A Theoretical Study of the Gas-Phase Reactions of Iodine Atoms ($^2P_{3/2}$) with H_2, H_2O, HI and OH

Sébastien CANNEAUX, Bertrand XERRI, Florent LOUIS, Laurent CANTREL

SUPPORTING INFORMATION

Table 1S: Vibrational Frequency Scaling Factors[a]

Level of theory		Vibrational Frequency Scaling Factors
MP2	**cc-pVTZ**	0.961
	cc-pVQZ	0.960
	6-311G(d,p)	0.955
MPW1K	**cc-pVTZ**	0.950
	cc-pVQZ	0.949
	6-311G(d,p)	0.947
BHandHLYP	**cc-pVTZ**	0.949
	cc-pVQZ	0.948
	6-311G(d,p)	0.946

[a] The *ab initio* and DFT vibrational frequencies were multiplied by an appropriate scaling factor, which was obtained at each level of theory by plotting observed fundamentals for H_2[1S], OH[1S], HI[1S], I_2[1S], and H_2O[3S-4S] versus calculated frequencies.

Table 2S: Optimized geometry parameters[a] for reactants and products at different levels of theory

Level of theory		Species					
		H_2	**OH**	**HI**	**I_2**	**H_2O**	
		r	*r*	*r*	*r*	*r*	θ
MP2	**cc-pVTZ**	0.737	0.967	1.598	2.657	0.959	103.5
	cc-pVQZ	0.736	0.966	1.589	2.636	0.958	104.0
	6-311G(d,p)	0.738	0.966	1.606	2.714	0.958	102.4
MPW1K	**cc-pVTZ**	0.740	0.962	1.606	2.646	0.951	105.0
	cc-pVQZ	0.739	0.962	1.603	2.643	0.949	105.2
	6-311G(d,p)	0.741	0.963	1.612	2.678	0.950	104.4
BHandHLYP	**cc-pVTZ**	0.737	0.962	1.607	2.672	0.950	105.3
	cc-pVQZ	0.736	0.961	1.604	2.668	0.949	105.6
	6-311G(d,p)	0.738	0.962	1.613	2.701	0.950	104.7
Literature		*0.741*[b]	*0.970*[b]	*1.609*[b]	*2.666*[b]	*0.958*[c]	*104.5*[c]

[a] Bond lengths *r* are in Angstroms and bond angles θ are in degrees. The values in italics are taken from ref. 1S[b], ref. 2S[c].

Table 3S: Calculated unscaled vibrational frequencies (in cm^{-1}) for reactants and products at different levels of theory

Level of theory		Species				
		H_2	**OH**	**HI**	**I_2**	**H_2O**
MP2	**cc-pVTZ**	4526	3822	2424	234	1652, 3855, 3976
	cc-pVQZ	4519	3824	2463	238	1642, 3855, 3978
	6-311G(d,p)	4533	3854	2415	222	1667, 3906, 4014
MPW1K	**cc-pVTZ**	4489	3876	2413	238	1675, 3967, 4071
	cc-pVQZ	4483	3877	2417	238	1671, 3972, 4076
	6-311G(d,p)	4494	3886	2432	234	1669, 3988, 4089
BHandHLYP	**cc-pVTZ**	4517	3872	2403	229	1685, 3967, 4068
	cc-pVQZ	4512	3875	2405	229	1681, 3971, 4071
	6-311G(d,p)	4519	3882	2418	224	1683, 3981, 4077
Literature		*4401*[a]	*3738*[a]	*2309*[a]	*215*[a]	*1595*[b], *3657*[b], *3756*[c]

The experimental values of the vibrational frequencies are in Italics. These values are taken from ref. 1S[a], ref. 3S[b], ref. 4S[c].

Table 4S: Calculated unscaled vibrational frequencies (in cm^{-1}) for transition states and molecular complexes at different levels of theory

I ($^2P_{3/2}$) + H_2 → HI + H (R_1)

Level of theory		Species		
		MCR1	**TS1**	**MCP1**
MP2	**cc-pVTZ**	51, 97, 97, 4526	443, 443, 1770, 872i	51, 51, 68, 2423
	cc-pVQZ	91, 126, 187, 4508	432, 432, 1833, 836i	93, 93, 111, 2460
	6-311G(d,p)	69, 110, 144, 4529	458, 458, 1591, 1102i	28, 28, 40, 2415
MPW1K	**cc-pVTZ**	23, 38, 65, 4486	234, 234, 2200, 244i	77, 105, 105, 2385
	cc-pVQZ	27, 41, 65, 4481	234, 234, 2193, 253i	48, 146, 146, 2331
	6-311G(d,p)	20, 41, 65, 4491	306, 306, 2110, 351i	125, 169, 169, 2385
BHandHLYP	**cc-pVTZ**	41, 62, 93, 4514	188, 188, 2268, 111i	40, 162, 162, 2310
	cc-pVQZ	40, 66, 89, 4510	196, 196, 2259, 132i	57, 155, 155, 2321
	6-311G(d,p)	78, 109, 143, 4511	277, 277, 2155, 265i	117, 182, 182, 2349

