Modelling of iodine atmospheric chemistry

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Outline

- Context

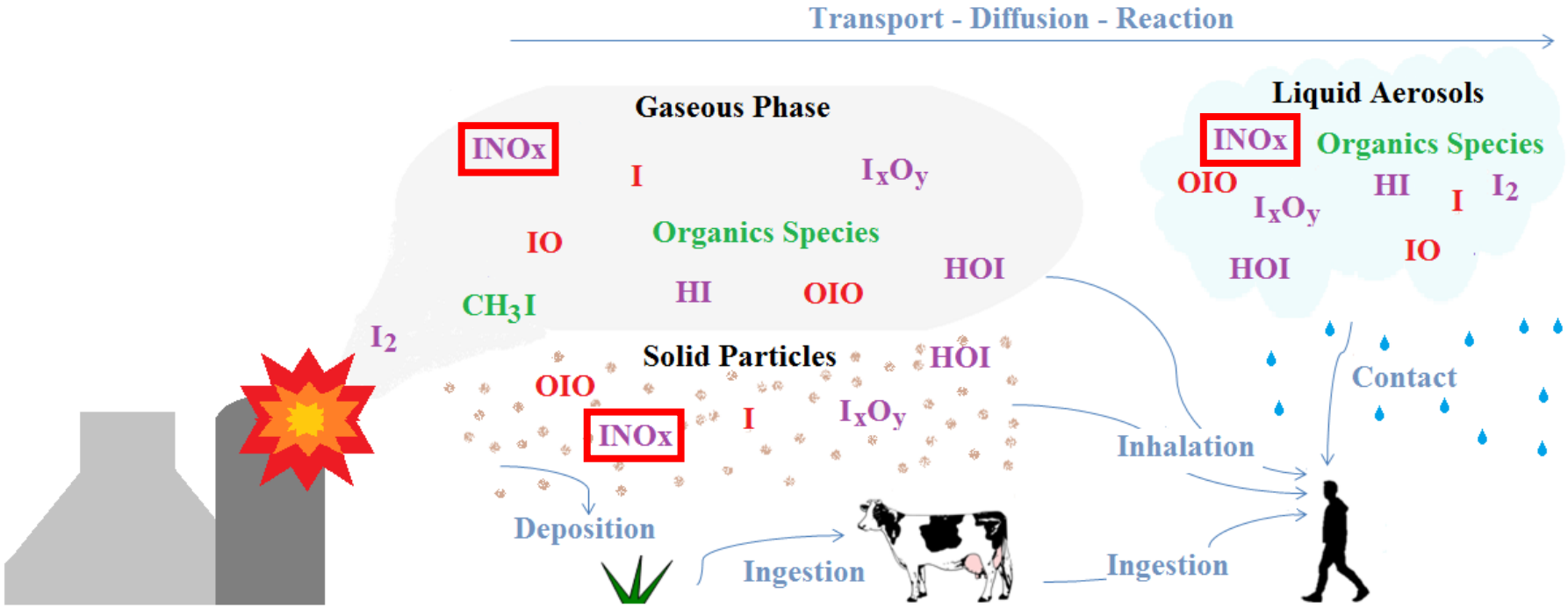
- Thermodynamic properties (gas phase)
  - *Computational methods*
  - *Results*

- Microhydration (gas phase)

- Henry's law constants (aqueous phase)
  - *Computational methods*
  - *Results*

Context

- Radioactive iodine (^{131}I) released in the atmosphere in case of a nuclear power plant accident.



- Speciation of iodine species: gas phase, aerosols.
  - Need to determine their gas-phase stability (thermodynamic properties, reactivity) and their mass transfer to liquid phase (k_H, α).

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INOx computational methods

➢ Aim: Thermochemical properties within **chemical accuracy** (± 4.18 kJ mol^{-1})

Step 1

Structures:

- Optimized geometries and vibrational frequencies calculated at the UωB97XD/ aug-cc-pVTZ level of theory (**ECP28 for I**).
- Test systematically the stability of the DFT and HF wave functions.

Difficulties associated to the presence of heavy elements

Step 2

Energetics:

- Potential energies calculated at the UωB97XD/aug-cc-pV5Z and UCCSD(T)/CBS (T,Q,5) with ωB97XD optimized geometries.

Electron correlation
Within valence electrons and chemical bonds

Multiconfigurational wave functions ?
Unpaired electrons

Step 3

Spin-orbit coupling (SOC in kJ mol^{-1}):

- RASSCF/CASPT2/RASSI

Relativistic effects
Heavy elements

INO	INO_2	Cis-IONO	Trans-IONO	$IONO_2$	ICl	IBr	HI
-4.93	-5.51	-6.76	-5.96	-7.22	-6.78	-7.57	-2.26

INOx computational methods

Step 4

Thermochemical properties ($\Delta_f H°_{298K}$, $\Delta_r H°(T)$, $\Delta_r G°(T)$):

- Isogyric reaction is used to determine the standard enthalpy of formation.

  "A reaction in which the number of electron pairs is conserved" from IUPAC Gold Book"

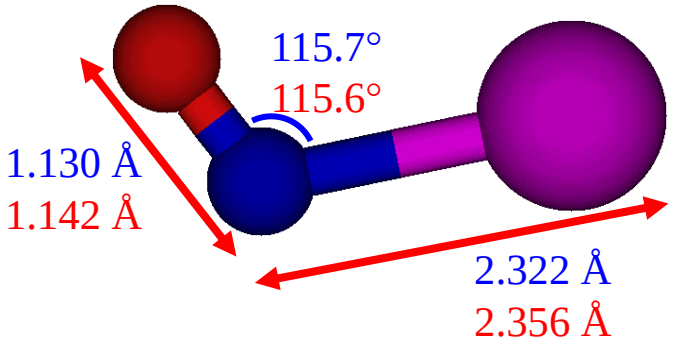
  - Set of 4 reactions (x = 1, 2, and 3)
    - INOx + H = I + HNOx
    - INOx + H_2 = HI + HNOx
    - INOx + HCl = ICl + NOx
    - INOx + HBr = IBr + NOx
  - Standard enthalpies of formation for reference species (kJ mol^{-1}) (JPL 2015)

