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Towards accurate tunneling rates on a surface:

A case study of H + $H_2O_2 \longrightarrow H_2O + OH$

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European Research Council
Established by the European Commission

- H_2O network in relation to H_2O_2 observations
- What can be done?
- Methods
- Geometries
- Reaction rates!
- Outlook

Water formation network

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- Dense clouds:

$$O_2 \longrightarrow HO_2 \longrightarrow H_2O_2 \longrightarrow H_2O + OH$$

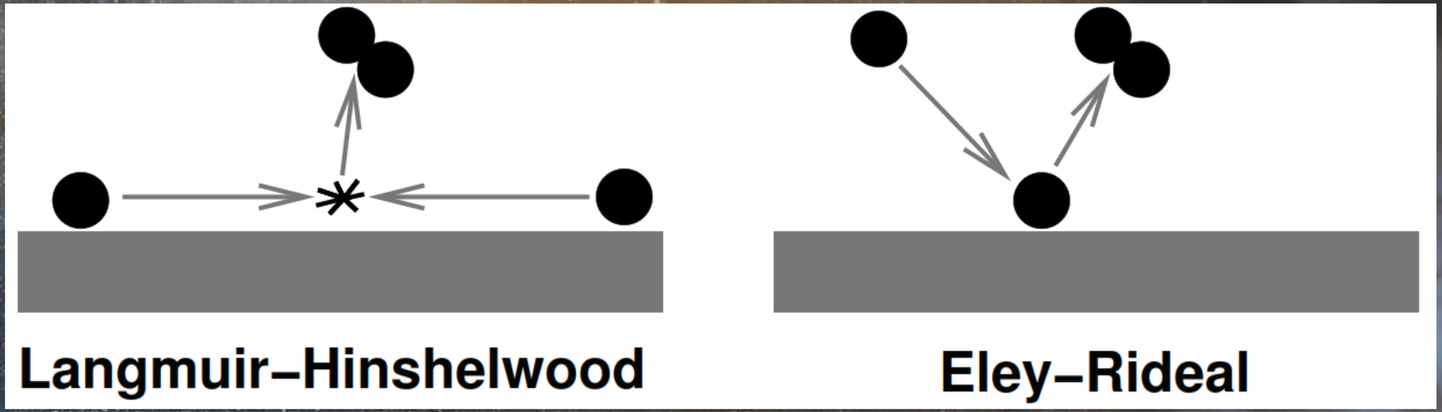
- Only final step high barrier
- Tunneling! (Kinetic Isotope Effect)
- H_2O_2 abundance seems to be strongly T-dependent
- Surface reaction – hydrogen bonds

H_2O network in relation to H_2O_2 observations

Taquet et al. 2013, Lamberts et al. 2014, Oba et al. 2014, Parise et al. 2014

Reaction rates?

- Surface chemistry mechanisms



What can be done?

Reaction rates?

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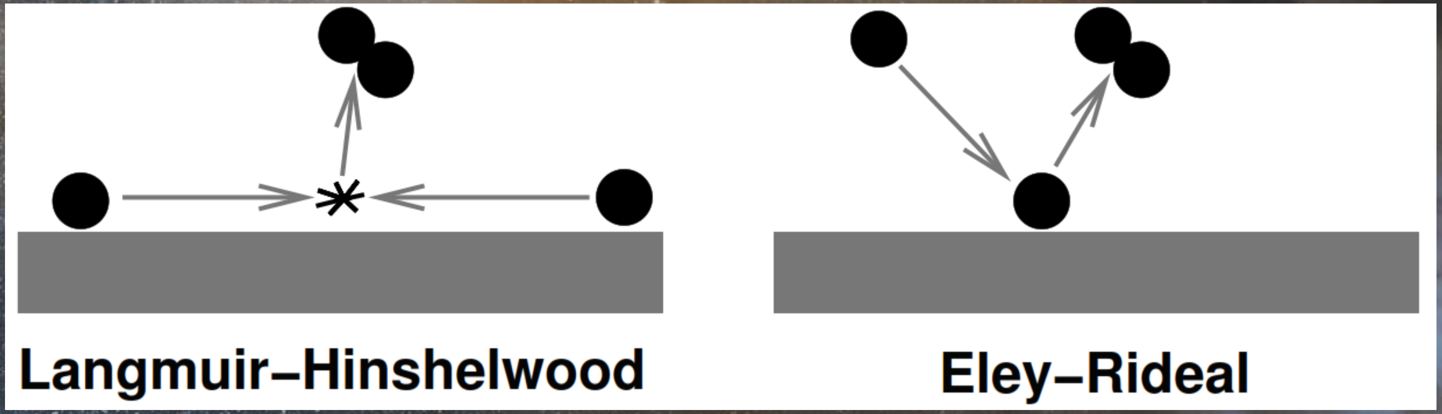
- Surface chemistry mechanisms



- Branching ratio: two reaction paths

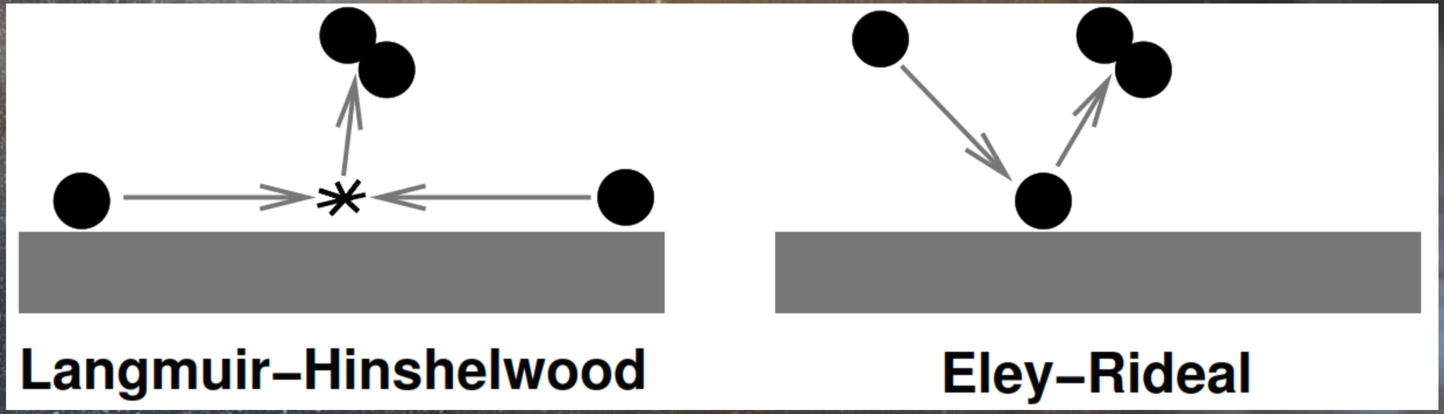
$$H + H_2O_2 \longrightarrow H_2O + OH$$

$$H + H_2O_2 \longrightarrow HO_2 + H_2$$

What can be done?

Reaction rates?

- Surface chemistry mechanisms



- Branching ratio: two reaction paths

$$H + H_2O_2 \longrightarrow H_2O + OH$$

$$H + H_2O_2 \longrightarrow HO_2 + H_2$$

- Gas vs. water clusters vs. surface

What can be done?

Methods

- **Ab initio methods**
  - Density functional theory
  - Functional and basis set chosen to match a CCSD(T)-F12 benchmark

- **Rate theory**
  - Taking into account tunneling
  - Instanton theory

Functional:
MPW1B95 & M05-2X

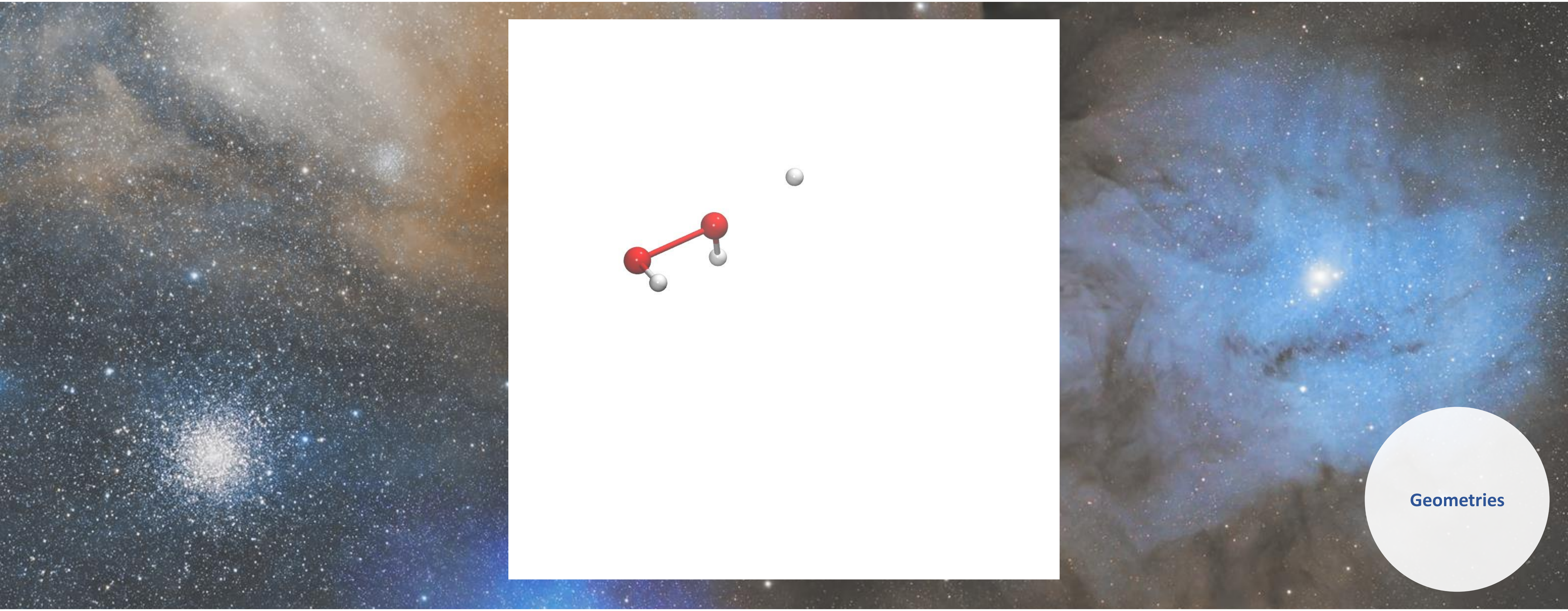
Basis set:
MG3S

NWChem

DL-find library in ChemShell

Ellingson et al. (2007), Kästner et al. (2009), Rommel et al. (2011)

