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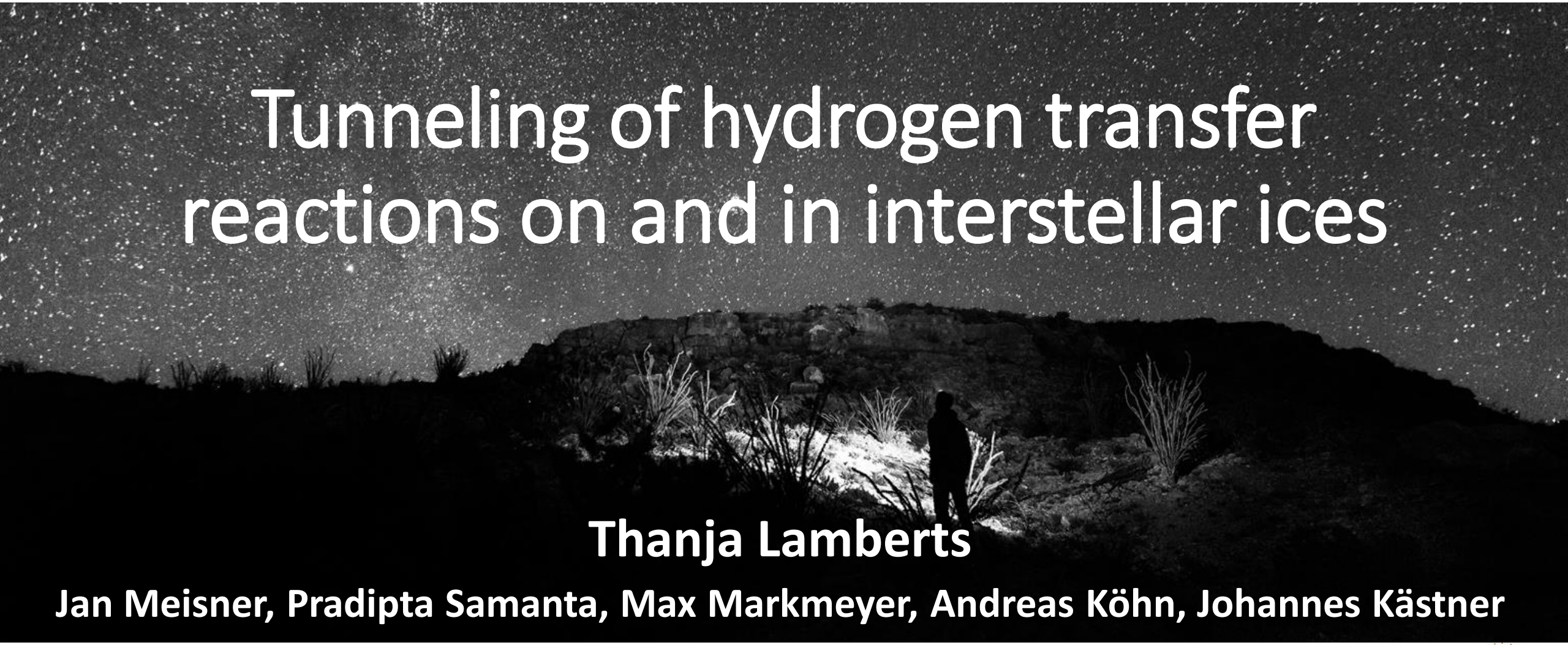

Tunneling of hydrogen transfer reactions on and in interstellar ices

Thanja Lamberts

Jan Meisner, Pradipta Samanta, Max Markmeyer, Andreas Köhn, Johannes Kästner

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Interstellar surface chemistry

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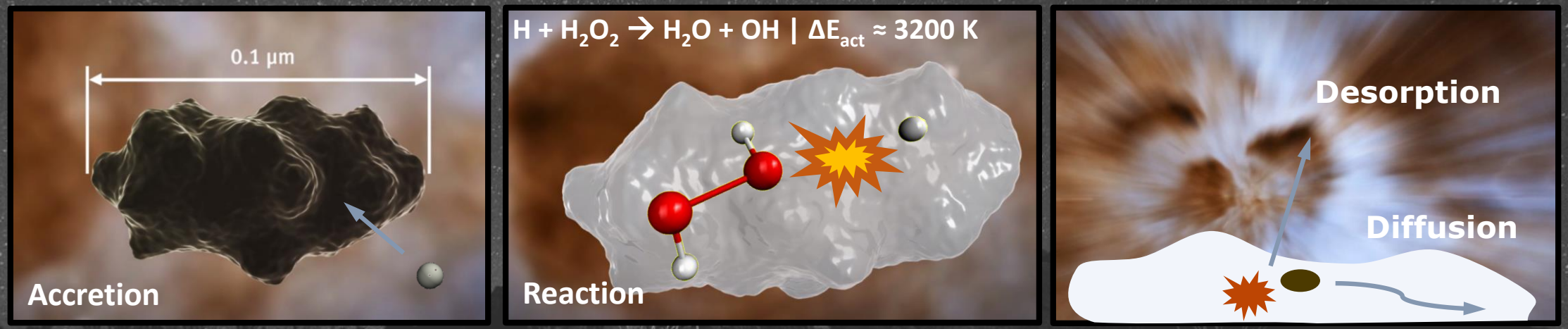
Germany



Accurate rate constants are needed as input for astrochemical models

Figure courtesy Ewine van Dishoeck

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Quantum tunneling

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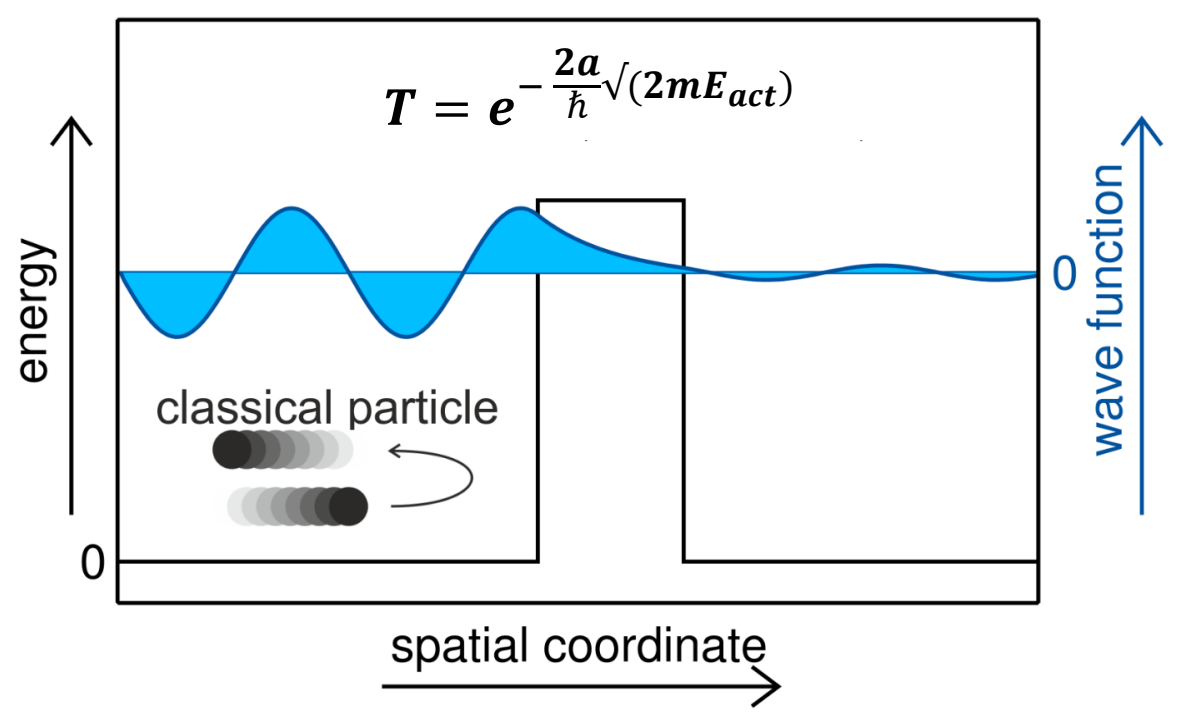

