Grain Surface Processes

Thanja Lamberts

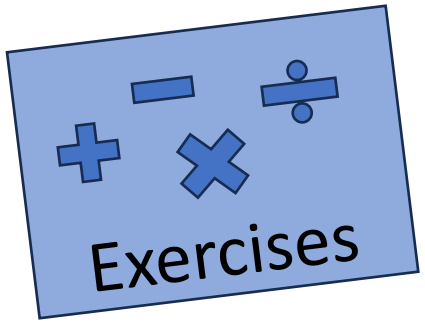
Groningen, 2024

Credit: Luís Dalí, assisted by MidJourney

Lecture Overview

- Introduction Astrochemistry

- Surface processes & Timescales
  - Dissipation (3rd body)
  - Adsorption
  - Desorption
  - Diffusion
  - Reaction
    - Energetics of a chemical reaction
    - Surface reaction mechanisms



- Energetic Processing & Non-thermal Desorption

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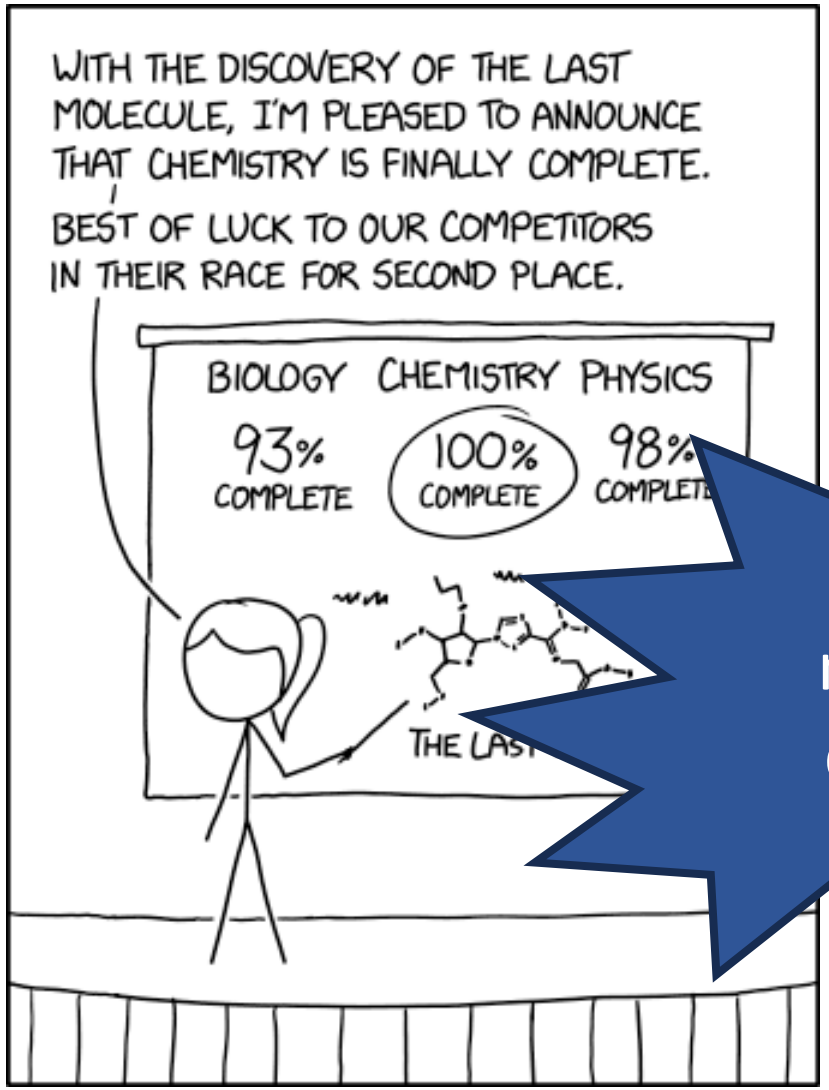
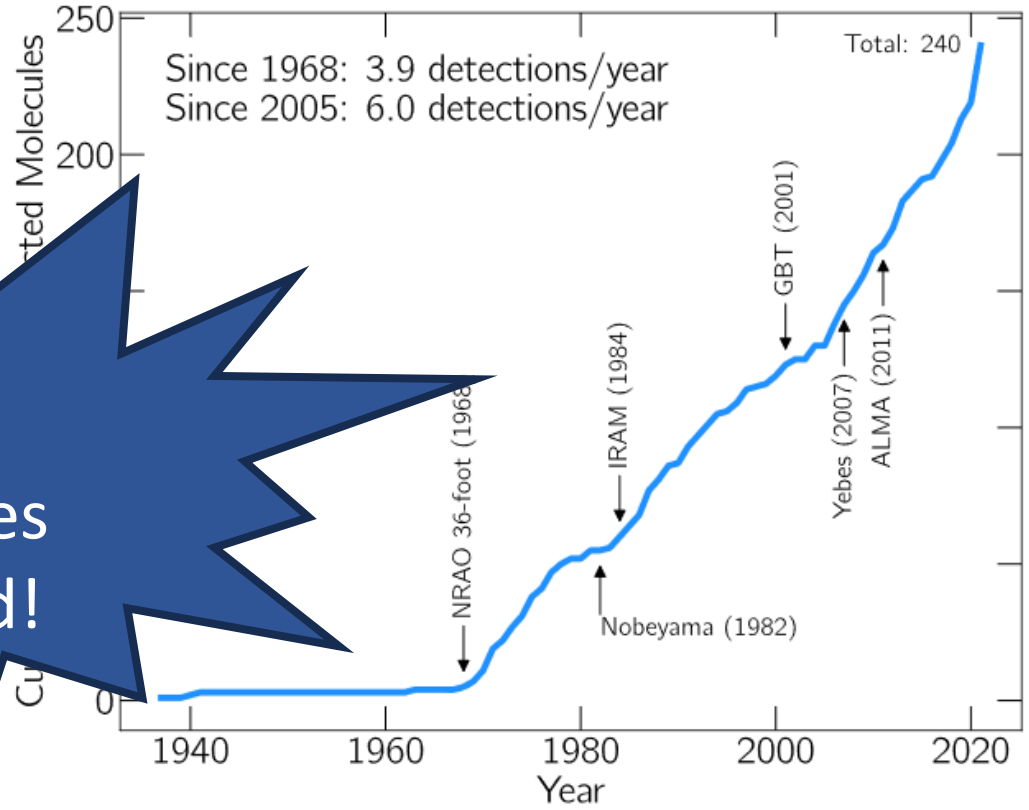


> 320 molecules detected!



Drivers of chemistry

- Not in thermodynamic equilibrium

- Low density & low temperature: chemistry needs to be driven
  - Starlight
  - Cosmic rays
  - (Exothermic) grain chemistry
  - Gas hydrodynamics

Different types of molecules are observed, why?

- N_2H+ ($N{\equiv}N\text{-}H^+$)
- HC_3N ($H\text{-}C{\equiv}C\text{-}C{\equiv}N$)
- C_2H
- $C{\equiv}O$
- H_2

- H_2O
- CH_4
- NH_3
- CH_3OH
- CO_2 ($O{=}C{=}O$)
- $C{\equiv}O$

High hydrogen content = saturation

$H + X \rightarrow HX$

Types of important gas-phase reactions

Two-body reactions with “two-body” products

Associative detachment

UV photoreactions

Dissociative recombination

Cosmic Ray ionization

Collisional dissociation

Cosmic Ray induced photoreactions

Ion-molecule reactions

Radiative association

Neutral-neutral reactions

Charge-transfer reactions

Ingredients: Radiation, Gas, and **Dust**

- Nucleates in the envelopes of cool stars, in novae and in supernovae
- The dust-to-gas ratio in our own Galaxy is ~ 1:100
- Size ranges from nm to μm
- Silicates and carbonaceous material (incl. metals, Mg, Fe, Si)
- Grains allow reactions of the form $A_{ads} + B_{ads} \rightarrow C_{ads}$ (e.g., H_2)

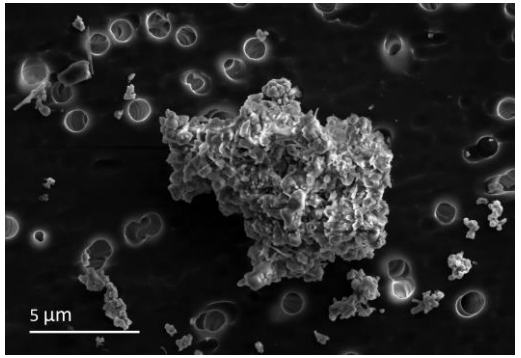
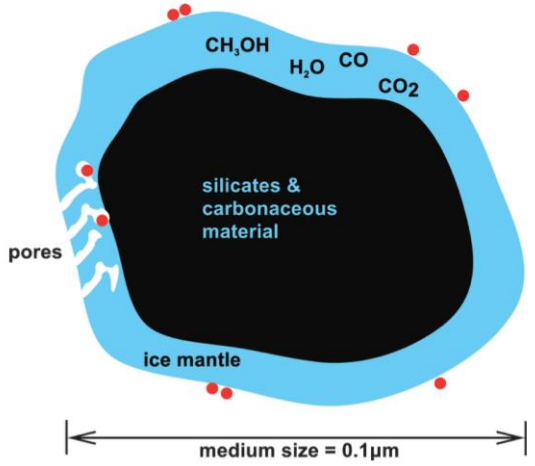


Figure courtesy:
Hope Ishii, University of Hawai'i



Karssemeijer et al. (2012)

Ices and the star formation process

NASA, ESA, CSA, STScI; Joseph DePasquale (STScI), Anton M. Koekemoer (STScI), Alyssa Pagan (STScI). Bill Saxton, NRAO, L. I. Cleeves

