Modelling of iodine oxides of environmental interest

Modélisation des oxydes d'iode d'intérêt environnemental

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Context

Nuclear

In a **pressurized water reactor**, during a severe accident

Release of radioactive iodine (gaseous I_2, CH_3I)

products of the air radiolysis

I_2 , CH_3I

$O^{\cdot}$, $OH^{\cdot}$ and e^-

Iodine oxides

High *T* (400 K, 1000 -1500 K … 2500 K)

Atmospheric

In the atmosphere **above oceans**

marine organisms (macroalgae, phytoplankton)

production

I_2 , CH_3I

hv, O_3 — photolyzed (UV-visible light) oxidation

Iodine oxides

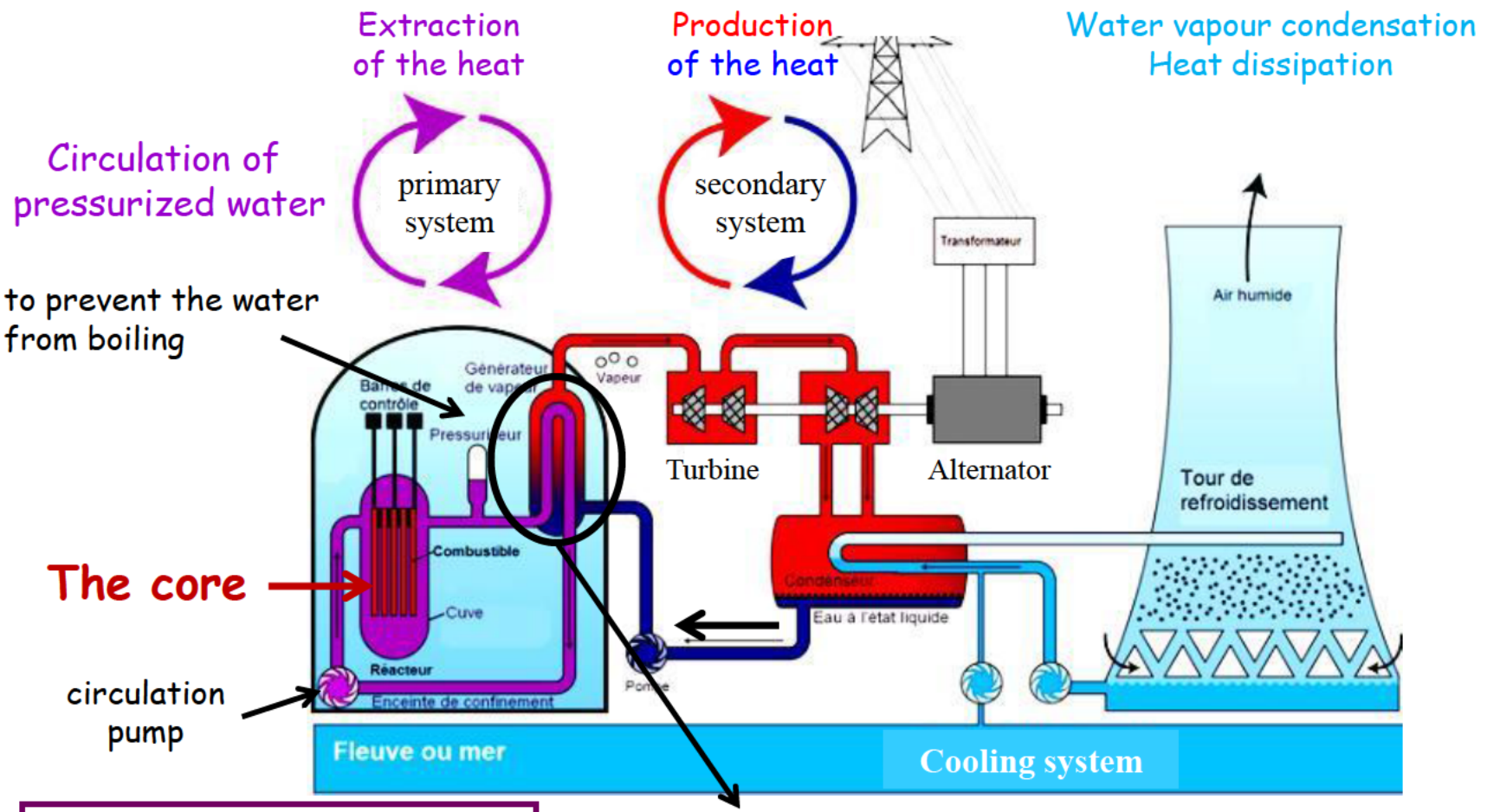
Tropospheric *T* (250-300 K)

Key issues

✓What are the **most important forms** of iodine oxides ?
→ Are they chemically **stable** ?
→ Do they **react** with molecules present in the conditions (*CO*, *OH*, *H*, *O* …) ?

Context

Pressurized water reactor (PWR)



- UO_2 fuel pellets, rods
- fission chain reaction
- emission of a considerable amount of heat

Steam generator

water of the primary system allows for the water of the secondary system to evaporate

Context

Pressurized water reactor (PWR)

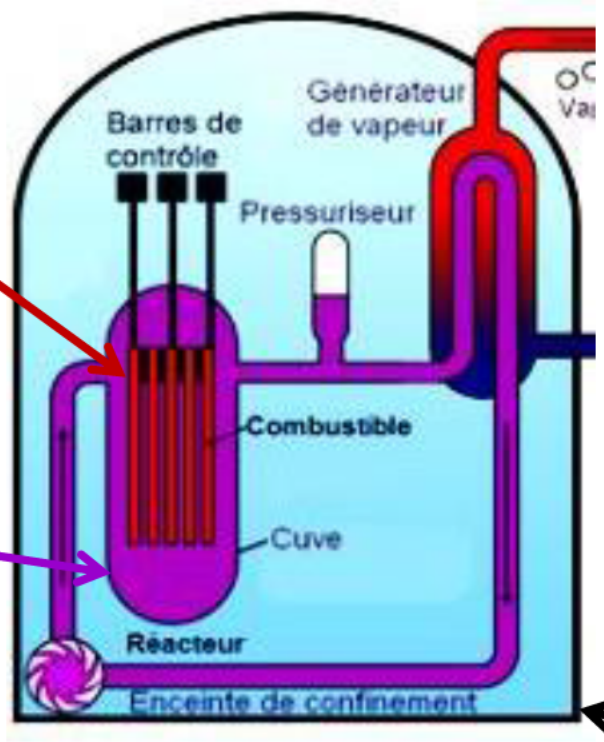
3 Containment barriers (safety)

1 Metal cladding

(containing the nuclear fuel)

2 Metal reactor vessel

(containing the fuel/cladding assemblies)



