

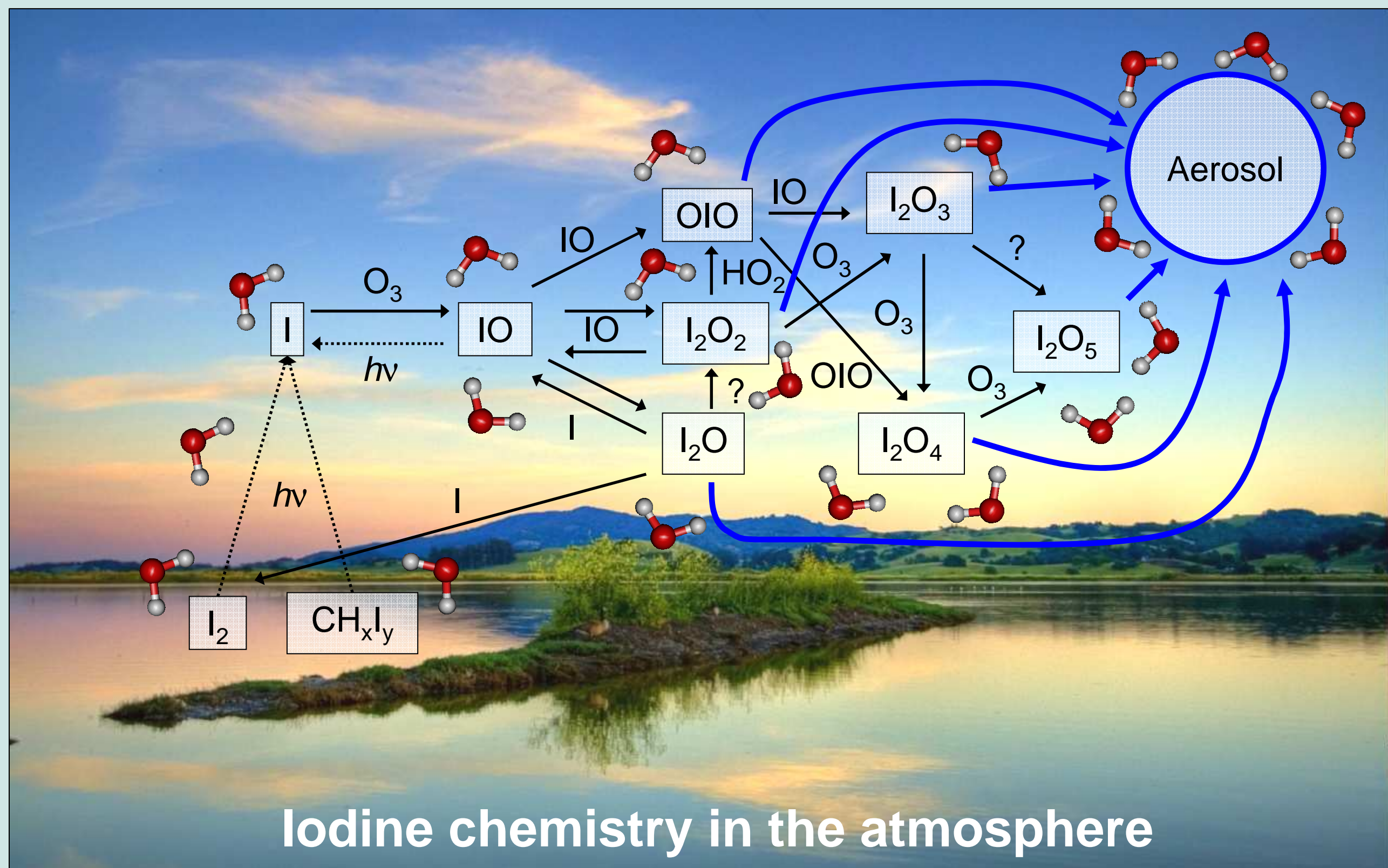
Quantum chemical investigation on iodine oxides and their role in the formation of atmospheric aerosols