Prestellar Core

n_H ~10^6 cm^{-3}

T ~ 10 K

Dense cloud

n_H ~1-10^4 cm^{-3}

T ~ 20 K

Protostar

n_H ~10^7 cm^{-3}

T ~ 100 K

Protoplanetary disk

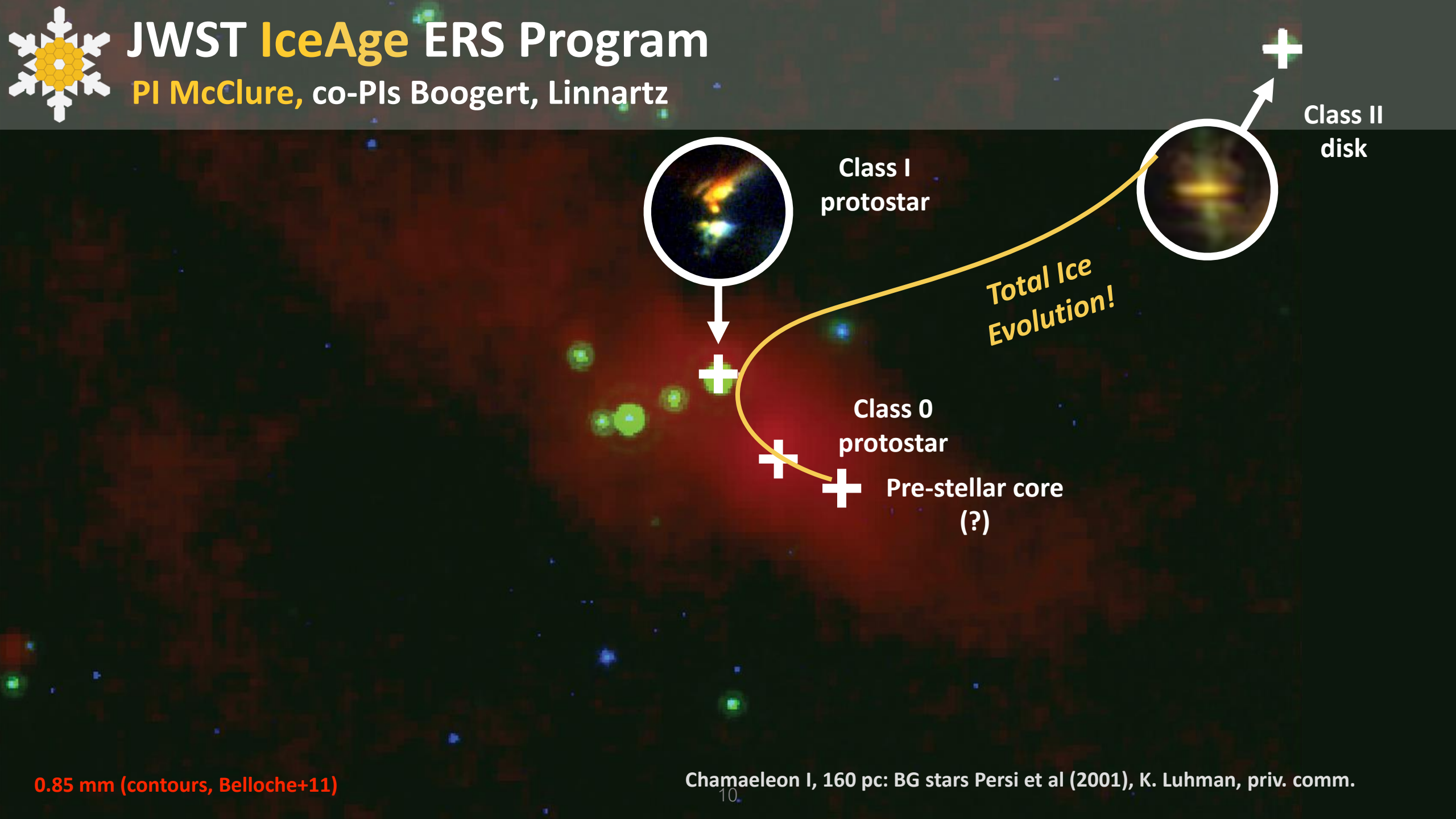
n_H ~10^9 - 10^{15} cm^{-3}

T ~ 10-10,000 K

Solar System

JWST IceAge ERS Program

PI McClure, co-PIs Boogert, Linnartz



0.85 mm (contours, Belloche+11)

Chamaeleon I, 160 pc: BG stars Persi et al (2001), K. Luhman, priv. comm.

Which (physical) conditions are important for surface chemistry to efficiently occur?

- Low temperature
- High density (H/H_2 <<1)
- UV-shielded ("high Av")

Region	n_H (cm^{-3})	T (K)
Coronal gas	$< 10^{-2}$	5×10^5
HII regions	> 100	1×10^4
Diffuse gas	100-300	70
Molecular clouds	10^4	10
Pre-stellar cores	10^5-10^6	10-30
Star Forming Regions	10^7-10^8	100-300
Protoplanetary disks	10^4(outer)-10^{10}(inner)	10(outer)-500(inner)
Envelopes of Evolved stars	10^{10}	2000-3500

Strong lines at mm wavelengths, so-called low-J transitions

Sneak-peak at the molecular scales

- Introduction Astroch mistry
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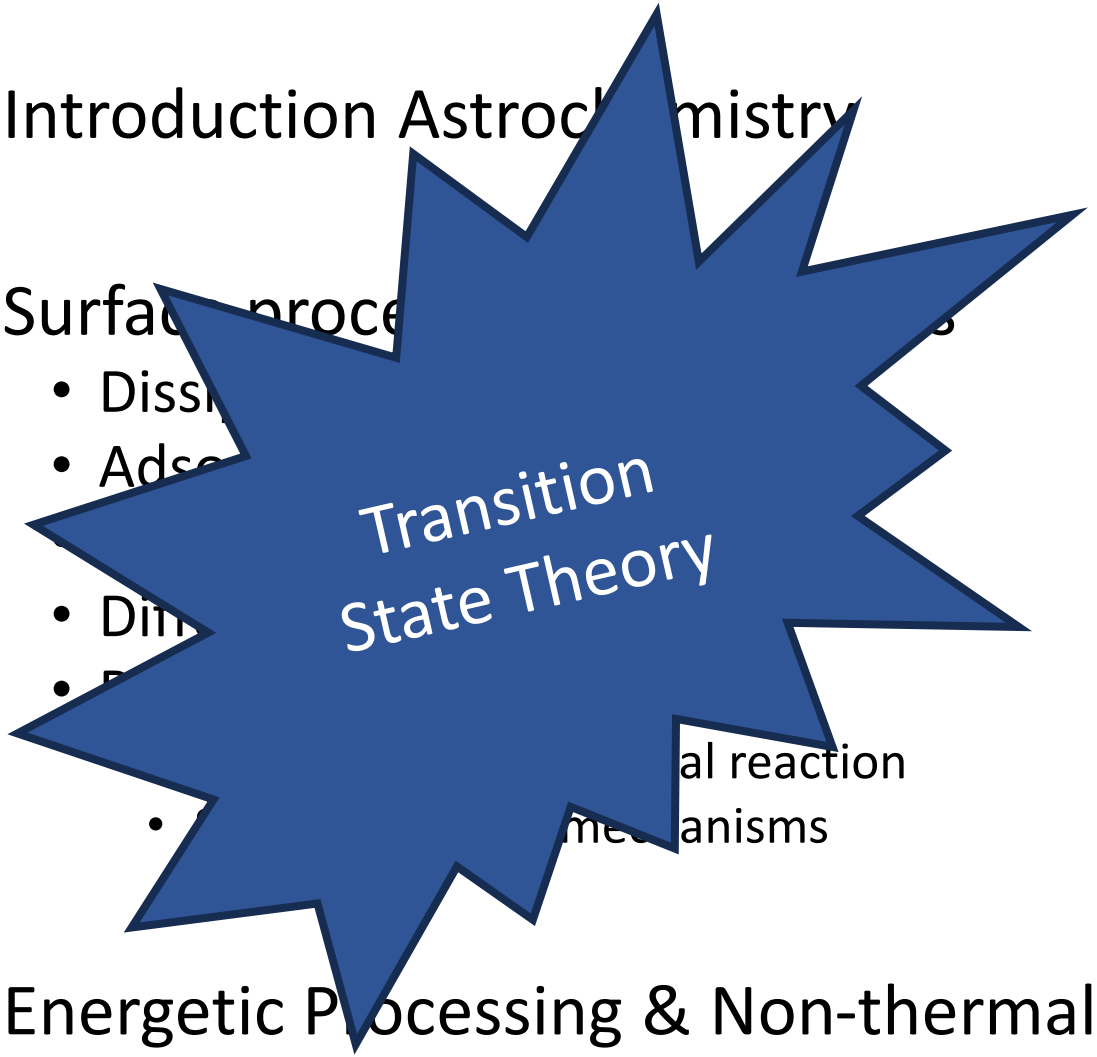
  - Diss
  - Ads
  - Di
  - al reaction
    - anisms
- Energetic P ocessing & Non-thermal Desorption



Reminder: Transition State Theory

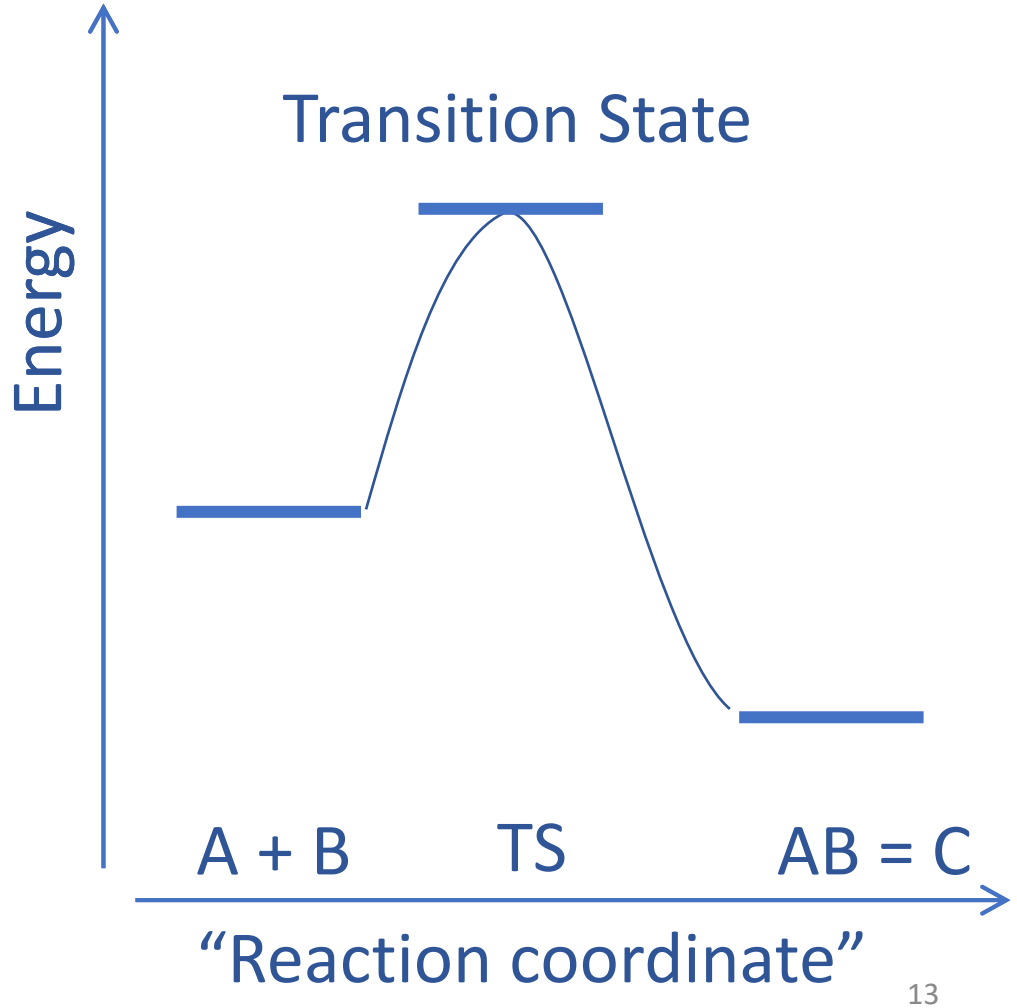
Reaction rate = $v\ [\mathrm{TS}]$

$= k\ [\mathrm{A}][\mathrm{B}]$

therefore $k = v \cdot \frac{[\mathrm{TS}]}{[\mathrm{A}][\mathrm{B}]} = v\ \mathrm{K}$

