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

Supplementary Material

Theoretical Treatment of IO-X (X = N_2, CO, CO_2, H_2O) complexes

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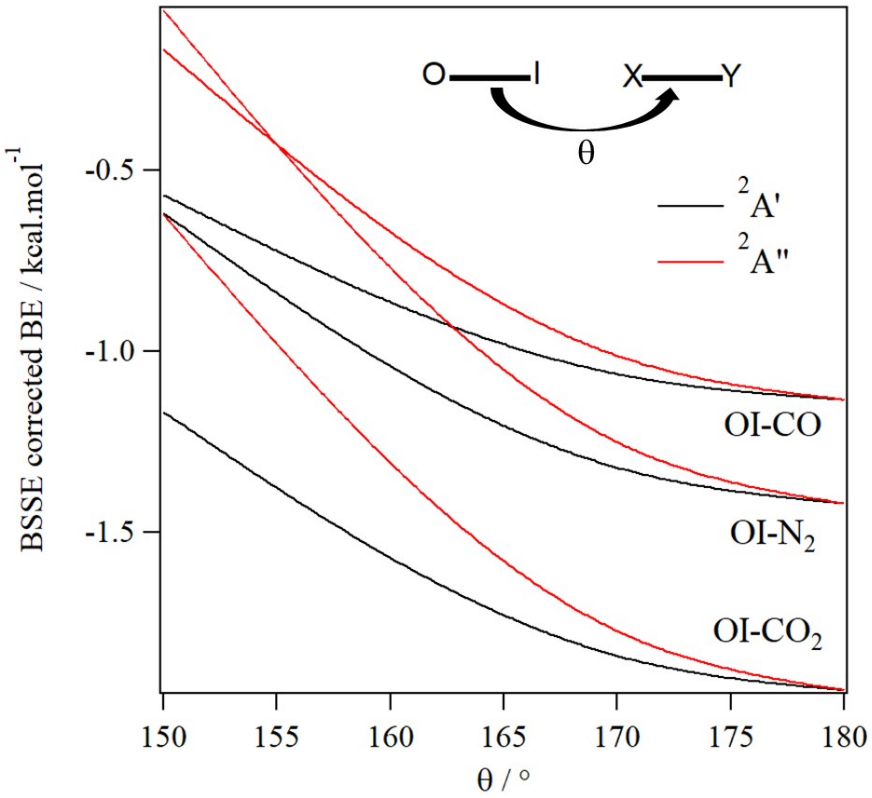

Figure S1: RCCSD(T)/aug-cc-pVTZ(PP) one-dimensional cuts of the potential energy surfaces of the OI-XY (XY = CO, N_2 and CO_2) complexes along the θ angle as defined in this figure. At linearity all complexes have a $^2\Pi$ symmetry. The reference energy is that of the separated monomers.

Table S1: Optimized equilibrium geometric parameters (R_i in Å and θ_i degree) of the I-bonded complexes between IO and N_2, CO, CO_2 or H_2O as computed using PBE0(+D3) and M05-2X(+D3) DFTs in conjunction with the aug-cc-pVTZ(PP) basis set.

	PBE0	PBE0-D3	M05-2X	M05-2X-D3		PBE0	PBE0-D3	M05-2X	M05-2X-D3
OI-N_2					**OI-CO**				
R_1	1.879	1.880	1.903	1.903	R_1	1.125	1.125	1.122	1.122
R_2	3.326	3.326	3.173	3.229	R_2	3.349	3.348	3.388	3.383
R_3	1.089	1.089	1.083	1.083	R_3	1.878	1.879	1.902	1.902
θ_1	180.0	180.0	179.7	179.9	θ_1	180.0	180.0	179.9	179.9
OI-CO_2					**OI-H_2O**				
R_1	1.157	1.157	1.154	1.154	R_1	- [a]	- [a]	2.804	2.796
R_2	3.234	3.239	3.100	3.102	R_2	- [a]	- [a]	0.958	0.958
R_3	1.879	1.879	1.903	1.903	R_3	- [a]	- [a]	1.909	1.910
θ_1	180.0	180.0	180.0	180.0	θ_1	- [a]	- [a]	126.5	126.4
θ_2	179.5	179.5	187.8	188.0	θ_2	- [a]	- [a]	180.0	180.0
θ_3	180.0	179.9	180.0	180.0					

a) No convergence.

Table S2: Optimized equilibrium geometric parameters (R_i in Å and θ_i degree) of the O-bonded complexes between IO and N_2, CO, CO_2 or H_2O as computed using PBE0(+D3) and M05-2X(+D3) DFTs in conjunction with the aug-cc-pVTZ(PP) basis set.

	PBE0	PBE0-D3	M05-2X	M05-2X-D3		PBE0	PBE0-D3	M05-2X	M05-2X-D3
IO-N_2					**IO-CO**				
R_1	1.878	1.877	1.899	1.899	R_1	1.877	1.877	1.904	1.904
R_2	3.483	3.287	3.322	3.167	R_2	3.207	3.116	3.087	3.030
R_3	1.090	1.090	1.084	1.084	R_3	1.124	1.1243	1.120	1.120
θ_1	100.0	94.4	87.4	91.1	θ_1	101.3	99.1	108.1	105.8
θ_2	95.9	100.0	88.6	88.2	θ_2	101.8	101.9	97.4	97.8
IO-CO_2					**IO-H_2O**				
R_1	2.968	2.909	2.797	2.802	R_1	0.962	0.962	0.960	0.960
R_2	1.158	1.158	1.155	1.155	R_2	1.970	1.958	2.030	2.022
R_3	1.876	1.876	1.896	1.896	R_3	1.874	1.875	1.8930	1.893
θ_1	90.7	90.7	90.8	90.7	θ_1	105.1	105.0	105.5	105.4
θ_2	119.8	116.0	115.6	113.8	θ_2	167.7	166.1	170.5	172.3
					θ_3	111.4	107.5	106.4	103.6

Table S3: Non-vanishing spin-orbit integrals (SO, cm^{-1}) in Cartesian coordinates of OI-CO($X^2\Pi$), OI-N_2($X^2\Pi$), OI-H_2O and IO-H_2O complexes at equilibrium.