Gas vs. Clusters



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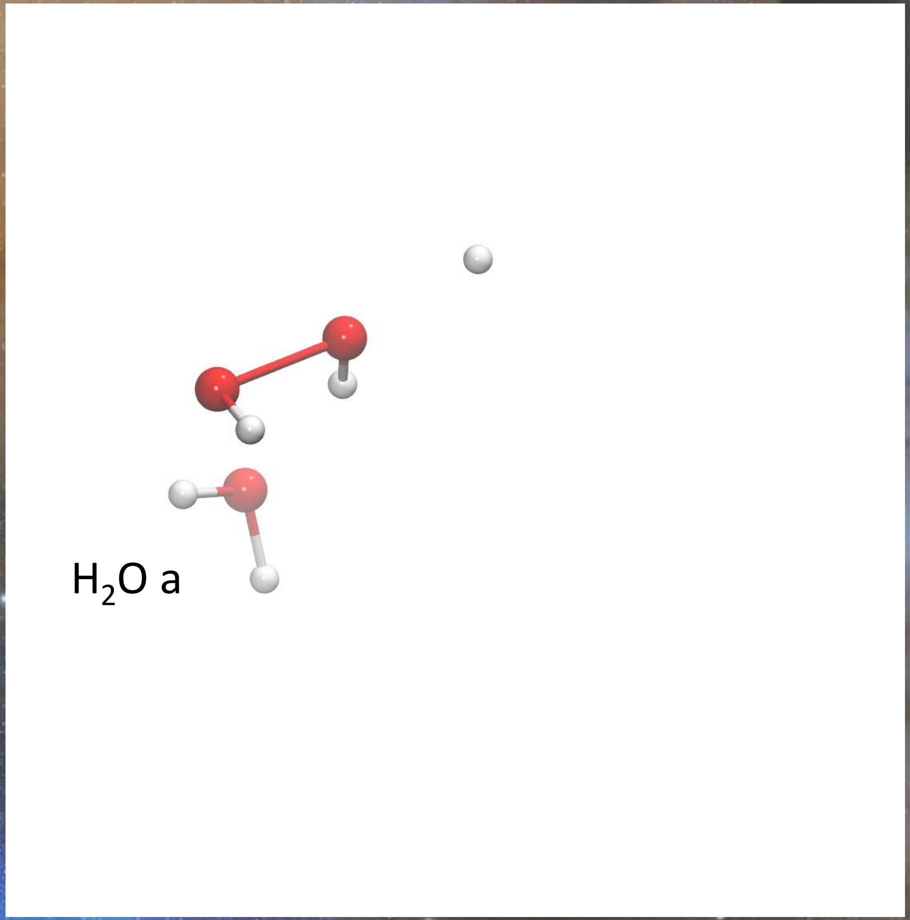
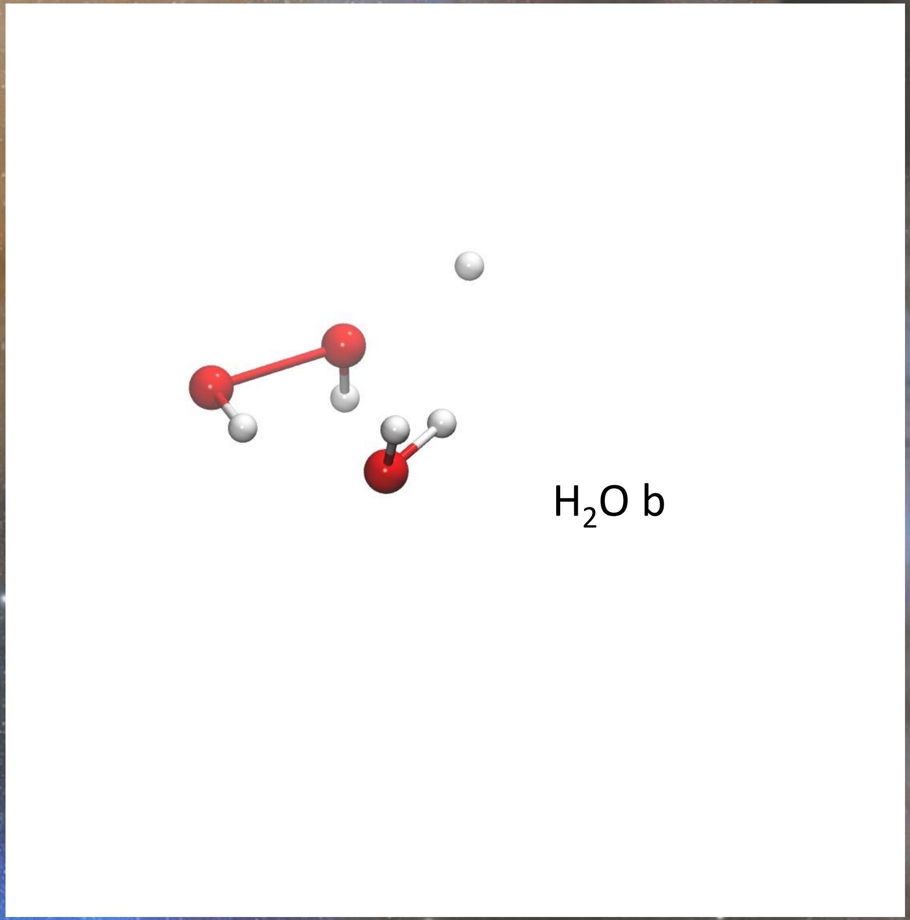
Gas vs. Clusters



Geometries

Gas vs. Clusters



Geometries

Gas vs. Clusters

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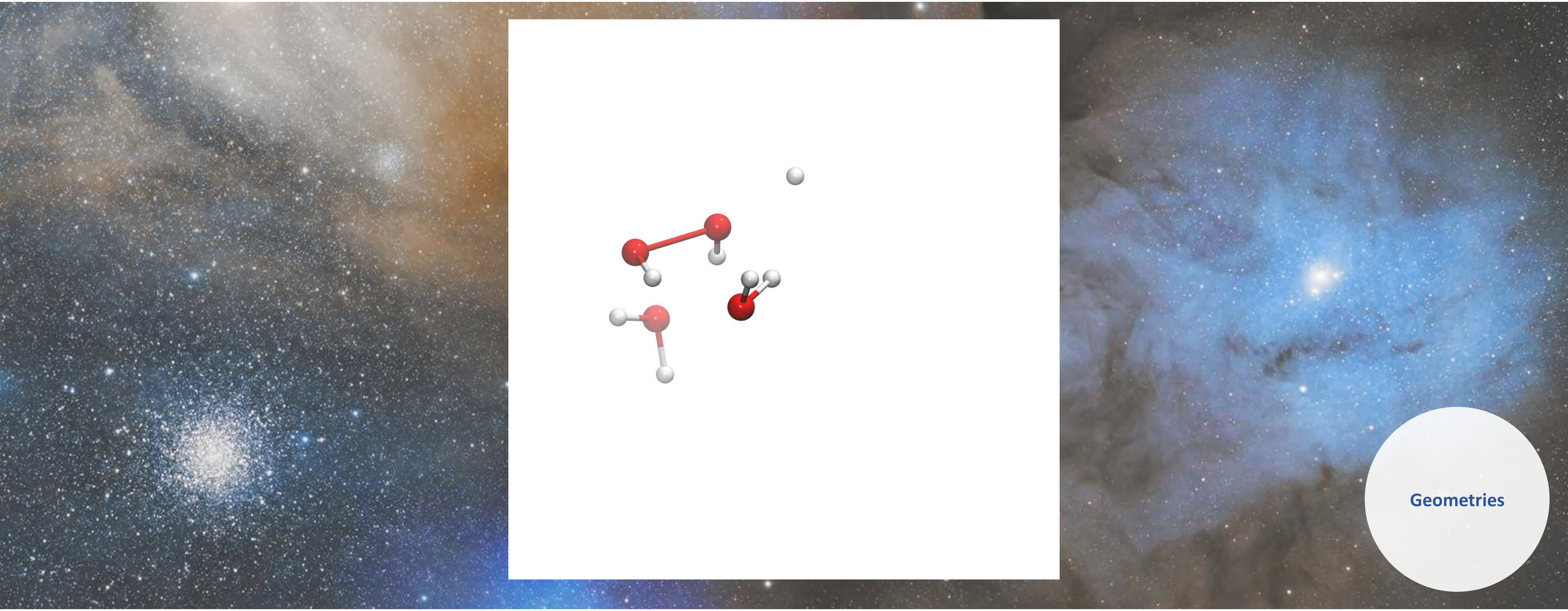
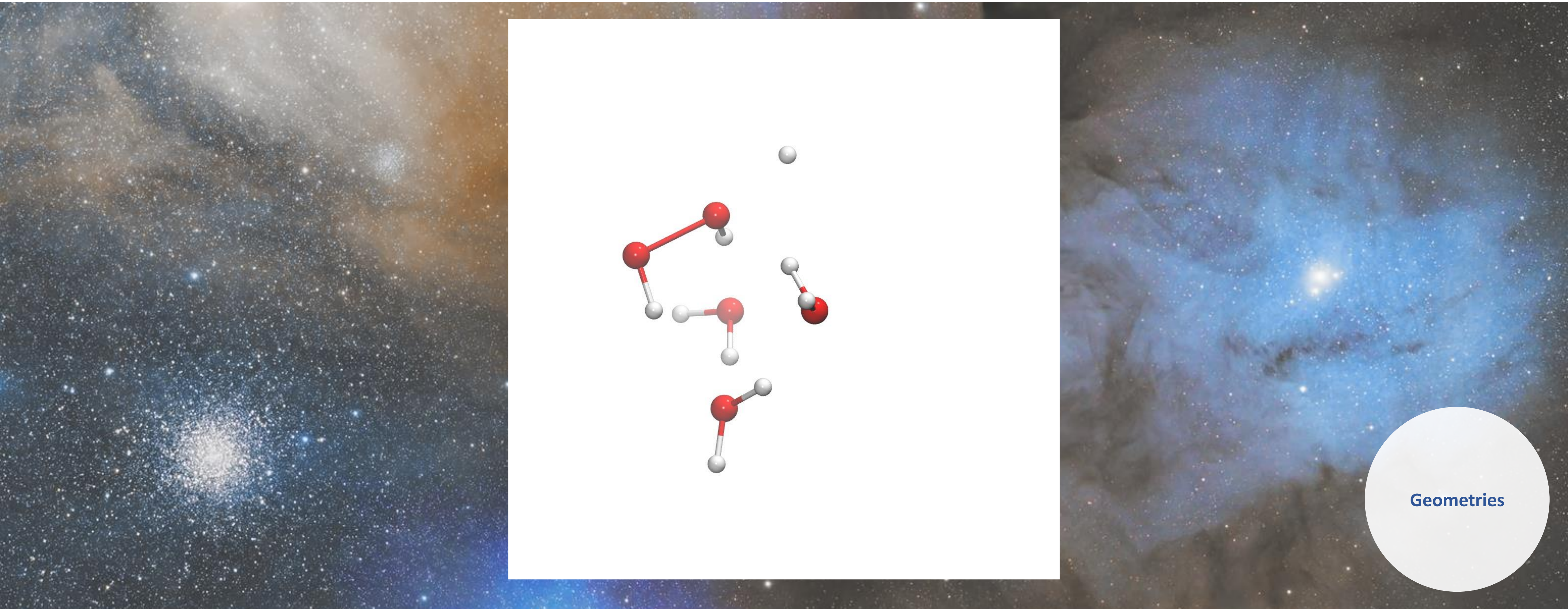