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Introduction

Atmospheric iodine has received considerable attention in the two past decades due to both its potential role in the catalytic destruction of ozone (1) and its contribution to the formation of aerosol particles (2), see Fig 1. Seaweeds and marine phytoplankton release iodocarbons and I₂ to the atmosphere, which are photo-oxidized, giving iodine oxides that polymerize to finally form iodine oxide particles (IOPs). In the last years, some laboratory studies have been done to investigate this process (see e.g. (3)), however the complete mechanism of formation of such particles and the role of water in this process, which could be specially relevant, have not yet been elucidated. In this context, quantum calculations could help to unravel essential steps of these processes, and in this contribution, for the first time, we present high level *ab initio* calculations to evaluate the formation of water-iodine oxides complexes.



Theoretical methods

- Iodine atom treated in quantum calculations with Averaged Relativistic Effective Potential (AREP) operators to substitute core electrons and AREP-optimized aug-cc-pVTZ basis sets obtained with MOLPRO2006.
- B3LYP and MP2/aug-cc-pVTZ geometries of iodine oxides and water complexes optimized with GAUSSIAN09.
- Thermodynamics properties calculated with ZPE-corrected B3LYP and MP2, frequencies obtained also with aug-cc-pVTZ basis sets with GAUSSIAN09.
- In exploratory calculation of simple species, Spin-orbit (SO) effects were included. SO were accounted for in spin-orbit DFT (SODFT) calculations using the SO operator part of the relativistic effective core potential (RECP) for iodine atom. SODFT calculations allow to treat explicitly the SO coupling. SODFT values obtained with NWChem 2.1.