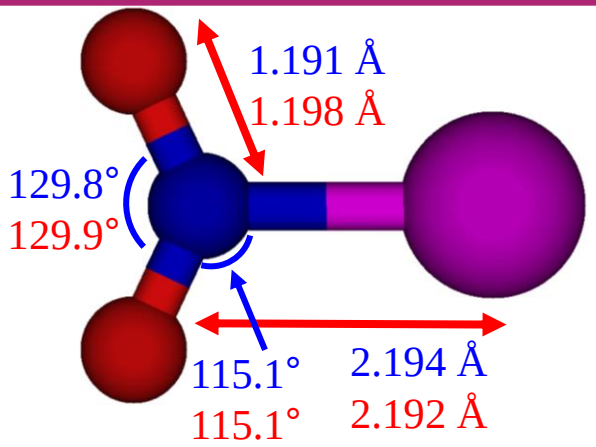
H	I	H_2	HCl	HBr	HI	ICl	IBr	HNO	HONO	HNO_3
217.997 ± 0.001	106.76 ± 0.04	0.00	−92.31 ± 0.10	−36.29 ± 0.16	26.50 ± 0.10	17.393 ± 0.040	40.807 ± 0.14	109.2 ± 2.1	−78.45 ± 0.80	−143.5 ± 0.5

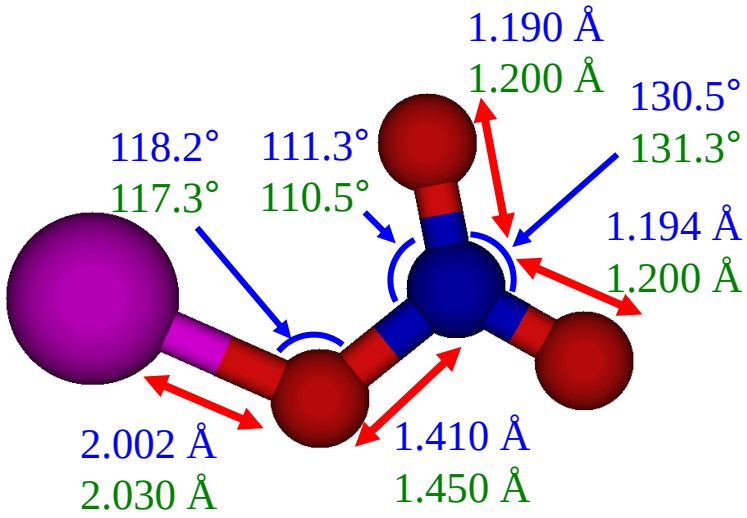
- Standard enthalpy of formation at 298 K calculations for target species:
  - $\Delta_r H°_{298K} = \Delta E + \Delta ZPE + \Delta ddH_{298K} + \Delta SOC$
  - $\Delta_r H°_{298K}$ is obtained using Hess' law

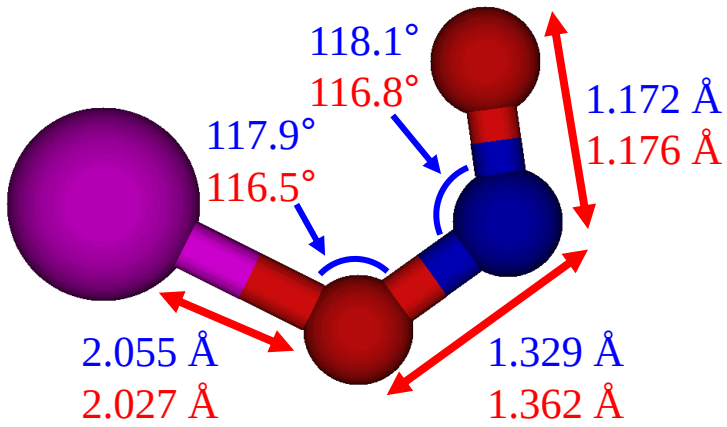
$$\Delta_f H°_{298K}(INO) = \underbrace{-\Delta_r H°_{298K}}_{\text{Calculations}} + \underbrace{\Delta_f H°_{298K}(HI) + \Delta_f H°_{298K}(NO) - \Delta_f H°_{298K}(H)}_{\text{From literature [JPL 2015]}}$$

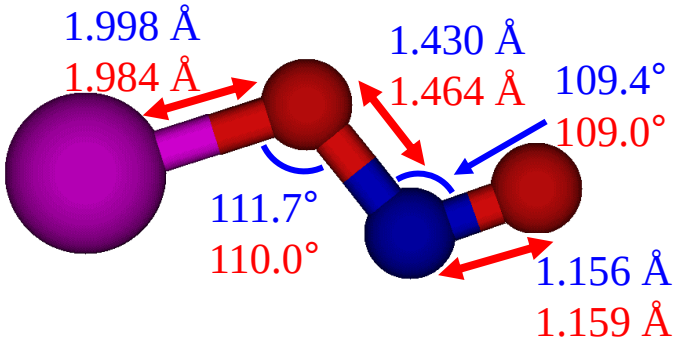
INOx structures











This work (UωB97XD/aug-cc-pVTZ)

[1] Peterson *et al.*, J. Chem. Phys., 140 (2014), 044308 (CCSD(T)-F12b)

[2] Allan *et al.*, J. Phys Chem. A, 106 (2002), 8634 (B3LYP)

INOx thermodynamics

UωB97XD/aV5Z//UωB97XD/aVTZ || UCCSD(T)/CBS//UωB97XD/aVTZ

Species	$\Delta_f H°_{298\ K}$ (kJ mol^{-1})	
	This work	Literature
INO	**121.9 ± 2.0** **141.9 ± 5.6**	**121.3 ± 4.2**[3]
INO_2	**68.2 ± 0.6** **69.8 ± 5.5**	**60.2 ± 4.2** [3]
Cis-IONO	**75.5 ± 2.4** **65.4 ± 5.6**	
Trans-IONO	**95.3 ± 2.4** **83.3 ± 5.6**	
$IONO_2$	**48.5 ± 0.9** **35.6 ± 5.5**	**33.1** [4]

[3] Troe *et al.*, J. Chem. Phys., 64 (1976), 736 (experiments)
[4] Kaltsoyannis *et al.*, Phys. Chem. Chem. Phys., 10 (2008), 1723 (CCSD(T) calculations)

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- Microhydration (gas phase)
- Henry's law constants (aqueous phase)
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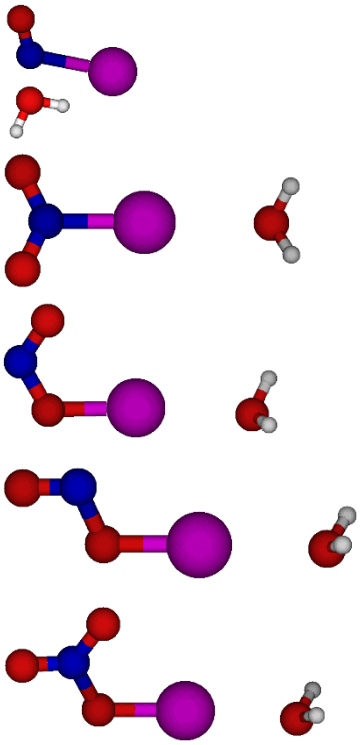
INOx microhydration thermodynamics

