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Unveiling the non-covalent interactions of molecular homodimers by dispersion-corrected DFT calculations and collision-induced broadening of ro-vibrational transitions: application to $(CH_2F_2)_2$ and $(SO_2)_2$

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Supporting Information

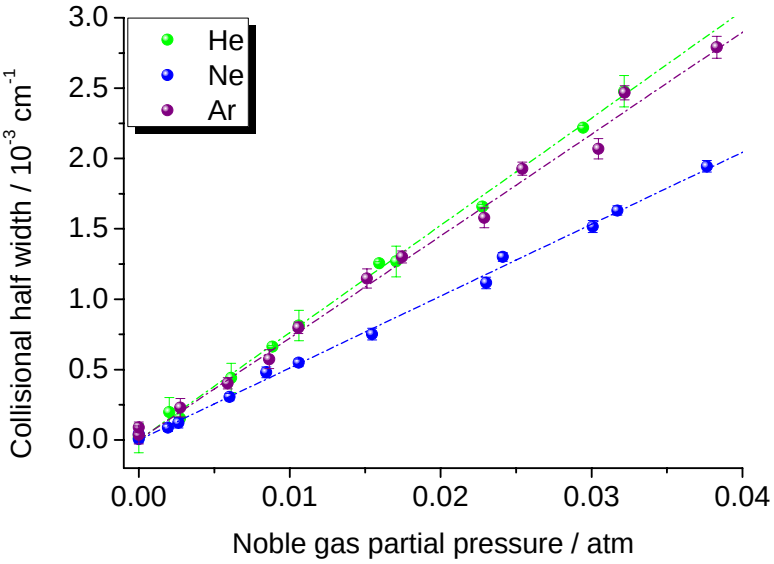

Figure S.1. Collisional half widths and corresponding linear fits for the $25_{10,15} \leftarrow 24_{9,15}$ ro-vibrational transition of the ν_7 band of CH_2F_2 perturbed by noble gases (cyrcles: experimental half widths; straight line: linear fit of Lorentzian half widths against the buffer gas partial pressure).

Table S.1. Relative energies (kcal mol^{-1}) of the stationary points on the PES of $(CH_2F_2)_2$ and $(SO_2)_2$ at CCSD(T)/CBS, DFT-D3/def2-TZVP and DFT/def2-TZVP levels of theory.

$(CH_2F_2)_2$	CCSD(T)/CBS	BLYP-D3	TPSS-D3	B3LYP-D3	PBE0-D3	TPSSh-D3	PW6B95-D3	BLYP	TPSS	B3LYP	PBE0	TPSSh	PW6B95
Struct1	1.7	1.3	1.2	1.4	1.2	1.1	1.6	0.4	0.5	0.5	0.7	0.4	1.3
Struct2	1.1	0.7	0.6	0.8	0.7	0.6	1.0	0.3	0.2	0.3	0.4	0.2	0.8
Struct3	0.4	0.3	0.3	0.3	0.3	0.3	0.4	0.3	0.2	0.2	0.2	0.1	0.3
Struct4	0.5	0.2	0.2	0.3	0.3	0.3	0.6	0.0	0.0	0.0	0.1	0.0	0.5
Struct5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.1	0.0	0.0	0.0
Struct6	0.6	0.3	0.3	0.4	0.4	0.3	0.6	0.1	0.1	0.1	0.2	0.1	0.5

$(SO_2)_2$	CCSD(T)/CBS	BLYP-D3	TPSS-D3	B3LYP-D3	PBE0-D3	TPSSh-D3	PW6B95-D3	BLYP	TPSS	B3LYP	PBE0	TPSSh	PW6B95
Struct1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
Struct2	0.4	0.4	0.4	0.5	0.5	0.5	0.6	0.6	0.5	0.6	0.6	0.5	0.6
Struct3	1.7	1.5	1.1	1.7	1.4	1.6	1.6	0.5	0.5	0.9	1.0	0.4	1.3
Struct4	1.4	1.0	0.7	1.2	1.0	1.2	1.1	0.1	0.2	0.4	0.6	0.0	0.9
Struct5	0.7	0.9	0.7	1.0	0.8	1.0	0.8	0.2	0.3	0.4	0.5	0.2	0.6
Struct6	0.1	0.3	0.3	0.3	0.3	0.4	0.4	0.2	0.2	0.2	0.2	0.1	0.4
Struct7	0.6	0.4	0.2	0.4	0.4	0.4	0.7	0.4	0.3	0.4	0.4	0.2	0.7
Struct8	0.8	0.4	0.3	0.6	0.4	0.5	0.8	0.0	0.1	0.2	0.3	0.0	0.6
Struct9	1.9	1.6	1.3	1.7	1.6	1.8	1.5	1.5	1.2	1.7	1.6	1.1	1.5

Table S.2. Boltzmann weights of the stationary points on the PES of $(CH_2F_2)_2$ and $(SO_2)_2$ employed to compute Boltzmann averaged dissociation energies at CCSD(T)/CBS, DFT-D3/def2-TZVP and DFT/def2-TZVP levels of theory