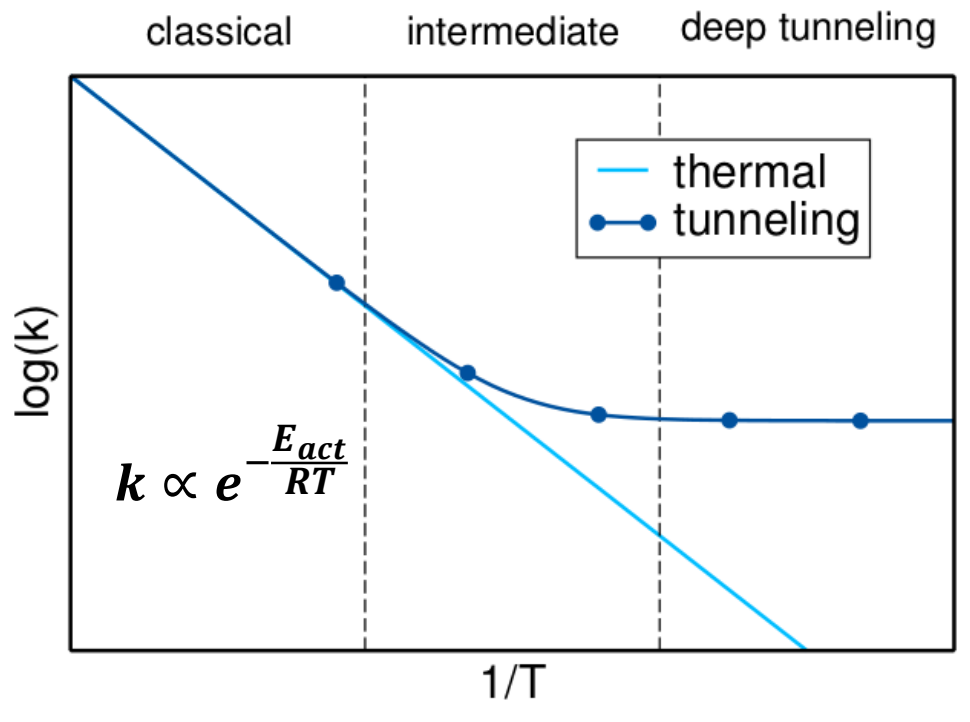

Minimum energy path is not a good approximation to the tunneling path for thin barriers

Figure courtesy Meisner & Kästner ACIE (2016)

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Rate constants including tunneling!

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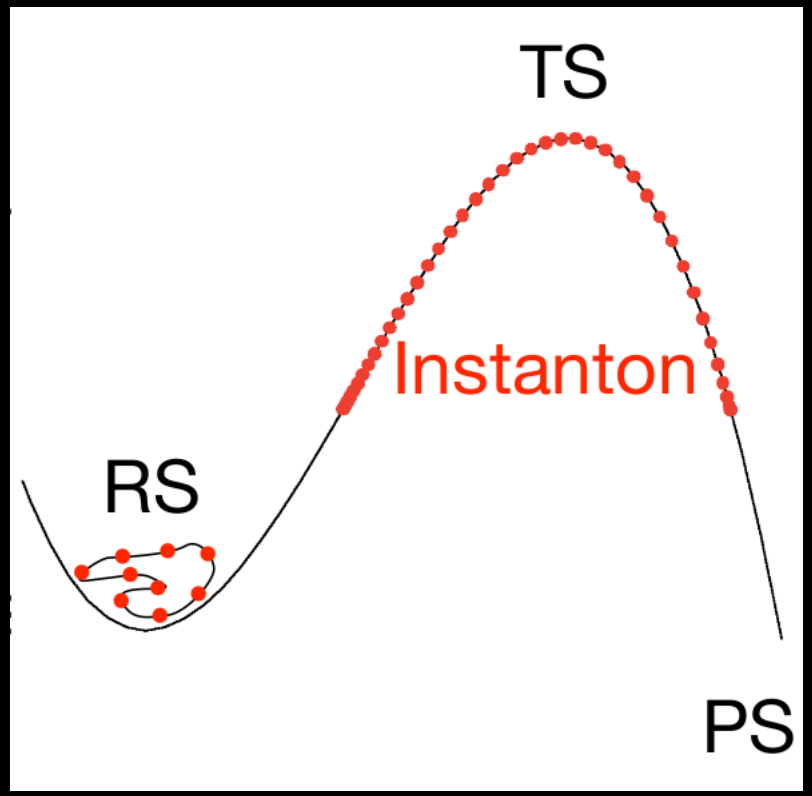
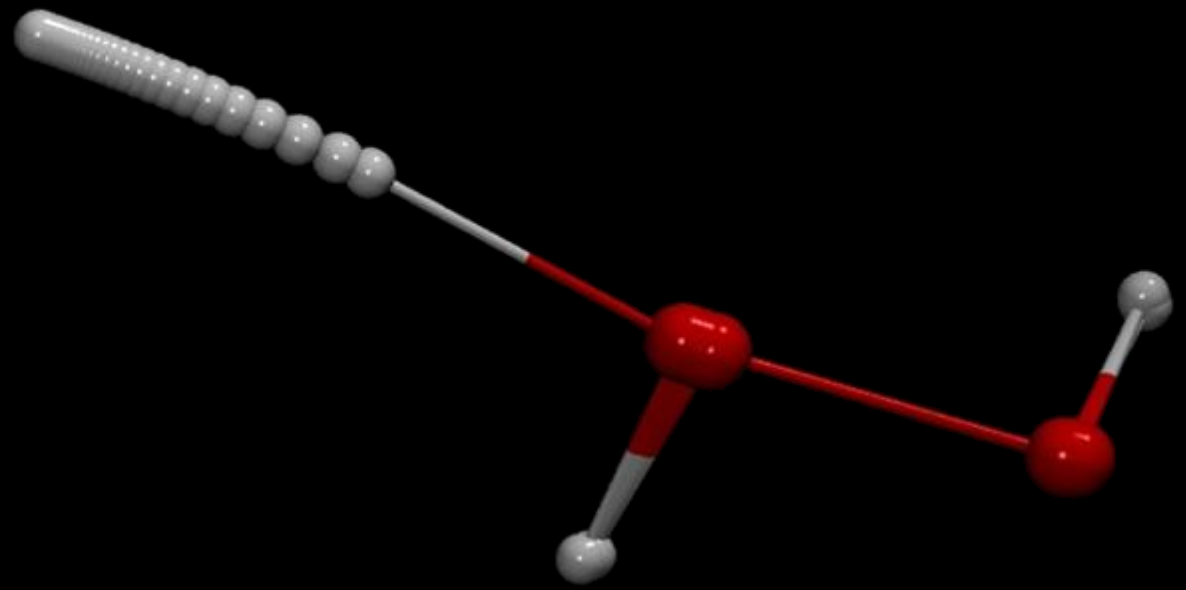
Instanton theory





Langer (1967), Miller (1975), Callan & Coleman (1977), Rommel *et al.* (2011), Kästner *et al.* (2014), Richardson (2016)

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Typical approach

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Benchmark DFT to CCSD(T)-F12

- Gas-phase reaction
- Interaction energies (dimers)

Energy profile (gas phase)

