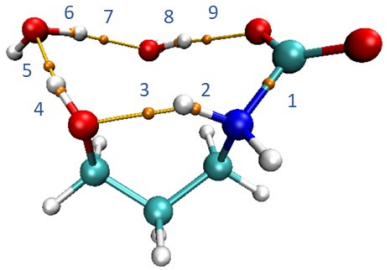
		2	H_{W1}---O_{CO2}	0.042	0.145	increased Overall energy is decreased w.r.t. TS1
		3	H_{W1}---O_{W1}	0.314	-2.191	
		4	H_{W2}---O_{W1}	0.041	0.148	
		5	H_{W2}---O_{W2}	0.314	-2.219	
		6	O_{W2}---H_N	0.022	0.073	
		7	H_N---N	0.317	-1.533	
		8	H_N---O_{OH}	0.025	0.078	
		9	O_{W2}---H_{OH}	0.031	0.113	
TS2		1	N---C_{CO2}	0.259	-0.622	Strength of N---C_{CO2} slightly increased Strength of H_{W1}---O_{CO2} slightly

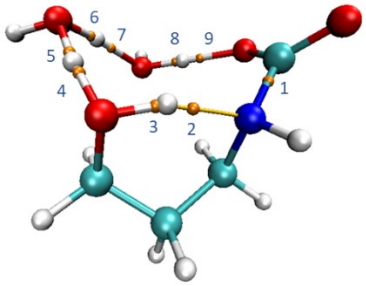
		2	H_{W1}---O_{CO2}	0.010	0.071	decreased Strength of H_{W1}---O_{W1} decreased Strength of H_{W2}---O_{W1} increased Strength of H_{W2}---O_{W2} decreased Strength of O_{W2}---H_N increased Strength of H_N---N decreased Strength of H_N---O_{OH} decreased Strength of O_{W2}---H_{OH} slightly decreased Overall energy is increased w.r.t IM
		3	H_{W1}---O_{W1}	0.235	-1.012	
		4	H_{W2}---O_{W1}	0.142	-0.129	
		5	H_{W2}---O_{W2}	0.183	-0.383	
		6	O_{W2}---H_N	0.190	-0.420	
		7	H_N---N	0.128	-0.156	
		8	H_N---O_{OH}	0.235	-1.012	
		9	O_{W2}---H_{OH}	0.020	0.063	
PC		1	N---C_{CO2}	0.318	-1.030	Strong N---C_{CO2} interaction leading to N- C bond formation Additional bond formations: H_{CO2}---

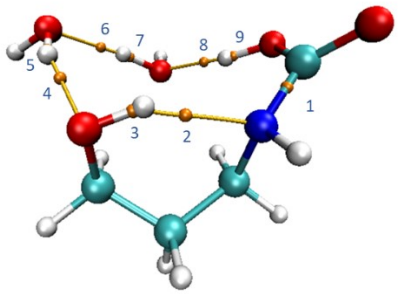
		2	H_{CO2}---O_{CO2}	0.315	-2.127	O_{CO2}, H_{W2}---O_{W2} and O_{W1}---H_{W1} Overall energy is decreased w.r.t. TS2
		3	H_{CO2}---O_{W2}	0.042	0.142	
		4	H_{W2}---O_{W2}	0.327	-2.282	
		5	H_{W2}---O_{W1}	0.030	0.110	
		6	O_{W1}---H_{W1}	0.332	-2.301	
		7	H_{W1}---N	0.018	0.0519	
		8	H_N---O_{OH}	0.024	0.075	
		9	H_{OH}---O_{W1}	0.026	0.095	
		10	H_{W2}---O_{OH}	0.014	0.048	
CO_2-3A1P-2H_2O involving four proton transfer						

Species	Figure	Critical point	Interaction type	Electron density (a.u.)	Laplacian	Analysis
RC		1	$N\text{---}C_{CO2}$	0.019	0.061	
		2	$H_N\text{---}O_{OH}$	0.020	0.060	
		3	$H_{OH}\text{---}O_{W1}$	0.036	0.136	
		4	$H_{W1}\text{---}O_{W2}$	0.037	0.134	
		5	$H_{W2}\text{---}O_{CO2}$	0.017	0.059	
		6	$O_{W1}\text{---}C_{CO2}$	0.012	0.049	
TS1		1	$N\text{---}C_{CO2}$	0.063	0.104	Strength of $N\text{---}C_{CO2}$ increased