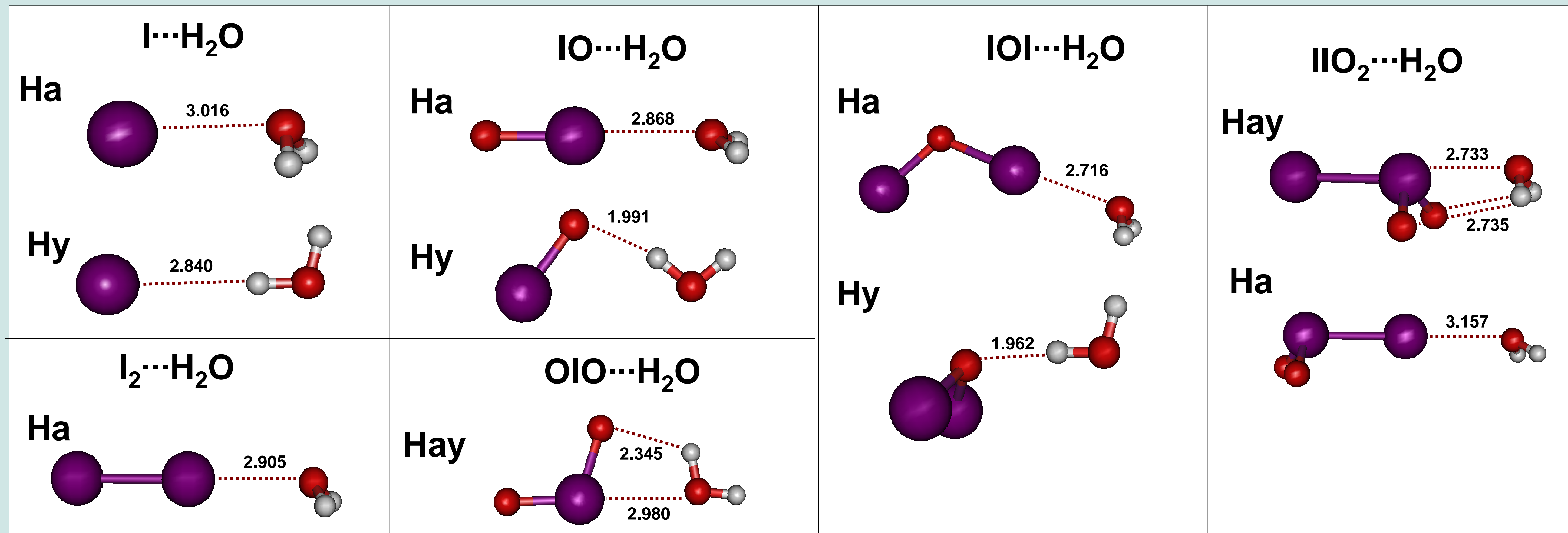
Benchmarking our methodology

	HI				I ₂		
	r _e /Å	ω _e /cm ⁻¹	D _e /Kcal.mol ⁻¹		r _e	ω _e	D _e
AREP B3LYP aTZ	1.610	2306	3.40		2.694	212	1.77
AREP MP2 aTZ	1.600	2390	3.35		2.663	226	1.93
SODFT-RECP-B3LYP aTZ	1.614	2332	3.35		2.713	201	1.72
Experimental	1.609	2309	3.20		2.666	215	1.56

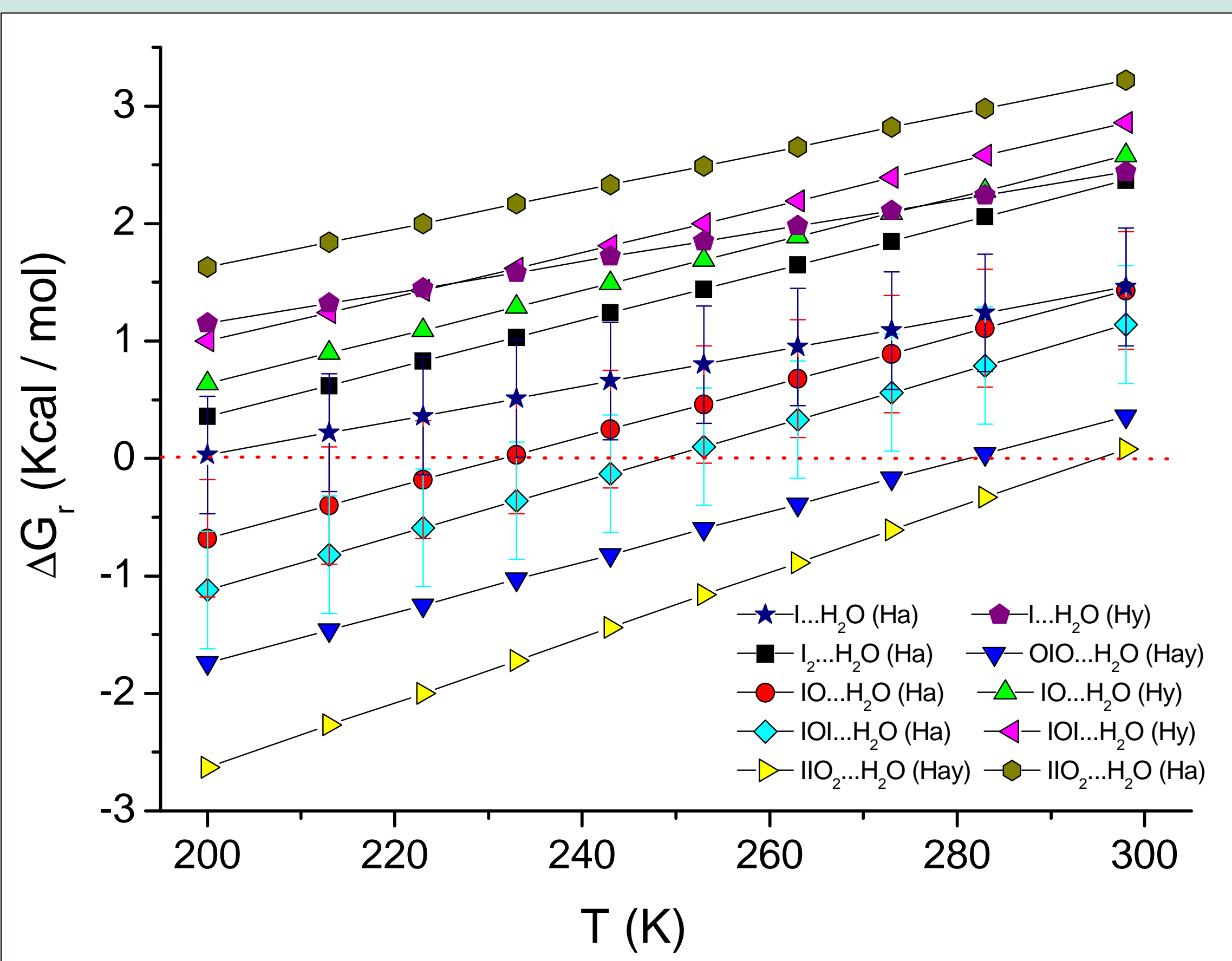
	IO				I ₃ ⁻ (Δ _f H ⁰ and Δ _f G ⁰ in Kcal.mol ⁻¹)		
	r _e	ω _e	D _e		ω _e	Δ _f H ⁰ ₂₉₈	Δ _f G ⁰ ₂₉₈
AREP B3LYP aTZ	1.868	690	2.58				
AREP MP2 aTZ	1.862	645	2.20		59, 118, 148	-253.8	-267.8
SODFT-RECP-B3LYP aTZ	1.865	705	2.63				
Experimental	1.868	682	2.35 ± 0.03		---, 112, 140	-252 ± 6	-266