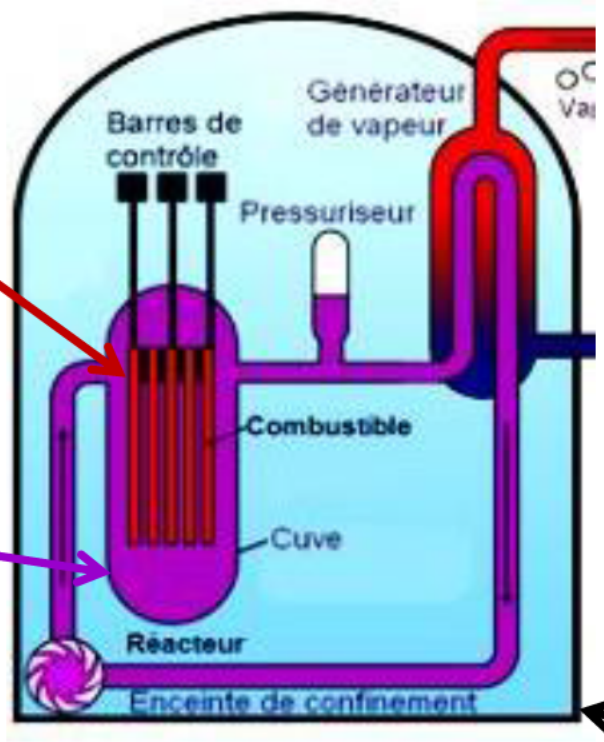
3 Containment building

(steel structure in concrete)

Context

Nuclear Accident

Core fusion/fuel melting



1 Met… g

(c… nuclear fuel)

Cladding degradation (1st barrier)

2 Metal re… ssel

(contain… / cladding …lies)

Corium can melt through the reactor vessel

3 Contain…

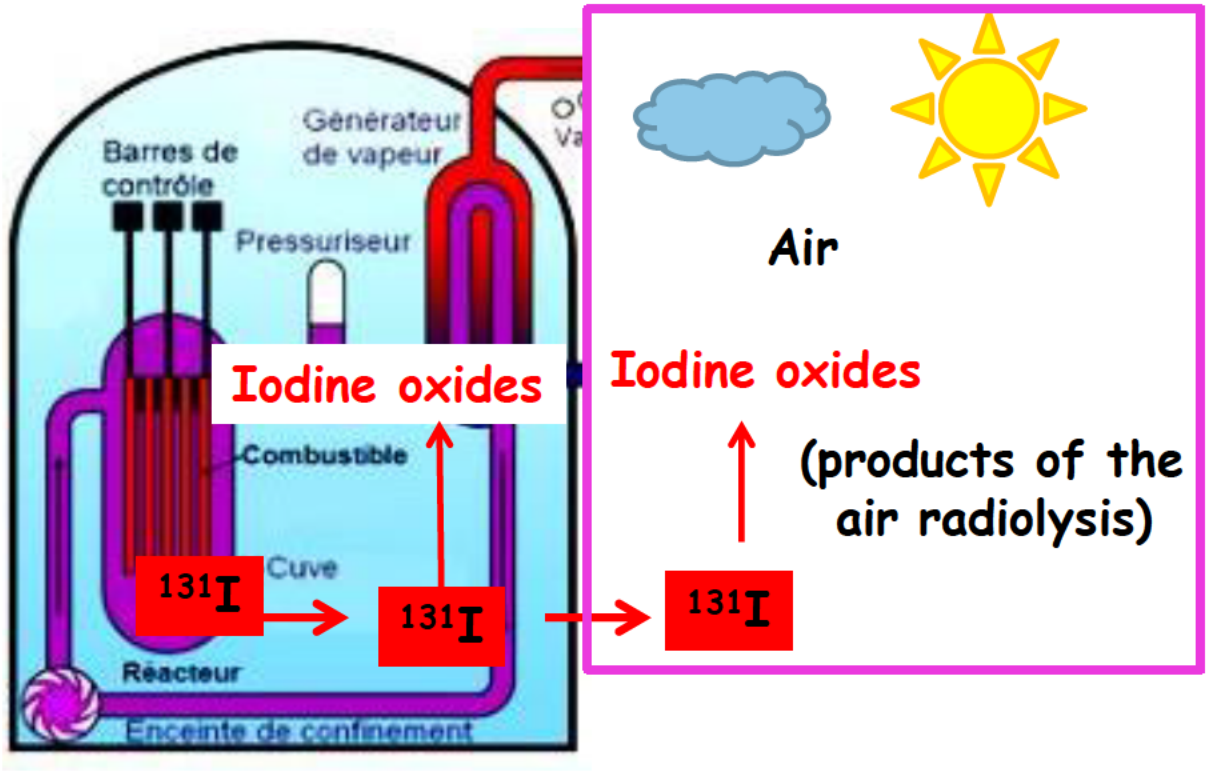
…e in concrete)

