Bridging static and dynamical descriptions of chemical reactions: an ab initio study of CO_2 interacting with water molecules: Supporting Information

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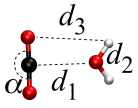
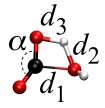
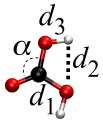
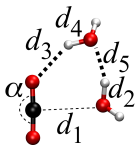
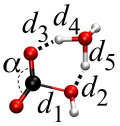
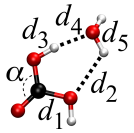
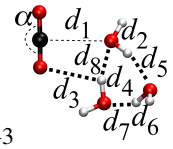
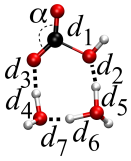
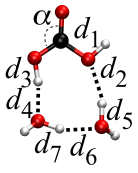
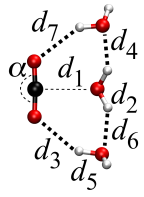
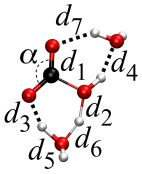
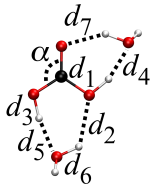
Table 1: Geometrical characteristics of reactant, TS and products(distances in (Å); angles in degrees)

(a) Complex	Parameters	PBE[a]	BLYP[a]	B3LYP[a]	B3LYP[a′]	M06[a′]	MP2[b]
 R$_1$	d_1	2.89	2.96	2.88	2.87	2.75	2.77
	d_2	0.97	0.97	0.96	0.96	0.96	0.96
	d_3	3.64	3.57	3.64	3.65	3.42	3.40
	α	178	178	178	178	178	178
 TS$_1$	d_1	1.70	1.74	1.69	1.68	1.65	1.68
	d_2	1.26	1.30	1.25	1.25	1.22	1.24
	d_3	1.24	1.22	1.23	1.24	1.24	1.23
	α	145	146	146	146	146	145
 P$_1$	d_1	1.37	1.38	1.36	1.36	1.35	1.36
	d_2	2.17	2.20	2.18	2.17	2.15	2.15
	d_3	0.97	0.97	0.96	0.97	0.96	0.97
	α	124	124	124	124	124	124

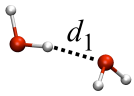
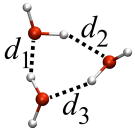
(b) Complex	Parameters	PBE[a]	BLYP[a]	B3LYP[a]	B3LYP[a′]	M06[a′]	MP2[b]
 R$_2$	d_1	2.90	2.95	2.87	2.84	2.93	2.76
	d_2	0.98	0.98	0.97	0.97	0.97	0.97
	d_3	2.17	2.24	2.20	2.19	2.18	2.13
	d_4	0.97	0.97	0.96	0.97	0.96	0.97
	d_5	1.90	1.95	1.94	1.94	1.96	1.92
	α	177	177	177	177	177	177
 TS$_2$	d_1	1.63	1.66	1.61	1.59	1.56	1.59
	d_2	1.26	1.30	1.27	1.26	1.24	1.25
	d_3	1.37	1.36	1.41	1.40	1.39	1.40
	d_4	1.11	1.12	1.08	1.09	1.08	1.08
	d_5	1.18	1.15	1.16	1.17	1.16	1.16
	α	139	140	139	139	139	139
 P$_2$	d_1	1.39	1.40	1.38	1.37	1.36	1.37
	d_2	2.27	2.40	2.40	2.42	2.20	2.29
	d_3	1.00	0.99	0.98	0.98	0.98	0.98
	d_4	1.72	1.77	1.77	1.76	1.78	1.74
	d_5	0.97	0.97	0.96	0.96	0.96	0.97
	α	126	126	125	125	126	125

(c) Complex	Parameters	PBE[a]	BLYP[a]	B3LYP[a]	B3LYP[a′]	M06[a′]	MP2[b]
 R_3	d_1	3.00	3.09	2.99	2.76	2.76	2.83
	d_2	0.99	0.99	0.98	0.98	0.98	0.98
	d_3	2.94	3.02	2.95	2.80	2.80	2.76
	d_4	0.98	0.98	0.97	0.97	0.97	0.97
	d_5	1.82	1.89	1.88	1.85	1.85	1.85
	d_6	0.99	0.98	0.97	0.97	0.97	0.98
	d_7	1.86	1.92	1.92	1.90	1.90	1.89
	d_8	1.90	1.97	1.97	1.97	1.96	1.96
	α	178	179	178	178	178	178
 TS_3	d_1	1.59	1.61	1.56	1.55	1.52	
	d_2	1.30	1.37	1.34	1.33	1.31	
	d_3	1.45	1.45	1.49	1.49	1.51	
	d_4	1.05	1.06	1.03	1.03	1.02	
	d_5	1.14	1.11	1.10	1.11	1.11	
	d_6	1.14	1.17	1.12	1.12	1.13	
	d_7	1.30	1.27	1.32	1.32	1.28	
	α	138	138	137	137	137	
 P_3	d_1	1.40	1.41	1.39	1.38	1.37	1.38
	d_2	1.91	1.97	1.99	2.00	1.94	1.94
	d_3	1.01	1.01	0.99	1.00	0.99	1.00
	d_4	1.62	1.67	1.68	1.66	1.69	1.65
	d_5	0.98	0.98	0.97	0.97	0.97	0.97
	d_6	1.74	1.80	1.80	1.79	1.81	1.80
	d_7	0.99	0.99	0.98	0.98	0.97	0.98
	α	126	126	126	126	126	126