$(CH_2F_2)_2$	CCSD(T)/CBS	BLYP-D3	TPSS-D3	B3LYP-D3	PBE0-D3	TPSSh-D3	PW6B95-D3	BLYP	TPSS	B3LYP	PBE0	TPSSh	PW6B95
Struct1	-	-	-	-	-	-	-	-	-	-	-	-	-
Struct2	0.07	0.12	0.15	0.10	0.13	0.14	0.09	0.21	0.21	0.19	0.17	0.22	0.11
Struct3	0.25	0.23	0.23	0.25	0.24	0.24	0.26	0.20	0.22	0.23	0.24	0.22	0.26
Struct4	0.20	0.27	0.25	0.25	0.24	0.24	0.18	0.35	0.29	0.31	0.27	0.28	0.20
Struct5	0.47	0.39	0.37	0.40	0.39	0.38	0.48	0.24	0.28	0.28	0.32	0.28	0.44
Struct6	-	-	-	-	-	-	-	-	-	-	-	-	-
$\langle \Delta E \rangle$ [a]	2.80	2.18	2.08	2.34	2.18	2.04	2.49	0.80	1.17	1.09	1.43	1.13	2.00
$\langle \Delta E \rangle_{all}$ [b]	2.81	2.19	2.08	2.35	2.18	2.04	2.54	0.78	1.15	1.08	1.41	1.10	2.04

$(SO_2)_2$	CCSD(T)/CBS	BLYP-D3	TPSS-D3	B3LYP-D3	PBE0-D3	TPSSh-D3	PW6B95-D3	BLYP	TPSS	B3LYP	PBE0	TPSSh	PW6B95
Struct1	0.34	0.32	0.29	0.34	0.32	0.35	0.41	0.27	0.27	0.31	0.31	0.23	0.40
Struct2	0.17	0.16	0.15	0.16	0.15	0.14	0.15	0.10	0.12	0.11	0.11	0.11	0.13
Struct3	-	-	-	-	-	-	-	-	-	-	-	-	-
Struct4	-	-	-	-	-	-	-	-	-	-	-	-	-
Struct5	-	-	-	-	-	-	-	-	-	-	-	-	-
Struct6	0.27	0.19	0.18	0.21	0.20	0.18	0.20	0.20	0.19	0.22	0.21	0.21	0.21
Struct7	0.13	0.18	0.19	0.16	0.17	0.17	0.13	0.15	0.17	0.14	0.16	0.18	0.12
Struct8	0.09	0.16	0.18	0.13	0.15	0.15	0.11	0.28	0.25	0.22	0.20	0.27	0.13
Struct9	-	-	-	-	-	-	-	-	-	-	-	-	-
$\langle \Delta E \rangle$ [a]	2.60	3.14	2.55	3.27	2.80	2.80	2.82	0.39	0.85	0.92	1.50	0.63	1.90
$\langle \Delta E \rangle_{all}$ [b]	2.49	3.02	2.42	3.15	2.67	2.68	2.68	0.37	0.79	0.84	1.39	0.61	1.77

[a] Boltzmann averaged theoretical dissociation energy obtained without considering transition state structures.
[b] Boltzmann averaged theoretical dissociation energy obtained considering all conformers.

Table S.3. Geometrical parameters for the most stable $(CH_2F_2)_2$ structure (Struct 5) and comparison to experimental values. [a]

	BLYP	TPSS	B3LYP	PBE0	TPSSh	PW6B95	Experimental [b]
Unit 1							
C1H2	109.6	109.3	109.0	109.2	109.0	108.6	108.4
C1H3	109.6	109.3	109.0	109.2	109.0	108.6	108.4
C1F4	138.9	137.8	136.9	135.7	137.0	135.7	135.1
C1F5	138.0	137.2	136.2	135.1	136.4	135.2	135.1
∠ H2C1H3	114.0	114.2	113.5	113.1	113.9	113.3	112.8
∠ F4C1F5	108.3	108.0	108.2	108.3	108.0	108.1	108.5
Unit 2							
C7H6	109.7	109.4	109.1	109.3	109.1	108.7	108.4
C7H8	109.6	109.2	108.9	109.2	109.0	108.5	108.4
C7F9	138.5	137.5	136.5	135.4	136.7	135.4	135.1
C7F10	138.5	137.5	136.5	135.4	136.7	135.4	135.1
∠ H6C7H8	114.7	114.7	114.1	113.6	114.5	113.8	112.8
∠ F9C7F10	108.1	108.0	108.0	108.1	107.9	107.9	108.5
Interfragment							
C1C2	355.9	366.5	353.0	356.6	360.9	356.1	354.4
H2F10	276.7	288.6	273.6	277.6	282.0	273.7	276.5
H3F9	276.7	288.6	273.6	277.6	282.0	273.7	276.5
H8F4	262.3	271.2	261.1	265.2	268.3	270.1	263.0
∠ C1H3F9	110.5	109.2	109.2	109.1	109.3	107.6	-
∠ C1H2F10	110.5	109.2	109.2	109.1	109.3	107.6	-
∠ C7H8F4	113.5	112.3	110.1	109.9	111.4	103.9	-
∠F5C1C7F9	-119.6	-119.5	-118.8	-118.9	-119.2	-117.0	-
α [c]	5.9	6.5	7.9	7.3	7.1	12.6	7.2
β [c]	7.0	8.6	8.8	8.5	8.3	10.5	8.9
MD lengths	1.6	4.8	-0.1	0.9	2.7	0.4	-
MAD lengths	1.8	4.8	1.4	0.9	2.7	1.4	-
MD angles	-0.1	0.2	0.3	0.0	0.2	1.2	-
MAD angles	1.2	0.9	0.6	0.4	0.8	1.6	-

