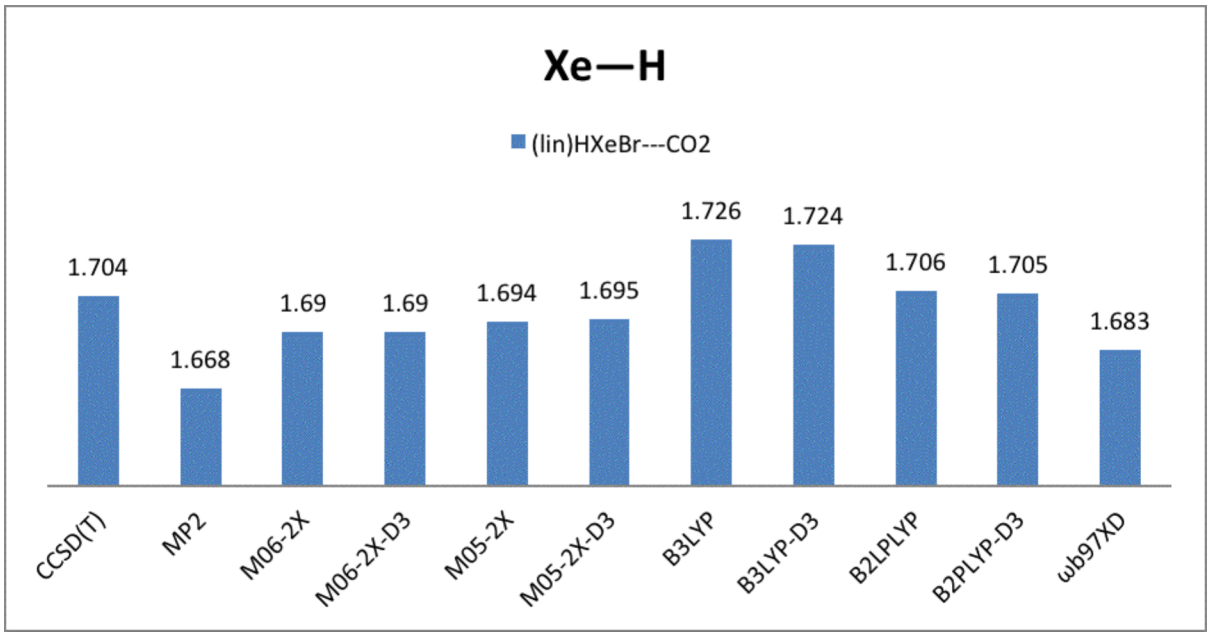
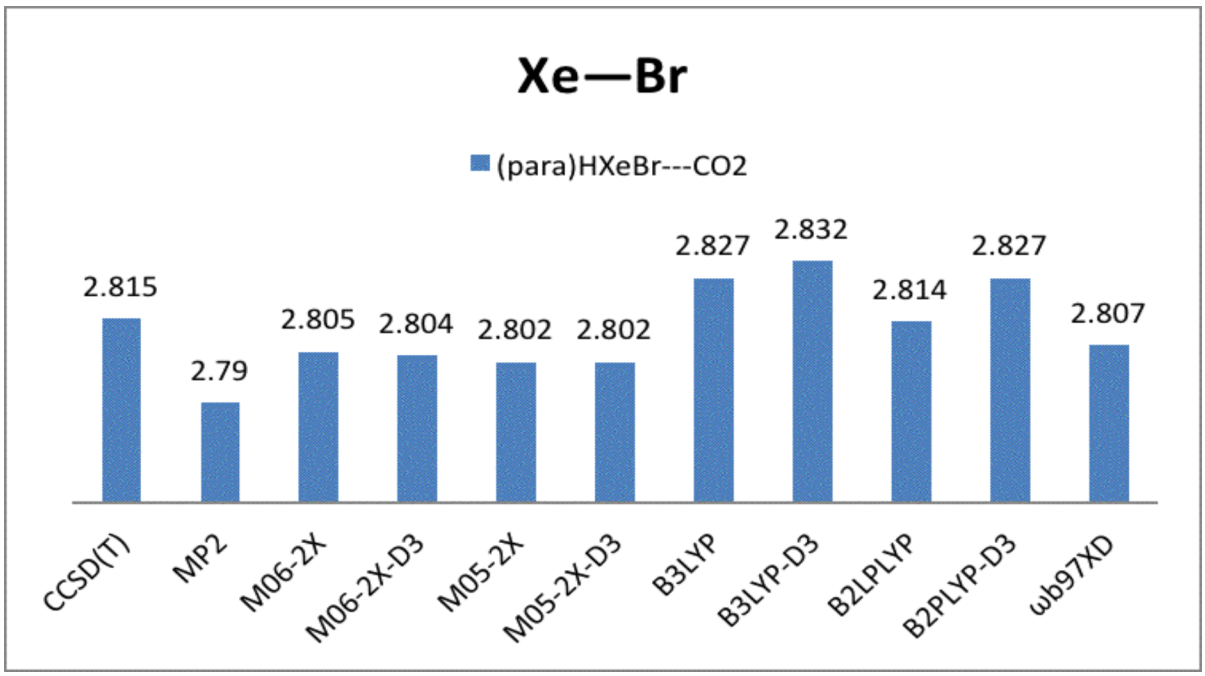
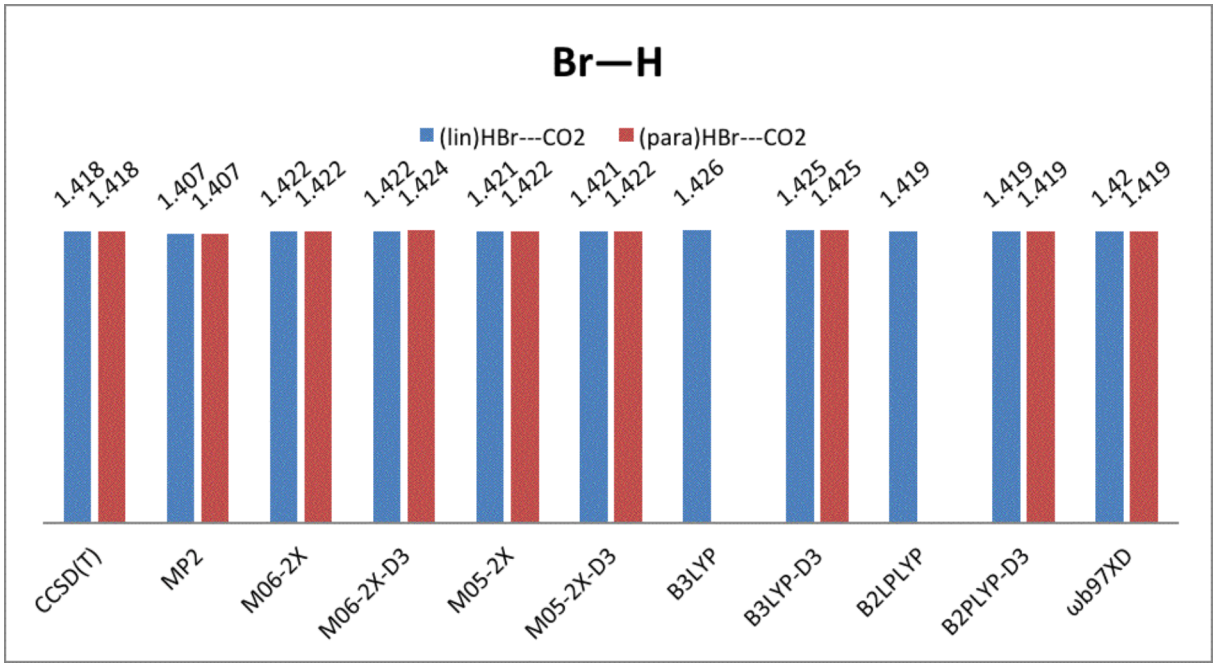
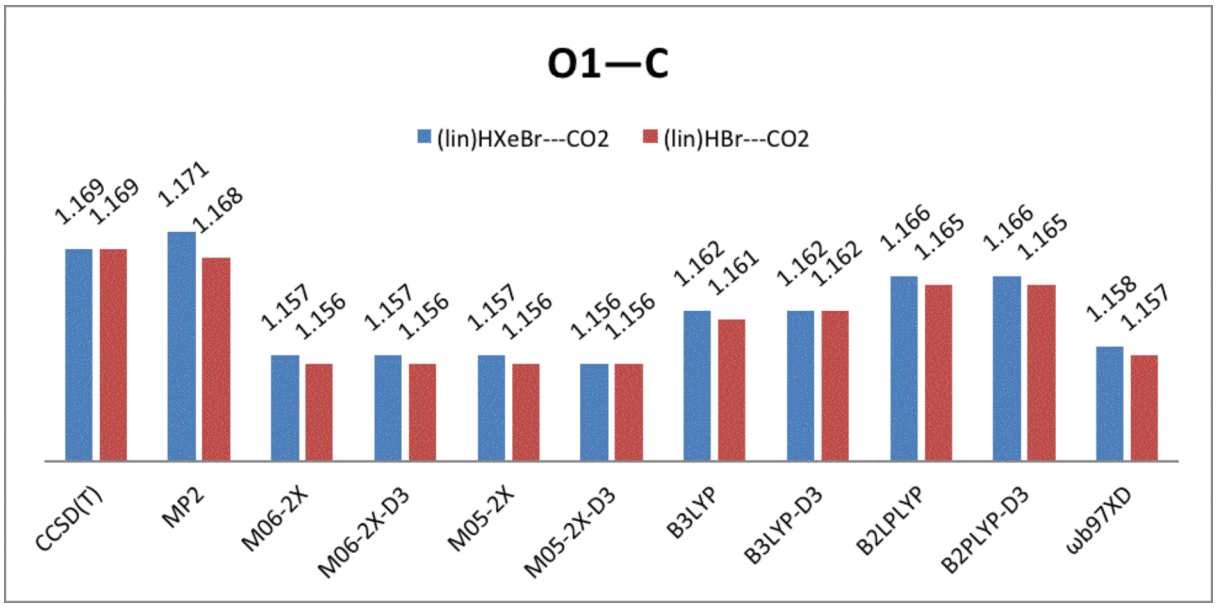
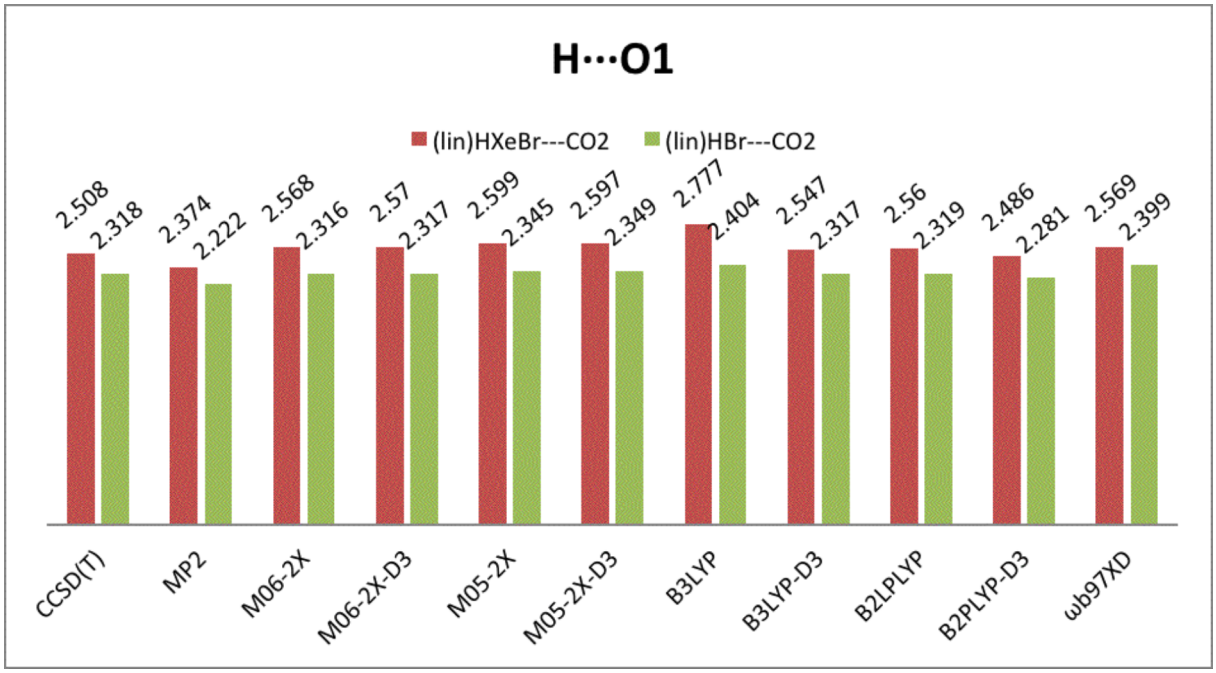
Figure 1S. Histograms showing how the selected intermolecular distances [Å] in the $HBr^{\cdots}CO_2$ and $HXeBr^{\cdots}CO_2$ complexes are dependent on the electron density functional used for calculations. For the purpose of comparison the results obtained using three various methods: CCSD(T), MP2 and DFT (9 different functionals) are shown. The calculations have been performed with Def2-TZVPPD basis set. The results achieved for the M05-2X (M05-2X-D3) are not discussed in the main text.