(d) Complex	Parameters	PBE[a]	BLYP[a]	B3LYP[a]	B3LYP[a′]	M06[a′]	MP2[b]
 R'_3	d_1	2.70	2.77	2.73	2.74	2.63	2.68
	d_2	0.97	0.97	0.97	0.97	0.97	0.97
	d_3	2.31	2.43	2.31	2.41	2.23	2.21
	d_4	1.99	2.07	2.04	2.08	2.00	2.02
	d_5	0.97	0.97	0.96	0.97	0.96	0.96
	d_6	1.98	2.05	2.03	2.05	1.99	2.02
	d_7	2.32	2.40	2.38	2.41	2.23	2.21
	α	175	176	176	176	175	176
 TS'_3	d_1	1.52	1.55	1.51	1.50	1.48	1.50
	d_2	1.21	1.26	1.23	1.22	1.22	1.21
	d_3	1.41	1.41	1.43	1.44	1.42	1.42
	d_4	1.61	1.75	1.72	1.68	1.74	1.67
	d_5	1.09	1.10	1.07	1.07	1.07	1.07
	d_6	1.22	1.19	1.19	1.20	1.18	1.19
	d_7	1.83	1.93	1.91	1.90	1.94	1.87
	α	134	135	135	135	135	135
 P'_3	d_1	1.36	1.37	1.36	1.35	1.34	1.35
	d_2	2.13	2.27	2.30	2.32	2.13	2.18
	d_3	1.00	0.99	0.98	0.99	0.98	0.99
	d_4	1.69	1.77	1.77	1.74	1.77	1.73
	d_5	1.72	1.77	1.77	1.76	1.78	1.75
	d_6	0.97	0.97	0.96	0.97	0.96	0.97
	d_7	1.84	1.94	1.94	1.91	1.92	1.91
	α	123	123	123	123	123	123

[a] This work: Pseudopotential-plane waves up to 100Ry cutoff.
[a′] This work: AE-aug-cc-pVTZ.
[b] Ref. 1: AE-aug-cc-pVTZ. No report is available on the TS_3 geometry.

Table 2: Water dimer and trimer. Hydrogen-bond distances (Å), binding energies E_B (E_B^{noZPE}) (kcal/mol) including (excluding) ZPE ($E_B = E(H_2O)_n - nE(H_2O)$), and deformation energies E_D (kcal/mol) in the structure of the water moieties (W_2^* and W_3^*) of R_2 and R_3 ($E_D = E(W_n^*) - E(H_2O)_n$)).

Complex	Parameters	PBE[a]	BLYP[a]	B3LYP[a]	B3LYP[a']	M06[a']	CCSD(T)[b]
	d_1	1.92	1.98	1.95	1.97	1.94	1.95
	E_B	−2.7	−2.2	−2.6	−2.4	−2.8	−3.0
	E_B^{noZPE}	−5.2[−5.1][c]	−4.3[−4.2][c]	−4.5[−4.6][c]	−4.6	−4.8	−5.0
	E_D	0.3	0.3	0.4	0.4	0.3	
	d_1	1.86	1.91	1.91	1.91	1.89	1.89
	d_2	1.87	1.94	1.93	1.95	1.92	1.91
	d_3	1.85	1.91	1.59	1.93	1.90	1.89
	E_B	−10.7	−8.0	−9.0	−9.3	−10.8	−10.6
	E_B^{noZPE}	−16.5[−16.2][c]	−13.6[−13.3][c]	−14.2[−14.3][c]	−14.5	−16.1	−15.9
	E_D	0.1	0.1	0.2	0.1	0.2	

[a] This work: Pseudopotential-plane waves up to 100Ry cutoff.
[a'] This work: AE aug-cc-pVTZ.
[b] Ref. 1: AE aug-cc-pVTZ ; MP2 geometries.
[c] Ref. 2: AE aug-cc-pV5Z; geometry optimization with aug-cc-pVTZ.