Corium can spread over the concrete of the containment building

Context

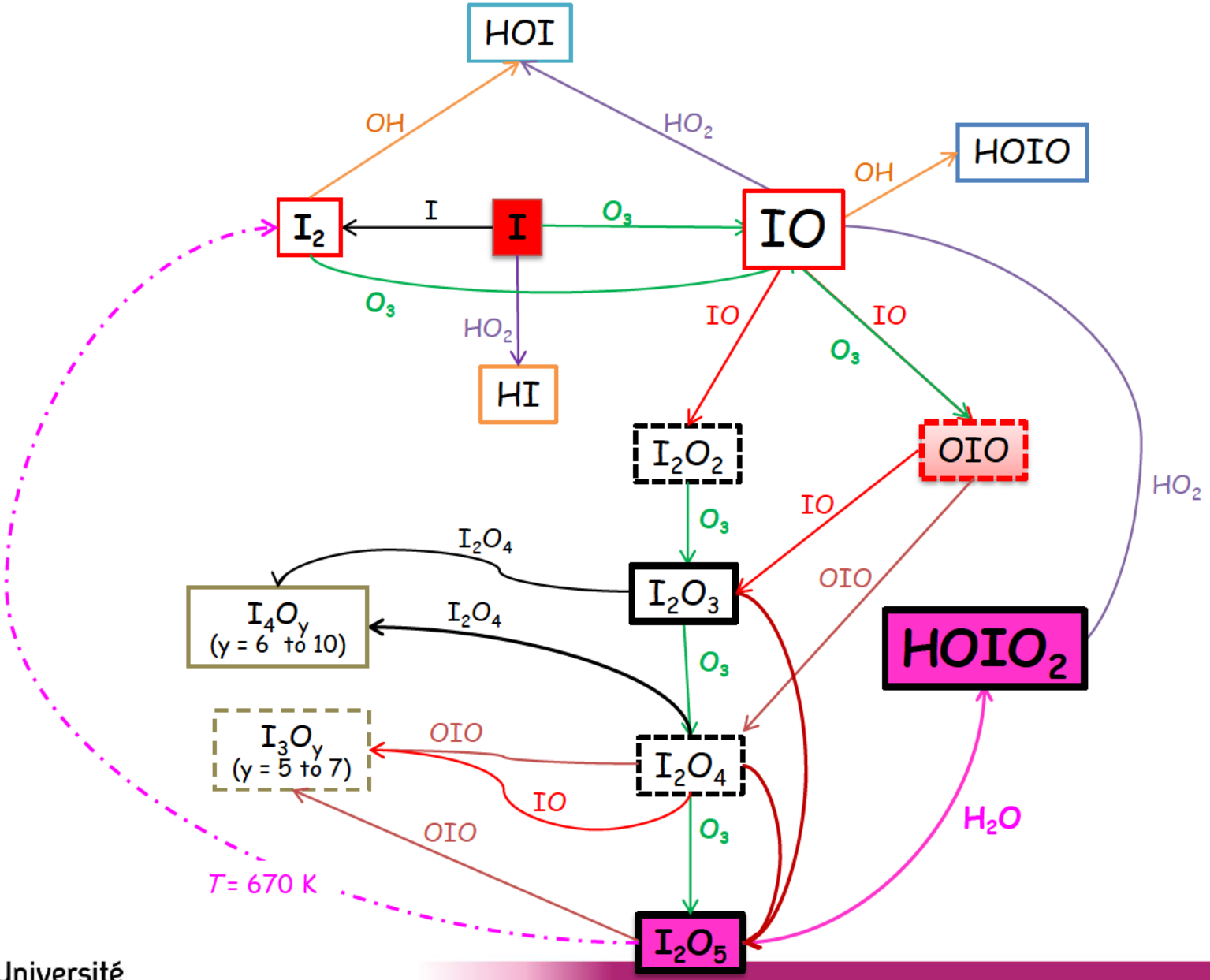
Nuclear Accident

Core fusion/fuel melting



Radioactive Iodine +++ harmful (respiratory system and thyroid gland)

Chemistry for gas phase iodine-containing species is complex and challenging !!



Outline

1. Reactivity of IO

➢ $IO + CO \longrightarrow I + CO_2$

2. Hydration and Reactivity of iodic acid ($HOIO_2$)

➢ Monohydrates of $HOIO_2$

➢ $HOIO_2$ + X (X = OH and H)

Gas phase: Methodology

Microhydration processes

Step 1

Geometry optimization
(DFT and *ab initio* methods)

Step 2

"dual level" approach

Energetics
CCSD(T)/aug-cc-pVnZ + pseudo-potential (Gaussian)
DK-CCSD(T)/ANO-RCC-VnZ (Molcas)

Step 3

Spin-orbit coupling
RASSCF/CASPT2/RASSI (Molcas)

Step 4

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

Gas phase reactivity

Step 1

Identification of the **Transition states**
(only 1 imaginary frequency)
IRC (forward and reverse)