Gas vs. Clusters



Gas vs. Clusters

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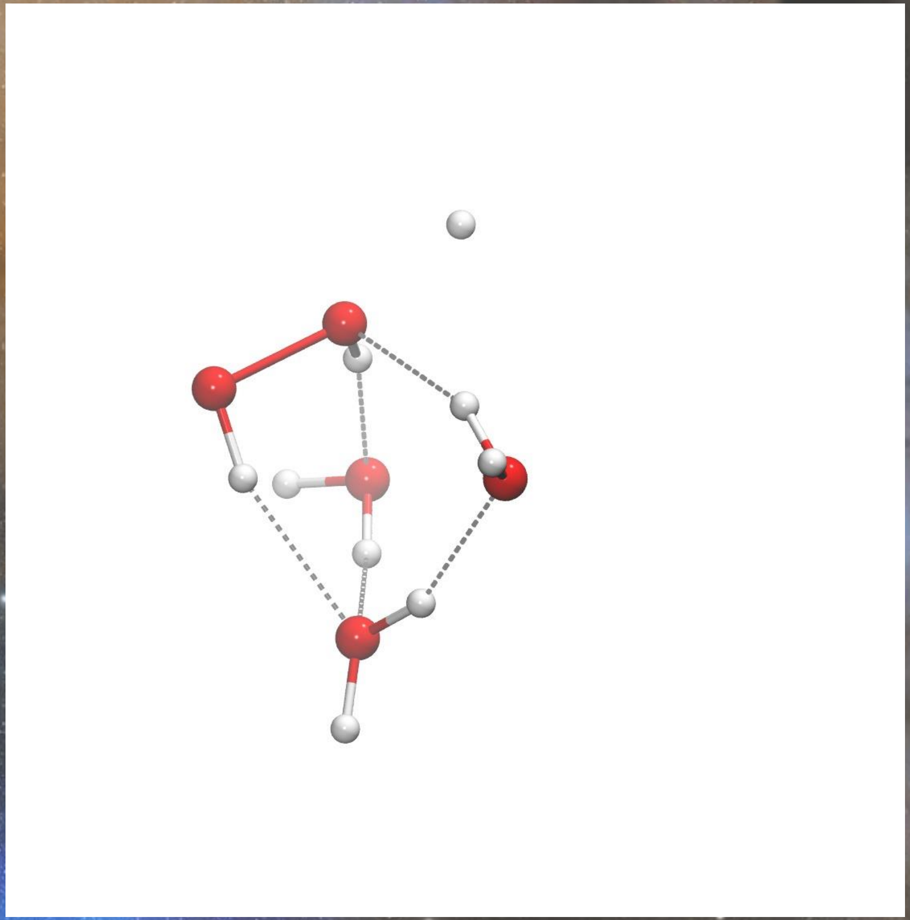

Geometries

Branching ratio

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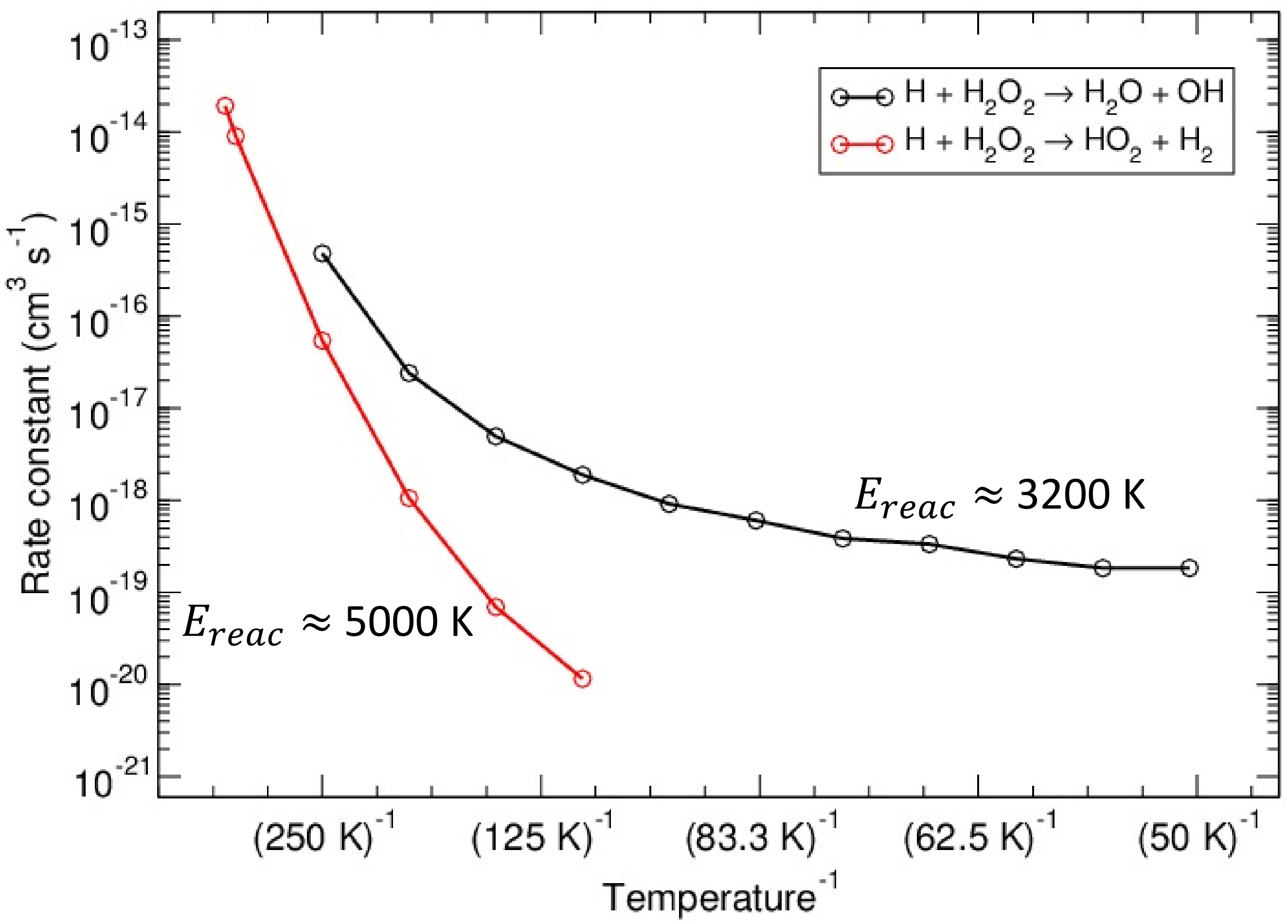

$E_{reac} \approx 3200$ K

$E_{reac} \approx 5000$ K

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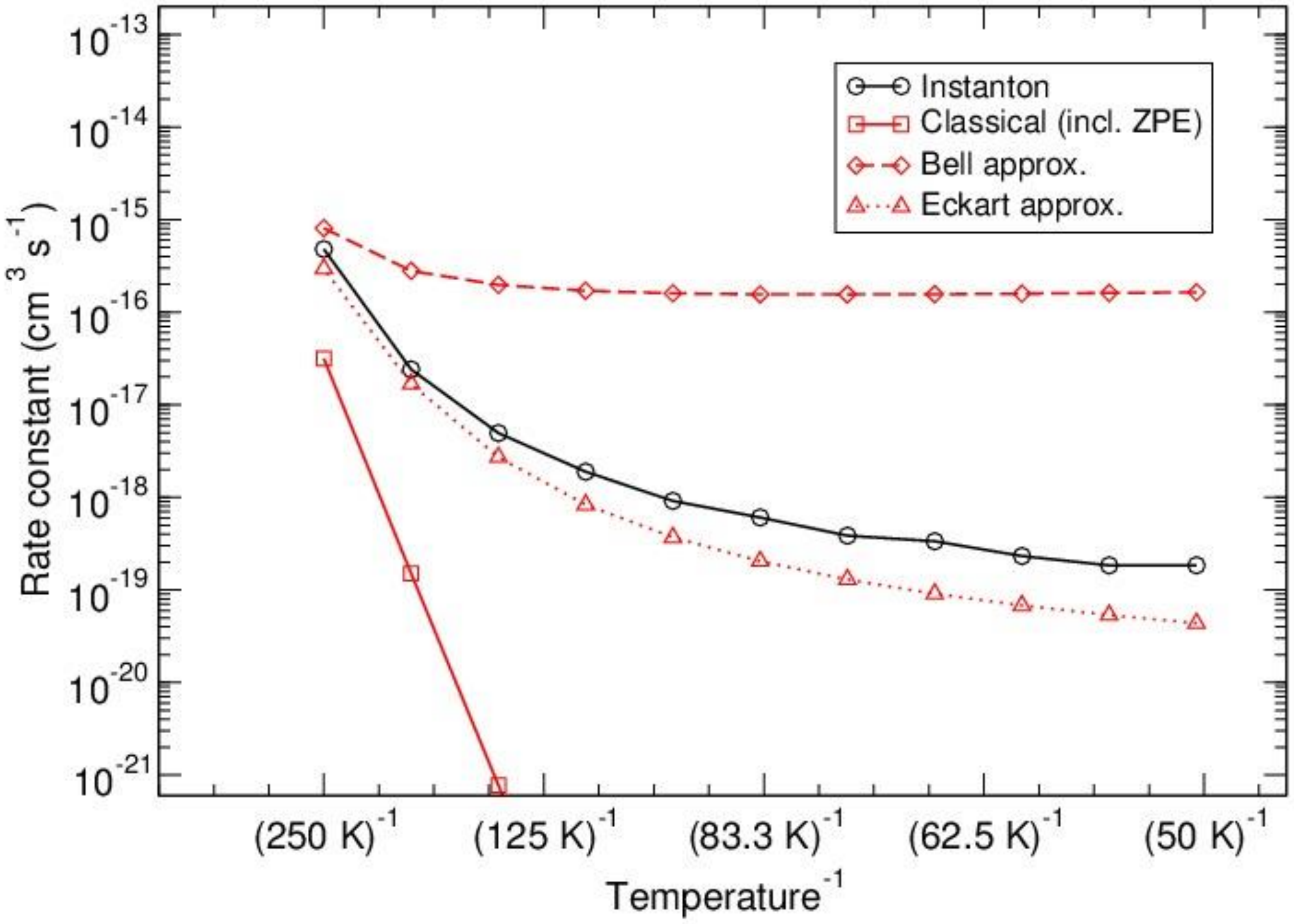
Classical vs. Bell/Eckart vs. Instanton