Table 3: Comparison of binding energies (kcal/mol) from BLYP and BLYP-D[3,4] including ZPE.

System	BLYP	BLYP-D	Δ
R_1	abs < 1	-1	-1
TS_1	46	45	-1
P_1	14	13	-1
R_2	-3	-6	-3
TS_2	25	22	-3
P_2	9	6	-3
R_3	-8	-13	-5
TS_3	16	10	-6
P_3	3	-2	-5
R_3'	-5	-10	-5
TS_3'	18	13	-6
P_3'	2	-4	-6

Table 4: ZPE contribution to the binding energies relative to the isolated molecules (kcal/mol)

System	PBE[a]	BLYP[a]	B3LYP[a]	B3LYP[a']	M06[a']	MP2[b]
R_1	0.9	1.4	1.3	1.0	0.9	0.9
TS_1	0.1	0.1	0.2	0.0	0.1	0.3
P_1	3.8	3.8	4.2	3.9	3.9	4.2
R_2	3.3	3.7	3.9	3.8	3.4	3.5
TS_2	2.6	2.4	2.7	2.9	2.5	3.2
P_2	6.0	5.9	6.1	6.3	5.8	6.3
R_3	6.2	6.5	6.5	6.2	6.6	6.2
TS_3	4.6	4.7	4.8	5.3	4.3	5.4
P_3	8.1	8.5	7.7	8.8	8.3	8.6
R_3'	5.2	5.4	5.1	4.9	5.1	5.0
TS_3'	5.1	5.2	4.7	5.7	5.1	5.6
P_3'	8.4	8.6	8.5	8.3	8.5	8.7

[a] This work: Pseudopotential-plane waves up to 100Ry cutoff.
[a'] This work: AE-aug-cc-pVTZ.
[b] Ref. 1: AE-aug-cc-pVTZ.

Table 5: ZPE contribution to the energy barrier (kcal/mol)

(a) Formation

n	PBE[a]	BLYP[a]	B3LYP[a]	B3LYP[a′]	M06[a′]	MP2[b]
1	−0.8	−1.2	−1.1	−1.0	−0.8	−0.6
2	−0.7	−1.2	−1.2	−0.9	−1.0	−0.2
3	−1.6	−1.8	−1.7	−0.8	−2.3	−0.8
3′	−0.1	−0.2	−0.4	0.8	abs<0.1	−0.5

(b) Dissociation

n	PBE[a]	BLYP[a]	B3LYP[a]	B3LYP[a′]	M06[a′]	MP2[b]
1	−3.7	−3.6	−4.0	−3.8	−3.8	−3.9
2	−3.3	−3.4	−3.4	−3.4	−3.4	−3.1
3	−3.4	−3.9	−2.9	−3.5	−4.0	−3.2
3′	−3.3	−3.4	−3.8	−2.6	−3.4	−3.2

Table 6: Entropic contribution to the free-energy barriers (kcal/mol) at room temperature: translational, rotational and vibrational components in the harmonic (H) and quasi-harmonic (QH) approximations.