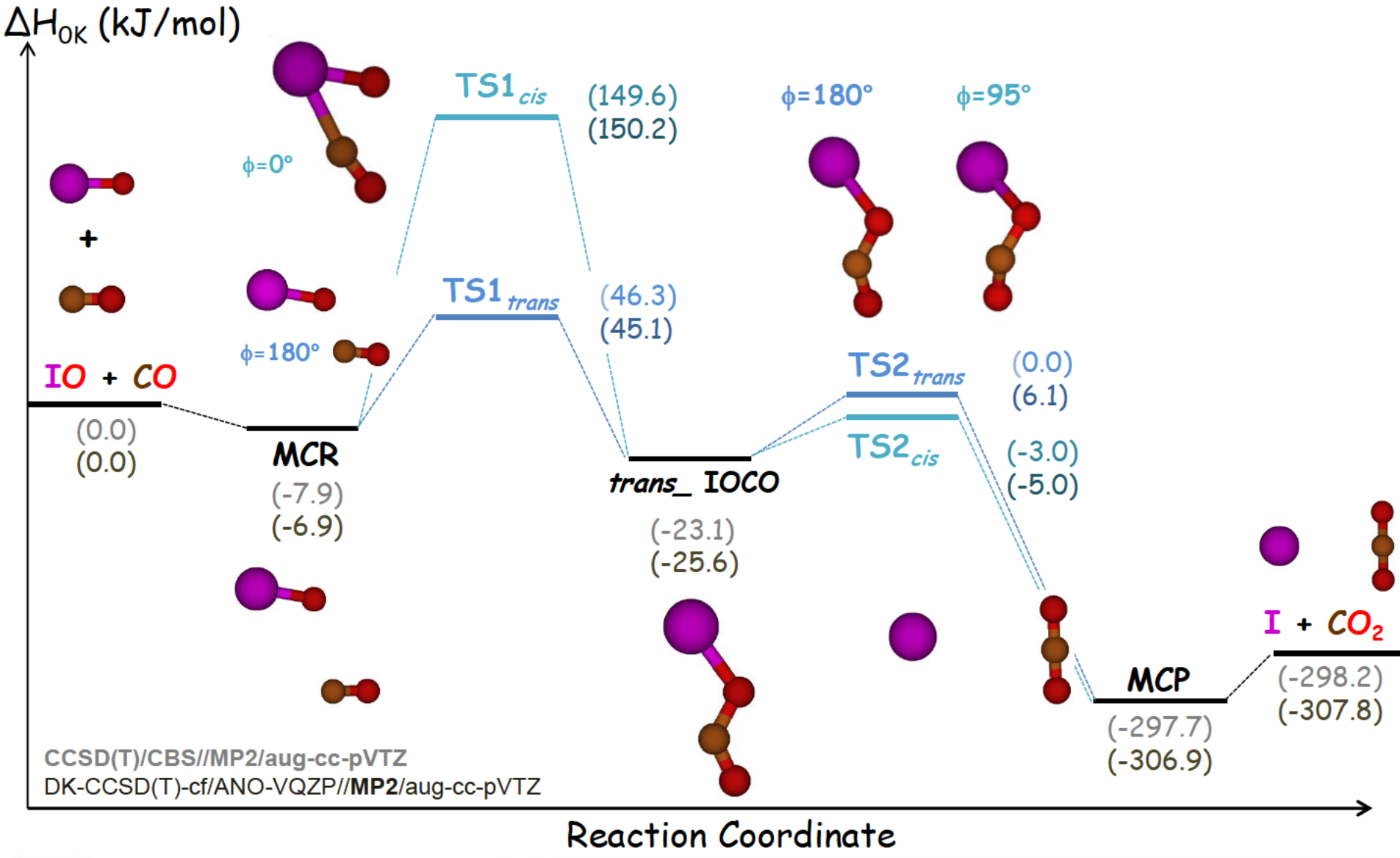
relativistic effects

Step 4

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

Reactivity of IO with CO

Trans pathway
Cis pathway



1st step: Formation of O-C bond

I-O increases while **IO ··· CO becomes shorter**

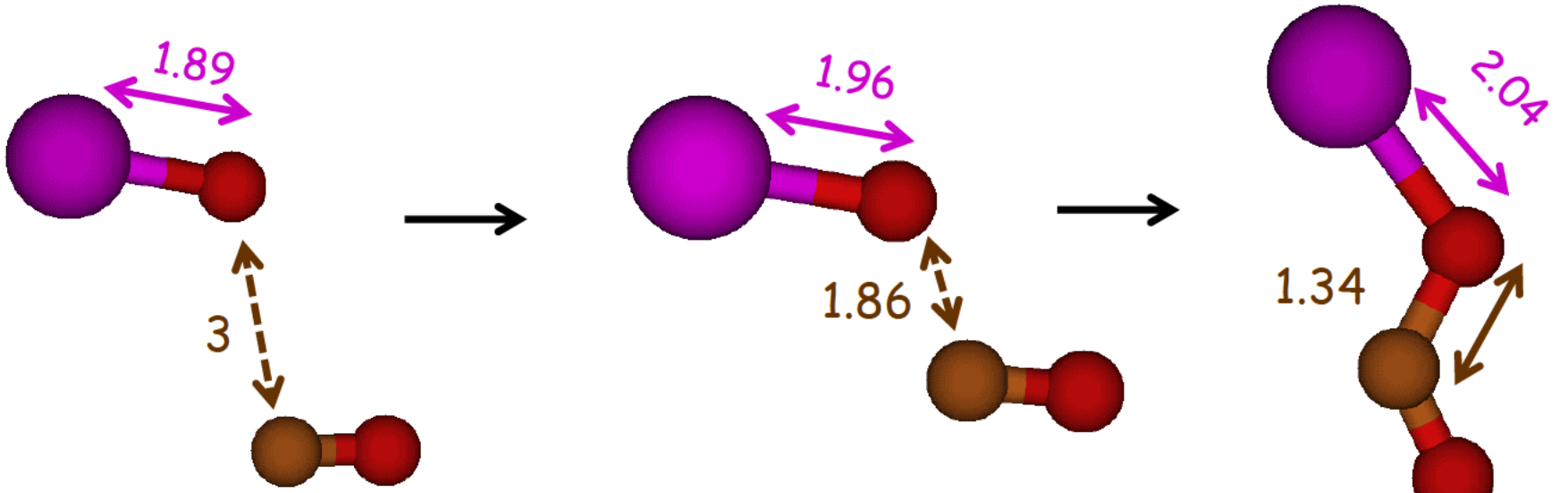
Molecular Complex on the Reactants side

Trans pathway

MCR

TS1 *trans*

trans _IOCO



ϕ=180°

ν_{im}=419i cm^{-1}

ϕ=180°

ϕ=180°

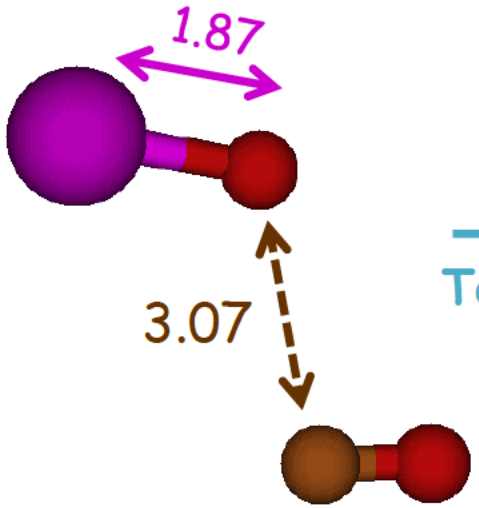
Geometries at the B3LYP/aVTZ level
Bond lengths in Å

1st step : Formation of O-C bond

I-O increases while **IO ··· CO becomes shorter**

Cis pathway

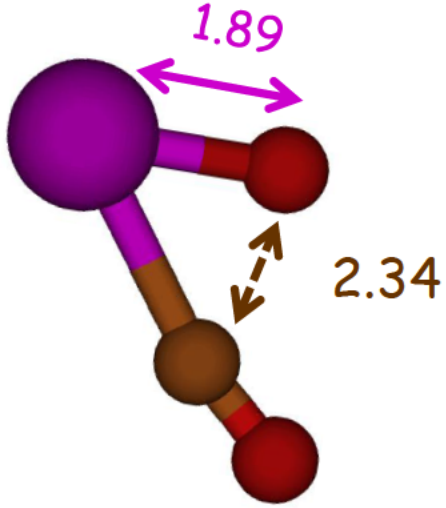
MCR



ϕ=180°

Torsion

TS1 *cis*

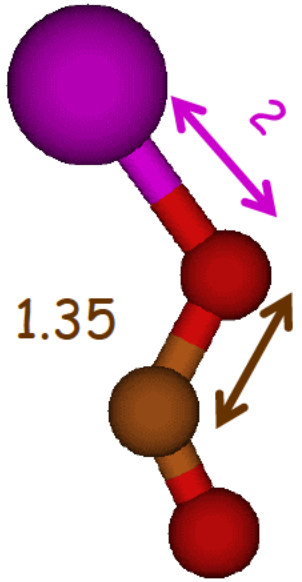


ν_{im}=711i cm^{-1}

ϕ=0°

Torsion

trans _IOCO



ϕ=180°

Geometries at the MP2/aVTZ level
Bond lengths in Å

Rate constant calculations

$$IO + CO \xrightarrow{TS1_{trans}} I + CO_2$$

Arrhenius expression:

$$k(T) = 1.49 \times 10^{-17} \times T^{1.77} \exp(-47.4/RT)$$

T = 250 - 2500 K

k : $cm^3\ molecule^{-1}\ s^{-1}$

A ($cm^3\ molecule^{-1}\ s^{-1}$)

E_a ($kJ\ mol^{-1}$)

- ✓ Atmospheric temperature $k_{250\text{-}300K} \sim 10^{-23} - 10^{-21}\ cm^3\ molecule^{-1}\ s^{-1}$
- ✓ Containment building $k_{400K} \sim 10^{-19}\ cm^3\ molecule^{-1}\ s^{-1}$
- ✓ Core melt accident $k_{1000\text{-}2500K} \sim 10^{-14} - 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$

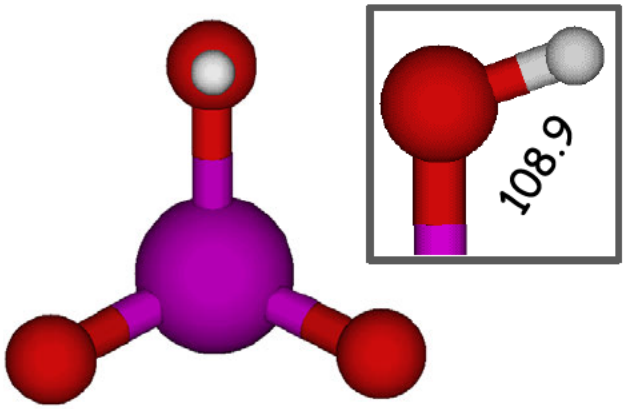
- ❑ In atmospheric conditions, k small compared to $OH + CO$ reaction ($10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$)
- ❑ At 1000 K, k is in the same order of magnitude than the one of $OH + CO$