with (stat. therm.) $\mathrm{K} = \frac{q}{q'_{\mathrm{A}} q'_{\mathrm{B}}}$

and $q' = \sum_i e^{-\epsilon_i / k_{\mathrm{B}} T}$



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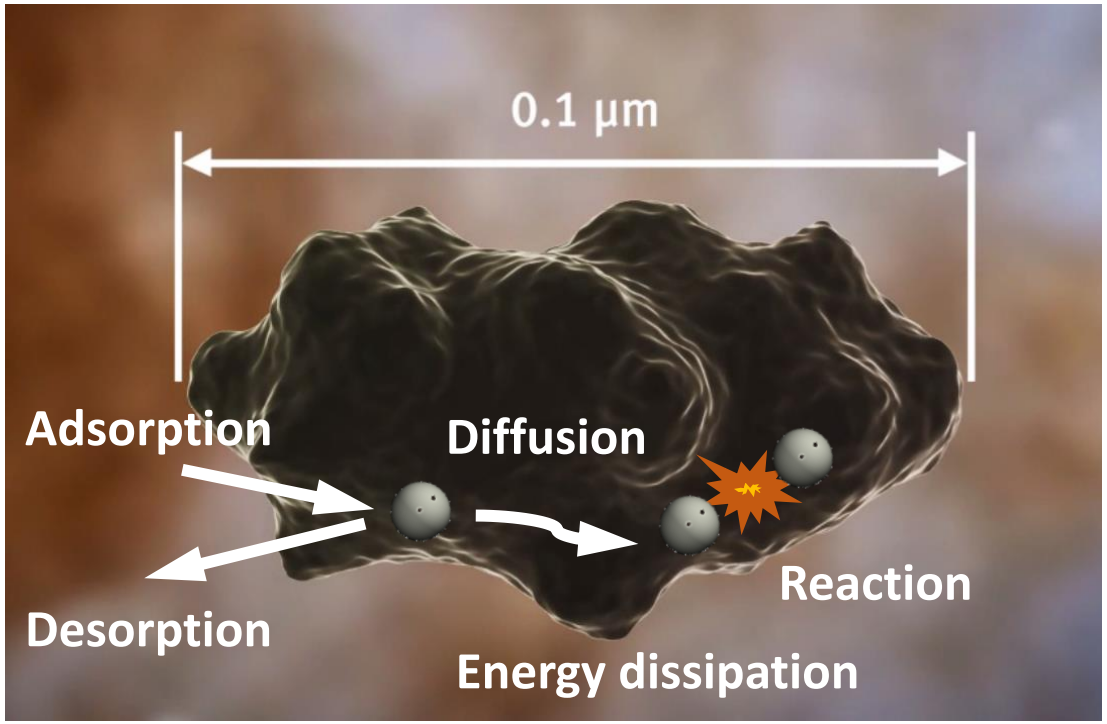
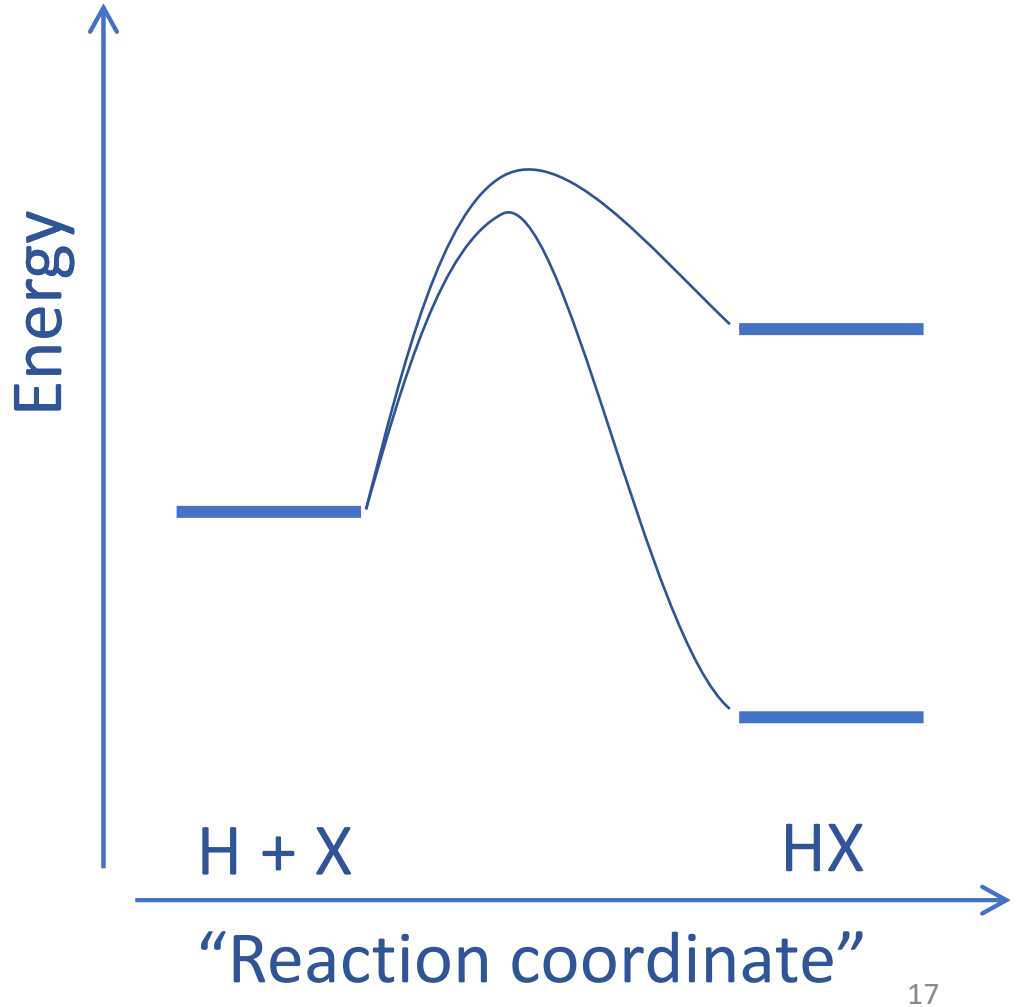
Movie courtesy: Ewine van Dishoeck & Thanja Lamberts, Background image: Hubble Space Telescope (Carina Nebula)

Overview of surface processes



Dissipation: excess energy

- At low T, a reaction should generate energy (exothermic, instead of endothermic)
- This needs to be dissipated: 3rd body = grain/ice
- Otherwise: radiative attachment = a slow process



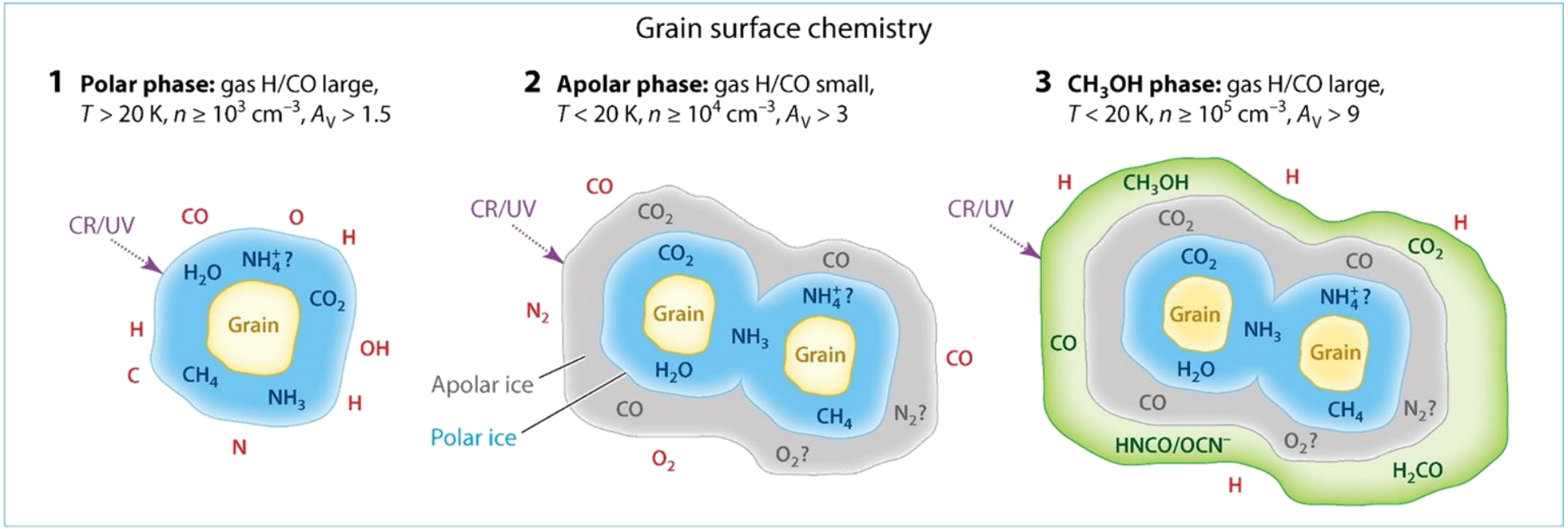
Adsorption

When an atom or molecule collides with a grain it “can” adsorb:

$$f_{acc,X} = S_X v_X n_{grain} \pi r^2 n_g(X) \quad \text{with} \quad v_X = \sqrt{\frac{8 k_B T_{gas}}{\pi m_X}}$$

- Sticking coefficient
- Gas-phase thermal velocity
- Grain number density
- Average grain cross section
- X number density
- Boltzmann constant
- Gas-phase temperature
- Mass of X

Interstellar ices



Boogert *et al*. ARAA 53, 541 (2015)

Different ways of binding

Physisorption vs. chemisorption.

