Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

ELECTRONIC SUPPLEMENTARY INFORMATION

Complexes Containing CO_2 and SO_2. Mixed Dimers, Trimers and Tetramers

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Figure S1. Molecular Electrostatic Potential (MEP) on the van der Walls (vdW) isodensity surface (±0.001 au). Black points are maxima and green points are minima in the electrostatic surface. Blue, green, yellow and red regions go from more negative to more positive values, in that order.

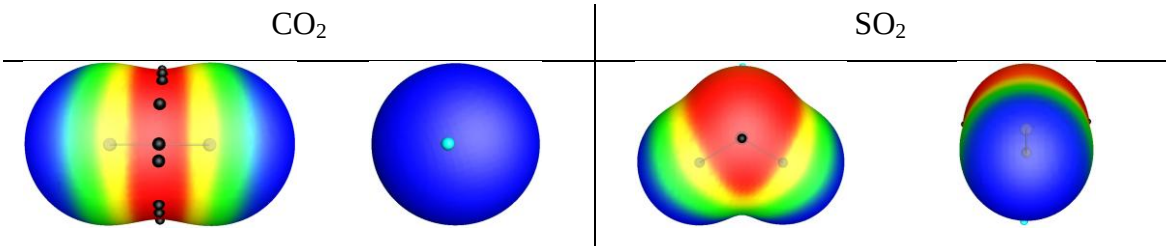
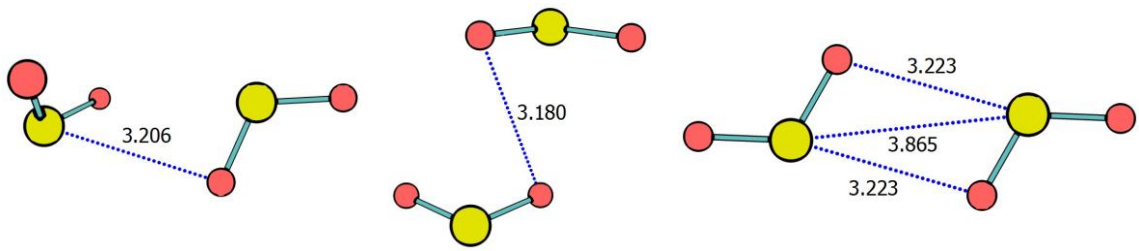


Table S1. Second-order perturbation NBO energy, $E(2)$ in kcal/mol, for the $(CO_2)_2$:SO_2 heterotrimers at ωB97XD/aug-cc-pVDZ computational level, applying an $E(2)$ threshold of 0.5 kcal/mol.

Complex	Donor/Acceptor	Type	$E(2)$
B1	$CO_2(1)/CO_2(2)$	$O_{lp}\rightarrow\pi^*(CO)$	0.93
	$SO_2/CO_2(1)$	$O_{lp}\rightarrow\pi^*(CO)$	0.75
	$SO_2/CO_2(1)$	$O_{lp}\rightarrow\pi^*(CO)$	0.75
	$CO_2(2)/SO_2$	$O_{lp}\rightarrow\pi^*(SO)$	0.81
B2	$CO_2(1)/CO_2(2)$	$O_{lp}\rightarrow\pi^*(CO)$	1.24
	$SO_2/CO_2(1)$	$O_{lp}\rightarrow\pi^*(CO)$	0.88
	$SO_2/CO_2(1)$	$O_{lp}\rightarrow\pi^*(CO)$	0.80
	$CO_2(2)/SO_2$	$O_{lp}\rightarrow\pi^*(SO)$	0.78
B3	$SO_2/CO_2(1)$	$O_{lp}\rightarrow\pi^*(CO)$	0.91
	$SO_2/CO_2(1)$	$O_{lp}\rightarrow\pi^*(CO)$	0.79
	$SO_2/CO_2(2)$	$O_{lp}\rightarrow\pi^*(CO)$	1.43
B4	$SO_2/CO_2(1)$	$O_{lp}\rightarrow\pi^*(CO)$	1.36
	$SO_2/CO_2(2)$	$O_{lp}\rightarrow\pi^*(CO)$	1.36

Figure S2. $(SO_2)_2$ homodimers at MP2/aug-cc-pVDZ computational level. Blue dot lines link atoms which present interatomic AIM BCPs, with distances in Å. Complexes are arranged in ascending order of energy.