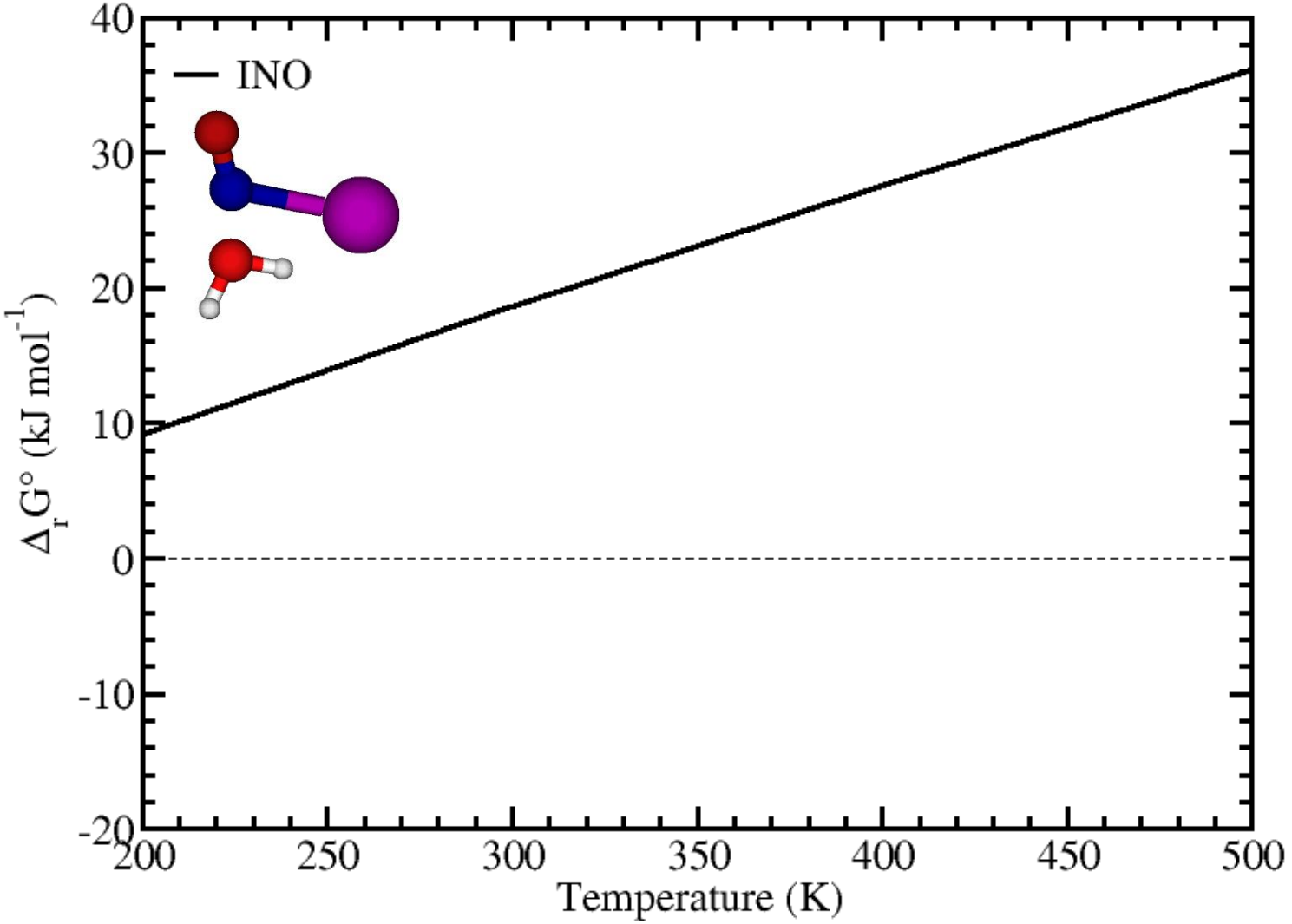
UωB97XD/aV5Z//UωB97XD/aVTZ

Species	$INOx + H_2O = INOx\text{-}H_2O$		
	Number of aggregates	$\Delta_r H°_{298\ K}$ (kJ mol^{-1})	$\Delta_r G°_{298\ K}$ (kJ mol^{-1})
INO	**1**	**−8.9**	**18.5**
INO_2	**3**	**−17.7**	**13.2**
Cis-IONO	**5**	**−21.7**	**10.6**
Trans-IONO	**7**	**−25.0**	**6.2**
$IONO_2$	**6**	**−32.0**	**−0.1**

- Exothermic processes.
- $IONO_2$ becomes spontaneous at ambient temperature.
- Halogen bonds except for INO



Microhydration as function of temperature



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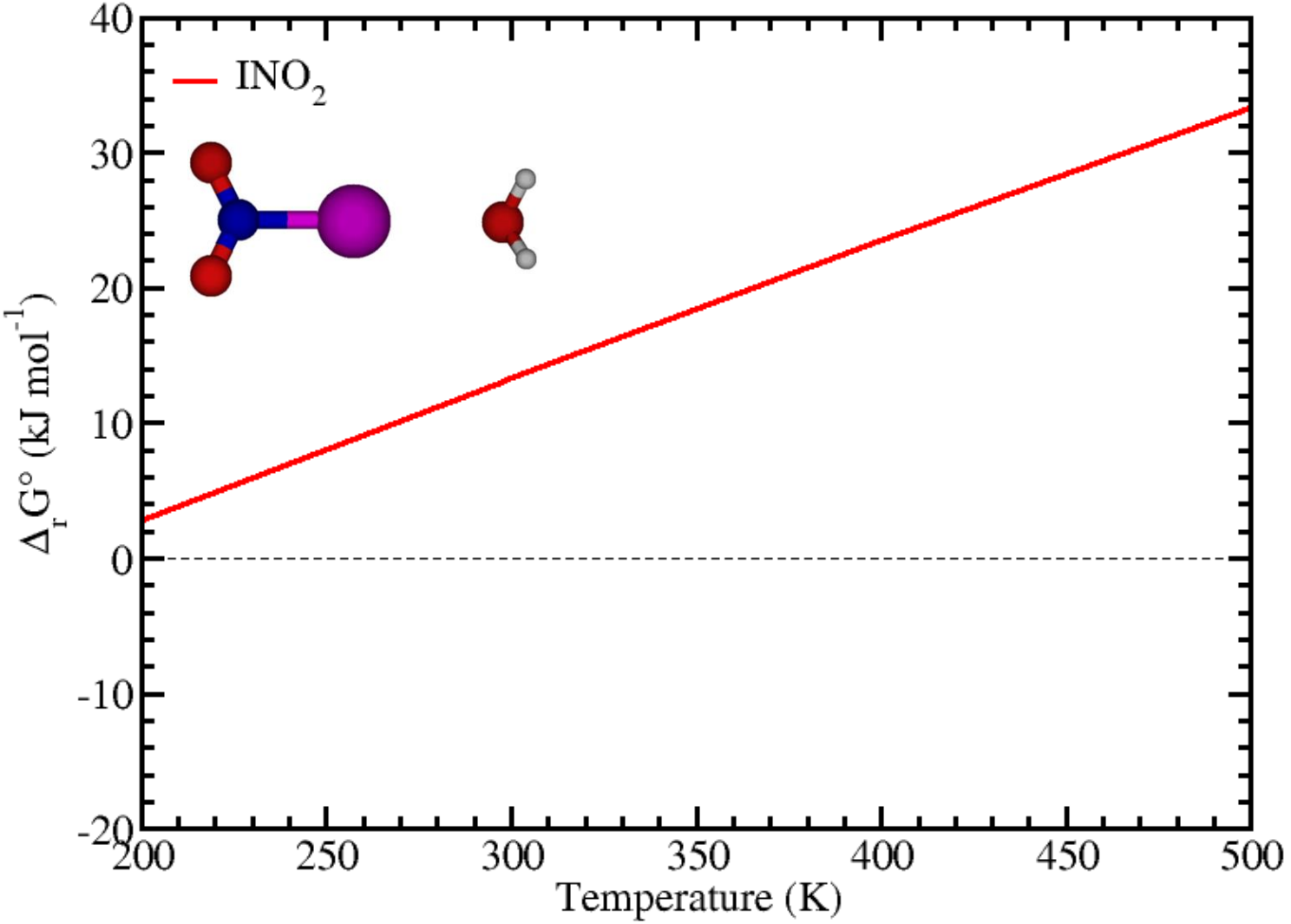