Van der Waals

Hydrogen bonded

Hemibonded

Covalently bonded

Ionic

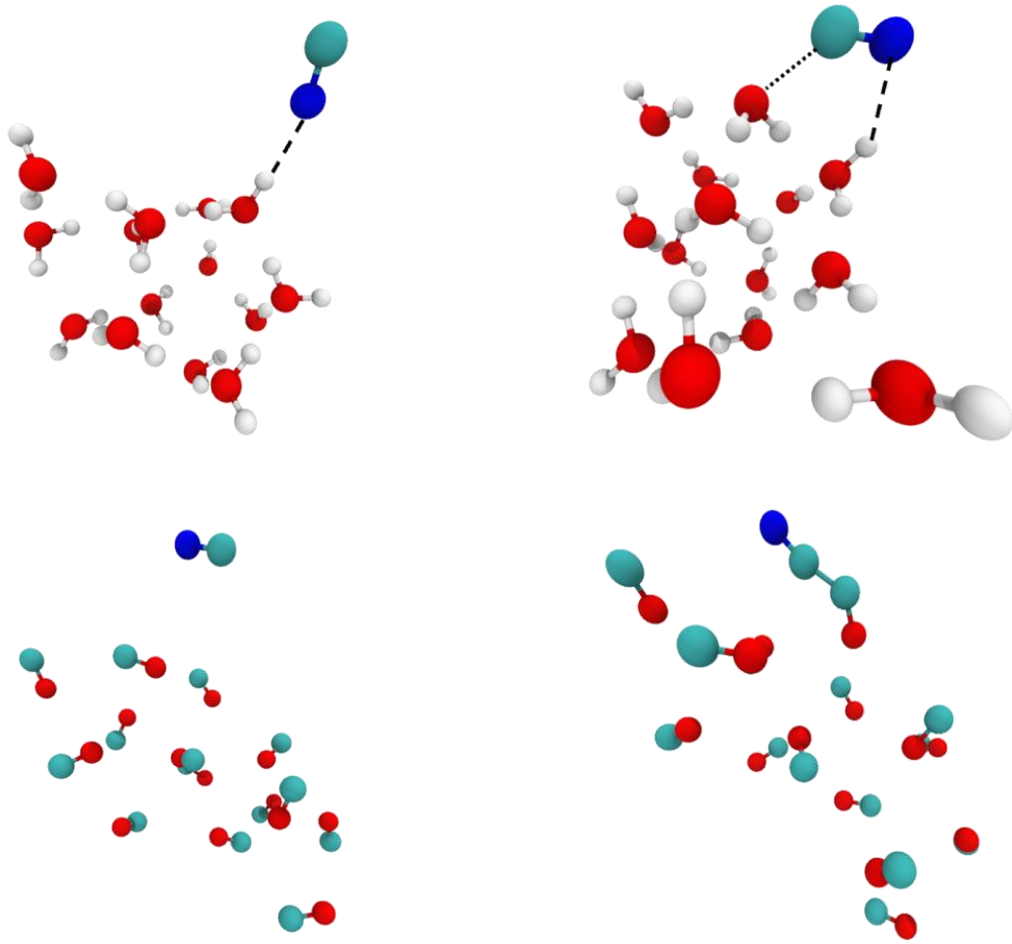
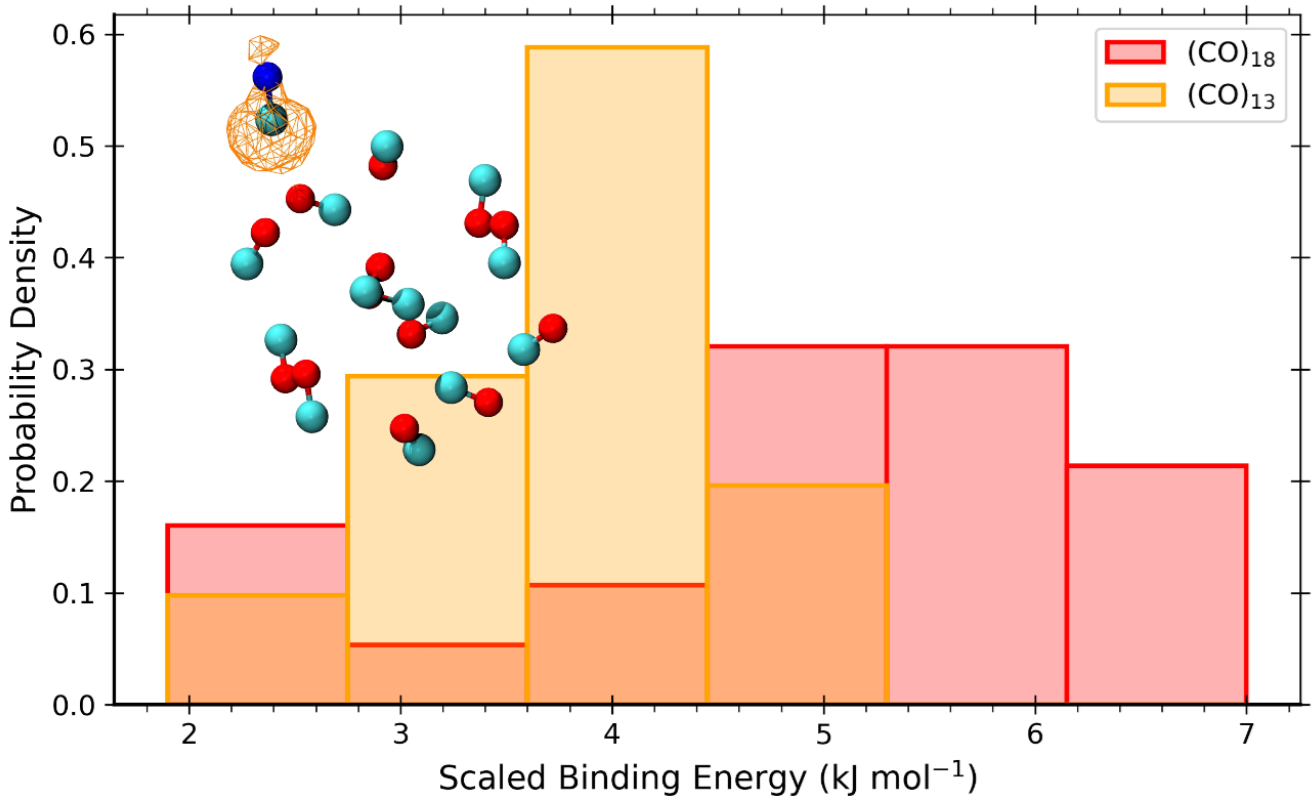


Figure courtesy: Joan Enrique-Romero

Example: Van der Waals binding only



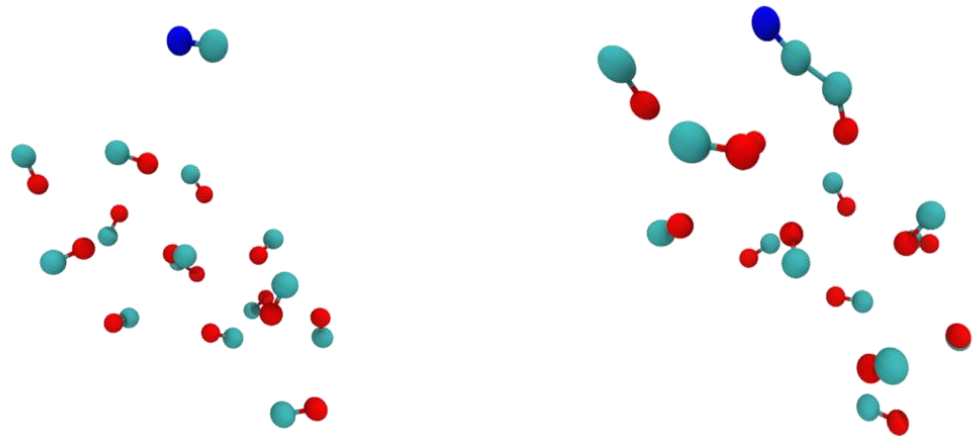
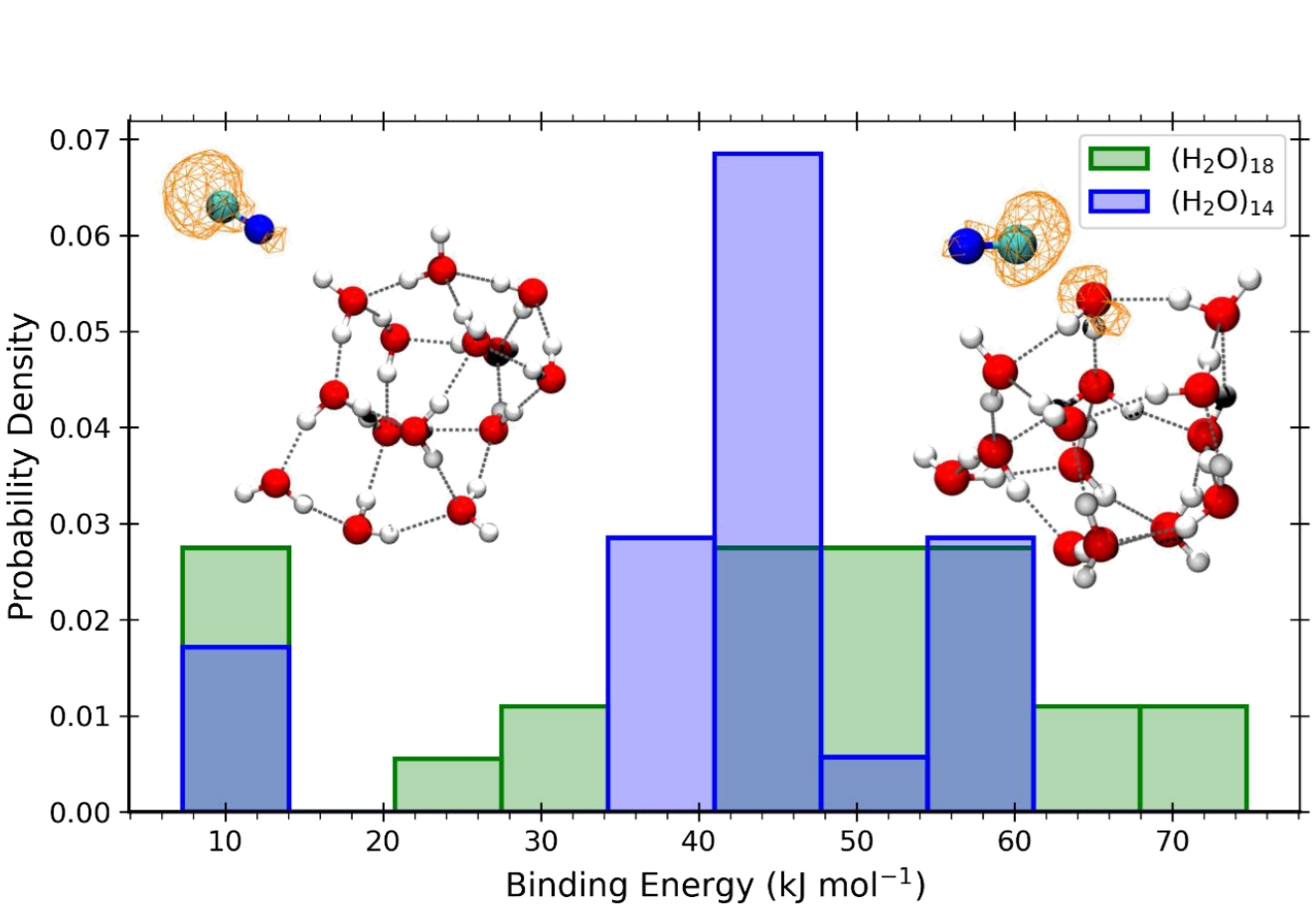