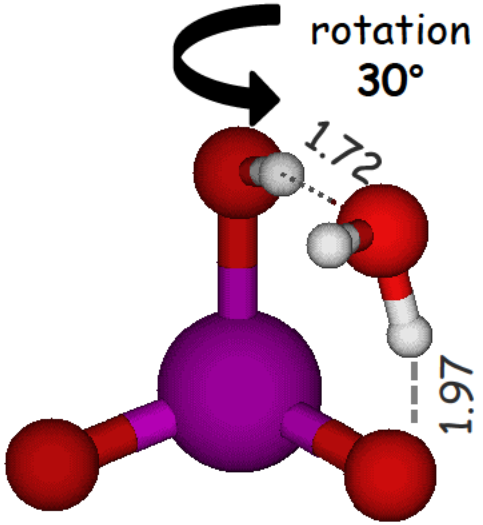
$HOIO_2$ mono-hydrates

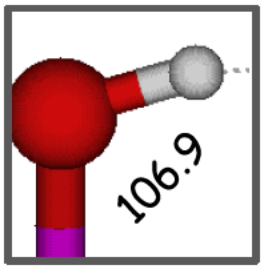
B3LYP/aug-cc-pVTZ level of theory

- **3** stable structures

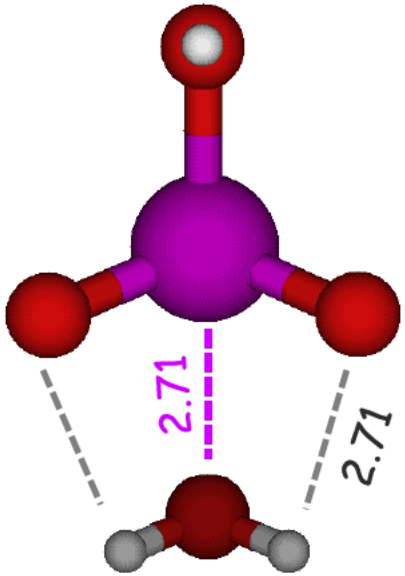
$HOIO_2$



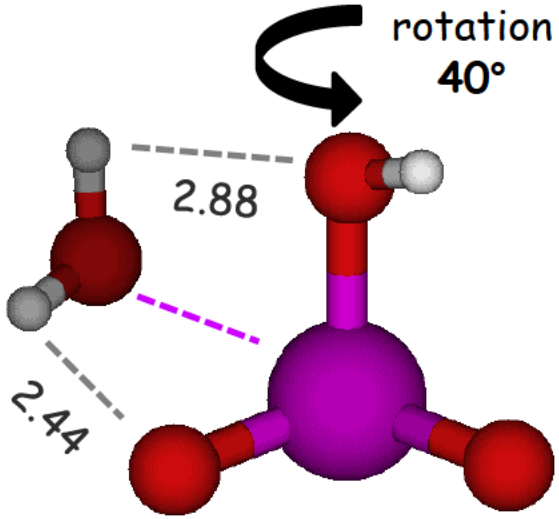


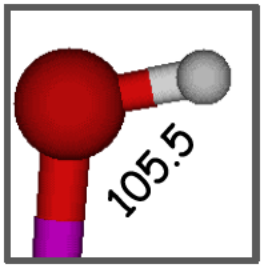


$HOIO_2$_1wa



$HOIO_2$_1wb





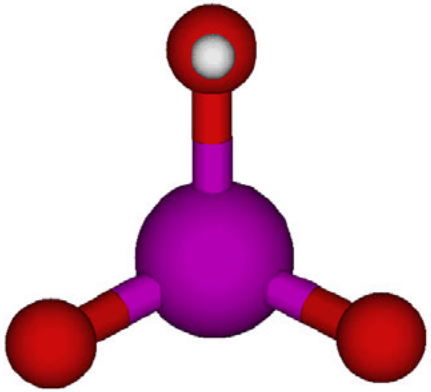
$HOIO_2$_1wc

$HOIO_2$ mono-hydrates

CCSD(T)/CBS//B3LYP/aug-cc-pVTZ level of theory

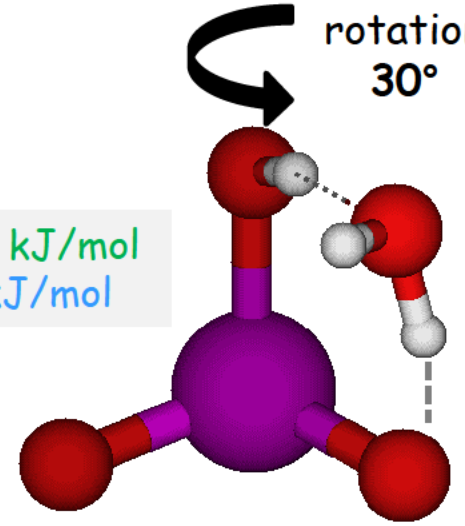
- **3 stable structures**

$HOIO_2$



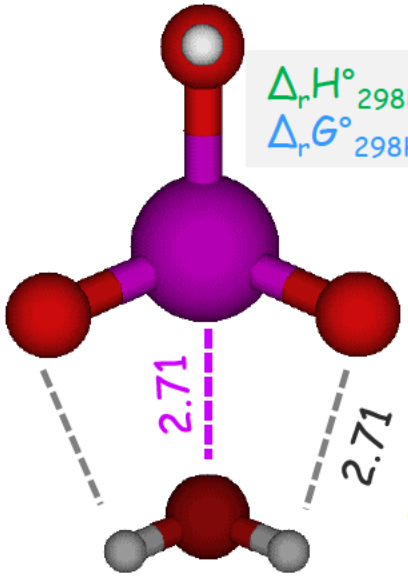
rotation 30°

$\Delta_r H°_{298K}$ = -43.8 kJ/mol
$\Delta_r G°_{298K}$ = -0.3 kJ/mol



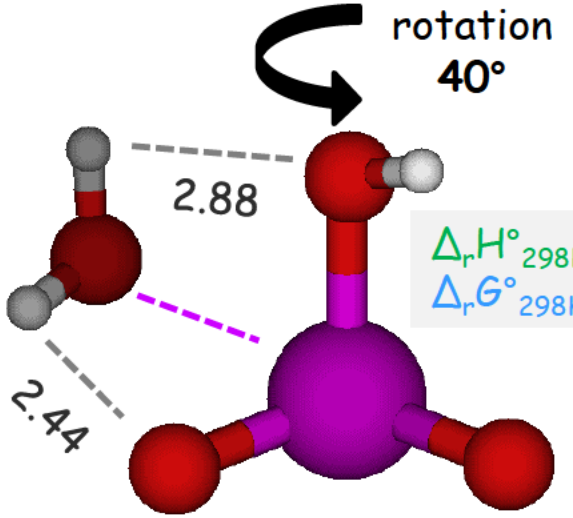
$HOIO_2$_1wa

$\Delta_r H°_{298K}$=-32.6 kJ/mol
$\Delta_r G°_{298K}$ = 4.1 kJ/mol



$HOIO_2$_1wb

rotation 40°



$\Delta_r H°_{298K}$ = -25.1 kJ/mol
$\Delta_r G°_{298K}$ = 13.0 kJ/mol

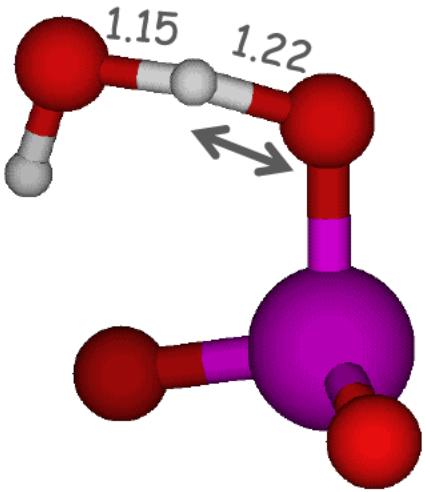