- Intrinsic reaction coordinate
- Encounter complex

Surface molecules

- Small clusters as test case
- QM/MM

Rate calculations

- Classical
- Eckart approximation
- Instanton theory

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Surface approximations

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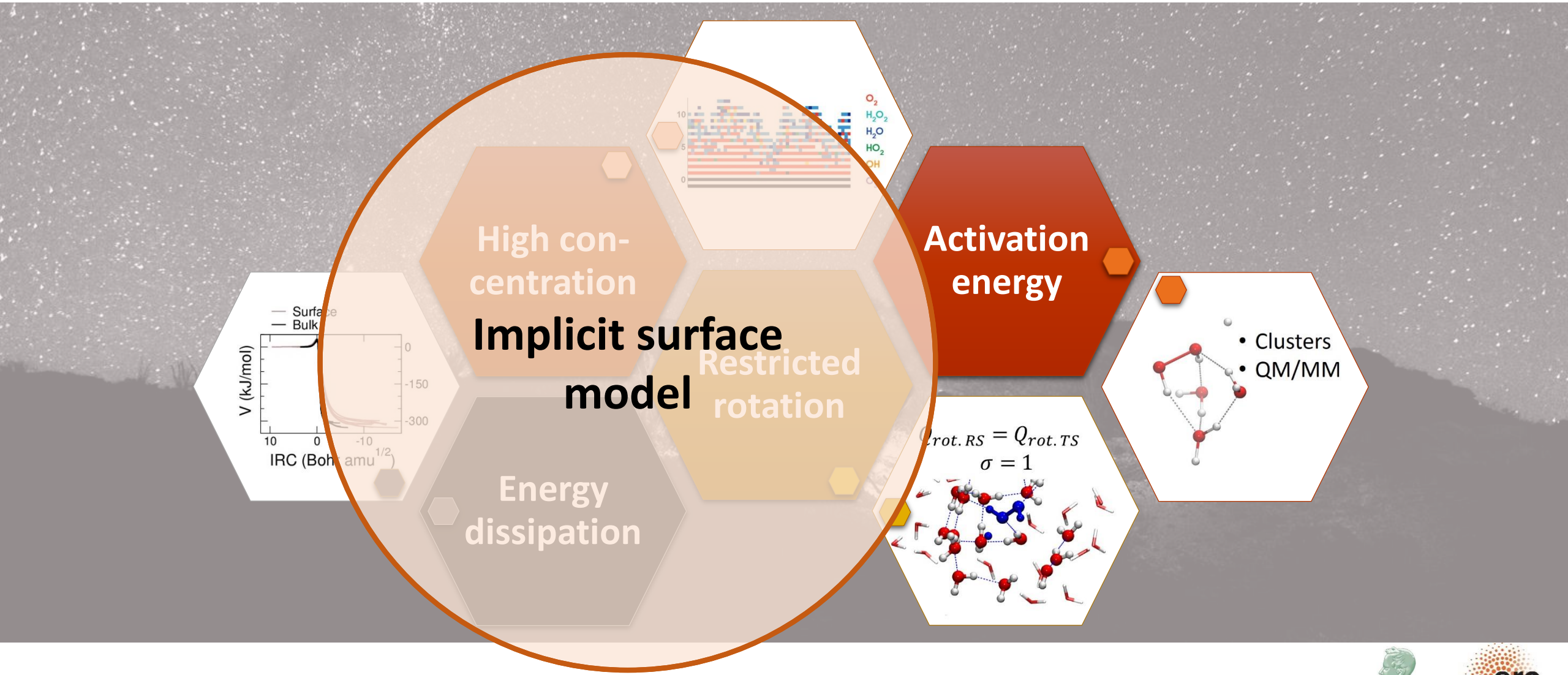

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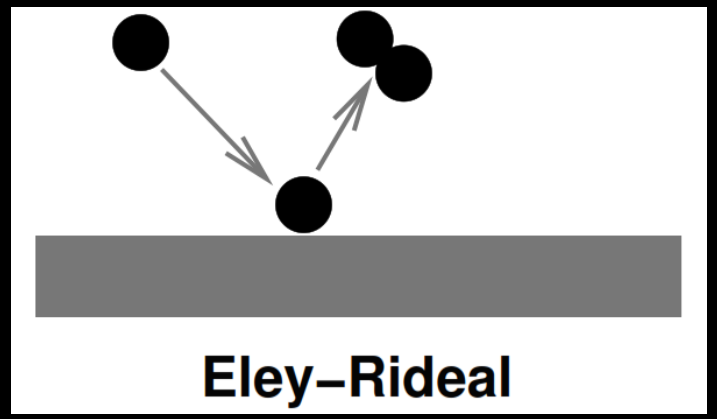
Surface chemistry mechanisms

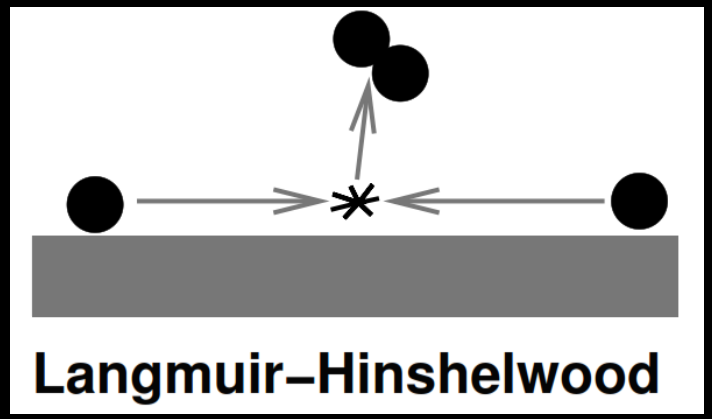
University of Stuttgart
Germany



Bimolecular

A adsorbed

+ gas-phase B



Unimolecular

both A and B adsorbed

+ diffusion

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Competition with diffusion

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$$R_{LH} = P_{react}.R_{diff}$$

$$= \frac{k_{react}}{k_{react} + k_{diff,A} + k_{diff,B}} \frac{k_{diff,A} + k_{diff,B}}{N_{sites}} n_A n_B$$

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Tunneled reactions: rate constants

University of Stuttgart
Germany

Studied reactions:

$H + C_2H_2 \longrightarrow C_2H_3$

$H + C_2H_4 \longrightarrow C_2H_3$

$HCOOH + H \longrightarrow HOCO + H_2$

$HCOOH + NH_2 \longrightarrow HOCO + NH_3$

$HCOOH + OH \longrightarrow HOCO + H_2O$

$CH_4 + OH \longrightarrow H_2O + CH_3$

$H + H_2O_2 \longrightarrow H_2O + OH$

$H_2 + OH \longrightarrow H_2O + H$

$H + H_2S \longrightarrow HS + H_2$

Within the framework of:

Cometary chemical inventory

'Complex' organic molecule precurors

Water formation

Sulfur chemistry

H. Kobayashi *et al.* (2017), Lamberts *et al.* (2016, 2017), Meisner *et al.* (2016, 2017), Markmeyer *et al.* in prep.

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$H + H_2O_2$ Gas vs. Clusters (I)

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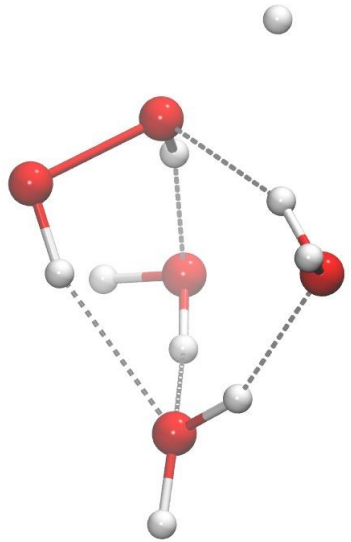