Databases

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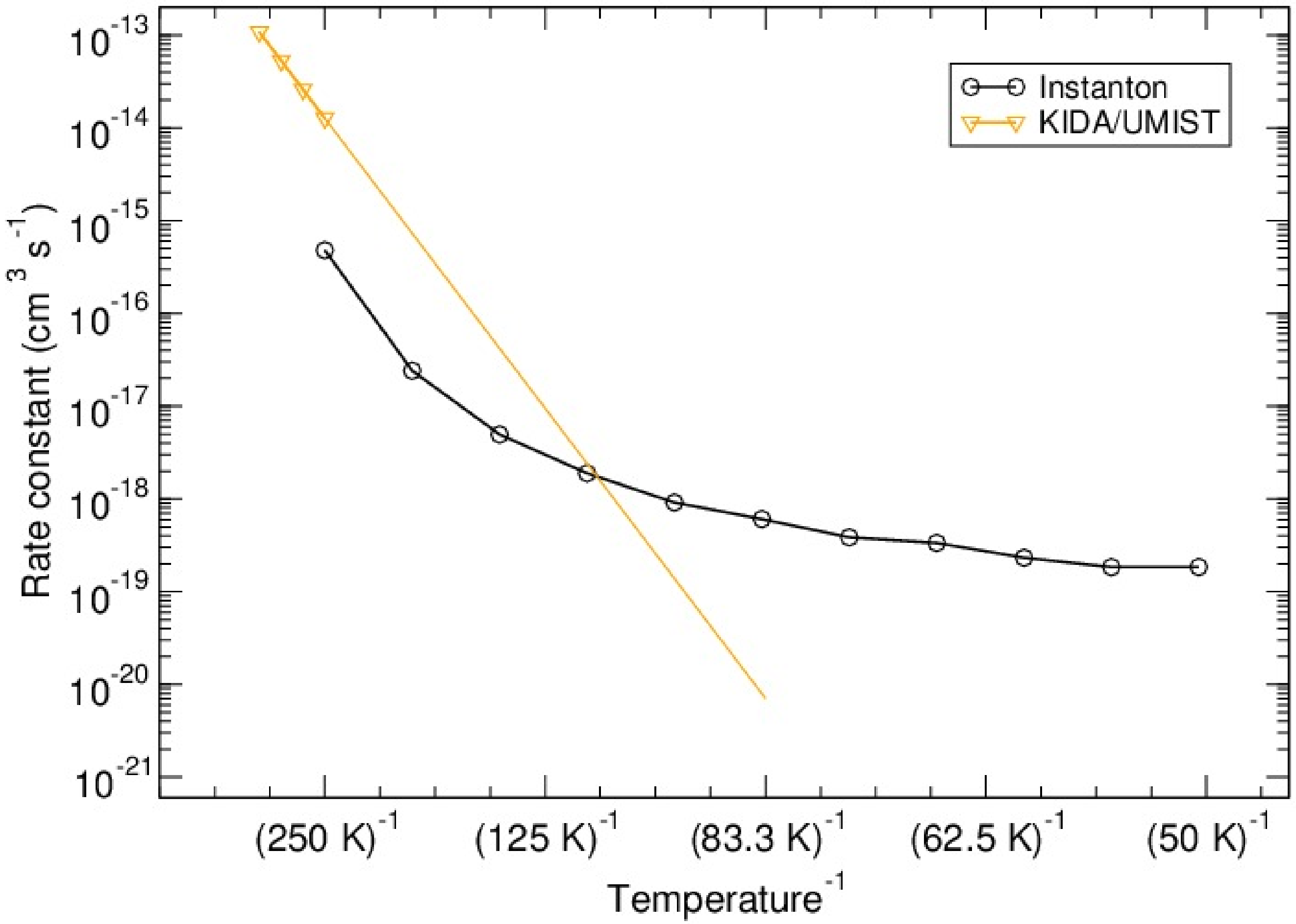

Geometries

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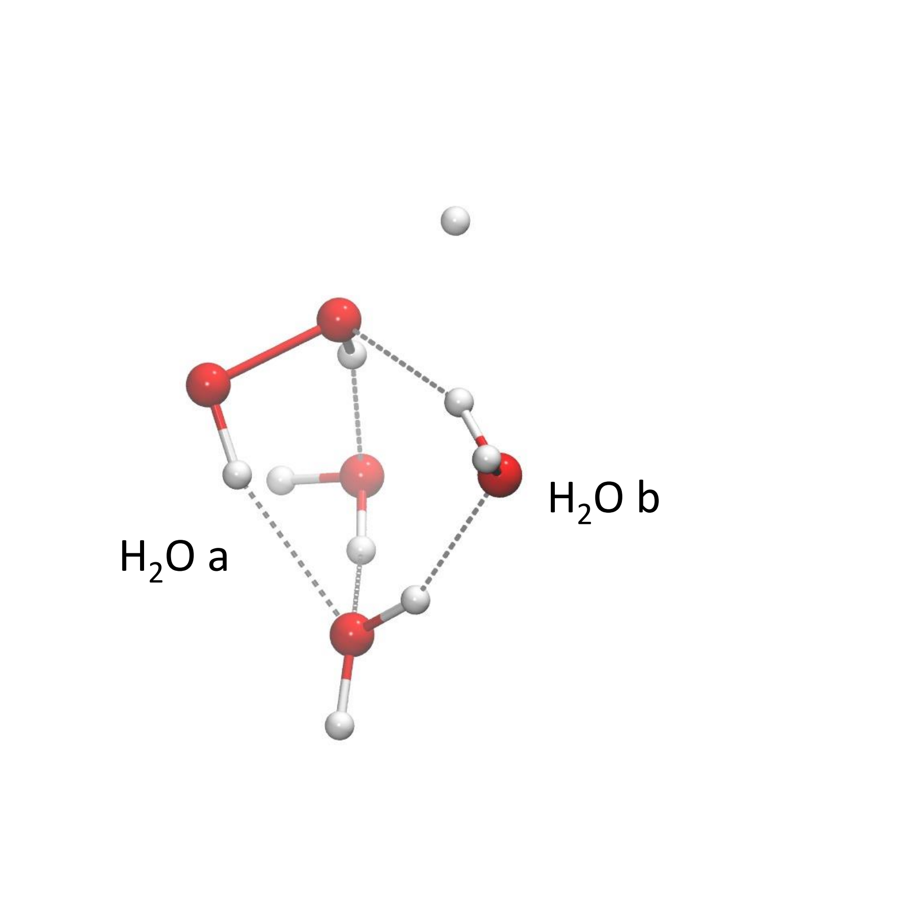
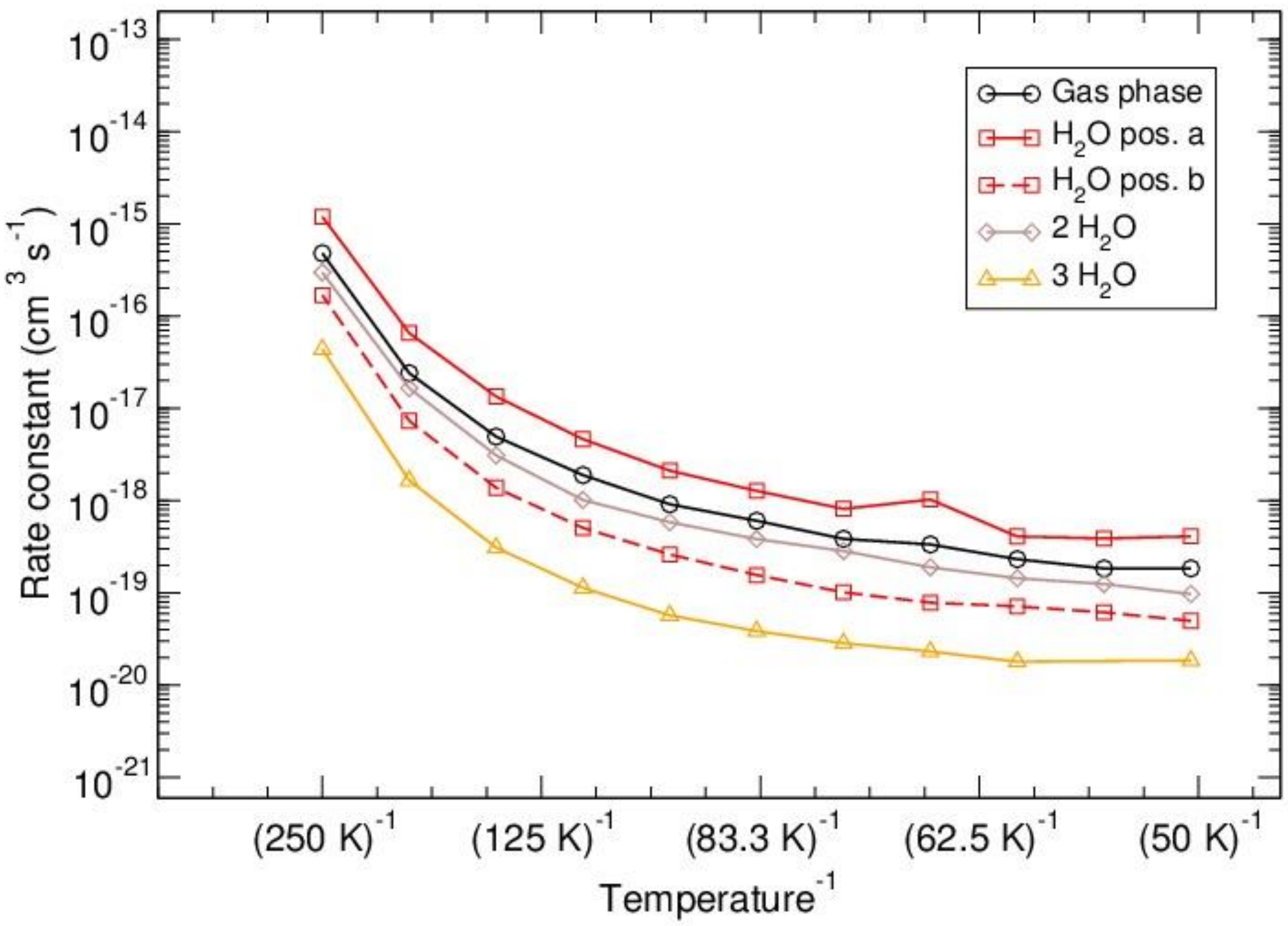


Reminder

Gas vs. Clusters



Unimolecular rates

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Rate equations: $k_{\text{uni}} \propto P_{\text{reac}} \cdot \nu \cdot (P_{\text{diff,A}} + P_{\text{diff,B}})$