I ($^2P_{3/2}$) + H_2O → HI + OH (R_2)

Level of theory		Species		
		MCR2	**TS2**	**MCP2**
MP2	**cc-pVTZ**	111, 238, 254, 1646, 3830, 3952	200, 326, 659, 1710, 3783, 589i	86, 138, 224, 312, 2376, 3804
	cc-pVQZ	110, 219, 225, 1636, 3828, 3951	186, 297, 650, 1801, 3785, 511i	88, 234, 257, 352, 2378, 3765
	6-311G(d,p)	109, 234, 258, 1658, 3882, 3993	221, 374, 682, 1434, 3814, 901i	85, 142, 229, 307, 2370, 3835
MPW1K	**cc-pVTZ**	125, 284, 295, 1664, 3946, 4052	183, 313, 494, 2040, 3865, 203i	78, 140, 231, 318, 2347, 3864
	cc-pVQZ	115, 273, 284, 1663, 3949, 4054	157, 287, 497, 2037, 3868, 231i	74, 129, 222, 302, 2352, 3867
	6-311G(d,p)	147, 318, 340, 1654, 3956, 4062	194, 374, 583, 1840, 3874, 386i	100, 159, 297, 363, 2338, 3870
BHandHLYP	**cc-pVTZ**	118, 253, 268, 1676, 3950, 4052	180, 288, 609, 1705, 3867, 429i	81, 126, 224, 293, 2357, 3863
	cc-pVQZ	108, 240, 251, 1675, 3954, 4055	155, 227, 604, 1680, 3872, 434i	77, 123, 211, 272, 2367, 3865
	6-311G(d,p)	136, 291, 314, 1669, 3961, 4062	205, 361, 659, 1514, 3876, 655i	97, 132, 224, 327, 2355, 3871

I ($^2P_{3/2}$) + HI → H + I_2 (R_3)

Level of theory		Species		
		MCR3	**TS3**	**MCP3**
MP2	**cc-pVTZ**	48, 174, 2417	148, 266, 634i	32, 87, 234
	cc-pVQZ	71, 211, 2454	135, 268, 577i	59, 164, 244
	6-311G(d,p)	25, 120, 2410	165, 251, 780i	13, 51, 222

I ($^2P_{3/2}$) + OH → HI + O (^3P) (R_4)

Level of theory		Species		
		MCR4	**TS4**	**MCP4**
MP2	**cc-pVTZ**	91, 227, 3796	191, 1151, 1549i	59, 141, 141, 2415
	cc-pVQZ	96, 224, 3793	187, 1224, 1494i	64, 146, 146, 2452
	6-311G(d,p)	89, 230, 3832	199, 1081, 1822i	64, 150, 150, 2412
MPW1K	**cc-pVTZ**	109, 369, 3846	171, 1550, 754i	57, 165, 2393
	cc-pVQZ	103, 363, 3847	165, 1533, 761i	49, 153, 2394
	6-311G(d,p)	124, 373, 3854	194, 1480, 940i	73, 207, 2404
BHandHLYP	**cc-pVTZ**	107, 296, 3850	165, 1197, 1023i	68, 132, 2388
	cc-pVQZ	100, 291, 3854	157, 1153, 1018i	61, 125, 2392
	6-311G(d,p)	122, 328, 3863	184, 1190, 1263i	78, 200, 2401

Table 5S: Literature[a] enthalpy of formation at 0 K

Compound	$\Delta_f H^o$(0 K), kJ mol^{-1}
H	216.035 ± 0,06
O (^{3}P)	246.79 ± 0.10
I ($^2P_{3/2}$)	107.16 ± 0.04
H_2	0.00
OH	38.390 ± 1.21
HI	28.535 ± 0.21
I_2	65.504 ± 0.092
H_2O	-238.921 ± 0.042

[a] All the values are taken from Chase et al.[5S]

REFERENCES FOR SUPPORTING INFORMATION:

(1S) NIST Chemistry Webbook, *NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg MD, 2005 (http://webbook.nist.gov).

(2S) Hoy, A. R.; Bunker, P. R. *J. Molecular Structure* **1979**, *74*, 1-8.

(3S) Shimanouchi, T., Tables of Molecular Vibrational Frequencies, Consolidated Volume 1, NSRDS NBS-39

(4S) Huber, K. P.; Herzberg, G., Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules,, Van Nostrand Reinhold Co., 1979

(5S) Chase, M. W.; Davies, C. A.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data*, **1985**, *14*, Suppl. N°1.