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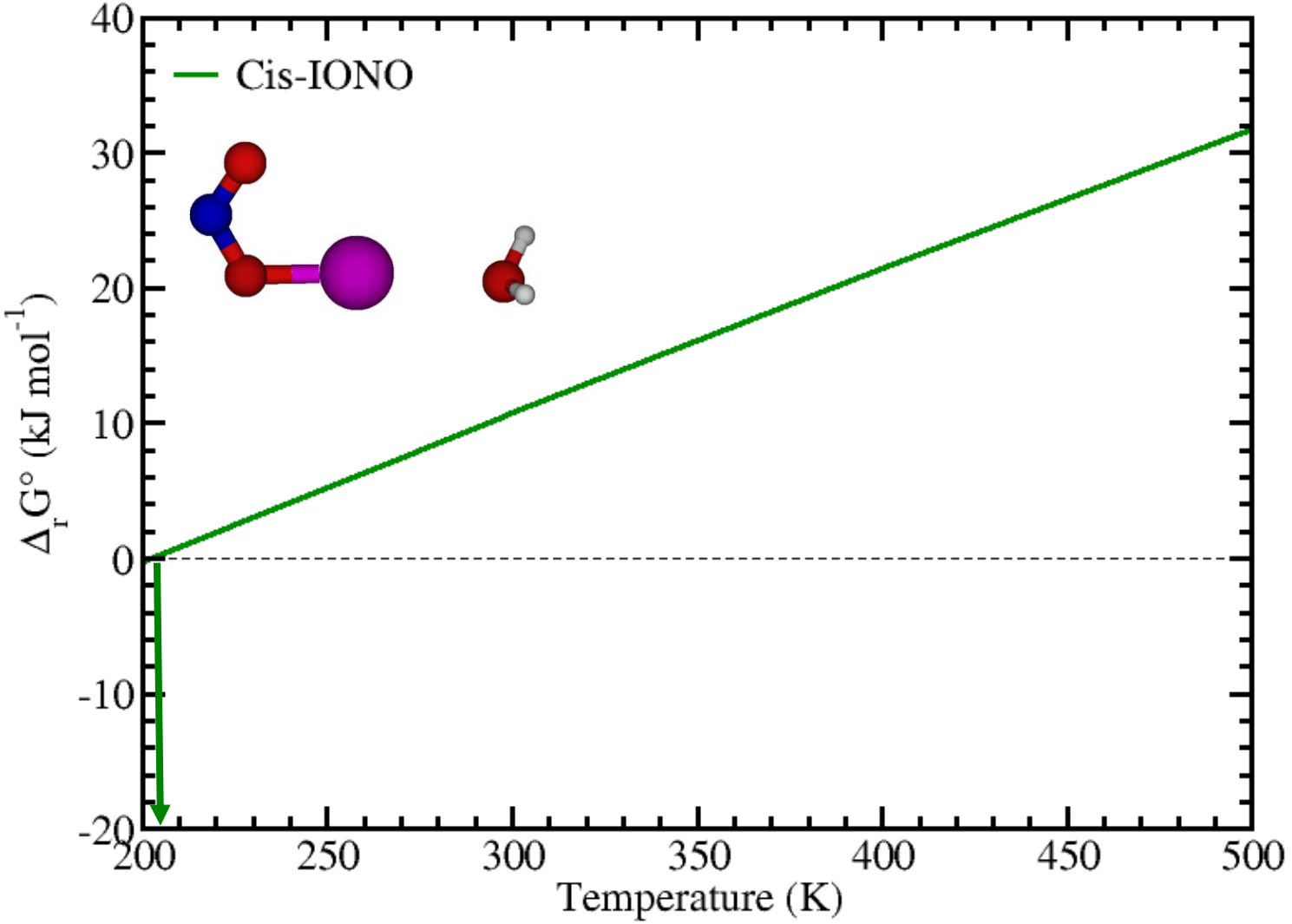