Figure courtesy: Joan Enrique-Romero

Example: Both hemi- and hydrogen bonding



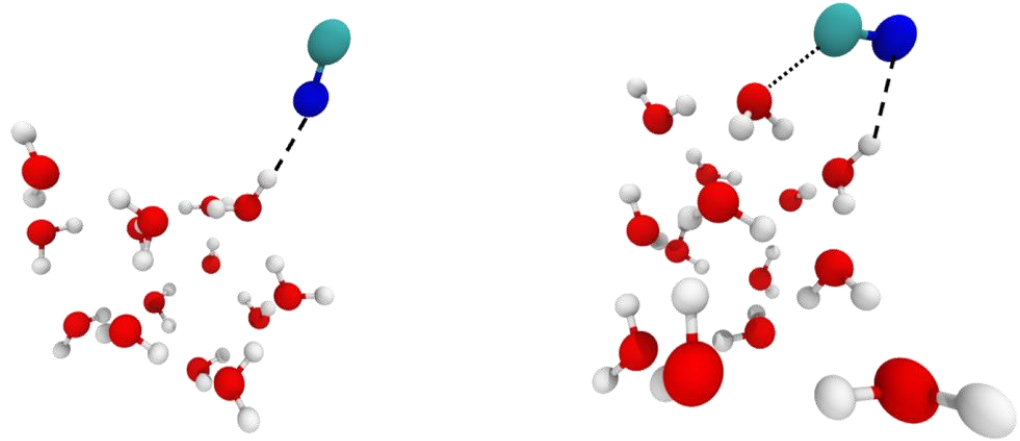
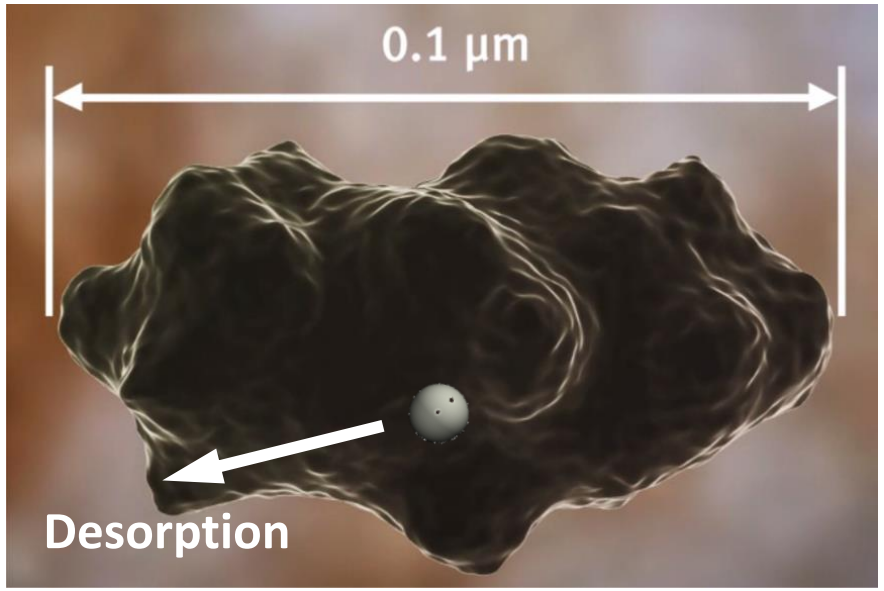


Figure courtesy: Joan Enrique-Romero

Desorption

Opposite of adsorption: return of a species to the gas phase. Governed by interaction with the surface: Binding energy



$$f_{des,X} = k_{des,X}\, n_s(X) \quad \text{with:}$$

$$k_{des,X} = \nu_{trial} \exp\left(-\frac{E_{bind,X}}{k_B T}\right) \quad \text{and} \quad \nu_{trial} = \sqrt{\frac{2 N_S E_{bind,X}}{\pi^2 m_X}}$$

Assumptions underlying typical formula

Transition state theory ☺

$$k = \nu \exp\left(-\frac{E_a}{k_B T}\right) \qquad \nu_{TST} = \frac{k_B T}{h}\frac{q^{\ddagger}}{q_{ads}}$$

$$\nu_{TST} = \frac{k_B T}{h} q^{\ddagger}_{tr,2D} q^{\ddagger}_{rot,3D}$$

$$q^{\ddagger}_{tr,2D} = \frac{A}{\Lambda^2} \qquad q^{\ddagger}_{rot,3D} = \frac{\sqrt{\pi}}{\sigma h^3}(8\pi^2 k_B T_{peak})^{3/2}\sqrt{I_x I_y I_z}$$

Up to 7 orders of magnitude difference!

ACS EARTH AND SPACE CHEMISTRY

http://pubs.acs.org/journal/aesccq

Thermal Desorption of Interstellar Ices: A Review on the Controlling Parameters and Their Implications from Snowlines to Chemical Complexity

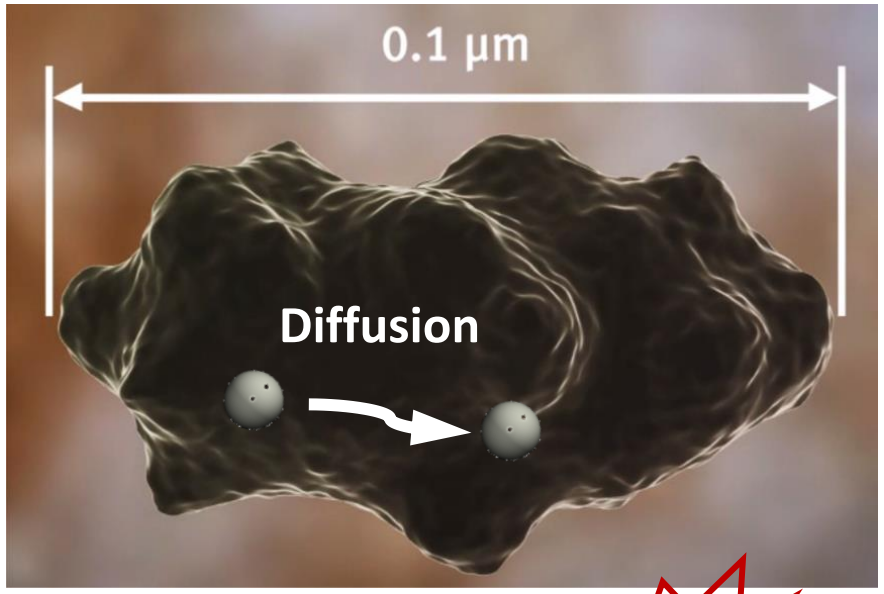
Marco Minissale,* Yuri Aikawa, Edwin Bergin, Mathieu Bertin, Wendy A. Brown, Stephanie Cazaux, Steven B. Charnley, Audrey Coutens, Herma M. Cuppen, Victoria Guzman, Harold Linnartz, Martin R. S. McCoustra, Albert Rimola, Johanna G.M. Schrauwen, Celine Toubin, Piero Ugliengo, Naoki Watanabe, Valentine Wakelam, and Francois Dulieu

Cite This: *ACS Earth Space Chem.* 2022, 6, 597–630

Read Online

Diffusion

Movement across the surface allows reactants to meet. Governed by interaction with the surface: Diffusion Barrier



$$k_{diff,X} = \nu_{trial} \exp\left(-\frac{E_{diff,X}}{k_B T}\right) \quad \text{and} \quad E_{diff,X} = \alpha \cdot E_{bind,X} \text{ with } \alpha < 1$$

Heavier/larger species, typically bind stronger, and diffuse slower.

Validity of the α factor

Monthly Notices of the ROYAL ASTRONOMICAL SOCIETY

MNRAS 510, 3063–3070 (2022)
Advance Access publication 2021 December 13

https://doi.org/10.1093/mnras/stab3631

Neural-network assisted study of nitrogen atom dynamics on amorphous solid water – II. Diffusion

Viktor Zaverkin, Germán Molpeceres and Johannes Kästner ★

Computational studies need to include many degrees of freedom

- Nudged Elastic Band approach for locating TS
- Surface-coverage dependence of diffusion (α > 1)

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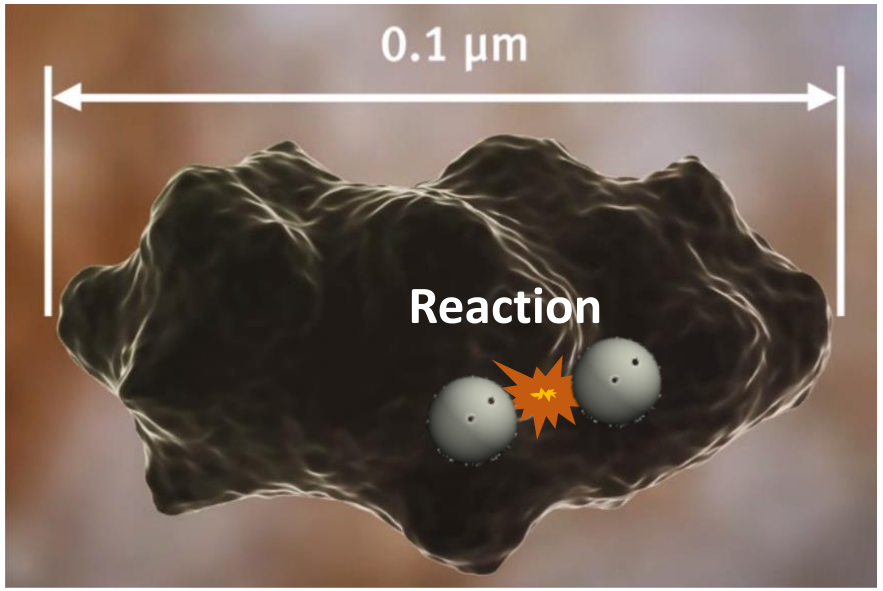
Reaction