DFT: MPW1B95 / MG3S

Lamberts *et al.* (2016)

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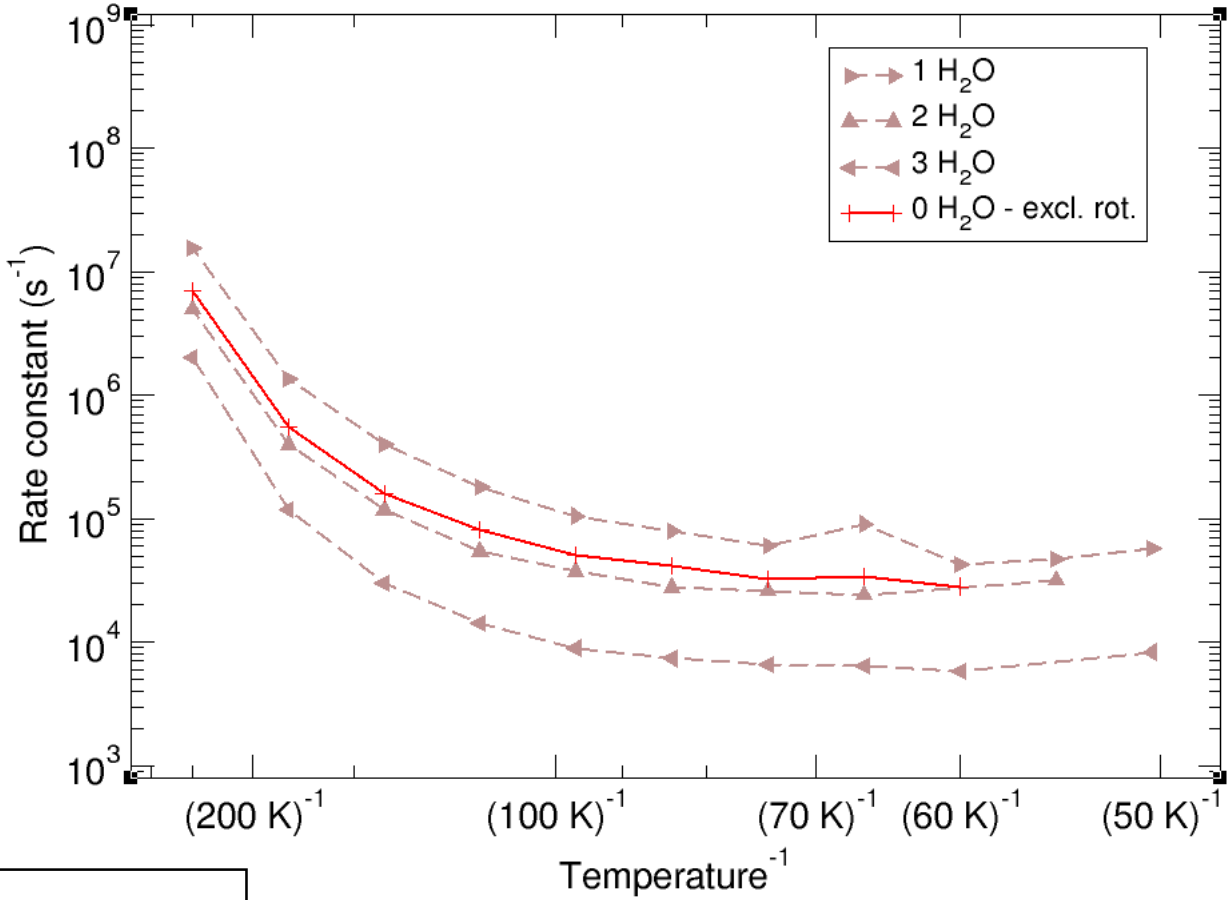
$H + H_2O_2$ Gas vs. Clusters (II)

University of Stuttgart
Germany



$E_{act.} \approx 2910 - 3200$ K

Lamberts *et al.* (2016)

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$H + H_2O_2$ Clusters vs. Surface (I)

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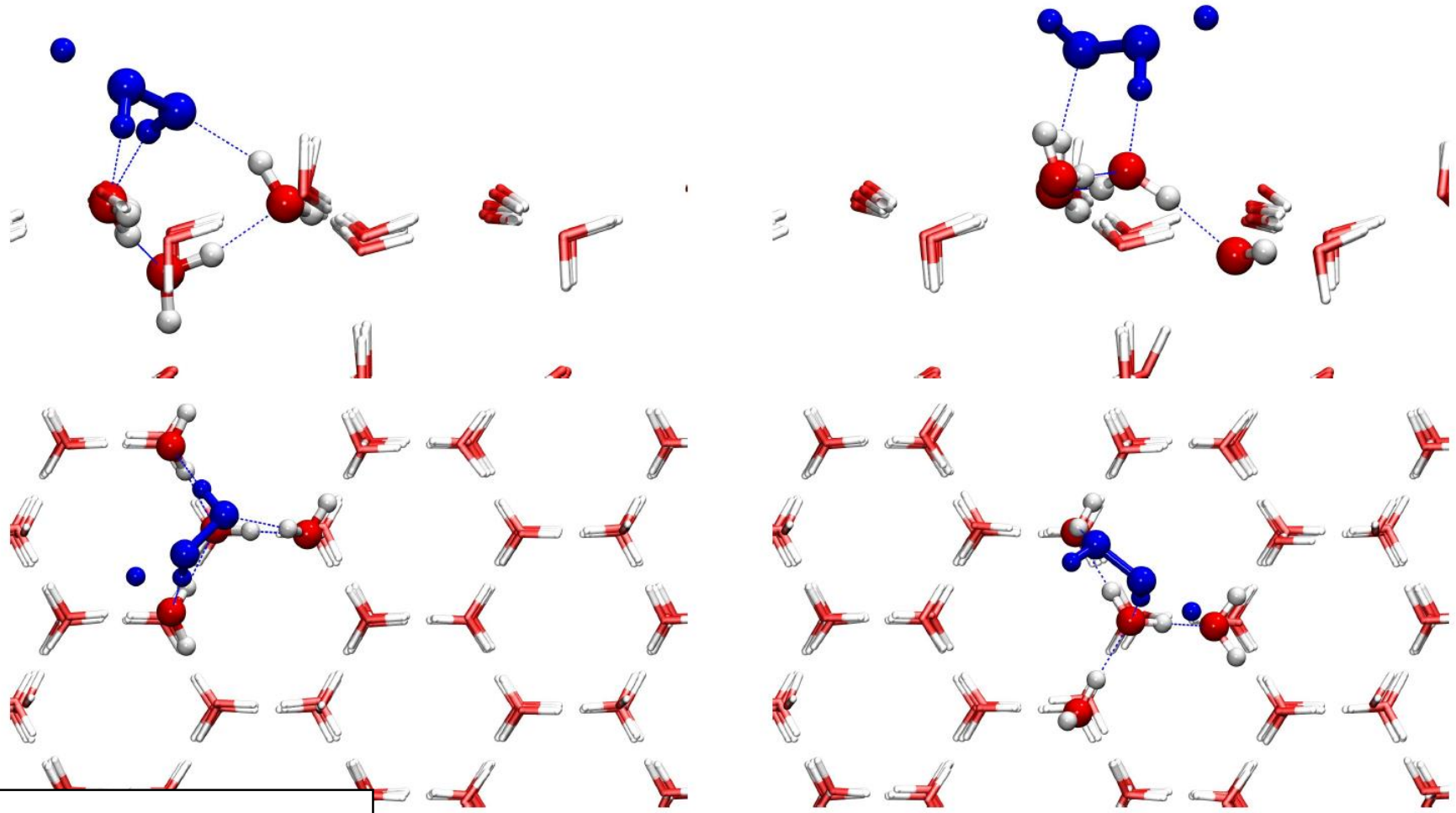