F1 (C_1) **F2** (C_i) **F3** (C_2)

Table S2. Interaction energy in kcal/mol at MP2/aug-cc-pVDZ and at CCSD(T)/aug-cc-pVTZ (single point) computational levels for the $(SO_2)_2$ homodimers.

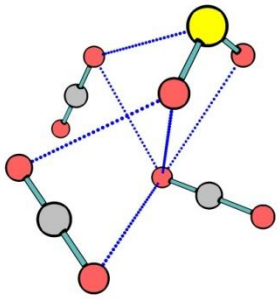
	MP2		CCSD(T)	
Complex	E_{int}	E_{int} + CC[a]	E_{int}	E_{int} + CC[a]
F1	–3.76	–2.39	–3.65	–3.02
F2	–3.39	–2.23	–3.23	–2.66
F3	–3.21	–1.88	–3.09	–2.52

[a]Counterpoise correction of the Basis Set Superposition Error (BSSE).

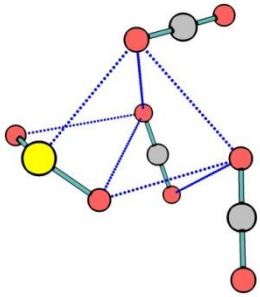
Table S3. Second-order perturbation NBO energy, $E(2)$ in kcal/mol, for the CO_2:$(SO_2)_2$ heterotrimers at ωB97XD/aug-cc-pVDZ computational level, applying an $E(2)$ threshold of 0.5 kcal/mol.

Complex	Donor/Acceptor	Type	$E(2)$
C1	$SO_2(1)/CO_2$	$O_{lp}\rightarrow\pi^*(CO)$	1.11
	$SO_2(1)/CO_2$	$O_{lp}\rightarrow\pi^*(CO)$	0.81
	$SO_2(2)/SO_2(1)$	$O_{lp}\rightarrow\pi^*(SO)$	1.37
	$SO_2(2)/SO_2(1)$	$\pi(SO)\rightarrow\pi^*(SO)$	0.51
C2	$SO_2(1)/CO_2$	$O_{lp}\rightarrow\pi^*(CO)$	0.88
	$SO_2(1)/CO_2$	$O_{lp}\rightarrow\pi^*(CO)$	0.98
	$SO_2(2)/SO_2(1)$	$O_{lp}\rightarrow\pi^*(SO)$	0.61
C3	$SO_2(1)/CO_2$	$O_{lp}\rightarrow\pi^*(CO)$	1.22
	$SO_2(2)/CO_2$	$O_{lp}\rightarrow\pi^*(CO)$	1.29
C4	$CO_2/SO_2(1)$	$O_{lp}\rightarrow\pi^*(SO)$	1.88
	$SO_2(1)/SO_2(2)$	$\pi(SO)\rightarrow\pi^*(SO)$	1.16
	$SO_2(2)/CO_2$	$O_{lp}\rightarrow\pi^*(CO)$	0.91
C5	$SO_2(1)/CO_2$	$O_{lp}\rightarrow\pi^*(CO)$	1.44
	$SO_2(2)/CO_2$	$O_{lp}\rightarrow\pi^*(CO)$	1.09
	$SO_2(2)/SO_2(1)$	$O_{lp}\rightarrow\sigma^*(SO)$	0.70
C6	$CO_2/SO_2(2)$	$O_{lp}\rightarrow\pi^*(SO)$	0.91
	$SO_2(1)/CO_2$	$O_{lp}\rightarrow C_{lv}$	2.02
	$SO_2(2)/SO_2(1)$	$O_{lp}\rightarrow\pi^*(SO)$	1.88
C7	$SO_2(1)/SO_2(2)$	$O_{lp}\rightarrow\pi^*(SO)$	0.66
	$SO_2(2)/CO_2$	$O_{lp}\rightarrow\pi^*(CO)$	1.47
C8	$CO_2/SO_2(2)$	$O_{lp}\rightarrow\pi^*(SO)$	0.85
	$SO_2(2)/CO_2$	$O_{lp}\rightarrow\pi^*(CO)$	0.84
C9	$SO_2(1)/CO_2$	$O_{lp}\rightarrow\pi^*(CO)$	1.39
C10	$SO_2(1)/CO_2$	$O_{lp}\rightarrow\pi^*(CO)$	1.33
	$SO_2(2)/CO_2$	$O_{lp}\rightarrow\pi^*(CO)$	1.44
C11	$SO_2(1)/CO_2$	$O_{lp}\rightarrow\pi^*(CO)$	1.45
	$SO_2(2)/CO_2$	$O_{lp}\rightarrow\pi^*(CO)$	1.45