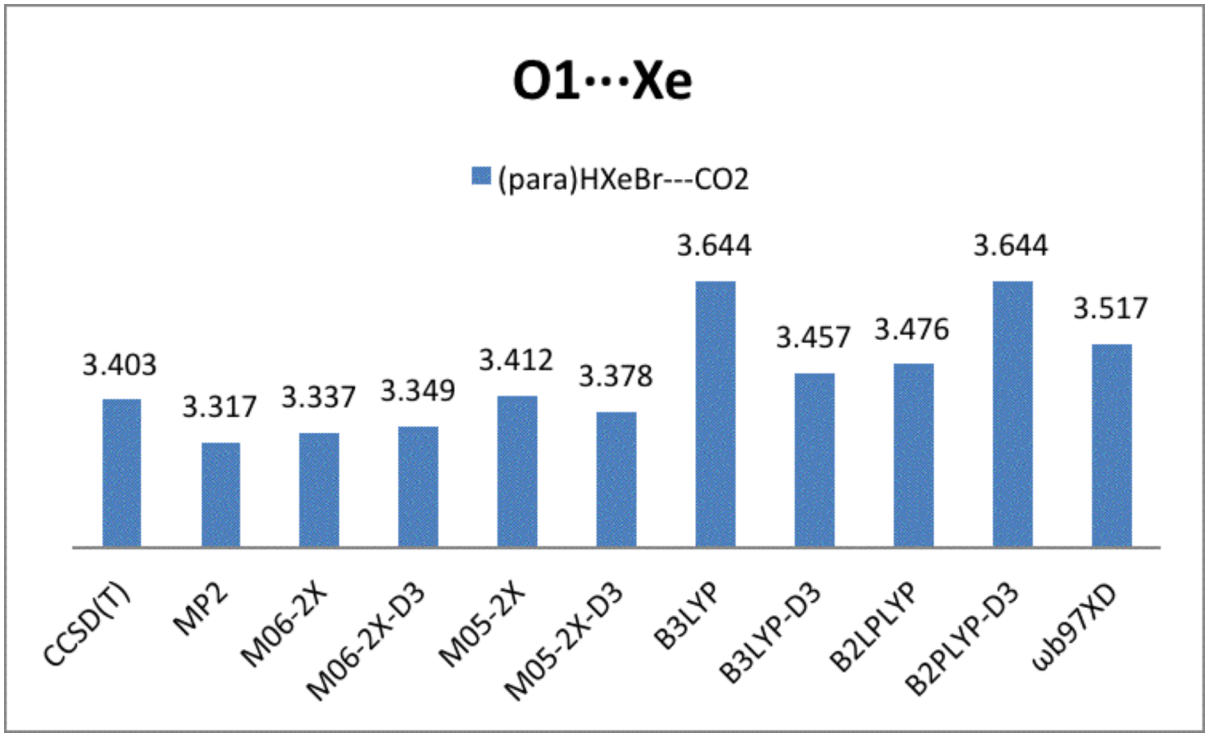


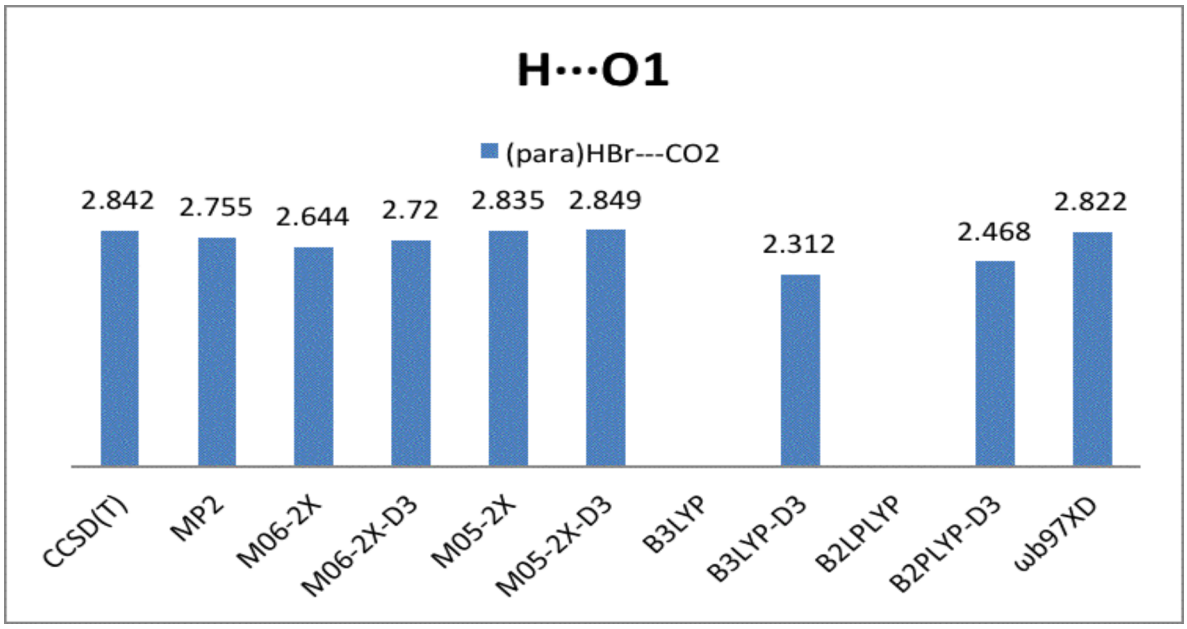



Br—H
(lin)HBr---CO2
(para)HBr---CO2
1.418
1.418
1.407
1.407
1.422
1.422
1.422
1.424
1.421
1.422
1.421
1.422
1.426
1.425
1.425
1.419
1.419
1.419
1.42
1.419
CCSD(T)
MP2
M06-2X
M06-2X-D3
M05-2X
M05-2X-D3
B3LYP
B3LYP-D3
B2LPLYP
B2PLYP-D3
ωb97XD


O1—C
(lin)HXeBr---CO2
(lin)HBr---CO2
1.169
1.169
1.171
1.168
1.157
1.156
1.157
1.156
1.157
1.156
1.156
1.156
1.162
1.161
1.162
1.162
1.166
1.165
1.166
1.165
1.158
1.157
CCSD(T)
MP2
M06-2X
M06-2X-D3
M05-2X
M05-2X-D3
B3LYP
B3LYP-D3
B2LPLYP
B2PLYP-D3
ωb97XD


H···O1
(lin)HXeBr---CO2
(lin)HBr---CO2
2.508
2.318
2.374
2.222
2.568
2.316
2.57
2.317
2.599
2.345
2.597
2.349
2.777
2.404
2.547
2.317
2.56
2.319
2.486
2.281
2.569
2.399
CCSD(T)
MP2
M06-2X
M06-2X-D3
M05-2X
M05-2X-D3
B3LYP
B3LYP-D3
B2LPLYP
B2PLYP-D3
ωb97XD