DFT: MPW1B95 / MG3S
FF: TIP3P

Lamberts *et al.* (2017)

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$H + H_2O_2$ Clusters vs. Surface (II)

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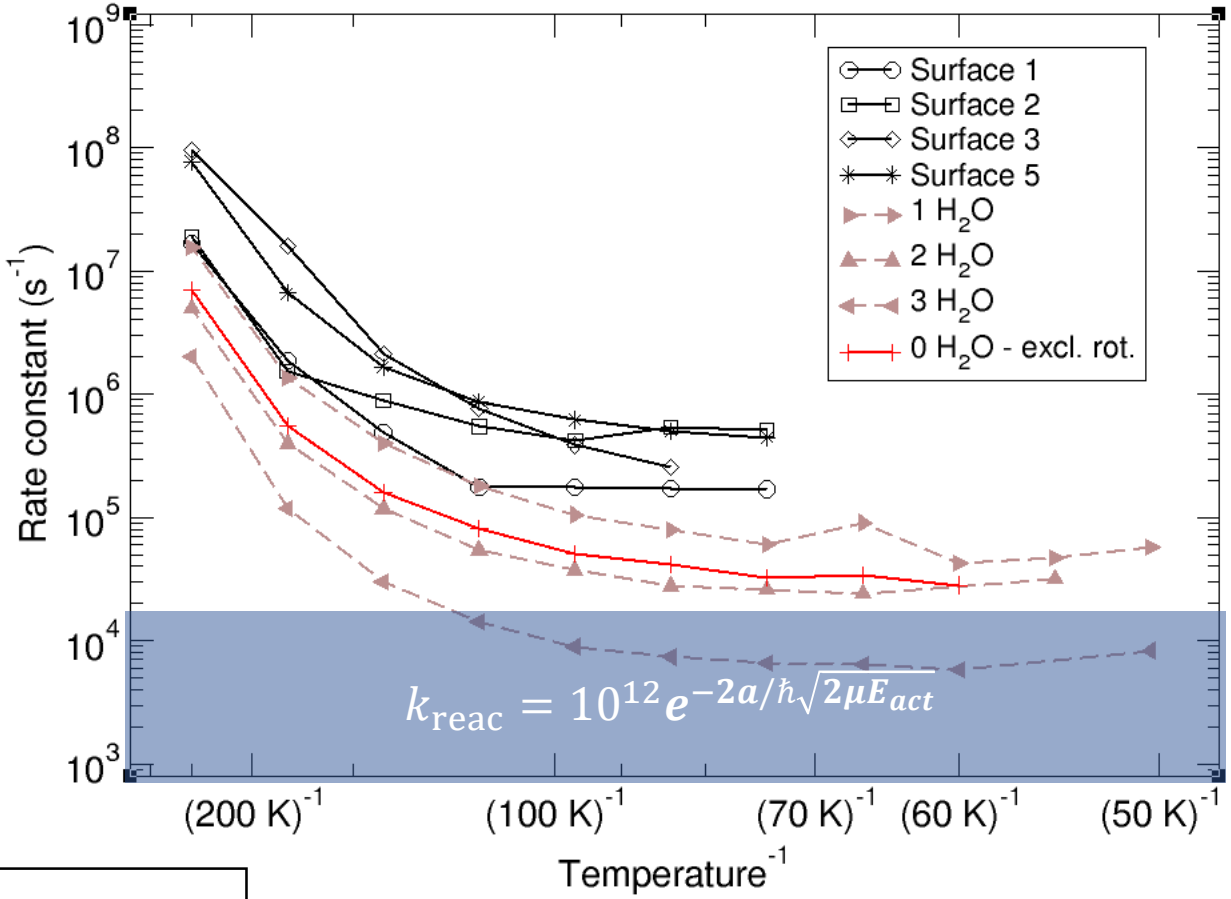

$E_{act.}$ ≈ 2740 – 3065 K

Lamberts *et al.* (2017)

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$H + H_2O_2$ Surface vs. Bulk (I)

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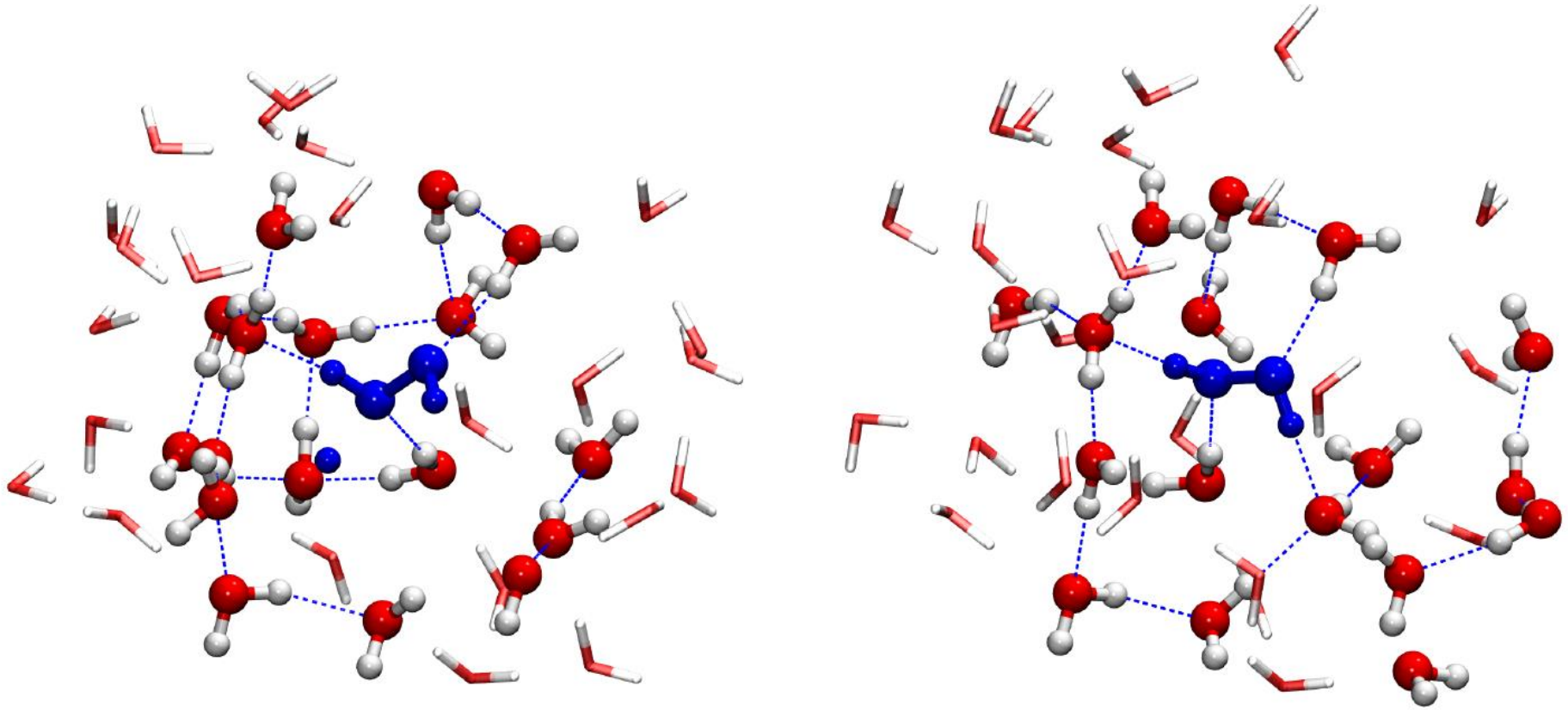