Results

We have calculated different water complexes of the most relevant iodine species involved in the aerosol formation. Halogen bond (Ha) and hydrogen bond (Hy) are the intermolecular links responsible for the complexes formation. Frequencies calculations have been done to both check that all the conformers are real minimum and to obtain thermodynamic values. Intermolecular values in Å at MP2 level are included.



	I...H ₂ O (Ha)	I...H ₂ O (Hy)	I ₂ ...H ₂ O (Ha)	IO...H ₂ O (Ha)	IO...H ₂ O (Hy)	OIO...H ₂ O (Hay)	IOI...H ₂ O (Ha)	IOI...H ₂ O (Hy)	IIO ₂ ...H ₂ O (Hay)	IIO ₂ ...H ₂ O (Ha)
ΔE, B3LYP	-2.35	-0.51	-2.32	-3.39	-2.51	-4.72	-4.13	-1.05	-5.65	-1.28
ΔE, MP2	-2.61	-1.31	-3.83	-5.04	-3.12	-6.09	-5.74	-2.91	-7.96	-2.19
ΔH _f , MP2	-2.88	-1.49	-3.75	-4.98	-3.32	-6.04	-5.71	-2.81	-8.17	-1.62
ΔG _f ²⁹⁸ , MP2	1.46	2.44	2.37	1.43	2.58	0.36	1.14	2.86	0.08	3.22
ΔG _f ²⁷³ , MP2	1.09	2.11	2.06	0.89	2.09	-0.17	0.56	2.39	-0.61	2.82



Conclusions

- The combination of AREP and the flexible basis set aug-cc-pVTZ optimized in this work, give accurate geometries and thermodynamic properties on all the different iodine species tested (see also our previous work in ref. 4).
- B3LYP and MP2 give similar results, although MP2 predict higher energies of formation on the complexes.
- Our methodology also allows us to include SO corrections, although in these systems they have a minor effect.
- Stable complexes are formed between iodine atom, I₂ or iodine oxides and water, giving negative energies and enthalpies of reaction of formation.
- Halogen bonding gives more stable conformers than hydrogen bonding, at ca. 1.5 kcal/mol.
- However, all reactions of formation of complexes are endoergonic at 298 K, although in the case of OIO and IIO₂, ΔG_f²⁹⁸ are approximately zero.
- When temperature decrease (from 298 to 200 K), ΔG_f of hydrate formation change to negative values for several species: IIO₂, OIO, IOI, IO and I. This result points to a sensitive role of temperature in controlling hydrate formation in the marine boundary layer.

References

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Acknowledgments

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