		2	H_N---O_{OH}	0.019	0.069	Strength of H_{W2}---O_{CO2} increased
		3	H_{OH}---O_{W1}	0.027	0.107	Strength of O_{W1}---C_{CO2} increased
		4	H_{W1}---O_{W2}	0.037	0.127	O_{W1}---C_{CO2} interaction disappeared
		5	H_{W2}---O_{CO2}	0.020	0.067	O_{OH}---H_{W2} interaction appeared
		6	O_{OH}---H_{W2}	0.027	0.092	Bending of CO_2 173^0 to 157^0 and overall the energy is increased w.r.t. RC
IM1		1	N---C_{CO2}	0.184	-0.189	Strength of N---C_{CO2} increased Overall energy is decreased w.r.t. TS1
		2	H_N---O_{OH}	0.026	0.094	
		3	H_{OH}---O_{W1}	0.024	0.093	
		4	H_{W1}---O_{W2}	0.039	0.133	
		5	H_{W2}---O_{CO2}	0.026	0.090	
		6	O_{OH}---H_{W2}	0.026	0.091	
TS2		1	N---C_{CO2}	0.195	-0.246	Strength of N---C_{CO2} slightly increased Strength of H_{OH}---O_{W1} slightly increased Strength of H_{W1}---O_{W2} slightly
		2	H_N---O_{OH}	0.032	0.114	

		3	H_{OH}---O_{W1}	0.042	0.143	decreased Strength of O_{OH}---H_{W2} slightly decreased Overall energy is slightly increased w.r.t. IM1
		4	H_{W1}---O_{W2}	0.030	0.107	
		5	H_{W2}---O_{CO2}	0.034	0.128	
		6	O_{OH}---H_{W2}	0.016	0.050	
IM2		1	N---C_{CO2}	0.203	-0.293	Strength of N---C_{CO2} slightly increased Strength of H_N---O_{OH} slightlly increased Strength of H_{OH}---O_{W1} slightlly increased Strength of H_{W1}---O_{W2} slightlly increased Strength of H_{W2}---O_{CO2} slightlly increased O_{OH}---H_{W2} interaction disappeared Overall energy is decreased w.r.t. TS2
		2	H_N---N	0.307	-1.504	
		3	H_N---O_{OH}	0.038	0.126	
		4	H_{OH}---O_{OH}	0.317	-2.156	
		5	H_{OH}---O_{W1}	0.045	0.150	
		6	O_{W1}---H_{W1}	0.318	-2.257	
		7	H_{W1}---O_{W2}	0.039	0.149	

		8	O_{W2}---H_{W2}	0.316	-2.236	
		9	H_{W2}---O_{CO2}	0.040	0.149	
TS3		1	N---C_{CO2}	0.265	-0.667	Strength of N---C_{CO2} increased Strength of H_N---N decreased Strength of H_N---O_{OH} increased Strength of H_{OH}---O_{OH} decreased Strength of H_{OH}---O_{W1} increased Strength of O_{W1}---H_{W1} decreased Strength of H_{W1}---O_{W2} slighly increased Strength of O_{W2}---H_{W2} decreased Strength of H_{W2}---O_{CO2} slightly increased Overall energy is increased w.r.t. IM2
		2	H_N---N	0.078	0.092	
		3	H_N---O_{OH}	0.260	-1.294	
		4	H_{OH}---O_{OH}	0.173	-0.303	
		5	H_{OH}---O_{W1}	0.155	-0.188	
		6	O_{W1}---H_{W1}	0.253	-1.338	
		7	H_{W1}---O_{W2}	0.086	0.126	

		8	O_{W2}---H_{W2}	0.258	-1.410	
		9	H_{W2}---O_{CO2}	0.082	0.135	
PC		1	N---C_{CO2}	0.306	-0.937	Strongest N---C_{CO2} interaction leading to N- C bond formation Additional bond formations: H_{OH}---O_{OH}, H_{W1}---O_{W1}, H_{W2}---O_{W2} and H_{CO2}---O_{CO2} Overall energy is decreased w.r.t. TS
		2	H_{OH}---N	0.029	0.087	
		3	H_{OH}---O_{OH}	0.334	-2.215	
		4	H_{W1}---O_{OH}	0.039	0.133	
		5	H_{W1}---O_{W1}	0.319	-2.221	
		6	O_{W1}---H_{W2}	0.046	0.152	
		7	H_{W2}---O_{W2}	0.306	-2.132	

		8	O_{W2}---H_{CO2}	0.056	0.166	
		9	H_{CO2}---O_{CO2}	0.296	-1.950	

The coordinates of all the species discussed in the manuscript are provided as a separate file in the xyz format.