DFT: MPW1B95 / MG3S
FF: TIP3P

Lamberts *et al.* (2017)

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$H + H_2O_2$ Surface vs. Bulk (II)

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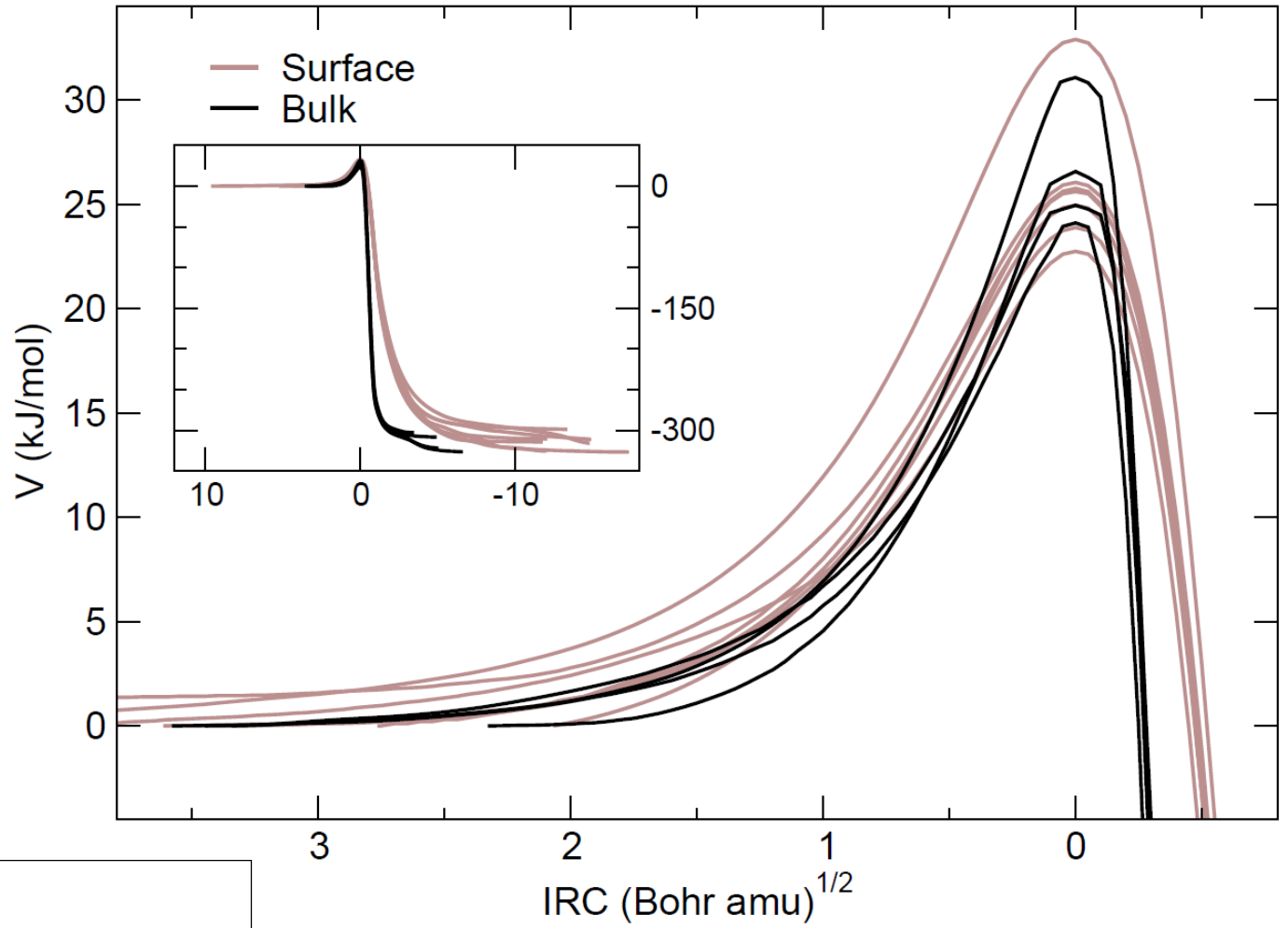

Lamberts *et al.* (2017)

$E_{act.} \approx 2500 - 2840$ K

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H_2 + OH Surface (I)

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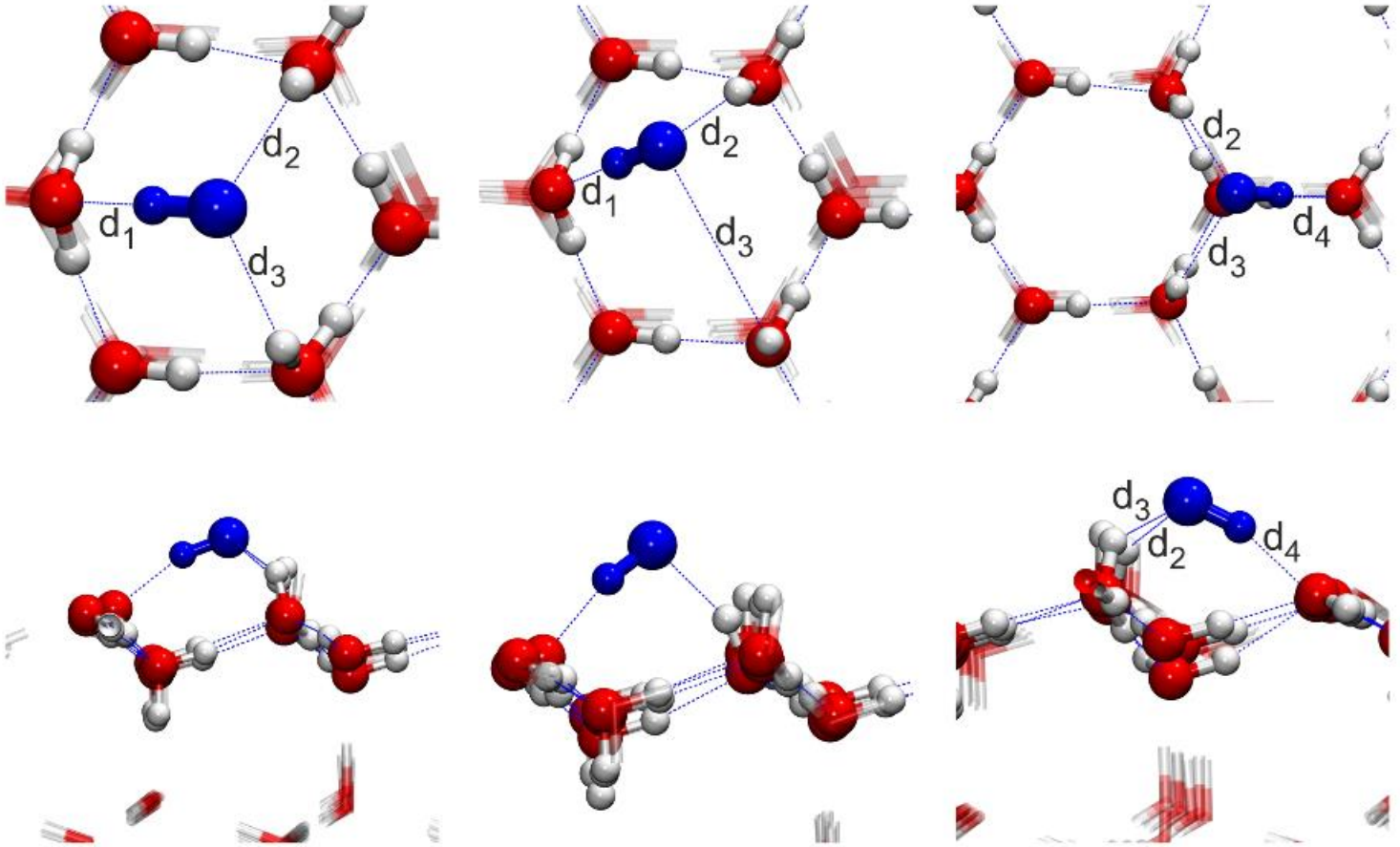