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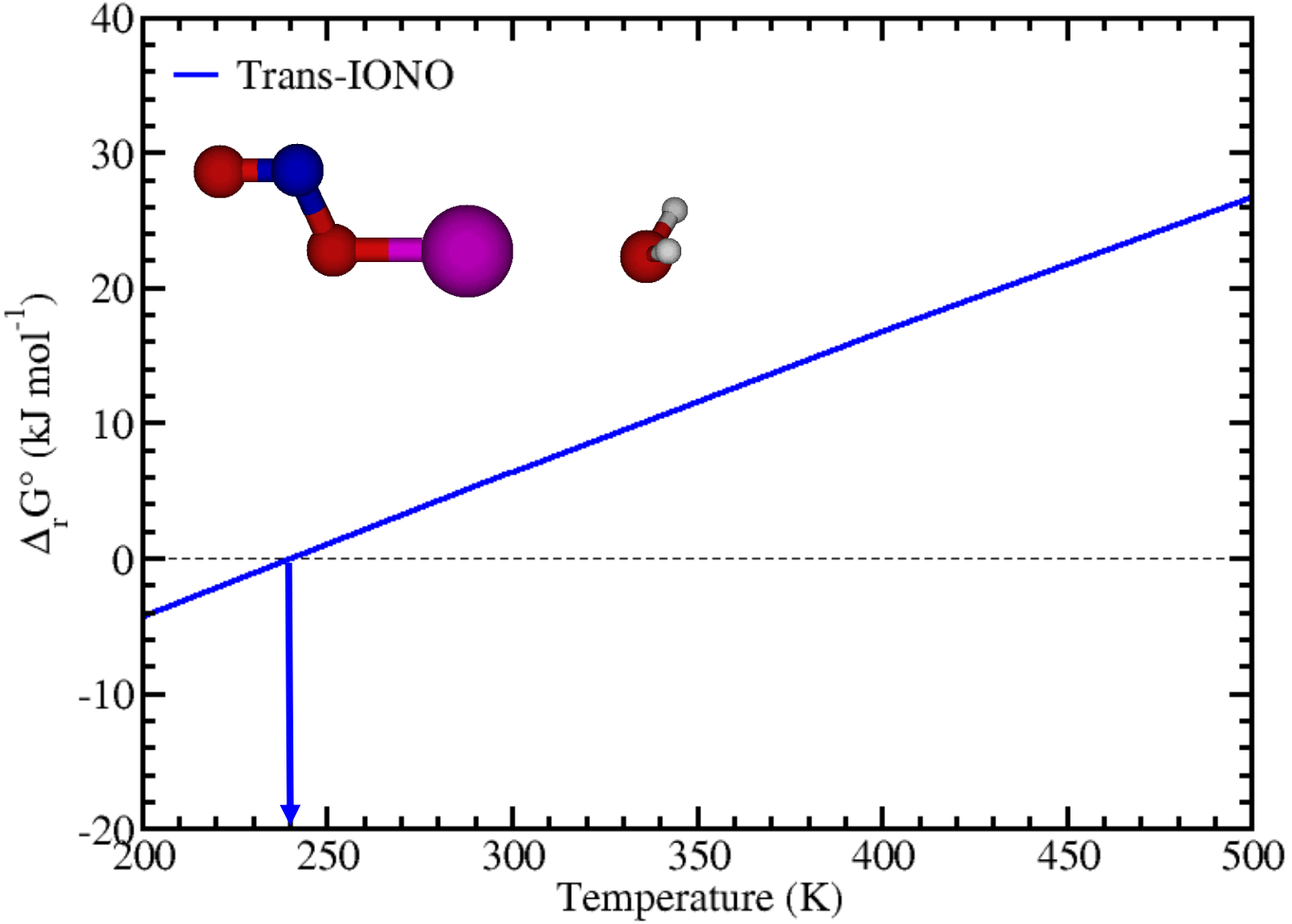

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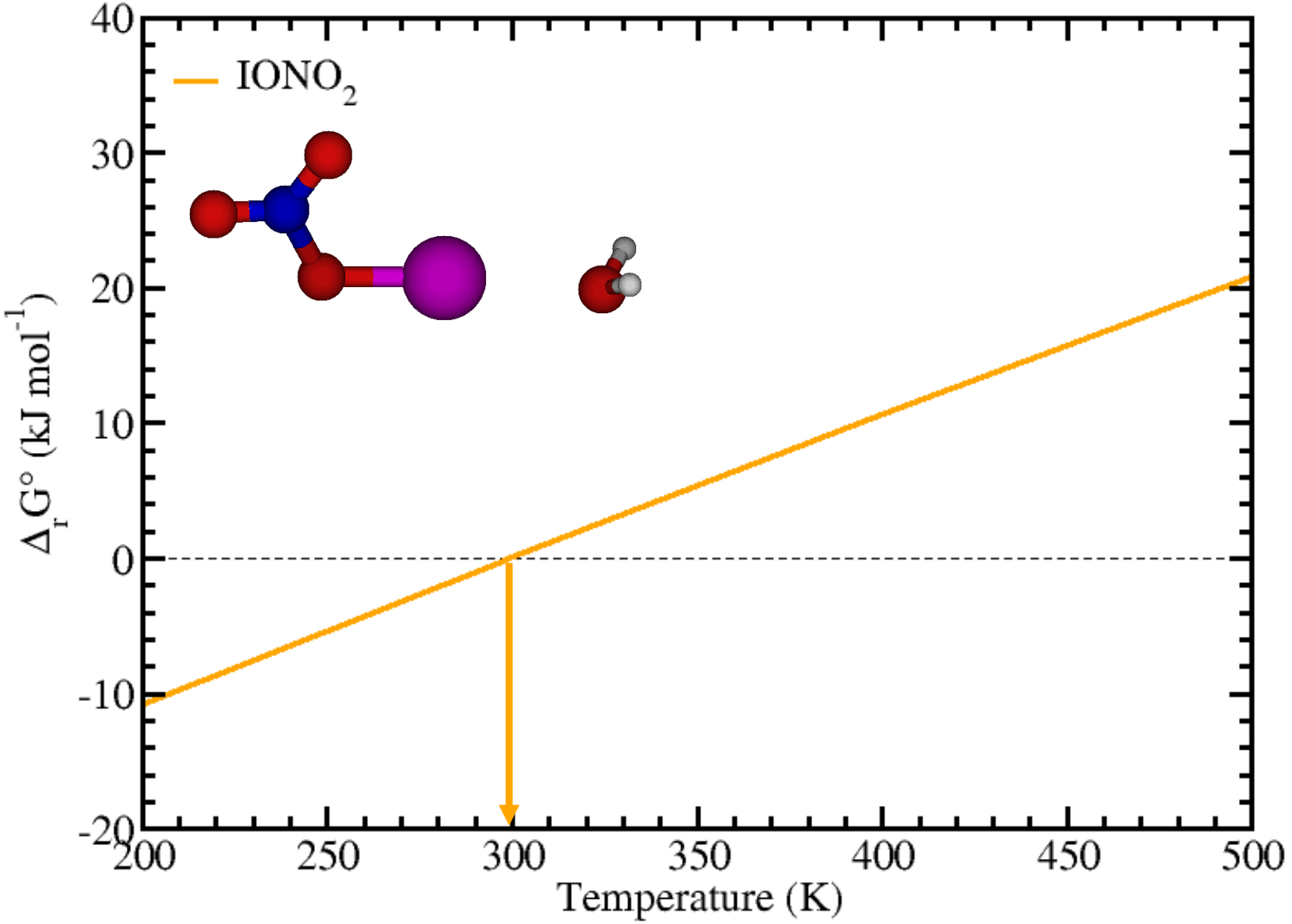