$HOIO_2$_1wc

B3LYP/aVTZ level
Bond lengths in Å

Reactivity of $HOIO_2$ with OH

H-abstraction: $HOIO_2 + OH \rightarrow IO_3 + H_2O$

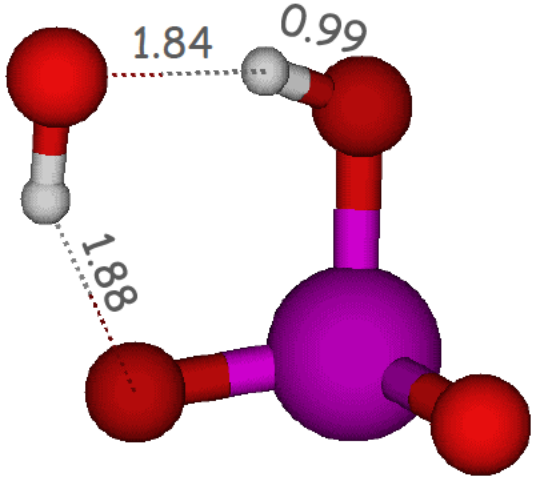
TS



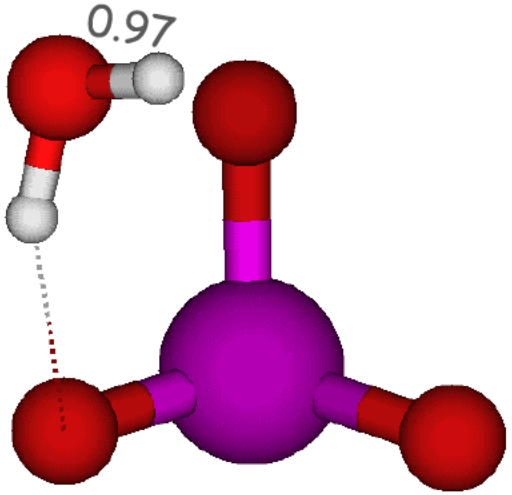
O-H increases

ν_{im}=1472i cm^{-1}

MCR



MCP

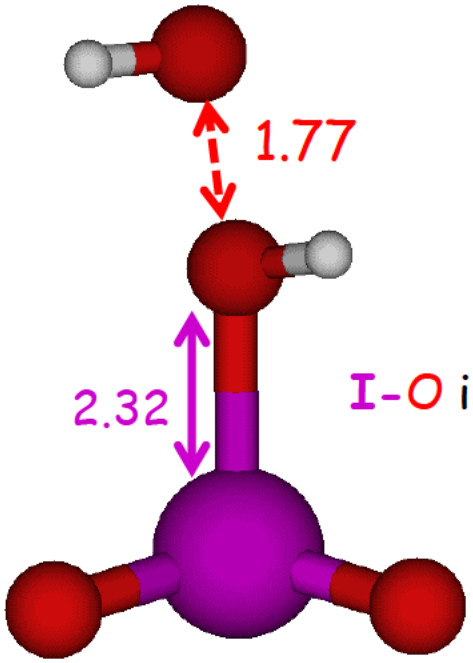


B3LYP/aVTZ level
Bond lengths in Å

Reactivity of $HOIO_2$ with OH

O(H)-abstraction: $HOIO_2 + OH \rightarrow OIO + H_2O_2$

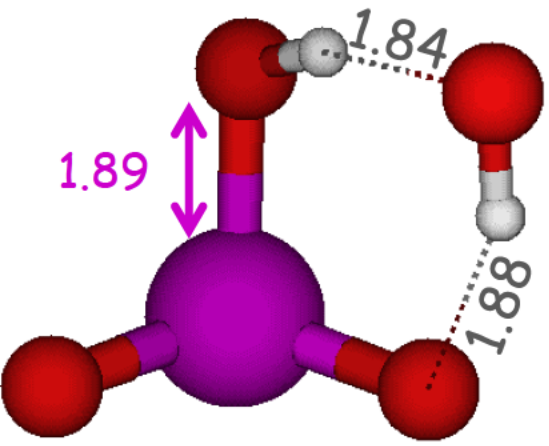
TS



I-O increases

ν_{im}=648i cm^{-1}

MCR



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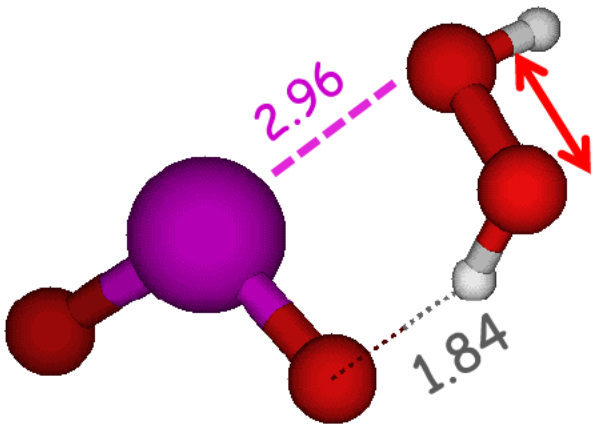


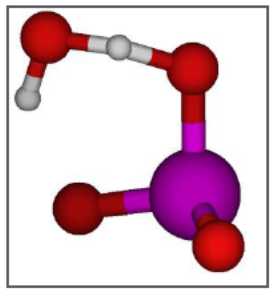
CCSD(T)/aVTZ//B3LYP/aVTZ

Reactivity of $HOIO_2$ with OH

O(H)-abstraction

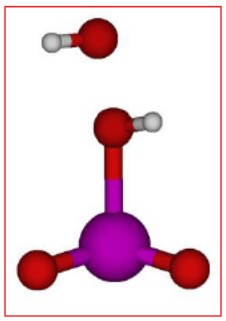
H-abstraction

ΔH_{0K} (kJ/mol)



TS

(93.9)



TS

(12.4)

(26.0)

$OIO + H_2O_2$

$HOIO_2 + OH$

(0.0)

(5.5)

$IO_3 + H_2O$

MCP

(-11.7)