KMC: $k_{\text{uni}} \propto \nu \cdot P_{\text{reac}}$

With $P_{\text{reac}} = e^{-E_{\text{reac}}/T}$

Effectively: both ν and E_{reac} fitting parameters,
e.g., $E_{\text{reac}} = 1900$ K vs. 2508 K vs. 3100 K

Langmuir - Hinshel wood

KIDA database, Taquet et al. (2012), this work

Unimolecular rates

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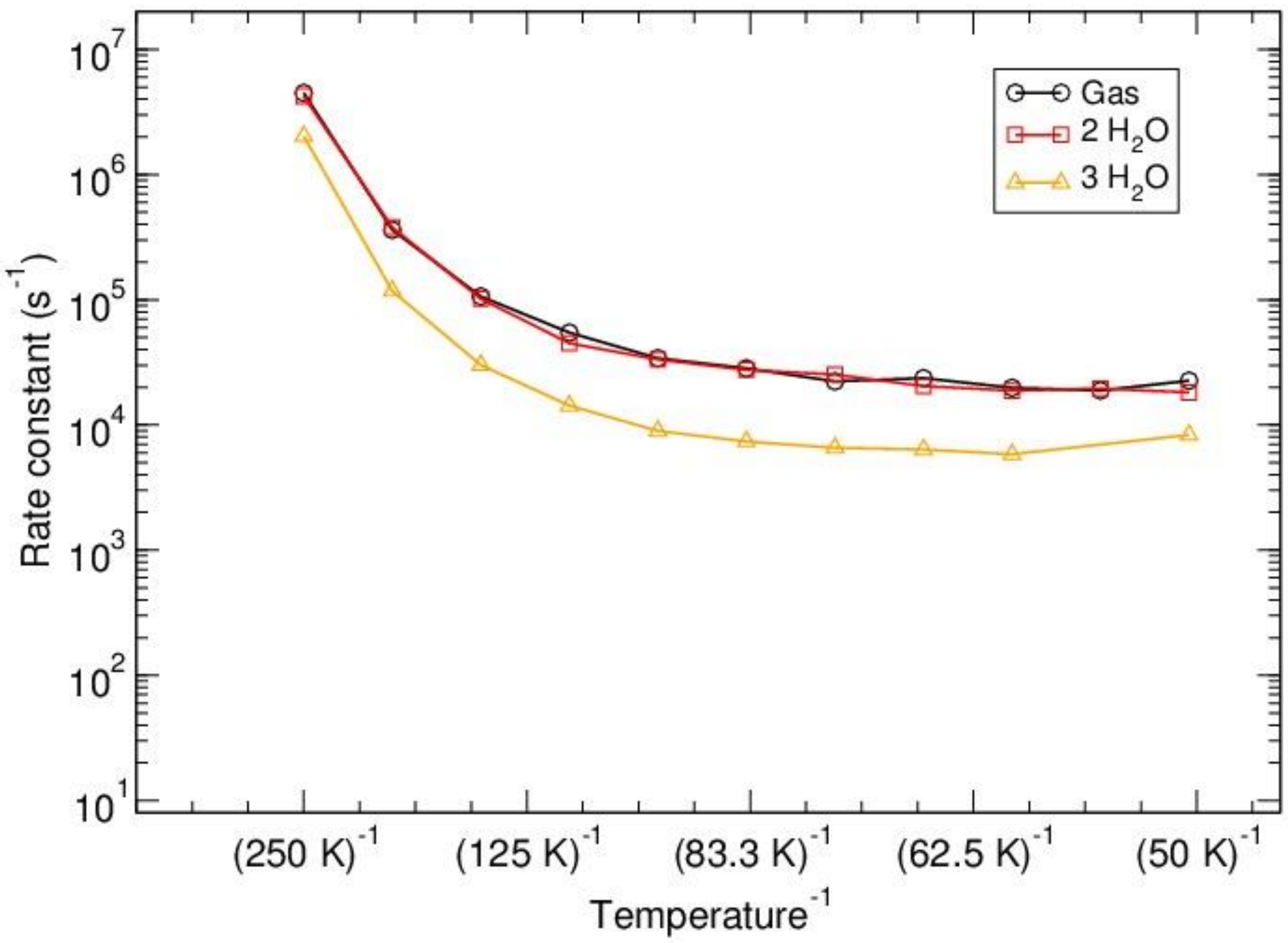

Langmuir - Hinshelwood

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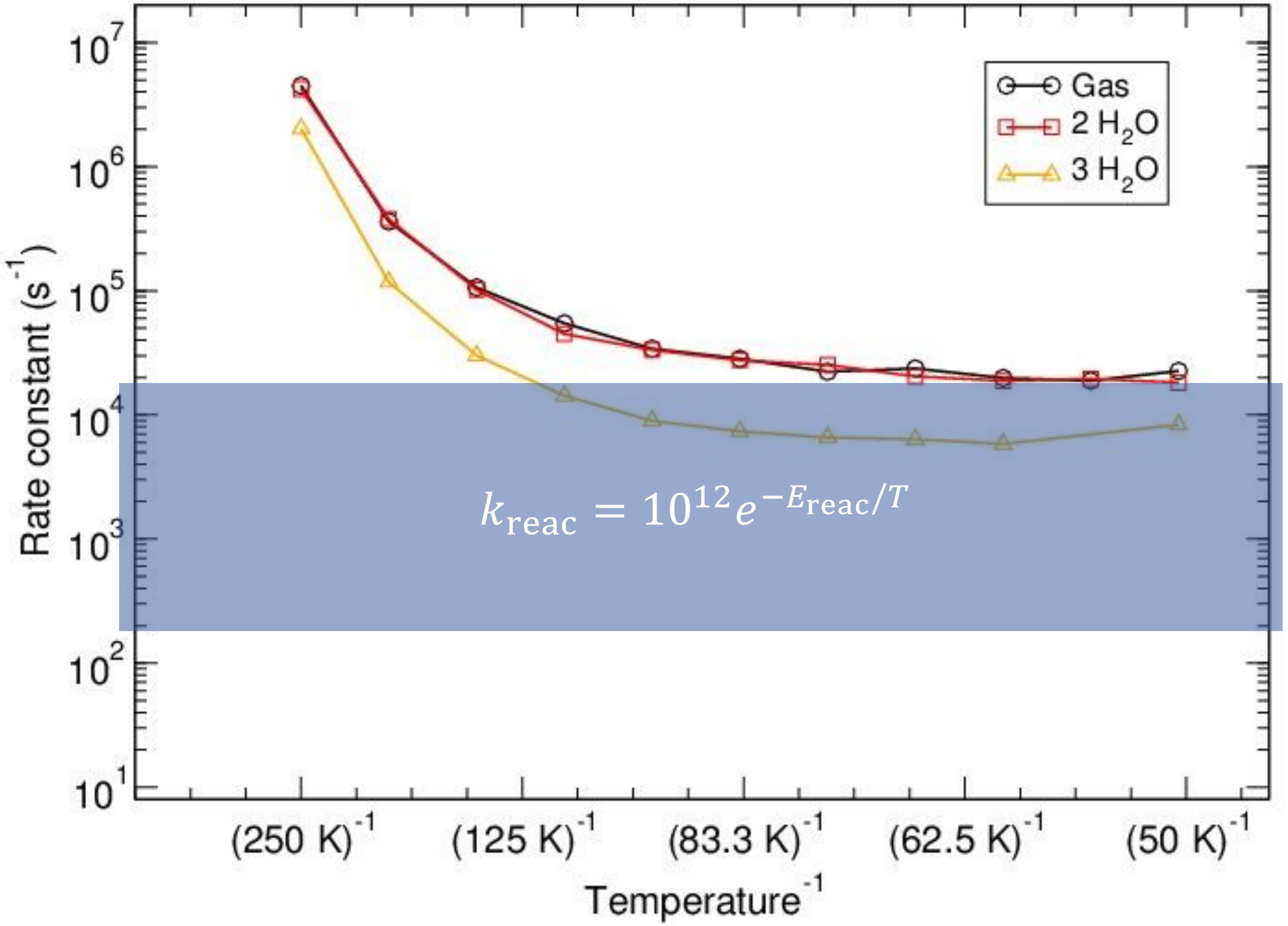
Unimolecular rates



$$k_{\mathrm{reac}} = 10^{12} e^{-E_{\mathrm{reac}}/T}$$

Langmuir - Hinshel wood

Kinetic Isotope Effect

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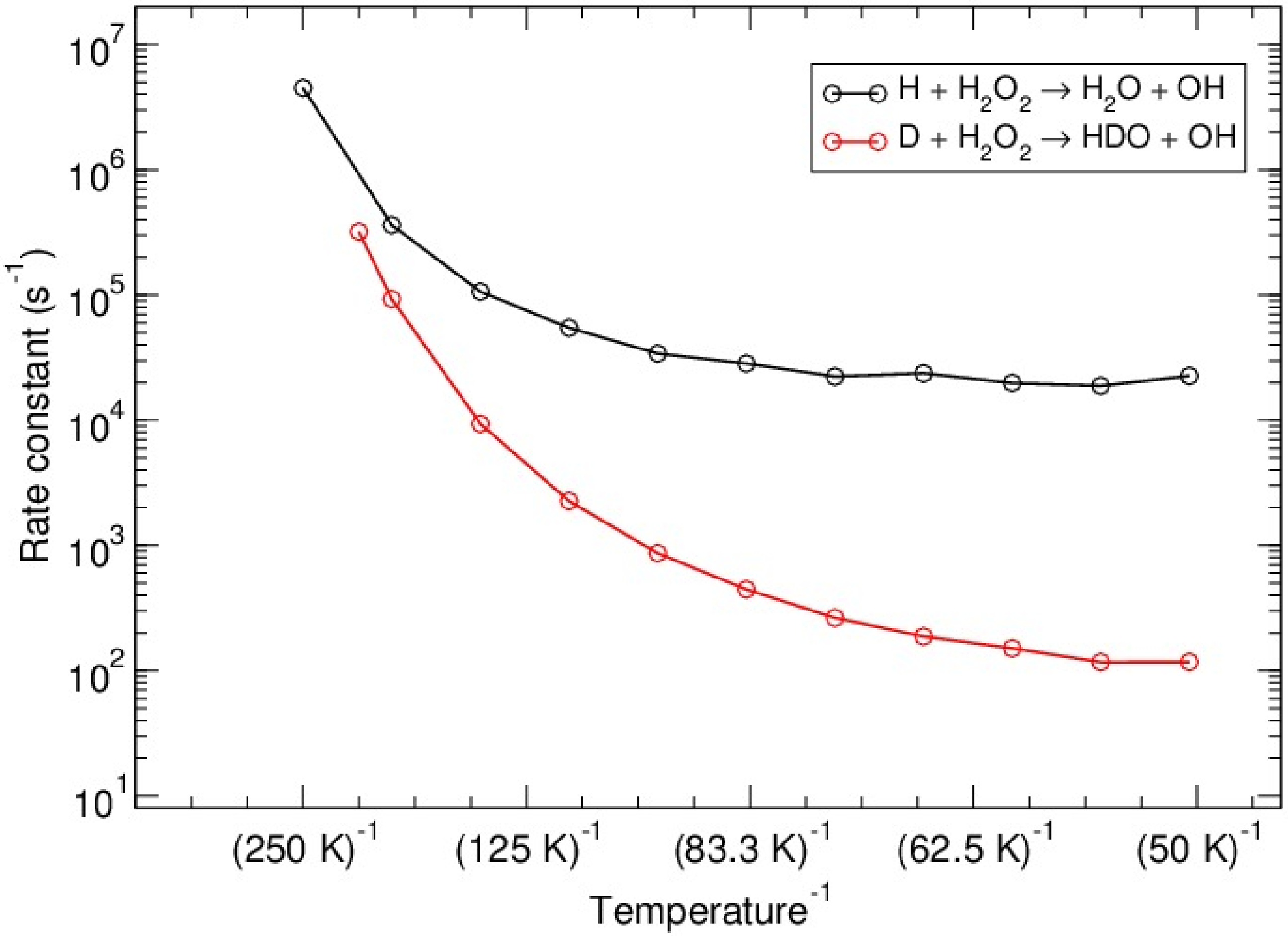