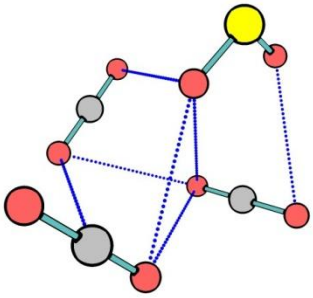
Figure S3. Most stable $(CO_2)_3$:SO_2 minima (less than 1 kcal/mol) at MP2/aug-cc-pVDZ computational level. Blue dot lines link atoms which present interatomic AIM BCPs. Complexes are arranged in ascending order of energy.



D1 (C_1)



D2 (C_1)

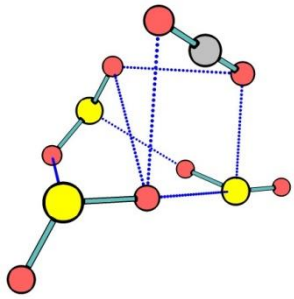


D3 (C_1)

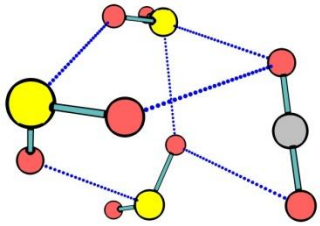
Table S4. Multi-body analysis in kcal/mol for the $(CO_2)_3$:SO_2 complexes at MP2/aug-cc-pVDZ computational level.

Complex	$\Sigma\Delta^2E$	$\Sigma\Delta^3E$	Δ^4E	total E_{int}
D1	–11.36	–0.59	0.00	–11.95
D2	–10.84	–0.56	0.00	–11.40
D3	–10.89	–0.43	0.01	–11.31
D4	–10.47	–0.42	0.02	–10.87
D5	–10.40	–0.44	0.03	–10.81
D6	–10.45	–0.36	0.04	–10.77
D7	–10.44	–0.35	0.02	–10.77
D8	–10.43	–0.38	0.04	–10.77
D9	–10.39	–0.37	0.02	–10.74
D10	–10.33	–0.36	0.02	–10.67
D11	–10.33	–0.31	0.06	–10.58
D12	–9.93	–0.44	0.06	–10.31
D13	–9.39	–0.22	–0.01	–9.62
D14	–9.25	–0.25	0.00	–9.50
D15	–8.16	0.08	–0.04	–8.12
D16	–6.99	–0.01	0.02	–6.98

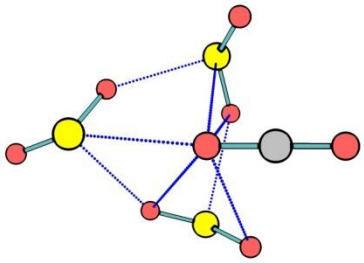
Figure S4. Most stable CO_2:$(SO_2)_3$ minima (less than 1 kcal/mol) at MP2/aug-cc-pVDZ computational level. Blue dot lines link atoms which present interatomic AIM BCPs. Complexes are arranged in ascending order of energy.