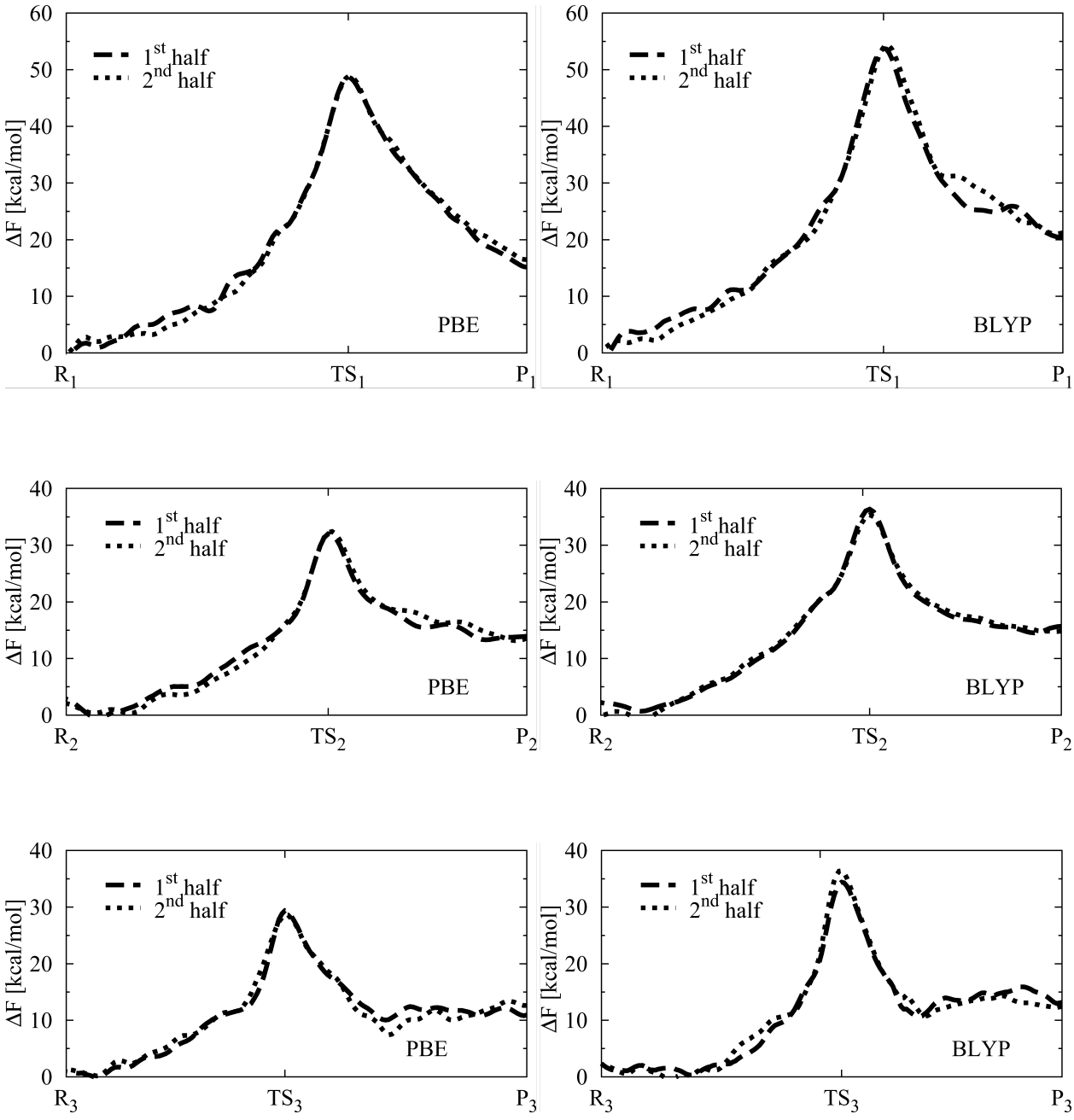
(a) Formation

	PBE[a]		BLYP[a]		B3LYP[a]		MP2[b]
n	H	QH	H	QH	H	QH	QH
1	−4.4	−4.8	−3.0	−3.5	−3.1	−3.6	−5.1
2	−6.1	−6.2	−5.0	−5.2	−4.4	−4.5	−6.3
3	−7.6	−7.8	−5.3	−5.5	−4.8	−4.9	−5.6
3′	−8.0	−7.7	−7.3	−7.1	−6.6	−6.3	−8.1

(b) Dissociation

	PBE[a]		BLYP[a]		B3LYP[a]		MP2[b]
n	H	QH	H	QH	H	QH	QH
1	1.3	0.0	1.4	0.1	1.5	0.1	0.1
2	−0.9	−1.9	−0.8	−1.8	−1.0	−1.9	−2.3
3	−1.3	−2.2	−1.0	−1.9	−1.6	−2.4	−2.6
3′	−0.8	−1.8	−1.1	−2.1	−0.4	−1.5	−2.4

[a] This work: Pseudopotential-plane waves up to 100Ry cutoff.
[b] Ref. 1: AE-aug-cc-pVTZ.