Kinetic Isotope Effect

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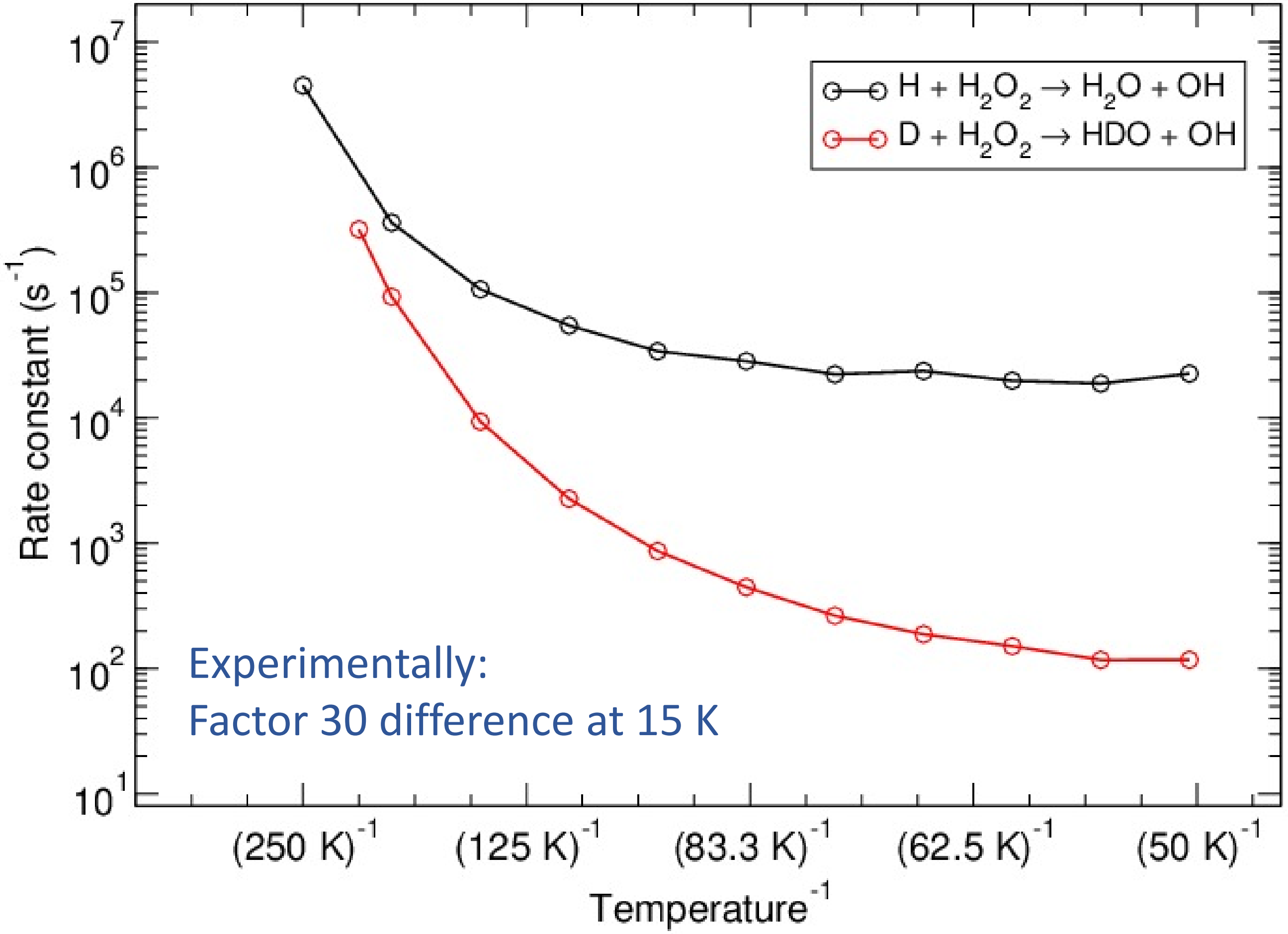

Experimentally:
Factor 30 difference at 15 K

Langmuir - Hinshel wood

Oba et al. 2014

What have we learned?

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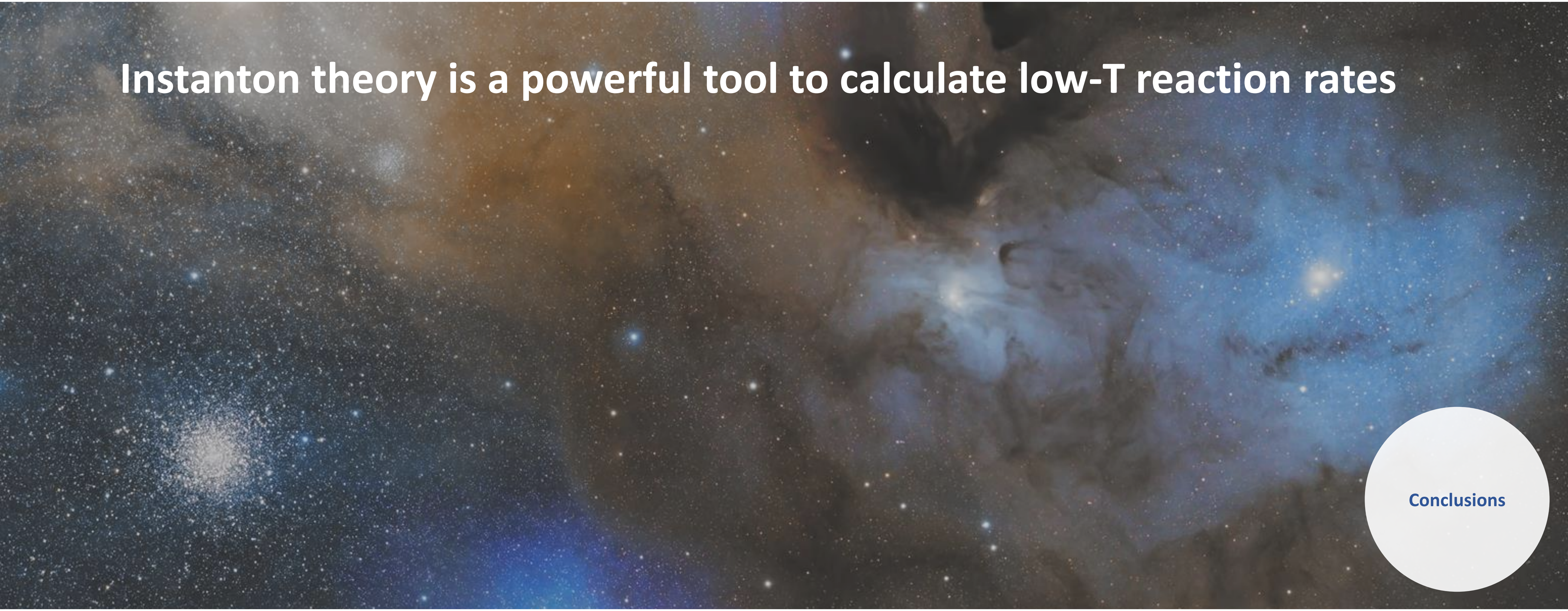

Instanton theory is a powerful tool to calculate low-T reaction rates

Conclusions

What have we learned?

Instanton theory is a powerful tool to calculate low-T reaction rates

- **Branching ratio:** *main product channel is H_2O + OH*
- **KIE:** *qualitative agreement with experiment*
- **Gas vs. Clusters:** *water in the vicinity of the reactive center impacts on the reaction rate*

What have we learned?

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Instanton theory is a powerful tool to calculate low-T reaction rates

- **Branching ratio:** *main product channel is H_2O + OH*
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Difference between bimolecular and unimolecular rates important to note!