When two reactants meet: possibility for a reaction to occur

Simplest and most abundant molecule is indeed formed on grain surfaces: H_2

$H\cdot_{ads} + H\cdot_{ads} \rightarrow H_{2\ ads}$

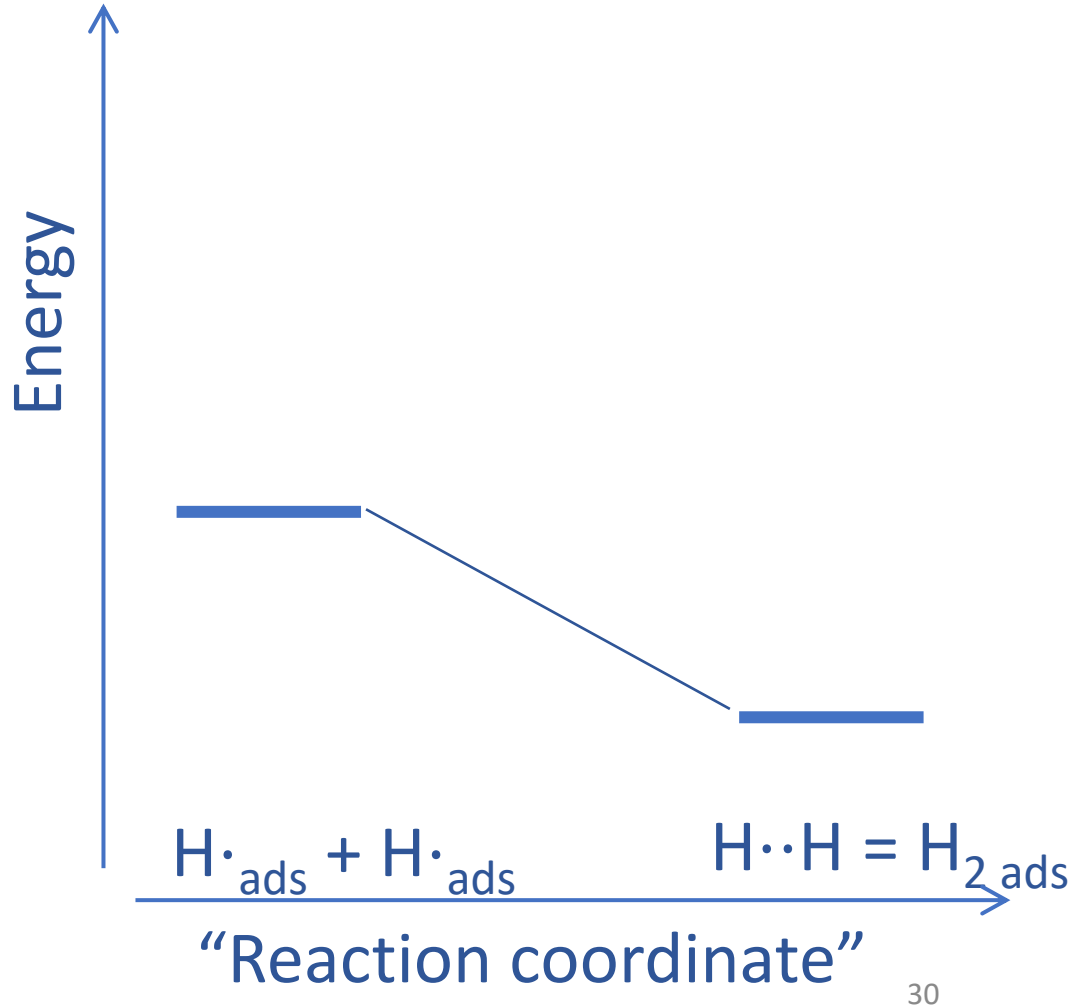
Barrierless and efficient! Detected “abundantly” despite UV radiation in PDR’s. NB: gas-phase routes are only relevant in the early Universe and in shocked regions

Reaction energetics: Radical-radical

"Electrons like to be paired"

Radical-radical reactions are barrierless (*)

(*) see exercises



Reaction energetics: Radical-neutral

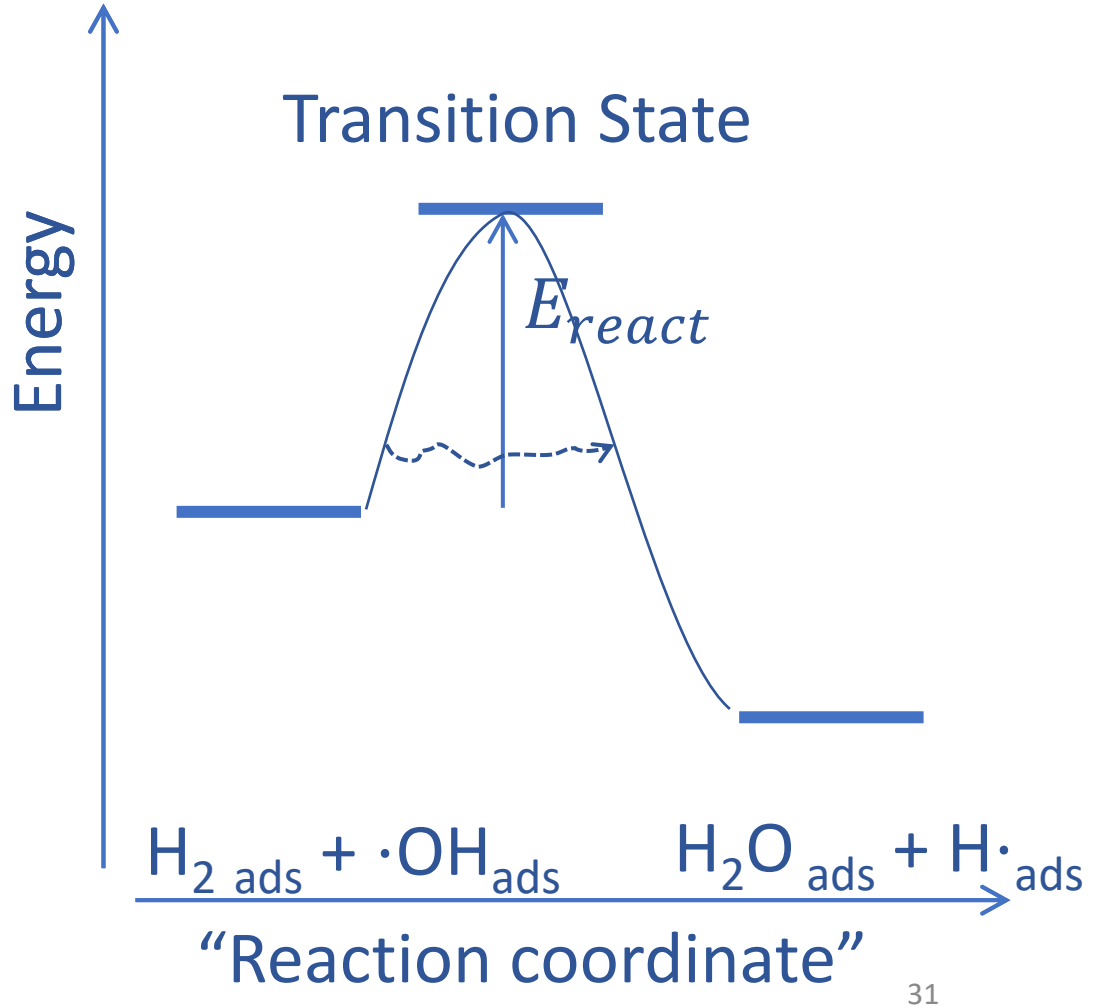
Usually a reaction with a barrier:

1. Thermally activated:

$$k_{LH} = \nu_{trial} \exp\left(-\frac{E_{react}}{k_B T}\right)$$

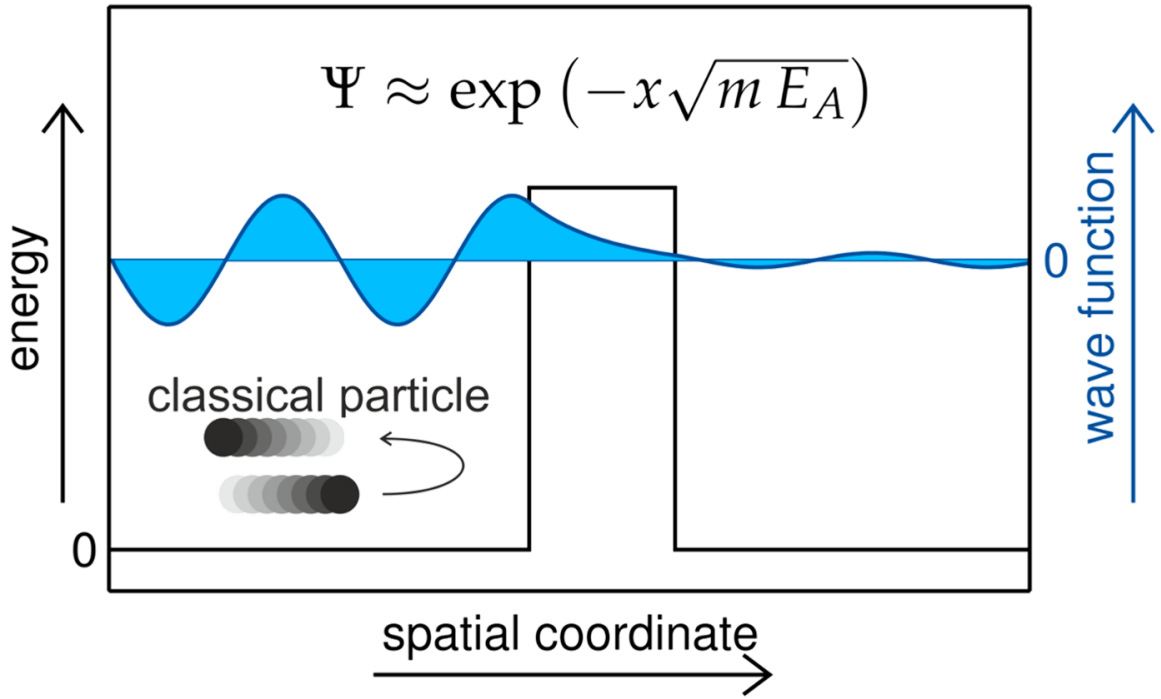
2. Tunneling mediated:

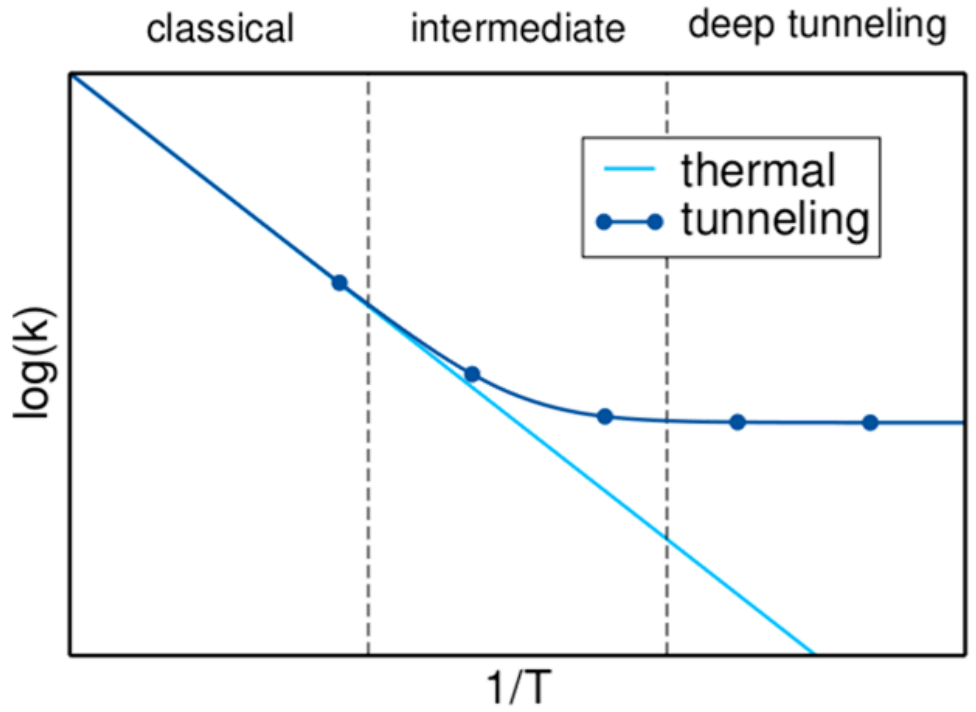
Depends on barrier height and width



Meisner et al. ACSESC 2017

Low-temperature effects: tunneling





Minimum energy path is not a good approximation to the tunneling path:
Rectangular barrier, Eckart, Instanton theory