1st half
2nd half
ΔF [kcal/mol]
PBE
BLYP
R1
TS1
P1
R2
TS2
P2
R3
TS3
P3

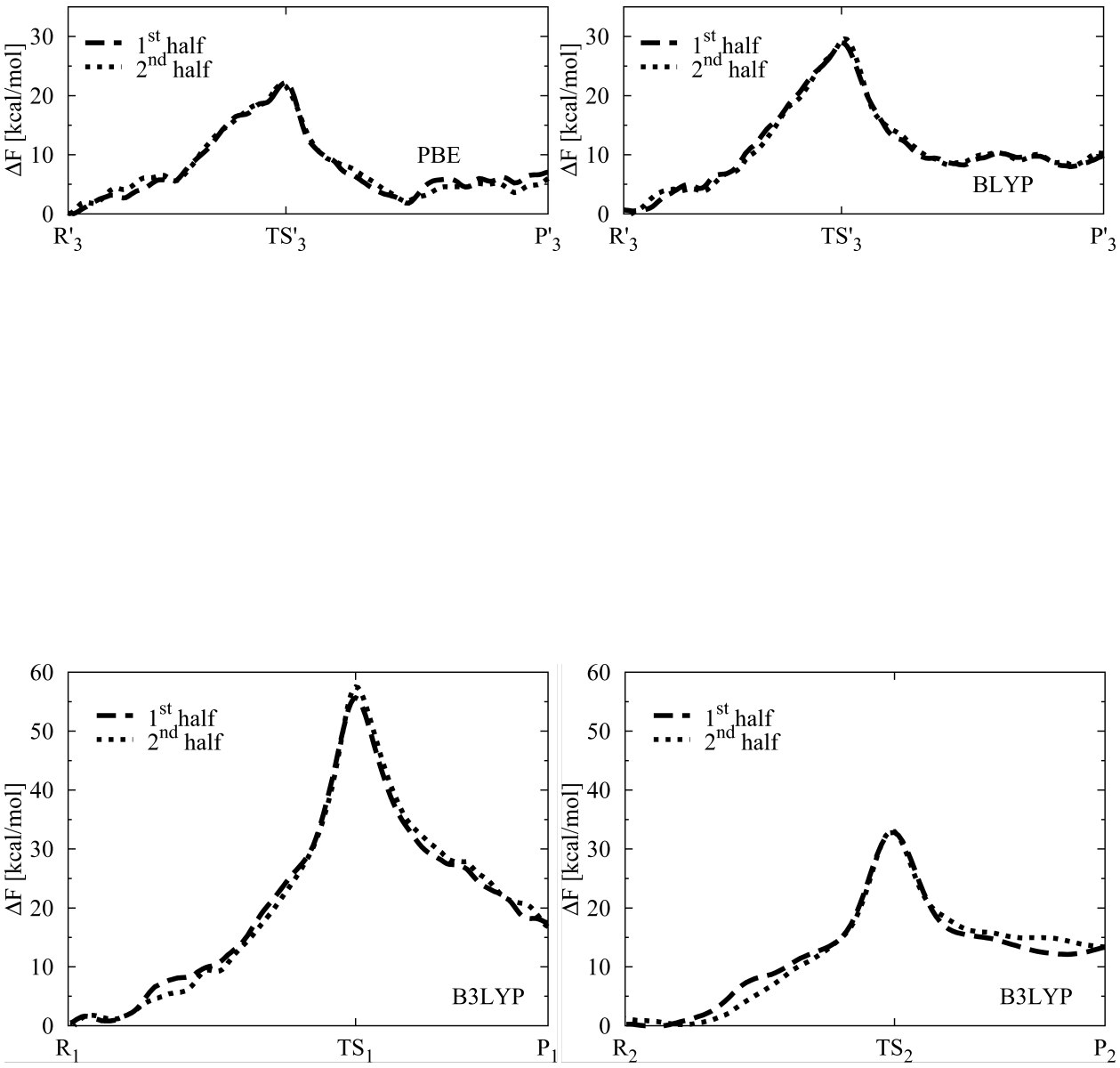