Conclusions

QM/MM

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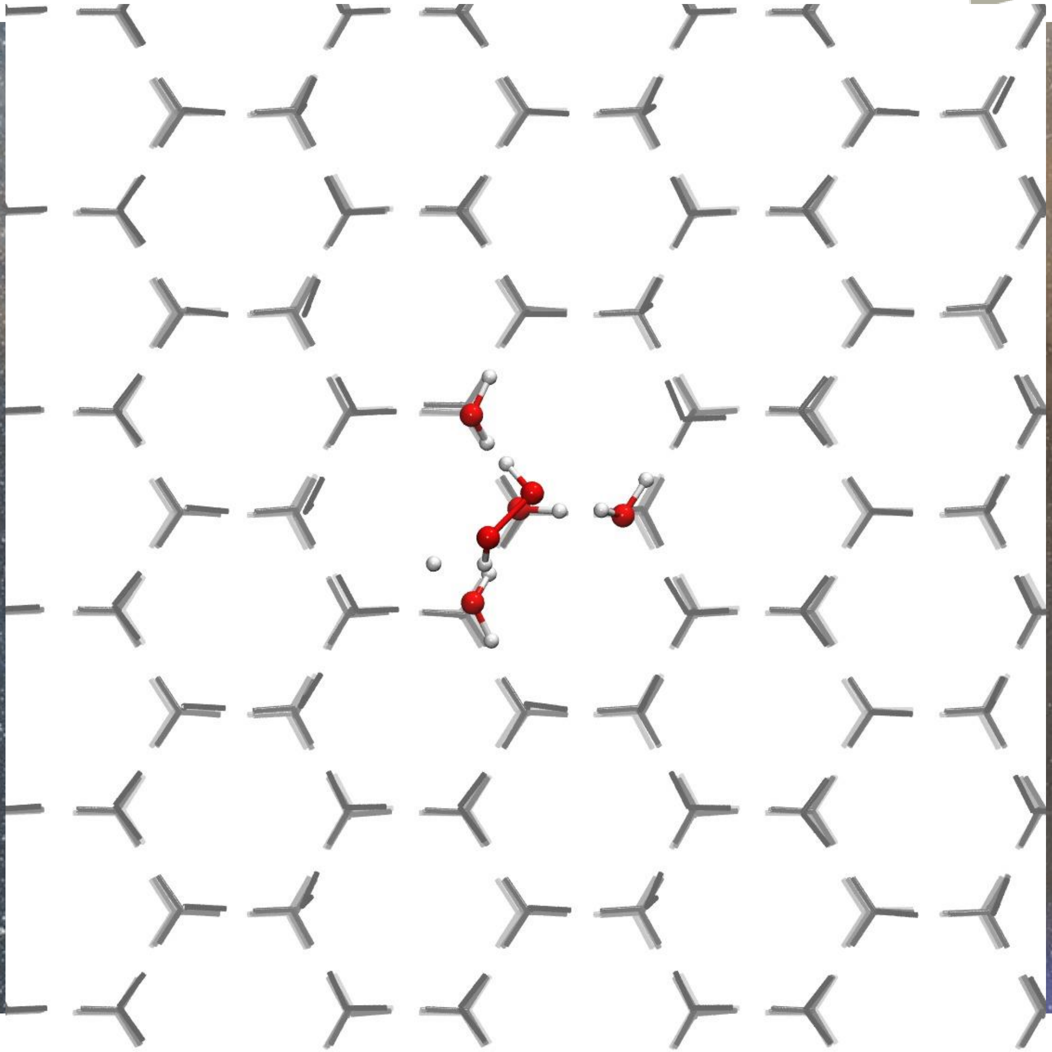
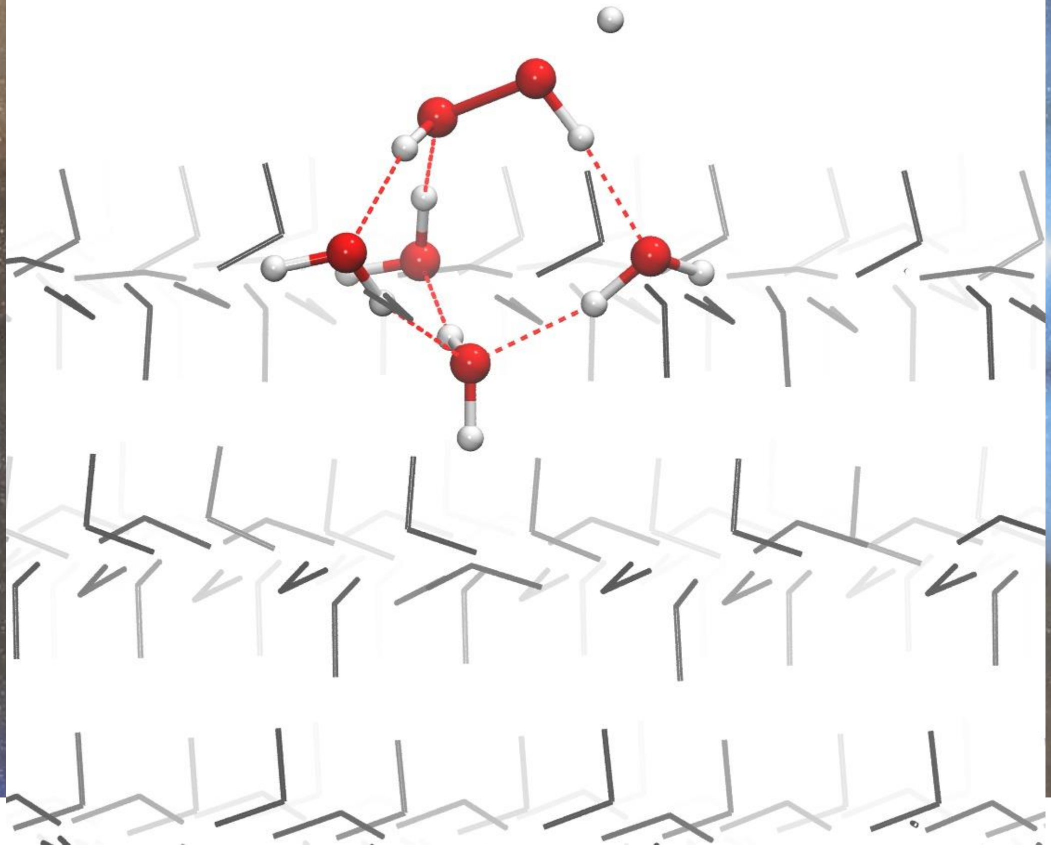


E_{bind} H_2O_2 = 74.22 kJ/mol = 8930 K

E_{reac} = 15.72 kJ/mol = 1890 K



Outlook

Thank you!

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Pradipta Kumar Samanta

Sonia Álvarez Barcia

Thomas Bissinger

BWForCluster Justus

European Research Council
Established by the European Commission
646717 TUNNELCHEM

Benchmark

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Method	Reaction 1 H + H_2O_2 → H_2O + OH		Reaction 2 H + H_2O_2 → HO_2 + H_2	
	kJ/mol	Kelvin	kJ/mol	Kelvin
CCSD(T)-F12 / VTZ-F12	**25.52**	**3069**	**39.38**	**4737**
ic-MRCCSD(T) / cc-pVQZ	**25.93**	**3111**	**--**	--
Ellingson et al. (2007)	**27.2**	**3260**	**41.4**	**4966**
MPW1B95 / MG3S	26.50	3187	23.66	2845
M05-2X / MG3S	45.86	5515	39.74	4779
PWB6K / MG3S	35.96	4325	35.40	4257
B3LYP / MG3S	11.22	1349	8.07	970
B3LYP / def2-TZVPD	10.78	1296	7.33	881

Energies in kJ/mol and Kelvin, without ZPE corrections, no dispersion correction

Benchmark and geometries

Ellingson et al. (2007)

Classical vs. Bell/Eckart vs. Instanton

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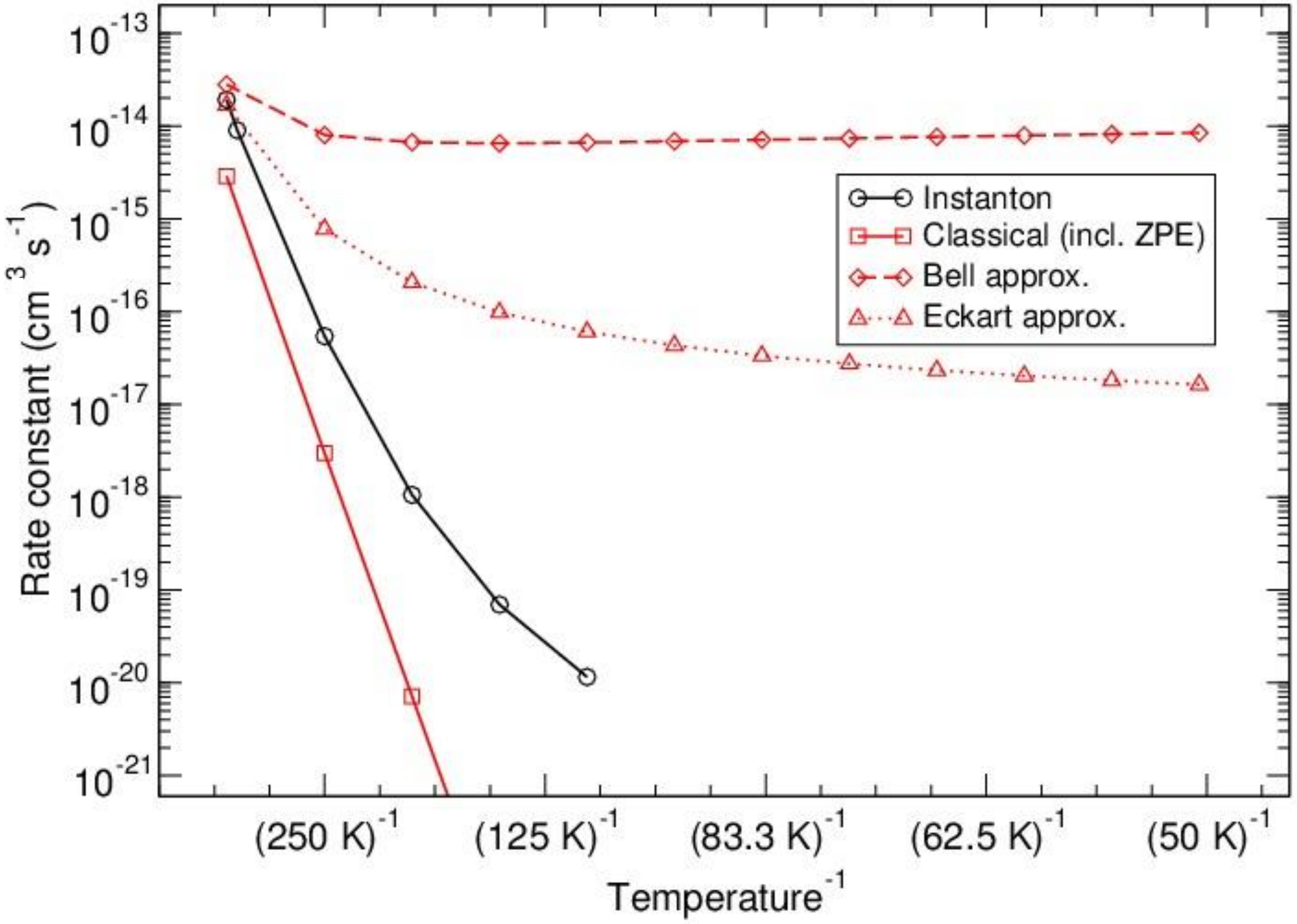
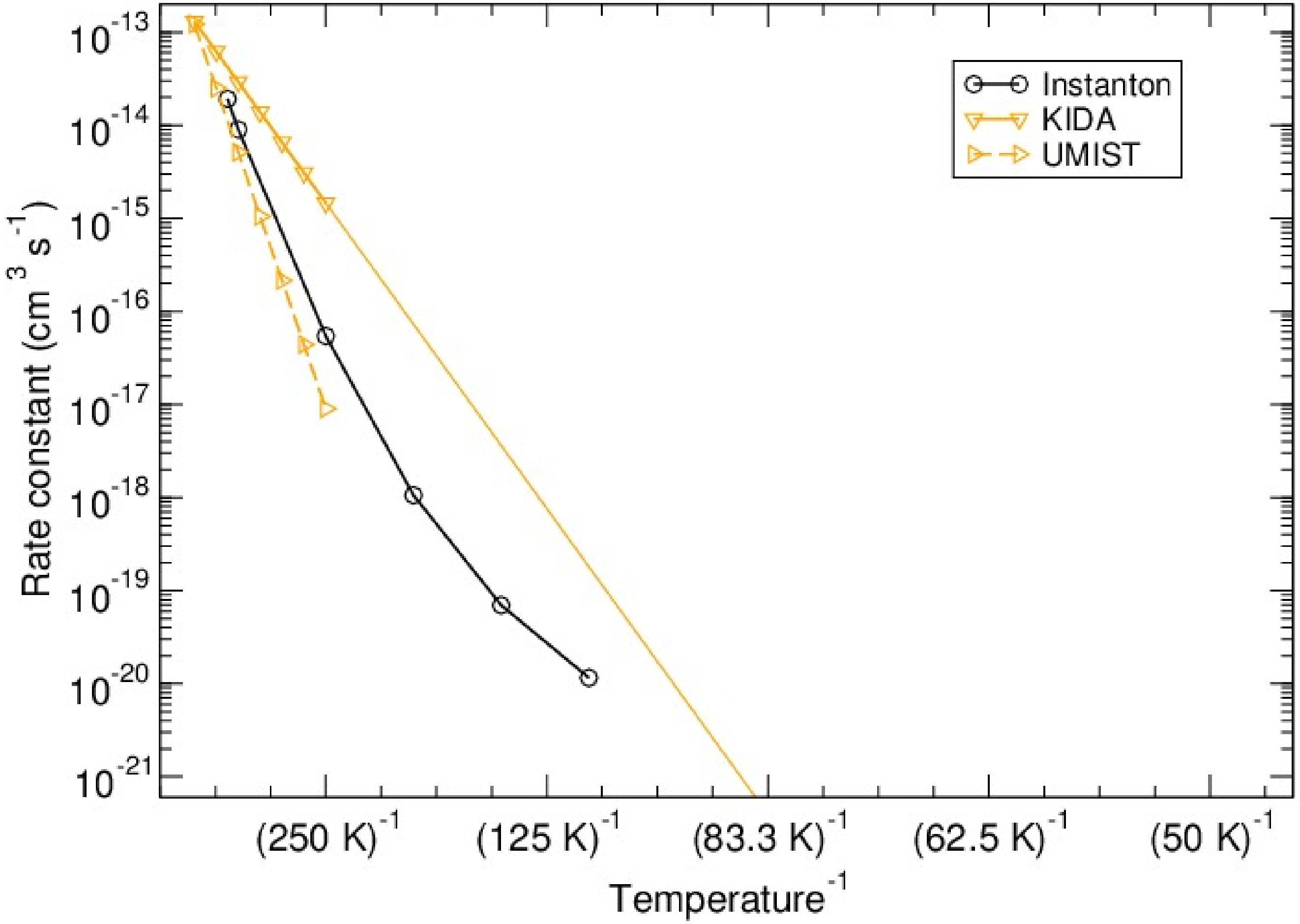


