Assessment of an effective quasirelativistic methodology designed to study astatine chemistry in aqueous solution

Julie Champion, Mahamadou Seydou, Andrea Sabatié-Gogova, Eric Renault, Gilles Montavon* and Nicolas Galland*

Electronic supplementary information

Section 1. Tables

Table S1 Calculated spectroscopic constants of At, HAt and At_2 species from literature (if available, the contribution of spin-orbit interactions is given in parentheses)

		DK-CASPT2 + RASSI-SO[a]	***2c* DK6-B3LYP**[b]	***2c* DK6-B3LYP/PP**[b]
At	*IE* (eV)	9.13 (-0.79)	9.24 (-0.85)	9.27 (-0.81)
	EA (eV)	2.22 (-0.82)	2.30 (-0.82)	2.37 (-0.77)
		***2c* CCSD(T)/RECP**[c]	***4c* B3LYP**[d]	***4c* CCSD(T)**[e]
HAt	D_e (eV)	2.19 (-0.68)	2.31	2.45 (-0.71)
	R_e (Å)	1.738 (+0.031)	1.743	1.718 (+0.029)
	ω_e (cm^{-1})	1924 (-182)	1947	1992 (-173)
		***4c* B3LYP**[d]	***4c* CCSD(T)**[f]	***2c* DK6-B3LYP**[b]
At_2	D_e (eV)	0.54	0.63	0.64 (-1.09)
	R_e (Å)	3.112	3.046	3.058 (+0.179)
	ω_e (cm^{-1})	102	108	107 (-46)

[a] B. O. Roos, R. Lindh, P.-A. Malmqvist, V. Veryazov and P.-O. Widmark, *J. Phys. Chem. A*, 2004, **108**, 2851-2858. [b] A. Mitin, V. and C. van Wullen, *J. Chem. Phys.*, 2006, **124**, 64305. [c] Y.-K. Han, C. Bae and Y. S. Lee, *J. Chem. Phys.*, 1999, **110**, 8969-8975. [d] T. Nakajima and K. Hirao, *J. Chem. Phys.*, 2003, **119**, 4105-4111. [e] A. S. P. Gomes and L. Visscher, *Chem. Phys. Lett.*, 2004, **399**, 1-6. [f] L. Visscher and K. G. Dyall, *J. Chem. Phys.*, 1996, **104**, 9040-9046.

Table S2 Log *K* values computed at different levels of theory for three complexation reactions

Reaction	B3LYP/mAVDZ[a]		Experiment
	CPCM-UAHF[b]	CPCM-UAKS[c]	
$At^+ + Br^- \rightleftarrows AtBr$	-6.4	-4.9	3.0 ± 0.2
$At^+ + 2Br^- \rightleftarrows AtBr_2^-$	2.0	4.5	4.1 ± 0.3
$AtCl + Cl^- \rightleftarrows AtCl_2^-$	8.7	9.7	0.4 ± 0.3

[a] Gas phase free energy of reaction based on B3LYP/mAVDZ calculations. [b] Solvation free energies based on CPCM-UAHF calculations. [c] Solvation free energies based on CPCM-UAKS calculations.

Table S3 Computed values of Log K_{exc} based on B3LYP/mAVDZ and CPCM-UAKS calculations

	$AtX + Y^- \rightleftharpoons AtY + X^-$		$AtOX + Y^- \rightleftharpoons AtOY + X^-$	
Log K_{exc} X^-/Y^-	**Cl^-/Br^-**	**Br^-/SCN^-**	**Cl^-/Br^-**	**Br^-/SCN^-**
	2.0	-0.5	0.8	-0.2
	$AtX_2^- + 2Y^- \rightleftharpoons AtY_2^- + 2X^-$		$AtOX_2^- + 2Y^- \rightleftharpoons AtOY_2^- + 2X^-$	
Log K_{exc} X^-/Y^-	**Cl^-/Br^-**	**Br^-/SCN^-**	**Cl^-/Br^-**	**Br^-/SCN^-**
	1.6	-1.2	0.7	-4.0

Section 2. Exponents and contraction coefficients of the modified aug-cc-pVDZ-PP basis set for astatine

mAVDZ

```
S
304.031000   0.0010310    0.0004960    0.0000000    0.0000000
22.4085000   -0.1018690   -0.0387430   0.0000000    0.0000000
14.0490000   0.5632730    0.2490070    0.0000000    0.0000000
7.5895000    -1.1045120   -0.5516910   0.0000000    0.0000000
1.8949400    1.0263640    0.8155580    0.0000000    0.0000000
0.9523580    0.3833240    0.2868020    0.0000000    0.0000000
0.3170410    0.0113590    -0.8682780   1.0000000    0.0000000
0.1224900    -0.0011400   -0.4694960   0.0000000    1.0000000
S
0.0404000    1.0000000
```

```
P
12.0093000  0.1631810   -0.0583630   0.0000000   0.0000000
8.0330000   -0.4244130  0.1606310    0.0000000   0.0000000
2.2239300   0.7031340   -0.3589420   0.0000000   0.0000000
1.0213300   0.4641680   -0.1621230   0.0000000   0.0000000
0.3012660   0.0302600   0.6248880    0.0000000   0.5562930
0.0999030   -0.0026180  0.5397840    1.0000000   0.5296780
P
0.0313000   1.0000000
D
21.3084000  0.0061410   0.0000000
7.0207600   -0.0706690  0.0000000
2.7689800   0.3190200   0.0000000
1.3731400   0.5044700   0.0000000
0.6368040   0.2924810   0.0000000
0.2593000   0.0514950   1.0000000
D
0.1073000   1.0000000
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