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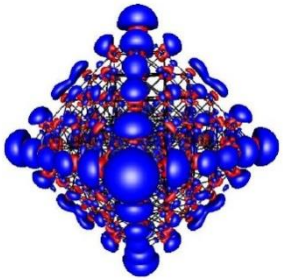
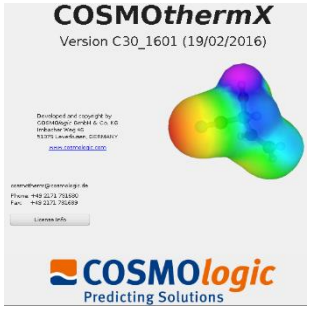
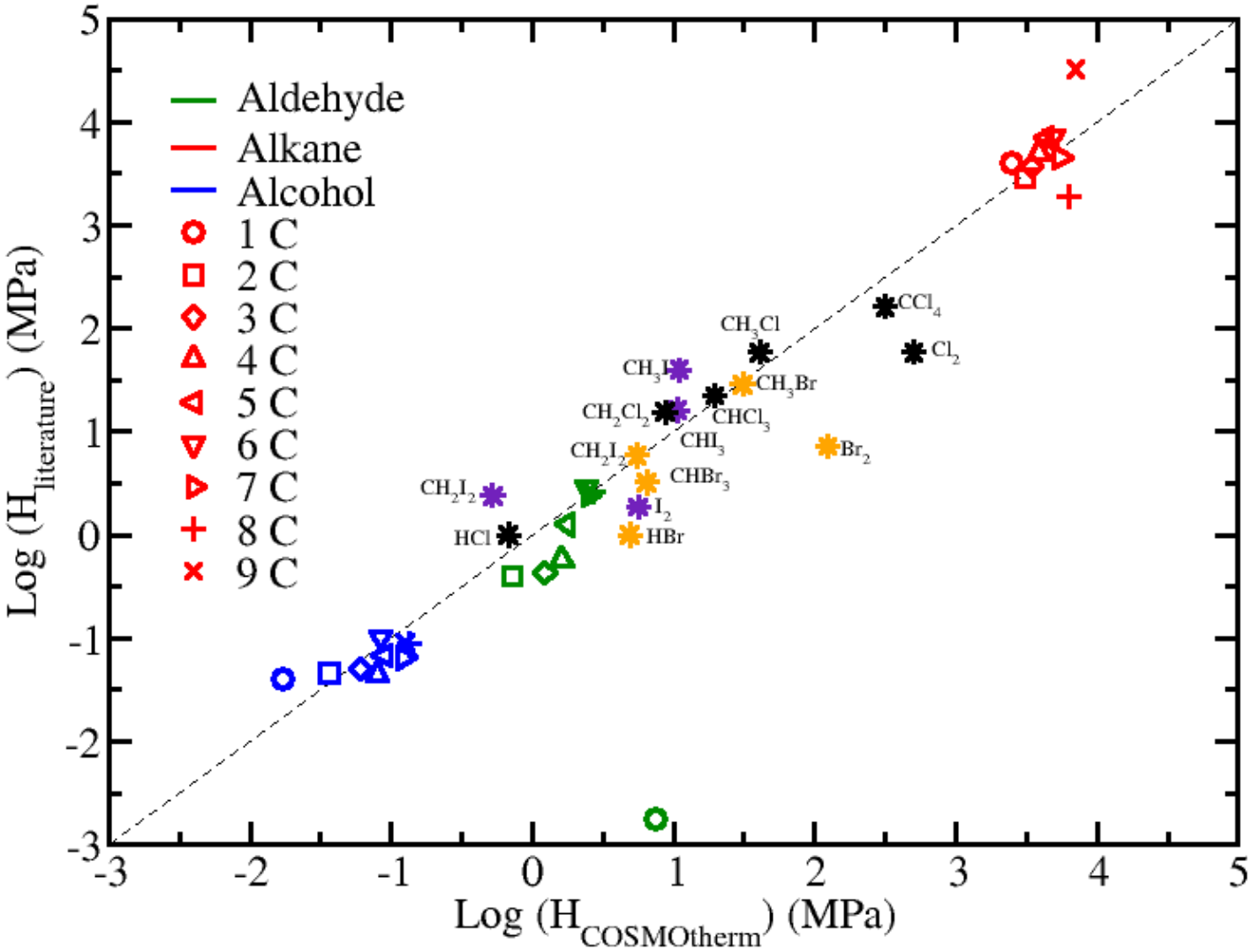
Henry's law constants computational methods

- Turbomole and COSMOthermX used in literature:
  - Parnis *et al.*, Atmos. Environ., 110 (2015), 27-35
  - Dougassa *et al.*, J. Chem. Thermo., 79 (2014), 49-60
- Optimized geometries at the BP/def-TZVP level of theory with m4 grid.
- ε_r dielectric constant set to ∞
- H_2O from COSMOthermX database
- Henry's Law Constant expressed in MPa (the volatility constant H) → conversion to mol L^{-1} atm^{-1} (k_H)