MCR

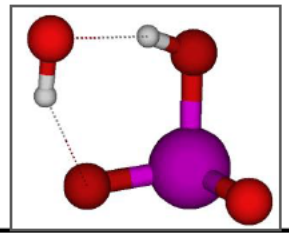
(-38.0)

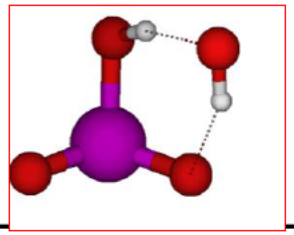
(-35.1)

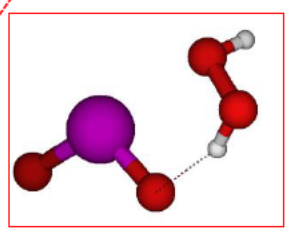
MCR

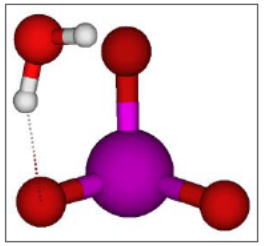
MCP

(-73.2)









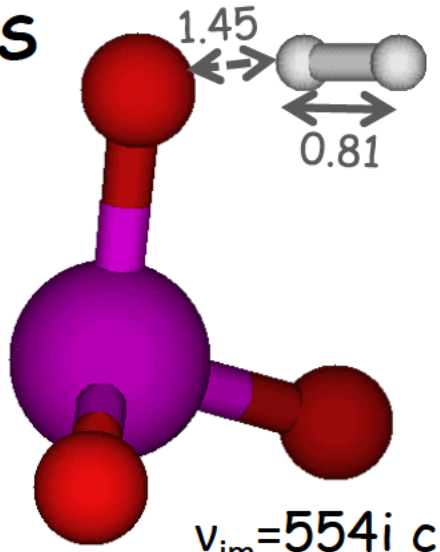
Reaction Coordinate

B3LYP/aVTZ level
Bond lengths in Å

Reactivity of $HOIO_2$ with H

H-abstraction: $HOIO_2 + H \rightarrow IO_3 + H_2$

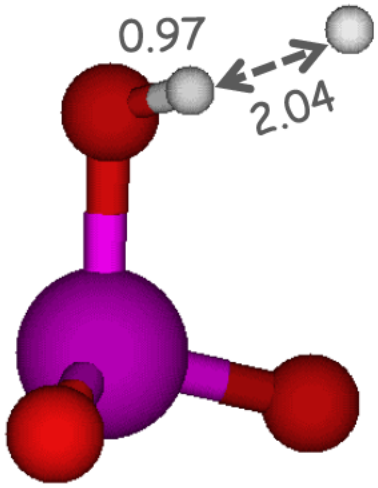
TS



O-H increases

ν_{im}=554i cm^{-1}

MCR



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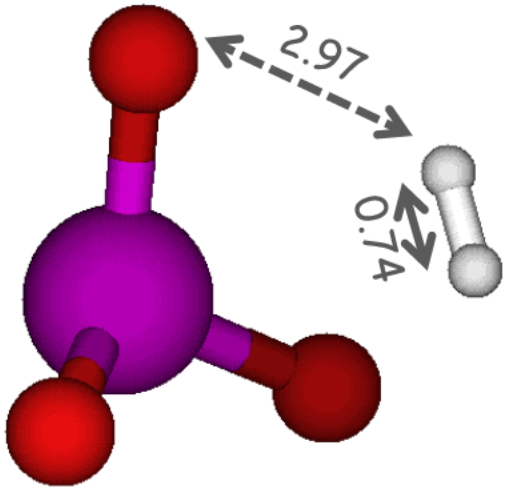
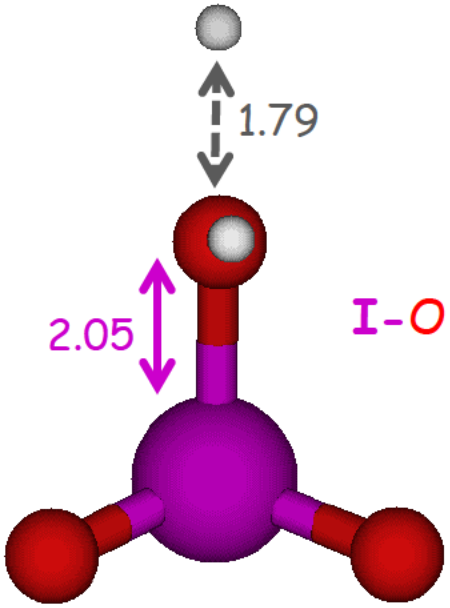