Complex	Integral	SO
OI-CO ($X^2\Pi$)	i<X $^2\Pi$|$\mathbf{L_zS_z}$|X $^2\Pi$>	-33.4 [a]
OI-N2 ($X^2\Pi$)	i<X $^2\Pi$|$\mathbf{L_zS_z}$|X $^2\Pi$>	-7.4 [a]
IO-N_2	i<1 $^2A''$|$\mathbf{L_xS_x}$|1 $^2A''$>	-0.1 [a]
	<1 $^2A'$|$\mathbf{L_yS_y}$|1 $^2A''$>	6.6 [a]
	i<1 $^2A'$|$\mathbf{L_zS_z}$|1 $^2A''$>	-1.75 [a]
IO-H_2O	i<1 $^2A'$|$\mathbf{L_xS_x}$|1 $^2A'$>	-49.3 [b]
	i<1 $^2A''$|$\mathbf{L_xS_x}$|1 $^2A''$>	-1.2 [b]
	<1 $^2A'$|$\mathbf{L_yS_y}$|1 $^2A''$>	8.1 [b]
	i<1 $^2A'$|$\mathbf{L_zS_z}$|1 $^2A''$>	-47.4 [b]
OI-H_2O	i<1 $^2B_1$|$\mathbf{LzSz}$|1 $^2B_2$>	-5.8 [b]

a) Computed at the full valence CASSCF/aug-cc-pVTZ(PP) level.
b) Computed at the full valence CASSCF/aug-cc-pVDZ(PP) level.

Table S4: Vibrational frequencies (υ_i in cm^{-1}) of the I-bonded complexes between IO and X (X = N_2, CO, CO_2, H_2O) as computed using PBE0(+D3) and M05-2X(+D3) DFTs in conjunction with the aug-cc-pVTZ(PP) basis set. For sake of simplicity, the modes are numbered by increasing energy.

Mode	PBE0	PBE0-D3	M05-2X	M05-2X-D3	Mode	PBE0	PBE0-D3	M05-2X	M05-2X-D3
OI-N_2					**OI-CO**				
υ_1	32	30	- [a]	- [a]	υ_1	24	23.80	- [a]	- [a]
υ_2	32	31	23	17	υ_2	28	27	20	37
υ_3	53	58	66	62	υ_3	50	55	22	37
υ_4	84	79	102	93	υ_4	57	57	61	61
υ_5	88	88	107	98	υ_5	65	65	115	134
υ_6	691	691	650	648	υ_6	691	694	642	643
υ_7	2482	2483	2556	2556	υ_7	2224	2224	2267	2268
OI-CO_2					**OI-H_2O**				
υ_1	21	20	- [a]	- [a]	υ_1	- [b]	- [b]	74	69
υ_2	21	20	16	16	υ_2	- [b]	- [b]	82	84
υ_3	48	47	33	30	υ_3	- [b]	- [b]	149	151
υ_4	48	49	46	45	υ_4	- [b]	- [b]	201	182
υ_5	60	59	71	72	υ_5	- [b]	- [b]	293	290
υ_6	681	682	653	652	υ_6	- [b]	- [b]	636	638
υ_7	682	682	697	697	υ_7	- [b]	- [b]	1612	1608
υ_8	693	692	697	697	υ_8	- [b]	- [b]	3860	3862
υ_9	1395	1394	1410	1410	υ_9	- [b]	- [b]	3960	3963
υ_{10}	2449	2449	2443	2443					

a) Imaginary frequency.
b) No convergence.

Table S5: Vibrational frequencies (υ_i in cm^{-1}) of the O-bonded complexes between IO and X (X = N_2, CO, CO_2, H_2O) as computed using PBE0(+D3) and M05-2X(+D3) DFTs in conjunction with the aug-cc-pVTZ(PP) basis set. For sake of simplicity, the modes are numbered by increasing energy.

Mode	PBE0	PBE0-D3	M05-2X	M05-2X-D3	Mode	PBE0	PBE0-D3	M05-2X	M05-2X-D3
IO-N_2					**IO-CO**				
υ_1	12	20	29	34	υ_1	24	24	20	37
υ_2	16	32	43	48	υ_2	26	40	22	37
υ_3	24	33	54	73	υ_3	42	51	61	61
υ_4	39	54	66	95	υ_4	88	100	115	134
υ_5	697	696	648	652	υ_5	698	698	642	643
υ_6	2480	2480	2549	2551	υ_6	2233	2233	2267	2268
IO-CO_2					**IO-H_2O**				
υ_1	16	24	41	52	υ_1	35	41	38	39
υ_2	31	34	66	70	υ_2	158	165	157	161
υ_3	59	71	88	93	υ_3	260	266	311	319
υ_4	100	111	137	138	υ_4	299	303	329	323
υ_5	673	671	642	645	υ_5	335	346	397	383
υ_6	685	686	688	689	υ_6	708	707	625	624
υ_7	702	701	704	705	υ_7	1650	1653	1635	1636
υ_8	1390	1390	1405	1405	υ_8	3778	3773	3812	3812
υ_9	2442	2441	2433	2432	υ_9	3892	3888	3910	3910

a) Low frequency mode.