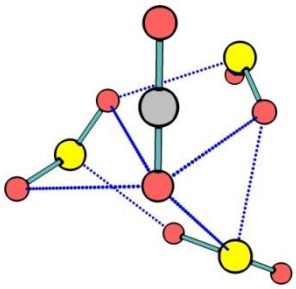
E1 (C_1)



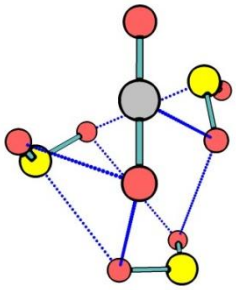
E2 (C_1)



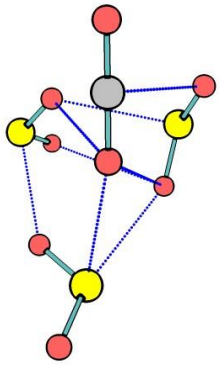
E3 (C_1)



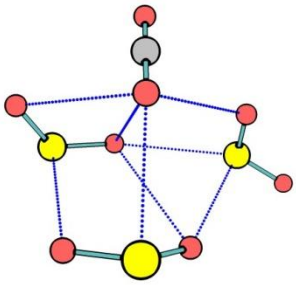
E4 (C_1)



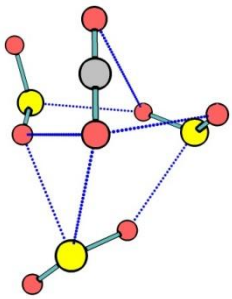
E5 (C_1)



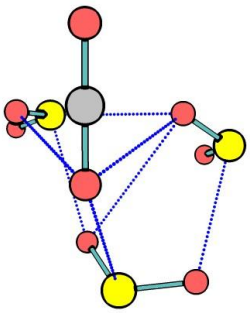
E6 (C_1)



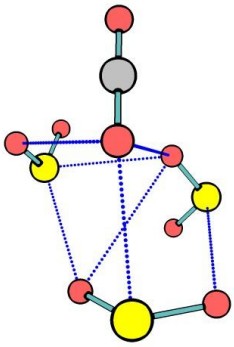
E7 (C_1)



E8 (C_1)



E9 (C_1)



E10 (C_1)

Table S5. Multi-body analysis in kcal/mol for the CO_2:$(SO_2)_3$ complexes at MP2/aug-cc-pVDZ computational level.

Complex	$\Sigma\Delta^2E$	$\Sigma\Delta^3E$	Δ^4E	total E_{int}
E1	–14.73	–1.04	0.01	–15.76
E2	–14.54	–1.11	0.02	–15.63
E3	–14.63	–0.97	0.00	–15.60
E4	–14.37	–1.06	–0.01	–15.44
E5	–14.11	–1.29	0.01	–15.39
E6	–14.28	–1.05	0.00	–15.33
E7	–14.60	–0.62	–0.01	–15.23
E8	–14.12	–0.84	0.02	–14.94
E9	–14.13	–0.79	–0.01	–14.93
E10	–14.06	–0.83	–0.02	–14.91
E11	–14.10	–0.63	–0.02	–14.75
E12	–14.12	–0.49	–0.07	–14.68
E13	–13.70	–0.75	–0.02	–14.47
E14	–13.48	–1.03	0.06	–14.45
E15	–13.50	–0.97	0.05	–14.42
E16	–13.76	–0.69	0.11	–14.34
E17	–13.81	–0.44	–0.08	–14.33
E18	–13.44	–0.74	–0.07	–14.25
E19	–13.26	–0.89	0.08	–14.07
E20	–13.51	–0.54	0.03	–14.02
E21	–13.45	–0.55	0.08	–13.92
E22	–13.46	–0.54	0.10	–13.90
E23	–13.52	–0.43	0.08	–13.87
E24	–13.46	–0.33	0.04	–13.75
E25	–13.24	–0.60	0.06	–13.78
E26	–12.98	–0.70	0.10	–13.58
E27	–13.27	–0.26	–0.02	–13.55
E28	–13.25	–0.39	0.09	–13.55
E29	–12.83	–0.43	0.06	–13.20
E30	–12.87	–0.27	0.08	–13.06
E31	–12.50	–0.35	0.08	–12.77
E32	–12.03	–0.44	0.08	–12.39
E33	–12.09	–0.33	0.10	–12.32
E34	–11.81	–0.27	0.03	–12.05
E35	–10.62	–0.43	0.03	–11.02
E36	–10.26	–0.42	0.01	–10.67
E37	–9.12	–0.04	0.03	–9.13
E38	–9.02	–0.11	0.01	–9.12