DFT: BHLYP / def2-SVPD
FF: TIP3P

Meisner *et al.* (2017)

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H_2 + OH Surface (II)

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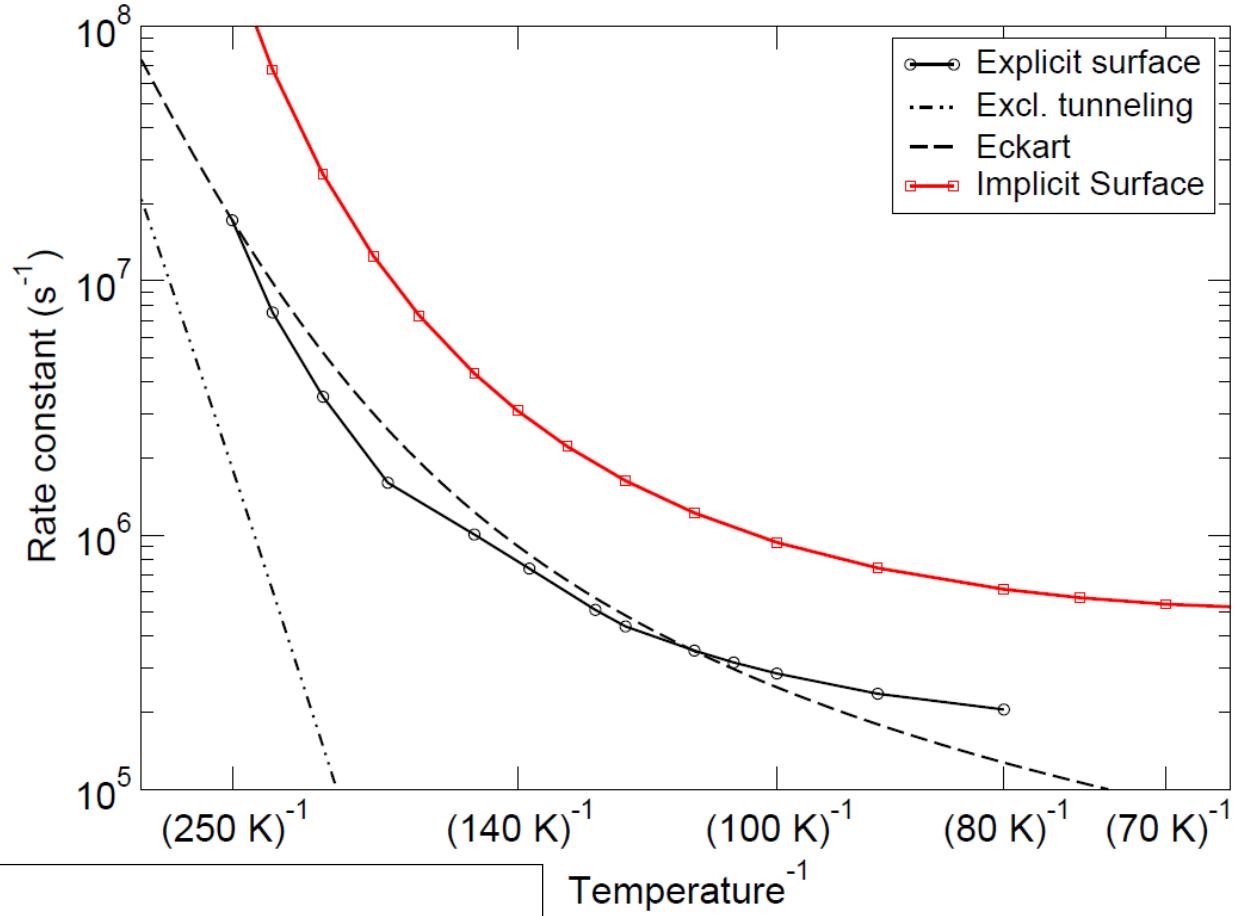

$E_{act.}$ ≈ 2700 – 2900 vs. 2935 K

Meisner *et al.* (2017)

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$H + H_2S$ Gas phase vs. Clusters (I)

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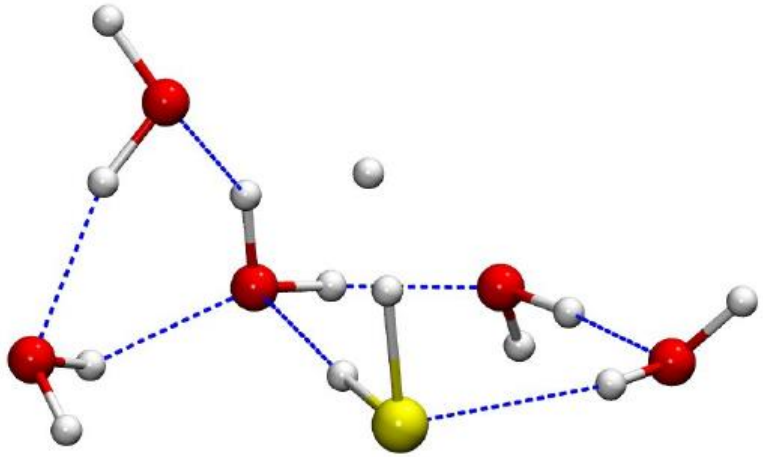

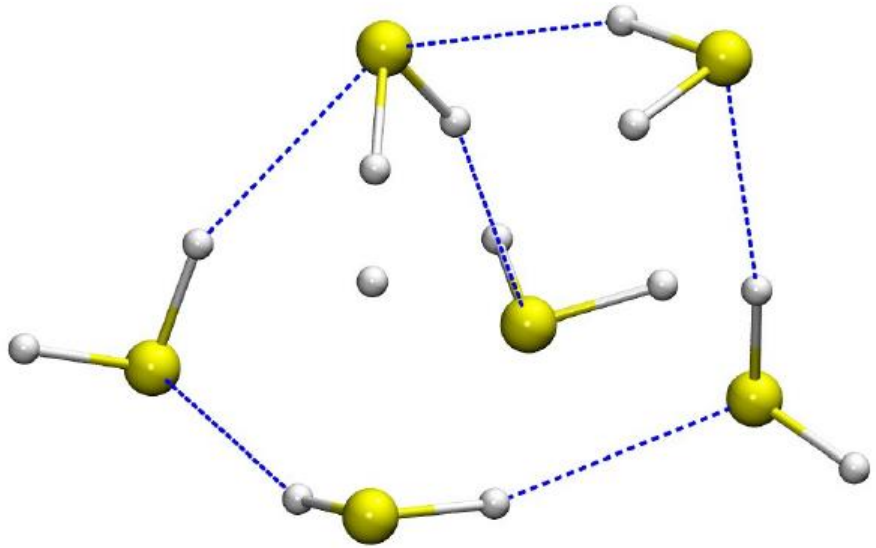

DFT: MPWB1K / def2-TZVP

Lamberts *et al.* (2017) in prep.

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Diffusion and binding energies?

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Germany

$$R_{LH} = P_{react}.R_{diff}$$

$$= \frac{k_{react}}{k_{react} + k_{diff,A} + k_{diff,B}} \frac{k_{diff,A} + k_{diff,B}}{N_{sites}} n_A n_B$$

Combination of activation and binding energy determines if a reaction is limited by diffusion: what about binding energy distributions?