B3LYP/aVTZ level
Bond lengths in Å

Reactivity of $HOIO_2$ with H

O(H)-abstraction: $HOIO_2 + H \rightarrow OIO + H_2O$

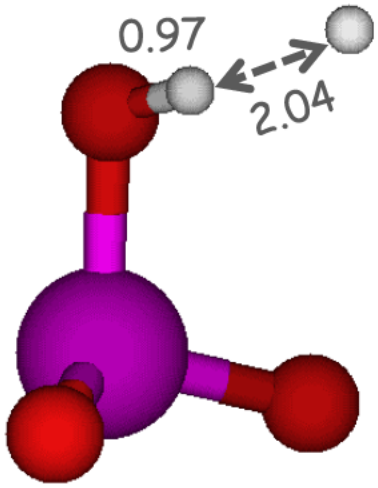
TS



I-O increases

ν_{im}=732i cm^{-1}

MCR



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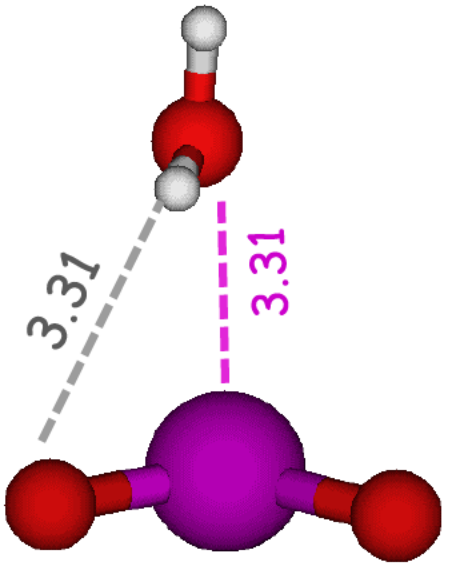
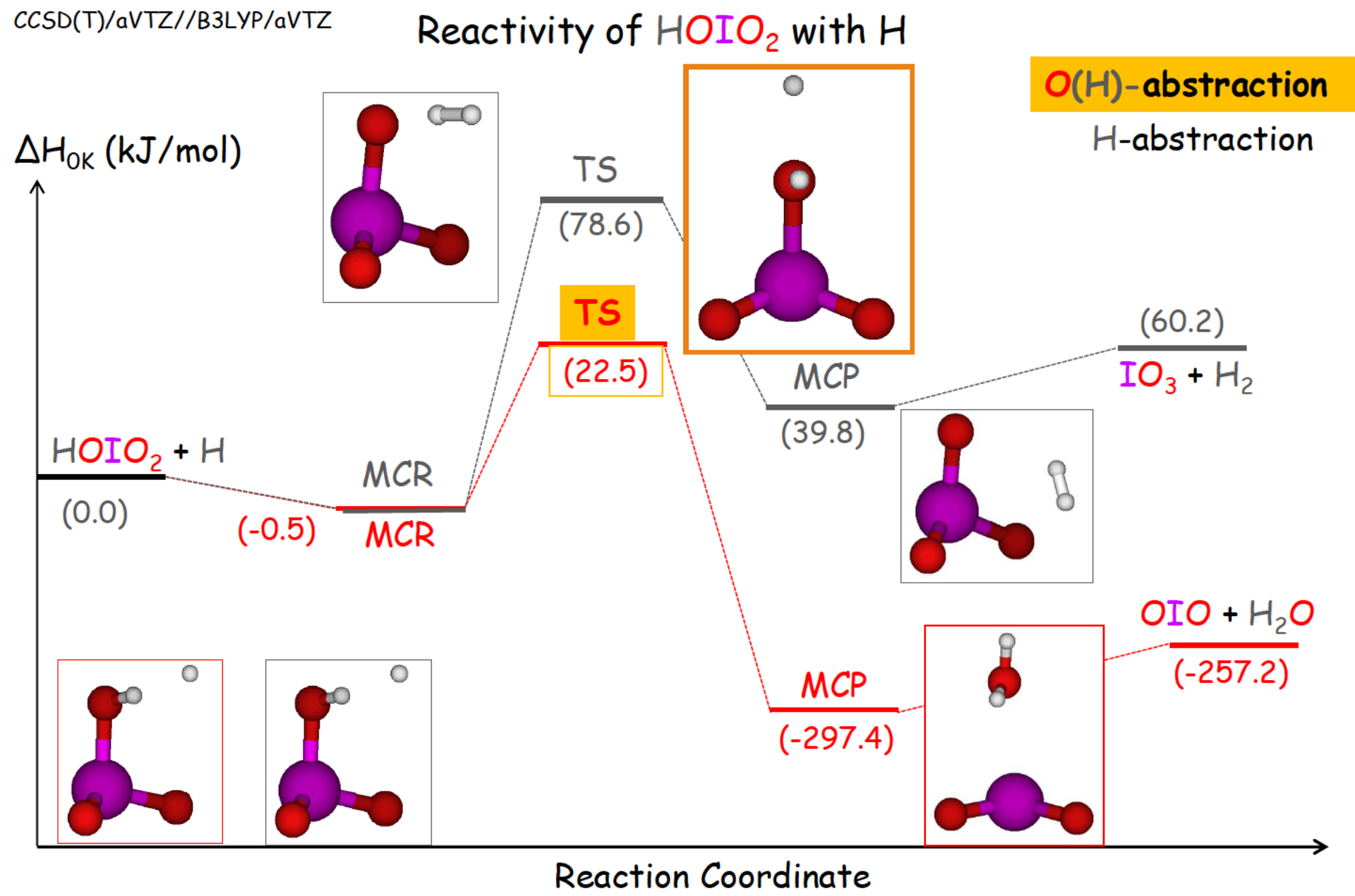


CCSD(T)/aVTZ//B3LYP/aVTZ

Reactivity of $HOIO_2$ with H

O(H)-abstraction

H-abstraction



Conclusions

$IO + CO \longrightarrow I + CO_2$

- ✓ 2 steps mechanism with a *trans* and a *cis* pathway
- ✓ Addition of CO is the rate determining step

$HOIO_2$ monohydrates

- ✓ 3 Structures identified ($HOIO_2$_1wa, 1wb, 1wc)
- ✓ Formation of monohydrates are **exothermic**
- ✓ $HOIO_2$_1wa is spontaneous where **hydrogen bonds** only are present

$HOIO_2$ reactivity

1. $HOIO_2 + OH$
   → **$IO_3 + H_2O$ (H_abs)**
   → $OIO + H_2O_2$ (O_abs)

   $E_0(TS_{H\text{-}abs}) < E_0(TS_{O\text{-}abs})$

2. $HOIO_2 + H$
   → $IO_3 + H_2$ (H_abs)
   → **$OIO + H_2O$ (O_abs)**

   $E_0(TS_{O\text{-}abs}) < E_0(TS_{H\text{-}abs})$

Acknowledgments

Labex CaPPA
Chemical and Physical Properties of the Atmosphere

ANR

"ANR-11-LABX-0005-01"
"ANR-11-RSNR-0013-01"

MIRE

RÉGION NORD PAS DE CALAIS

European Union
European Regional Development Fund

C3R
IRSN - CNRS – Lille 1

SLOVAK RESEARCH AND DEVELOPMENT AGENCY

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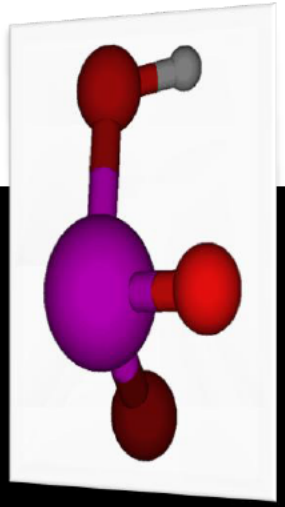

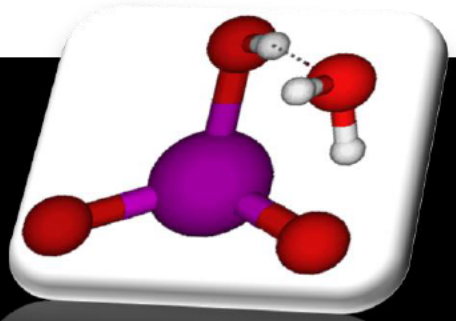

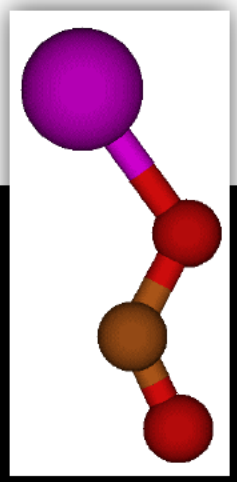

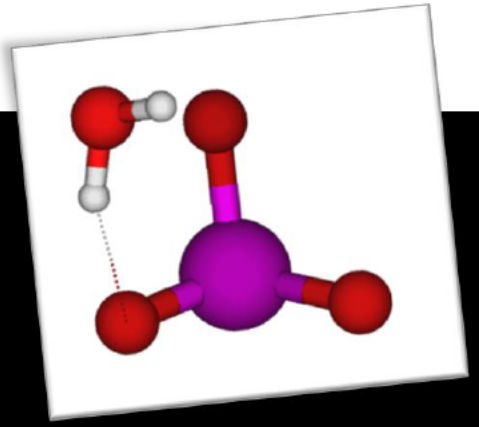

Thank you for your attention !