Figure courtesy Meisner & Kästner ACIE 55, 5400 (2016)

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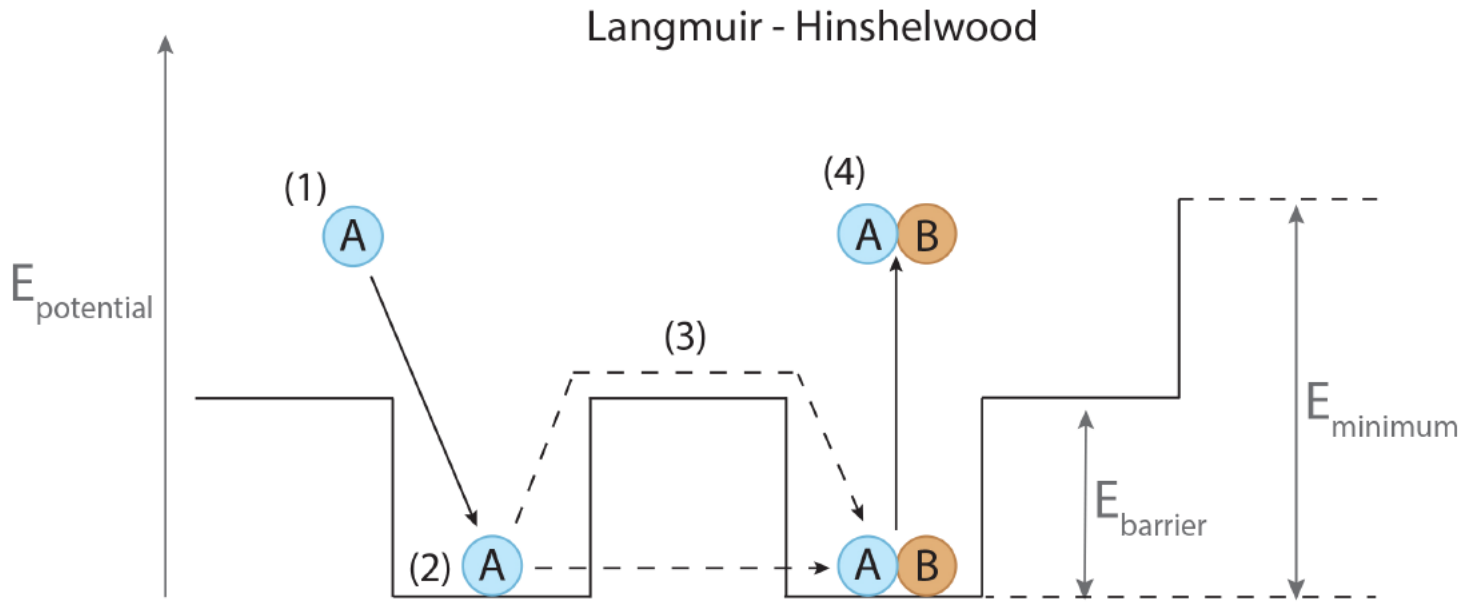
Reaction mechanism: Langmuir-Hinshelwood

Thermalized and diffusive:

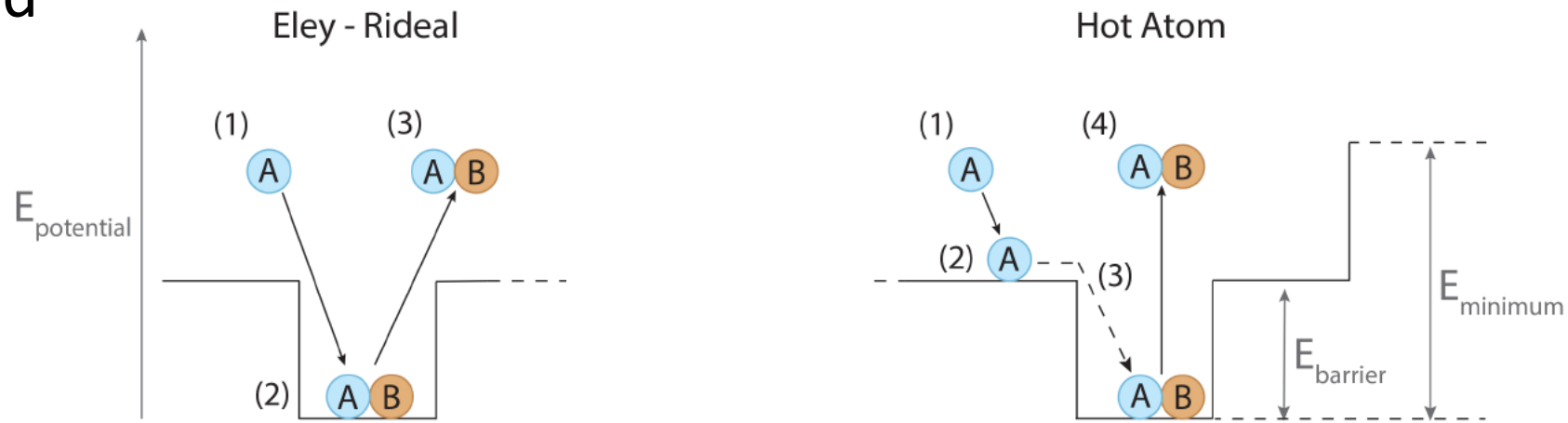


$A_{gas} + B_{ads} \rightarrow A_{ads} + B_{ads} \rightarrow (AB)_{ads} \rightarrow (AB)_{gas}$

$$k_{LH} = \nu_{trial} \exp\left(-\frac{E_{react,A+B}}{k_B T}\right)$$ with $E_{react,A+B}$ the reaction barrier

Reaction mechanism: Eley-Rideal or Hot Atom

Non-Thermalized



$A_{gas} + B_{ads} \rightarrow (AB)_{ads} \rightarrow (AB)_{gas}$

$A_{gas} + B_{ads} \rightarrow A_{not\text{-}ads} + B_{ads} \rightarrow (AB)_{ads} \rightarrow (AB)_{gas}$

Timescale comparisons (dark cloud @ 10 K)

Process	Timescale
Dissipation	Picoseconds – microseconds
Reaction	Microseconds – seconds
Diffusion	Microseconds – days
Adsorption	Days – months
Desorption	Seconds – months
Experiment	Days – weeks
Telescope lifetime	Years – decades
Molecular cloud	Million years

Surface processes in rate equation models

$$\frac{d}{dt}$$

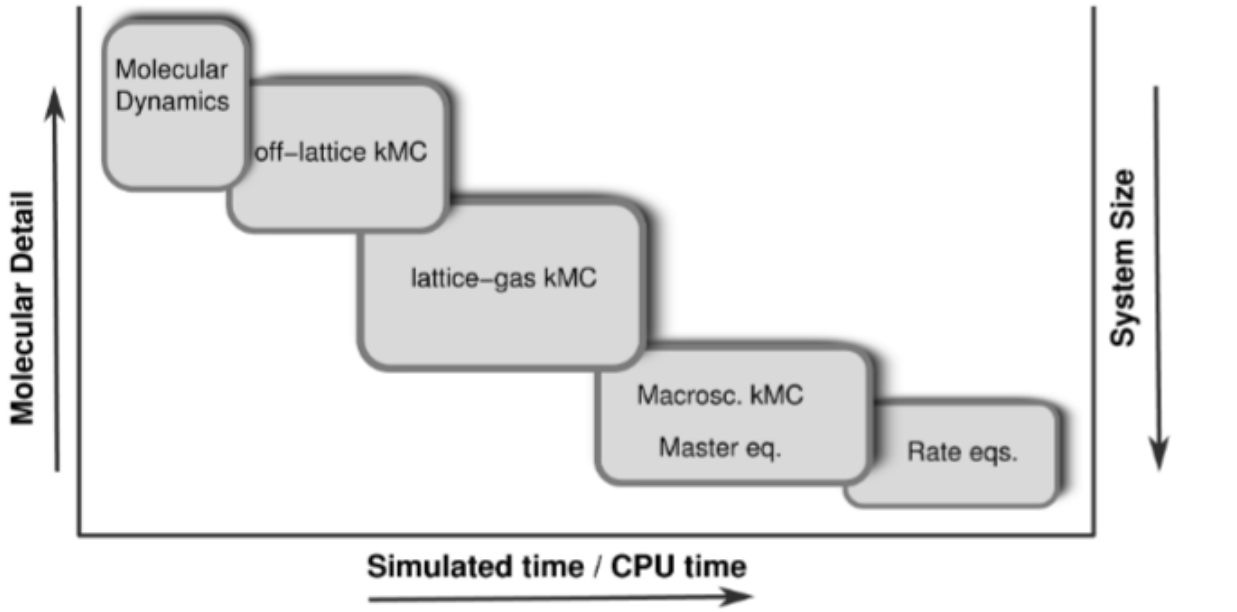
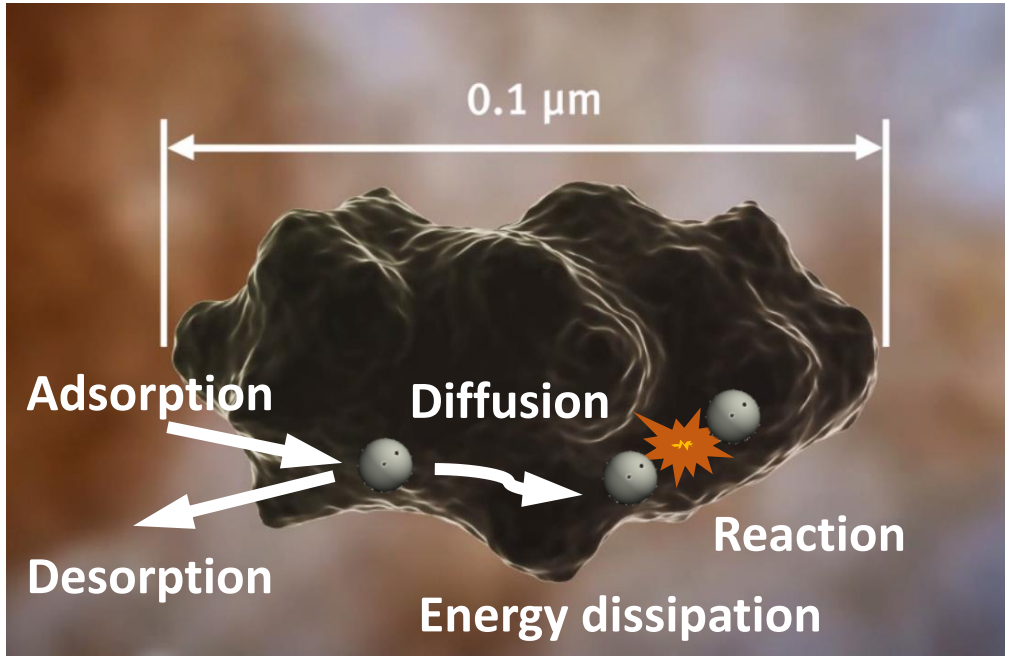


Figure 1. Overview of the different simulation methods mentioned in the present review.