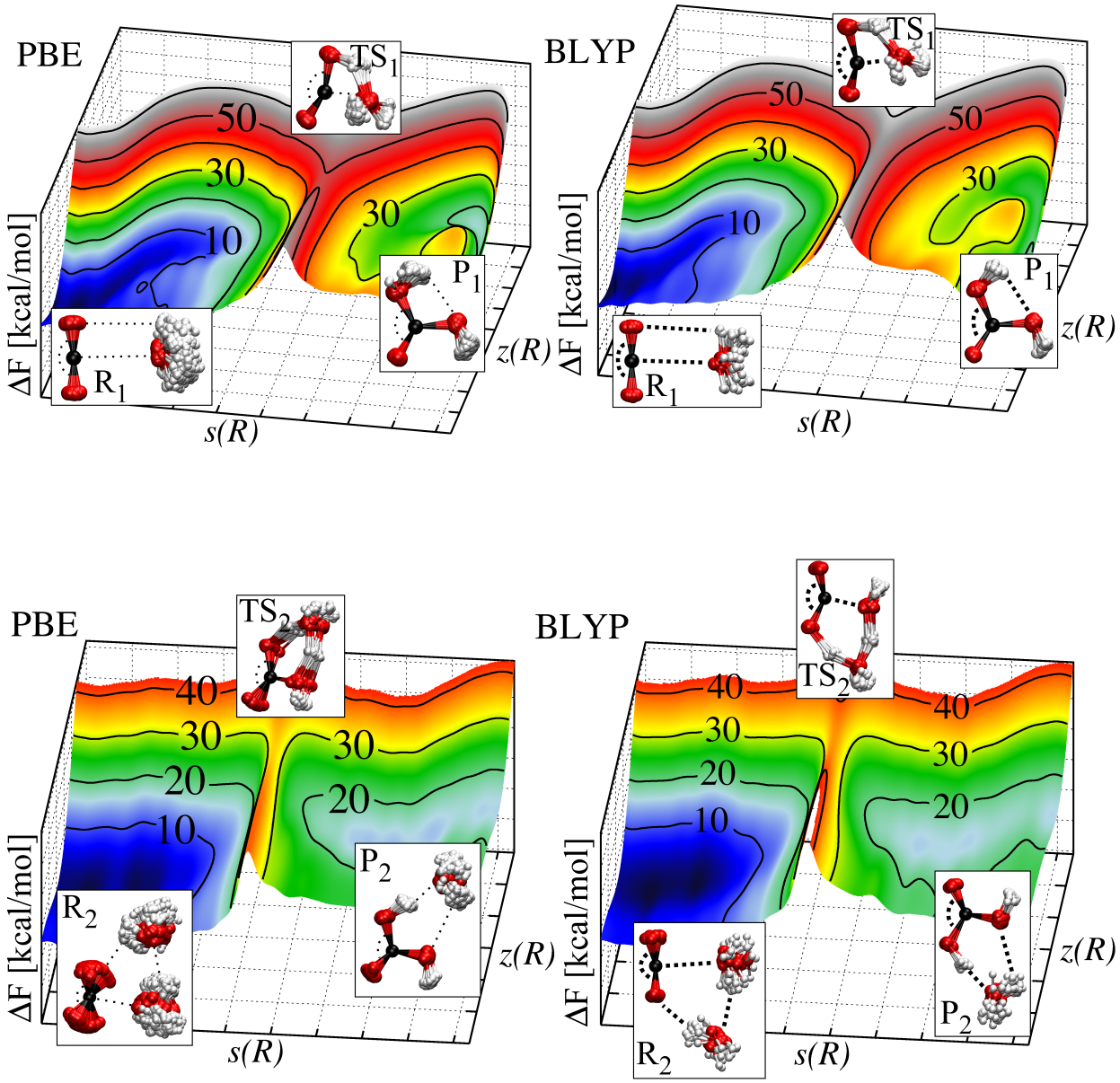
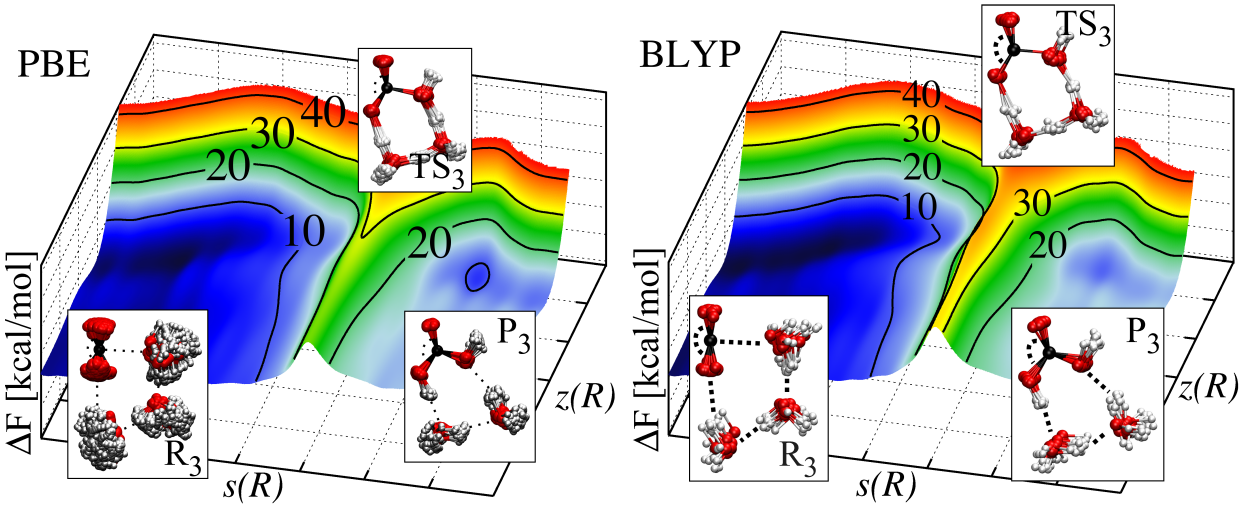
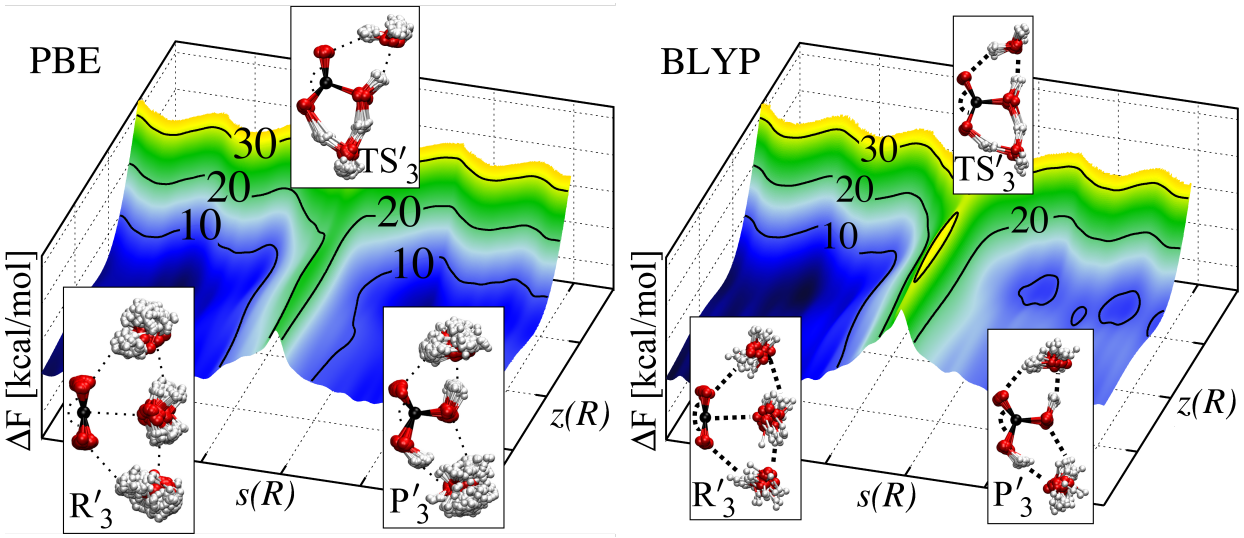