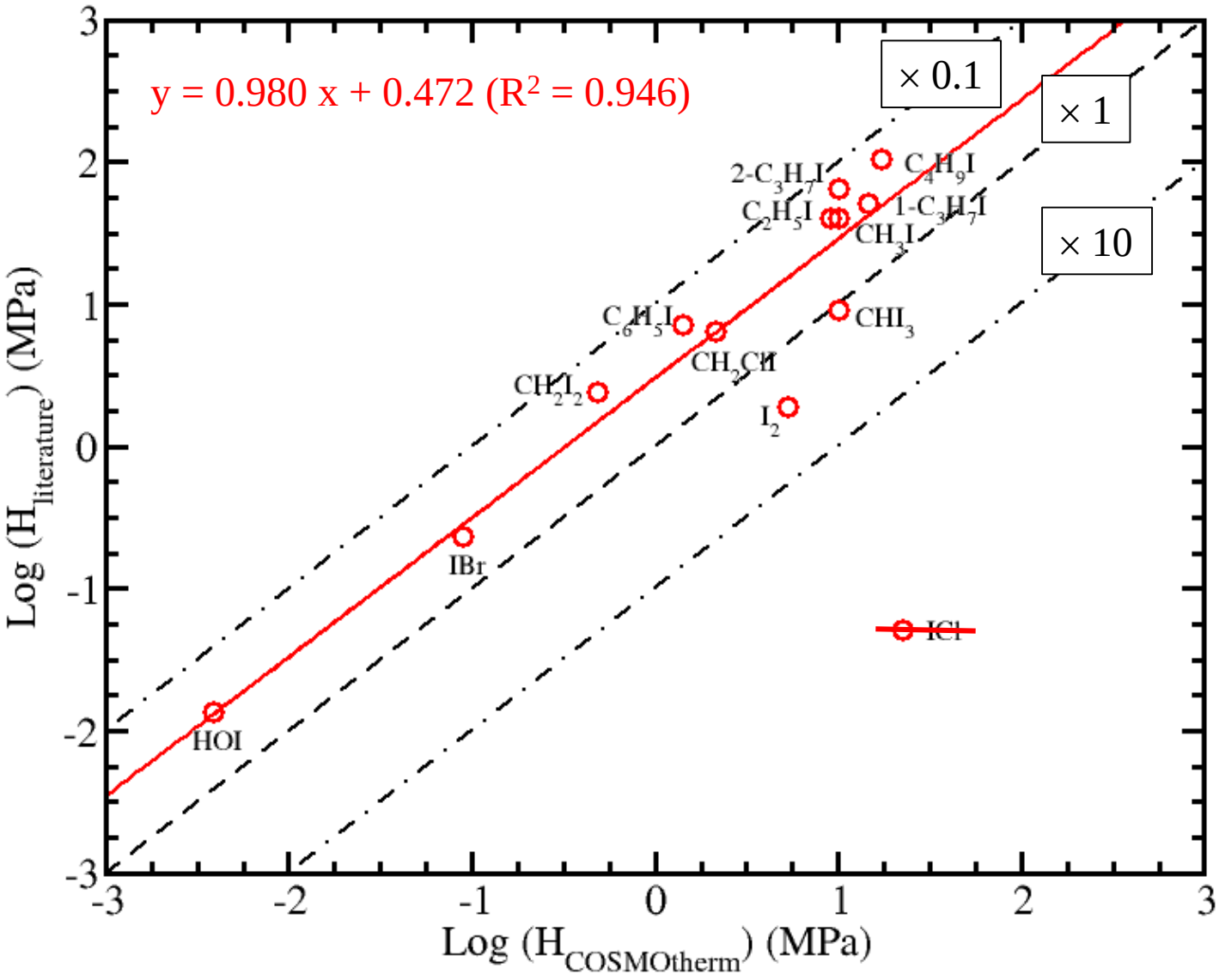


Henry's law constants



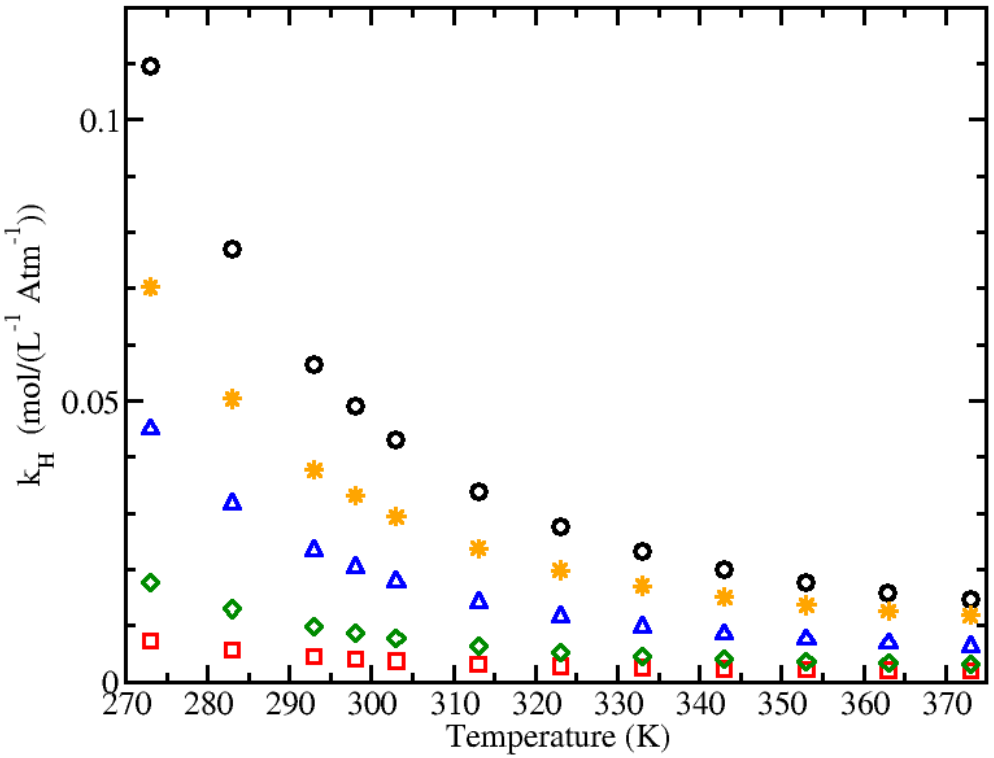
COSMOtherm V. 16

Henry's law constants



COSMOtherm V. 17 (December 2016)