Eley-Rideal

Databases


Instanton
KIDA
UMIST
Rate constant (cm^3 s^-1)
10^-13
10^-14
10^-15
10^-16
10^-17
10^-18
10^-19
10^-20
10^-21
(250 K)^-1
(125 K)^-1
(83.3 K)^-1
(62.5 K)^-1
(50 K)^-1
Temperature^-1


Eley-
Rideal

Branching ratio -- Extended

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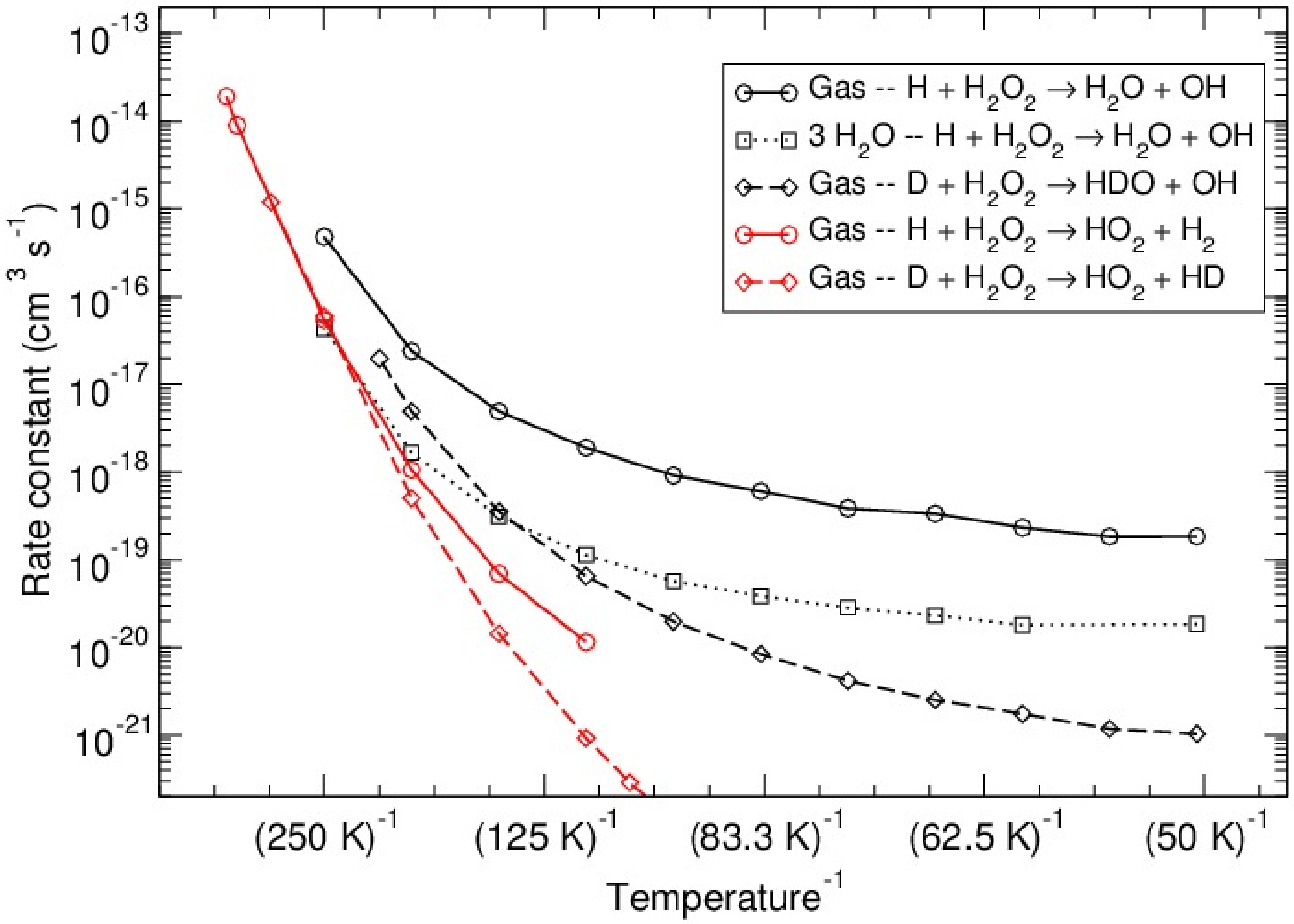

Extra

Flexible vs. Frozen

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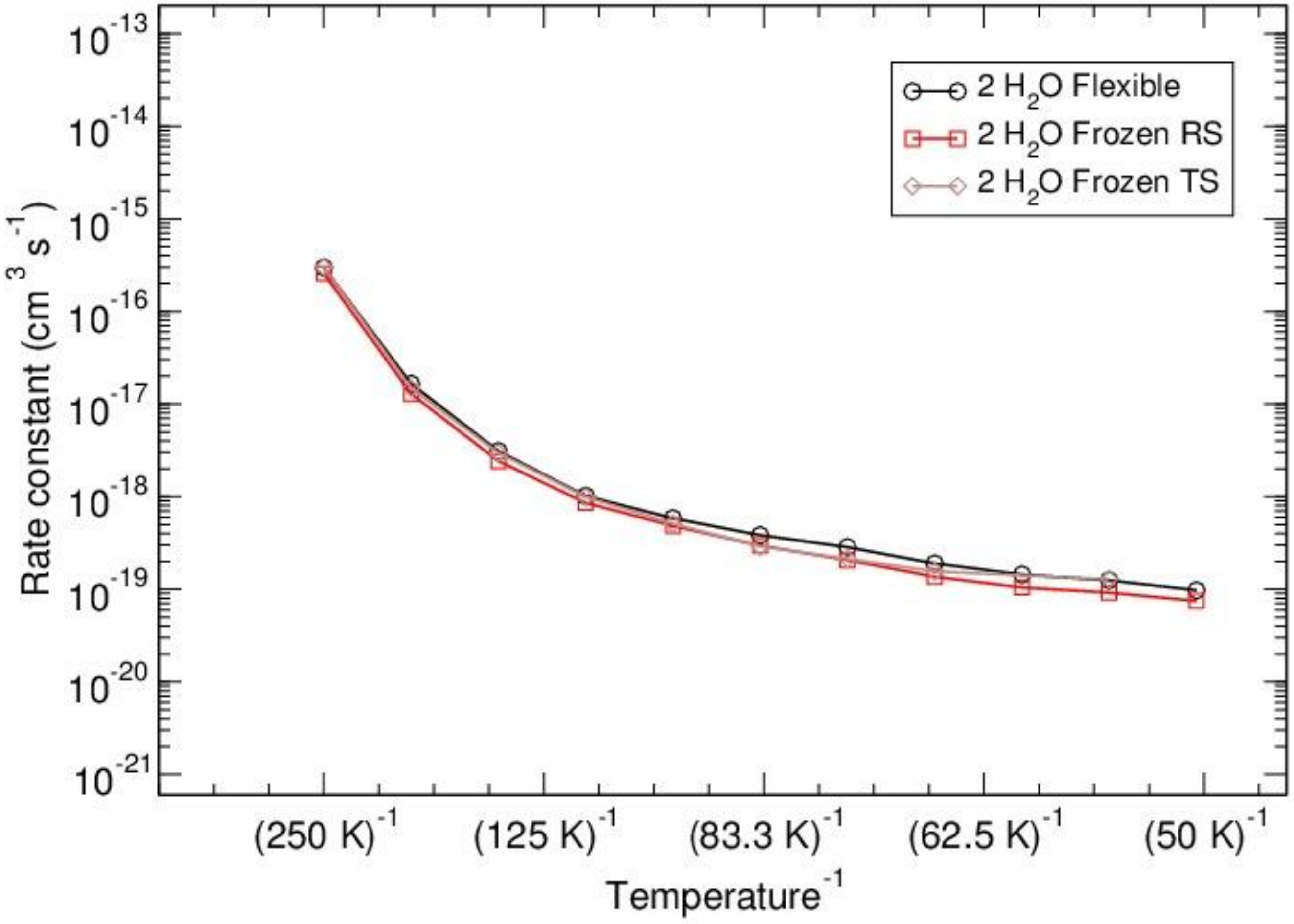

Extra

Isotopes bimolecular