[a] Lengths and degrees are expressed in pm and deg, respectively. For atom labeling see Figure S.2
[b] From Ref. [23].
[c] See Ref. [23] for definition of this angle.

Table S.4. Geometrical parameters for the most stable $(SO_2)_2$ structure (Struct 1) and comparison to experimental values.[a]

	BLYP	TPSS	B3LYP	PBE0	TPSSh	PW6B95	Experimental
Unit 1							
S1O2	146.6	145.7	144.2	143.4	144.7	143.1	143.1
S1O3	146.2	145.3	143.8	143.0	144.2	142.8	143.1
∠ O2S1O3	118.3	118.4	118.3	118.3	118.2	118.3	119.3
Unit 2							
S4O5	146.3	145.4	144.0	143.2	144.4	142.9	143.1
S4O6	146.3	145.4	144.0	143.2	144.4	142.9	143.1
∠ O5S4O6	118.4	118.5	118.3	118.4	118.3	118.3	119.3
Interfragment							
S1O5	353.5	359.2	350.7	355.7	344.3	344.4	-
S1O6	353.5	359.2	350.7	355.7	344.3	344.4	-
S1S4	370.6	381.8	371.0	375.6	358.5	374.4	-
S4O2	315.9	329.1	314.7	317.1	305.3	329.4	-
R_{cm}	369.8	378.9	368.1	372.6	359.0	368.8	382.2
∠ S1O2S4	100.0	99.7	101.3	102.7	99.4	96.8	-
∠ O2S4O5	82.6	80.0	81.0	81.1	83.9	76.3	-
∠ O2S4O6	82.6	80.0	81.0	81.1	83.9	76.3	-
∠ O3S1O2S4	-180.0	-180.0	-180.0	-180.0	-180.0	-180.0	-
∠ S1O2S4O5	-60.0	-60.8	-60.4	-60.4	-59.7	-62.1	-
∠ S1O2S4O6	60.4	60.8	60.4	60.4	59.7	60.4	-
θ_1 [d]	117.6	122.6	120.6	120.0	115.3	131.3	127
θ_2 [d]	53.8	53.3	54.8	55.8	53.4	51.3	60.5
MD lengths	0.1	1.2	-2.1	-1.8	-3.6	-2.8	-
MAD lengths	5.1	2.5	3.5	2.0	5.7	2.8	
MD angles	-4.5	-3.3	-3.5	-3.4	-5.2	-1.7	
MAD angles	4.5	3.3	3.5	3.4	5.2	3.9	

[a] Lengths and degrees are expressed in pm and deg, respectively. For atom labeling see Figure S.3
[b] From Ref. [29].
[c] Distance between the centers of mass of the two fragments.
[d] See Ref. [29] for definition of this angle.

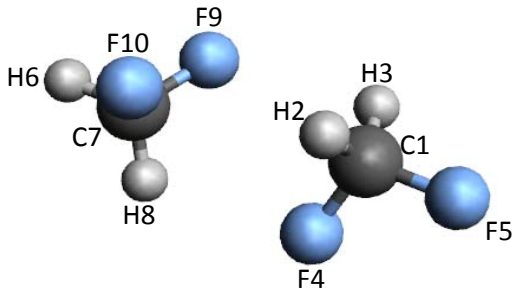

Figure S.2. Labeling of atoms within structure 5 of $(CH_2F_2)_2$.

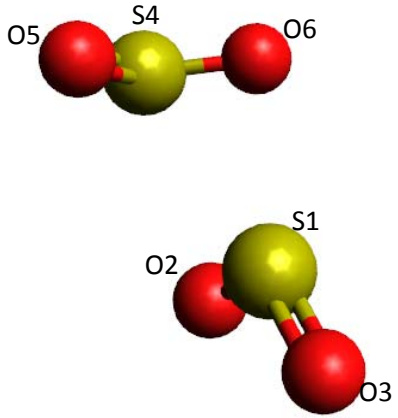

Figure S.3. Labeling of atoms within structure 1 of $(SO_2)_2$.