Henry's law constants

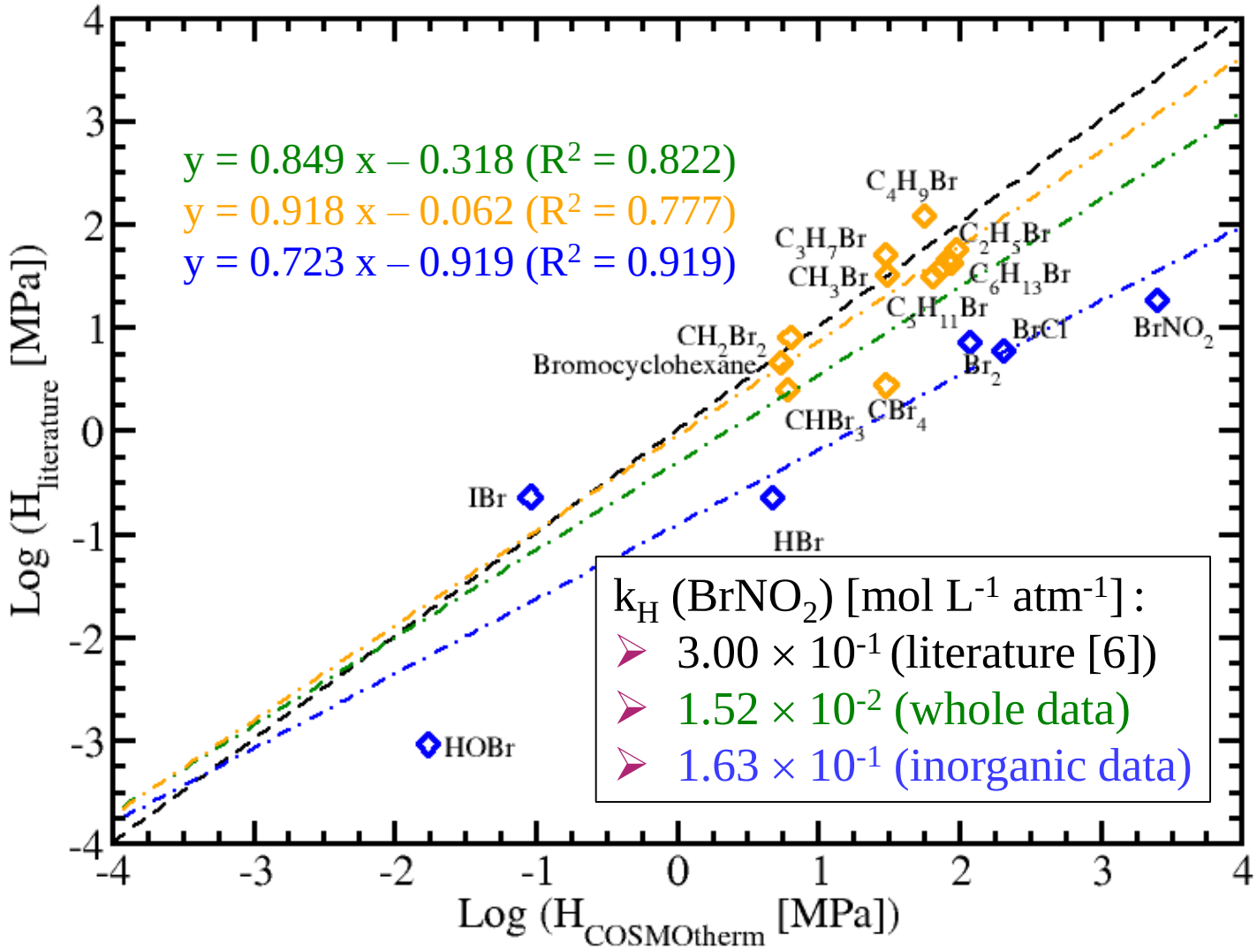


Species	k_H (298 K) (mol L^{-1} atm^{-1}) COSMOtherm
INO	4.90×10^{-2}
INO_2	4.14×10^{-3}
Cis-IONO	8.74×10^{-3}
Trans-IONO	2.04×10^{-2}
$IONO_2$	3.32×10^{-2}

- Note:
  - $k_H(298K)$ (INO_2) = 3.00×10^{-1} mol L^{-1} atm^{-1}
    → Valeur $BrNO_2$ [5]
  - $k_H(298K)$ ($IONO_2$) = 10^6 mol L^{-1} atm^{-1}
    → Virtual infinite solubility [5]: $IONO_{2\,(aq)} + H_2O_{(aq)} = HOI_{(aq)} + HNO_{3\,(aq)}$

[5] Saiz-Lopez *et al.*, Atmos. Chem. Phys., 2014, 14 (23), 13119.

Henry's law constants

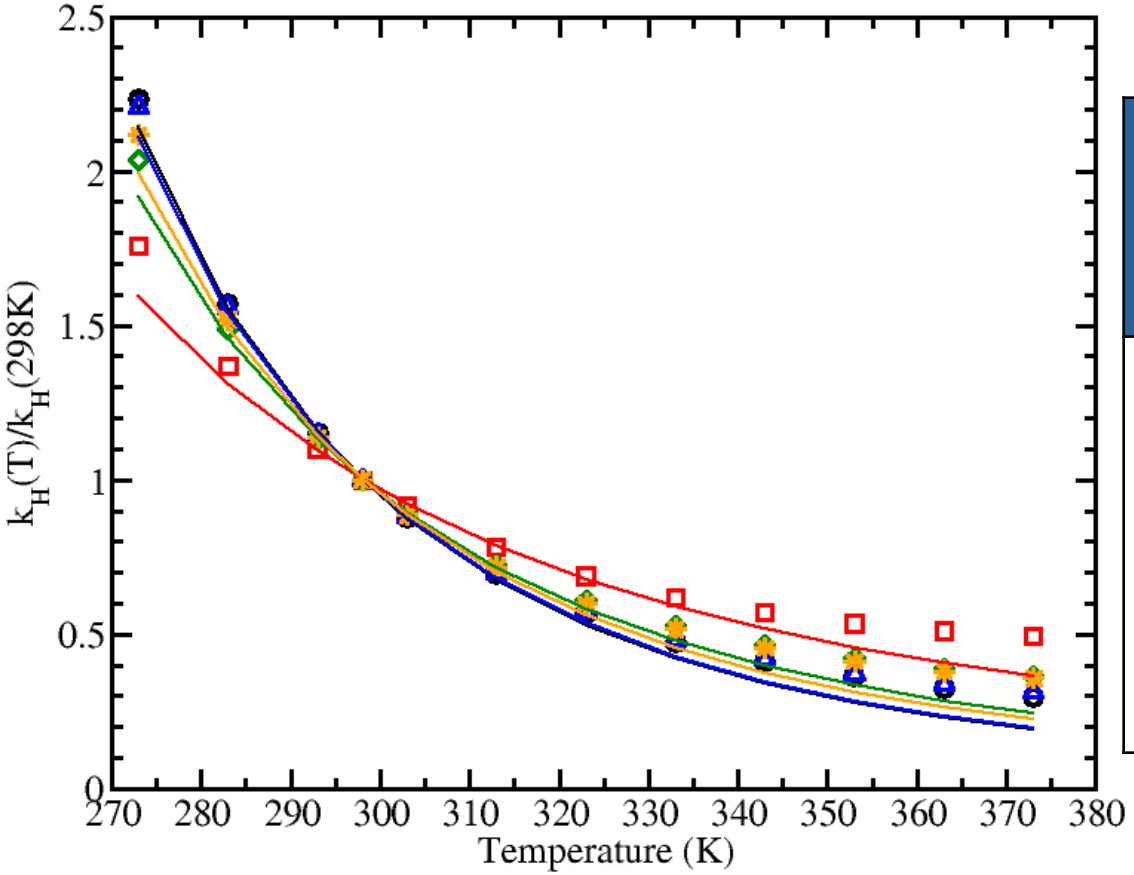


[6] Frenzel *et al.*, J. Phys. Chem. A, 102 (1998), 1329

COSMOtherm V. 17

Henry's law constants

$$\frac{k_H(T)}{k_H(298\ K)} = exp\left(\frac{-\Delta_{sol}H°}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right)$$



Species	$\Delta_{sol}H°$ (kJ mol^{-1}) COSMOthermX
INO	- 20.5
INO_2	- 12.5
Cis-IONO	- 17.5
Trans-IONO	- 20.1
$IONO_2$	- 18.5

Conclusions and outlook

- Reassessment of literature standard enthalpies of formation for INOx.
  - *Complete benchmark by performing CASPT2/CASSCF calculations,*
  - *Estimate the corrections due to higher correlation methods such as CCSDT(Q) (CFour).*

- Microhydration processes:
  - *Extend study to $IONO_2 + n\,H_2O = IONO_2_nH_2O$ (n = 2, 3, …)*

- Prediction of Henry's law constants for iodine-containing species.
  - *Complete study by using SMD methodology as implemented in Gaussian16*

Thank you for your attention

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