Figure 1: Free energy profile along the reaction path for all reactions studied : from the two halves of the path started from the reactant.


PBE
TS1
50
30
30
10
P1
R1
ΔF [kcal/mol]
s(R)
z(R)
BLYP
TS1
50
50
30
30
10
P1
R1
ΔF [kcal/mol]
s(R)
z(R)
PBE
TS2
40
30
30
20
20
10
P2
R2
ΔF [kcal/mol]
s(R)
z(R)
BLYP
TS2
40
40
30
30
20
20
10
P2
R2
ΔF [kcal/mol]
s(R)
z(R)


PBE
BLYP
ΔF [kcal/mol]
s(R)
z(R)
TS3
R3
P3
10
20
30
40


PBE
BLYP
ΔF [kcal/mol]
s(R)
z(R)
TS′3
R′3
P′3
10
20
30

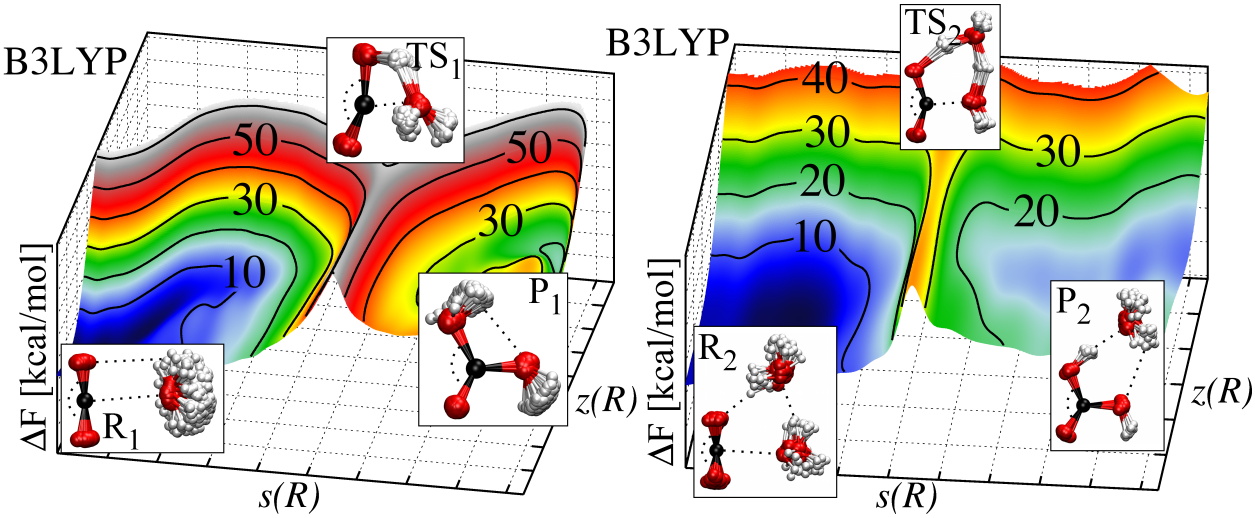


Figure 2: Free-energy surfaces in the relevant path-CV space: all cases studied

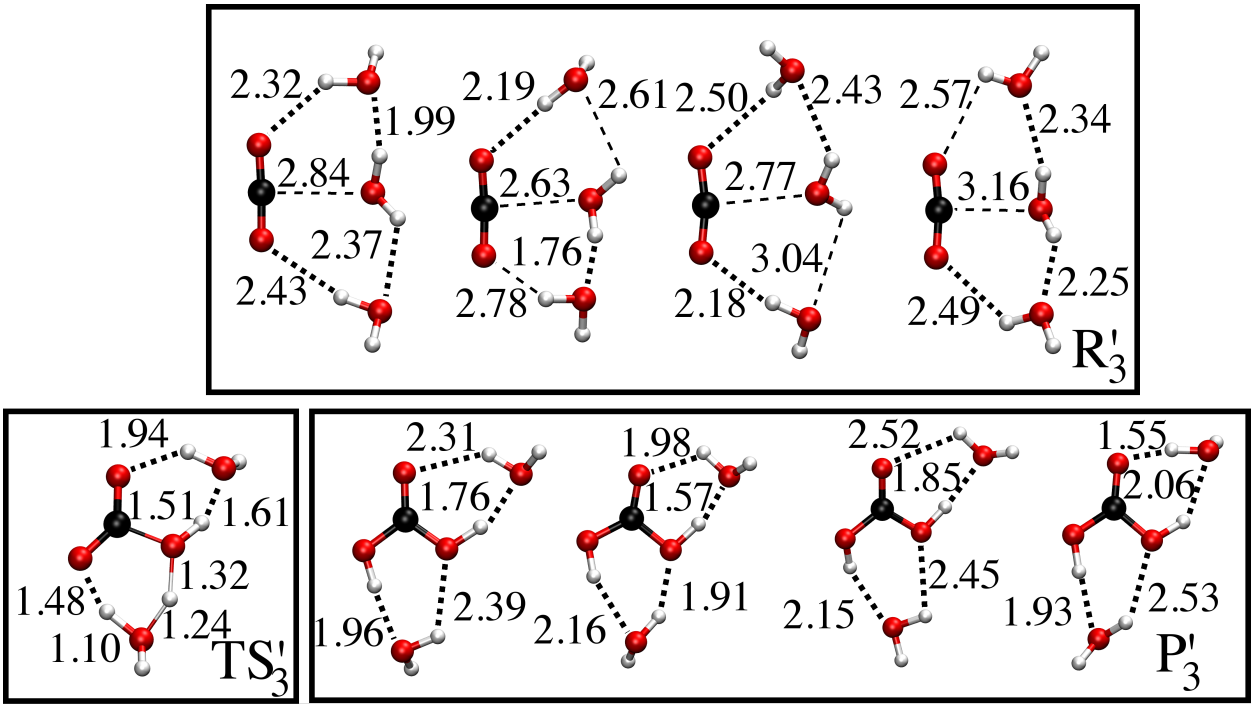


Figure 3: Cluster analysis of the FES (case denoted $n = 3'$)