O1···Xe
(para)HXeBr---CO2
3.403
3.317
3.337
3.349
3.412
3.378
3.644
3.457
3.476
3.644
3.517
CCSD(T)
MP2
M06-2X
M06-2X-D3
M05-2X
M05-2X-D3
B3LYP
B3LYP-D3
B2LPLYP
B2PLYP-D3
ωb97XD


H···O1
(para)HBr---CO2
2.842
2.755
2.644
2.72
2.835
2.849
2.312
2.468
2.822
CCSD(T)
MP2
M06-2X
M06-2X-D3
M05-2X
M05-2X-D3
B3LYP
B3LYP-D3
B2LPLYP
B2PLYP-D3
ωb97XD

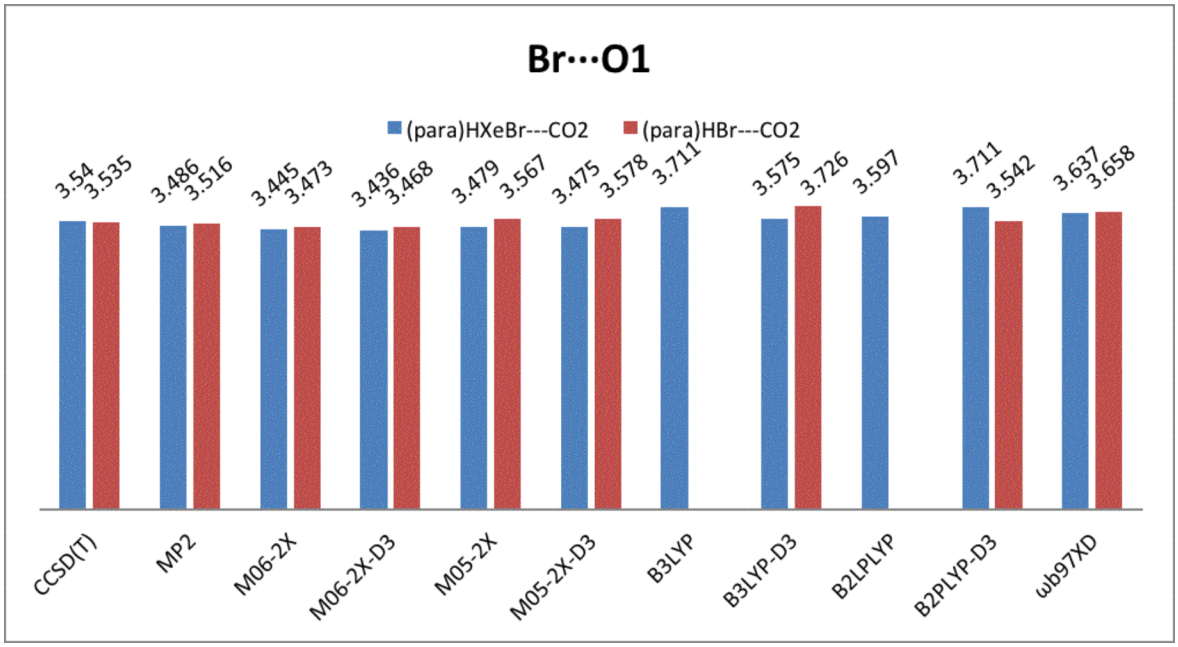

Br···O1
(para)HXeBr---CO2
(para)HBr---CO2
3.54
3.535
3.486
3.516
3.445
3.473
3.436
3.468
3.479
3.567
3.475
3.578
3.711
3.575
3.726
3.597
3.711
3.542
3.637
3.658
CCSD(T)
MP2
M06-2X
M06-2X-D3
M05-2X
M05-2X-D3
B3LYP
B3LYP-D3
B2LPLYP
B2PLYP-D3
ωb97XD

Figure 2S. Core and valence attractors localised for the Electron Localization Function (ELF) field for the C_s structures of the HBr···CO_2 and HXeBr···CO_2 complexes.