Song *et al.* (2016, 2017), Senevirathne *et al.* (2017), Ásgeirsson *et al.* (2017)

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Lessons learned

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Germany

- **Water ice:** may impact on barrier height and width
  may decrease the barrier
- **Hydrogen bonds:** restricted orientations
  determine binding energy
- **Binding energies:** a large spread
- **Rectangular barrier:** often underestimates rate constants
  often results in error in the KIE

- **Rate constants available for roughly a dozen reactions!**

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Thank you!

April Cooper

Sonia Álvarez Barcia

Computational Chemistry Group Stuttgart

Institut für Theoretische Chemie Stuttgart

University of Stuttgart
Germany

Alexander von Humboldt
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BWForCluster Justus

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Lessons learned

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Germany

- **Water ice:** may impact on barrier height and width
  may decrease the barrier
- **Hydrogen bonds:** restricted orientations
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  often results in error in the KIE

- **Rate constants available for roughly a dozen reactions!**

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In a nutshell

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Imaginary F theory: $k \propto \mathrm{Im}(F) = \frac{\mathrm{Im}(Q)}{\mathrm{Re}(Q)}$

Transition state theory: $k \propto \frac{Q_{TS}}{Q_{RS}}$

$Q_{TS} = tr[e^{-\beta H}] = \oint D\mathrm{x}\ e^{-\frac{1}{\hbar}S_E[\mathrm{x}]}]$ → **path integral formulation**

x that minimizes $S_E[\mathrm{x}]$ **is 'the instanton', discretized: P segments in 3N dimensions**

This ring-polymer with k=k(T) can be seen as wrapped around the barrier

Deviations from the most-likely tunneling path: harmonic approximation

Langer (1967), Miller (1975), Callan & Coleman (1977), Rommel *et* al. (2011), Kästner *et al.* (2014), Richardson (2016)

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Hydrogenation of H_2O_2

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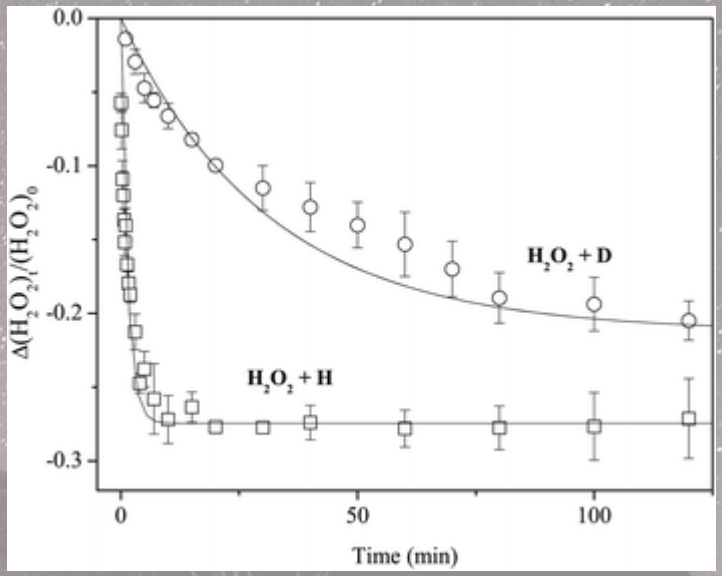
- **Experiments show a kinetic isotope effect**
  - $H_2O_2 + H$ vs. $H_2O_2 + D$
  - $D_2O_2 + H$ vs. $D_2O_2 + D$

- **In models**
  - Rectangular barrier approximation
  - Eckart barrier approximation



$$P_{\text{reac}} \propto e^{-2a/\hbar\sqrt{2\mu E_{act}}}$$

Taquet *et al.* (2013), Oba *et al.* (2014)

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Surface formation of water

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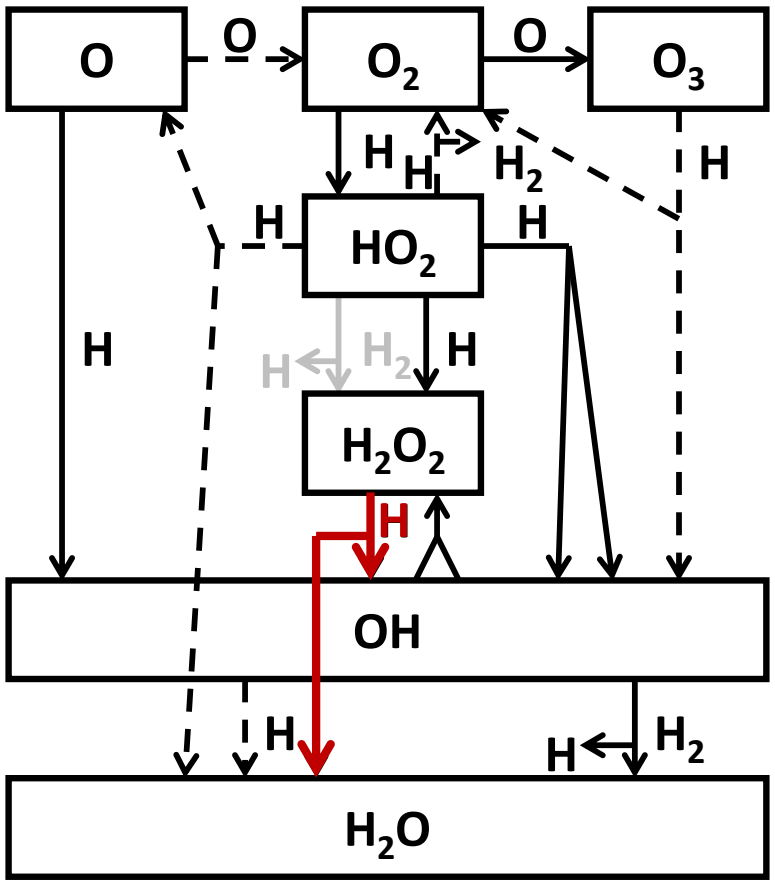

Radical-radical reactions: barrierless

Radical-neutral reactions: tunneling!

$H + H_2O_2 \rightarrow H_2O + OH : E_{act.} \approx 26$ kJ/mol

Tielens & Hagen (1982), Hiraoka *et al.* (1998) , Miyauchi *et al.* (2008), Ioppolo *et al.* (2008), (2010), Dulieu *et al.* (2010)
Lamberts *et al.* (2013), Lamberts *et al.* (2014), Lamberts *et al.* (2016), Meisner *et al.* (2017), Lamberts *et al.* (2017)

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Benchmark

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Method	Reaction 1 $H + H_2O_2 \rightarrow H_2O + OH$		Reaction 2 $H + H_2O_2 \rightarrow HO_2 + H_2$	
	kJ/mol	Kelvin	kJ/mol	Kelvin
CCSD(T)-F12 / VTZ-F12	25.5	3070	39.4	4740
ic-MRCCSD(T) / cc-pVQZ [1]	24.9	2995	38.3	4605
Ellingson et al. (2007)	27.2	3260	41.4	4970
MPW1B95 / MG3S	26.5	3190	23.7	2845
M05-2X / MG3S	45.9	5520	39.7	4780
PWB6K / MG3S	35.9	4330	35.4	4260
B3LYP / MG3S	11.2	1350	8.1	970
B3LYP / def2-TZVPD	10. 8	1300	7.3	880

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

Lamberts *et al.* (2016)

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Kinetic Isotope Effect

University of Stuttgart
Germany

	Instanton theory	Eckart Barrier	Rectangular Barrier
Eley-Rideal / bimolecular	197	27	6945
Langmuir-Hinshelwood / unimolecular	229	60	7033

All KIE's calculated at 50 K

Experimental KIE = 30 at 15 K, but … includes diffusion!

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