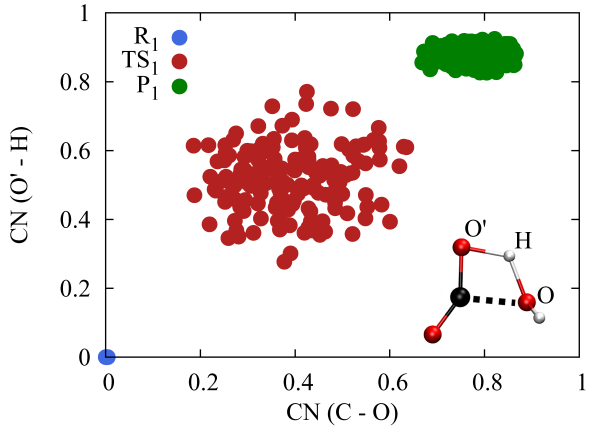


Figure 4: $n = 1$: Reactant, transition and product states from the FES calculated in this work (see Figure 5(a) of the paper), plotted in the space of the collective variables used by Kumar et al.[5]

References

(1) Nguyen, M. T.; Matus, M. H.; Jackson, V. E.; Ngan, V. T.; Rustad, J.; Dixon, D. A. *J. Phys. Chem. A* **2008**, *112*, 10386–10398.

(2) Santra, B.; Michaelides, A.; Scheffler, M. *J. Chem. Phys.* **2007**, *27*, 184104.

(3) Grimme, S. *J. Comp. Chem.* **2004**, *25*, 1463.

(4) Grimme, S. *J. Comp. Chem.* **2006**, *27*, 1787.

(5) Kumar, P. P.; Kalinichev, A. G.; Kirkpatrick, R. J. *J. Chem. Phys.* **2007**, *126*, 204315.