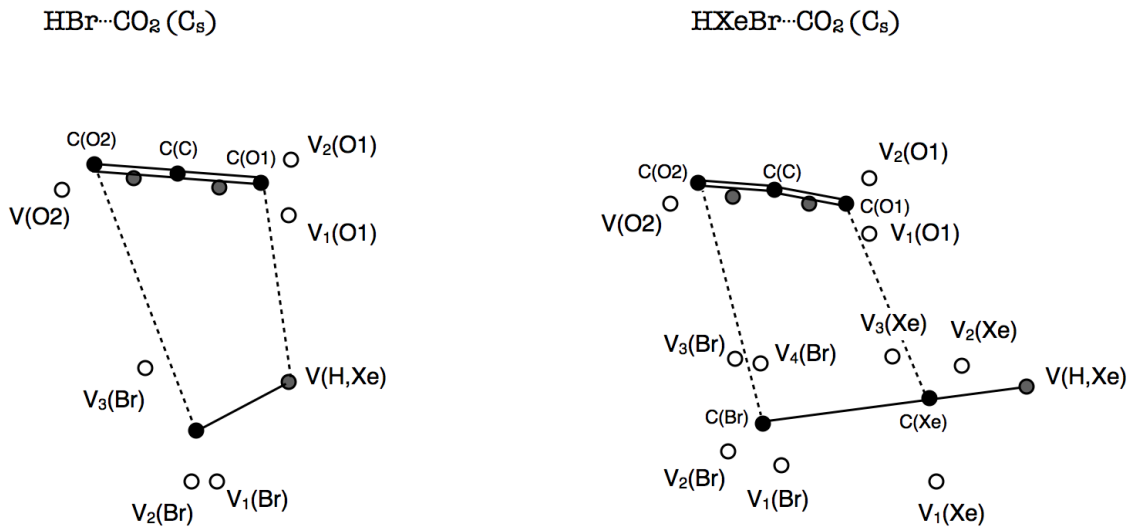


Table 2S. Total basin populations [e] for the linear ($C_{\infty v}$) and 'parallel' (C_s) geometrical structures of the $HBr^{\cdots}CO_2$ and $HXeBr^{\cdots}CO_2$ complexes calculated with different computational methods. The geometrical structures have been optimised using the CCSD(T)/def-TZVPPD method.

complex:	**$HBr^{\cdots}CO_2$**			**$HXeBr^{\cdots}CO_2$**			**$HBr^{\cdots}CO_2$**			**$HXeBr^{\cdots}CO_2$**		
structure:	**$C_{\infty v}$**						**C_s**					
method: basin	**DFT**	**MP2**	**CC**	**DFT**	**MP2**	**CC**	**DFT**	**MP2**	**CC**	**DFT**	**MP2**	**CC**
C(Xe)	-	-	-	45.74	45.75	45.75	-	-	-	45.75	45.74	45.63
C(Br)	27.71	27.67	27.76	27.68	27.72	27.72	27.67	27.71	27.70	28.05	27.70	27.61
C(C)	2.09	2.09	2.09	2.09	2.09	2.09	2.09	2.09	2.09	2.09	2.09	2.09
C(O1), C(O2)	2.13	2.13	2.13	2.13	2.13	2.13	2.13	2.13	2.13	2.12	2.12	2.13
V(O1)	4.53	4.69	5.26	4.87	4.96	5.02	5.17	5.15	5.18	5.24	5.18	5.25
V(O2)	4.53	4.37	4.97	4.87	4.96	5.02	5.11	5.12	5.14	5.11	5.13	5.19
V(Xe)	-	-	-	6.88	6.83	6.81	-	-	-	6.86	6.84	6.92
V(Br)	6.48	6.22	6.40	7.91	7.92	7.93	6.54	6.49	6.51	7.55	7.94	8.05
V(C,O1)	3.29	3.41	2.67	2.94	2.85	2.81	2.67	2.67	2.65	2.61	2.65	2.57
V(C,O2)	3.29	3.44	2.83	2.97	2.88	2.80	2.71	2.71	2.69	2.73	2.71	2.65
V(H,Br)	1.80	1.82	1.83	-	-	-	1.77	1.79	1.78	-	-	-
V(H,Xe)	-	-	-	1.76	1.74	1.75	-	-	-	1.75	1.75	1.76