Cuppen *et al.* 113 (2013) 8840

Competition

$$\kappa_{react} = \frac{k_{react}}{k_{react} + k_{diff} + k_{des}}$$

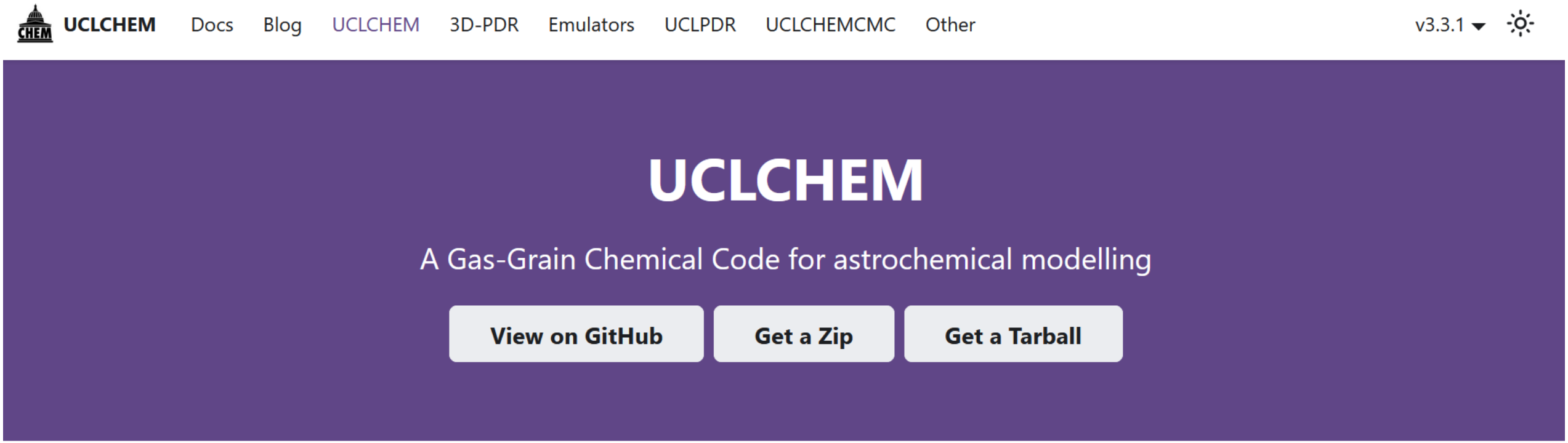
$$k_{react,\,thermal} = \nu \cdot e^{-E_{act}/k_B T}$$

$$k_{react,\,tunneling} = \text{not trivial}^{*}$$

$$k_{des} = \nu \cdot e^{-E_{bind}/k_B T}$$

$$k_{diff} = \nu \cdot e^{-E_{diff}/k_B T}$$

Surface processes in rate equation models



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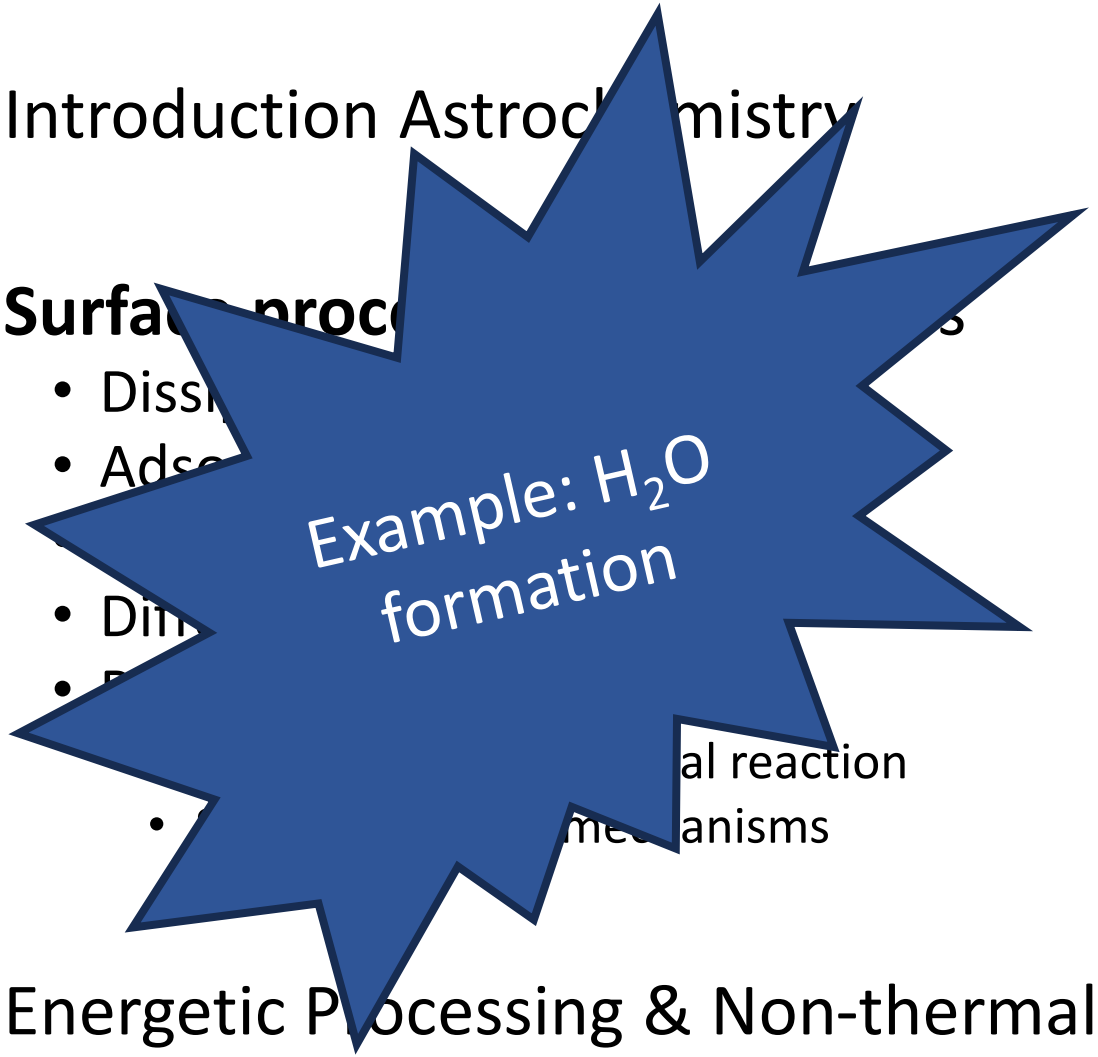
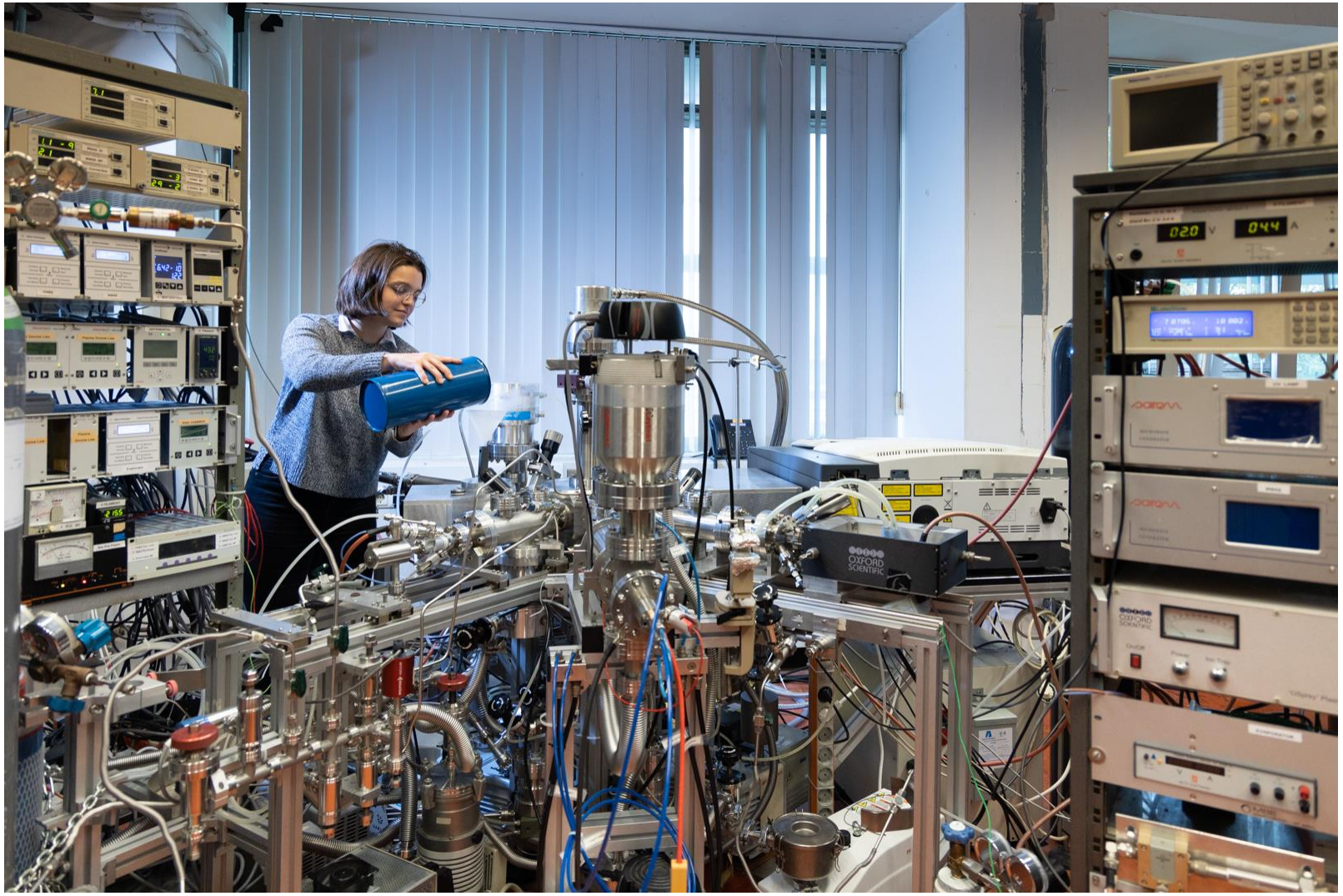
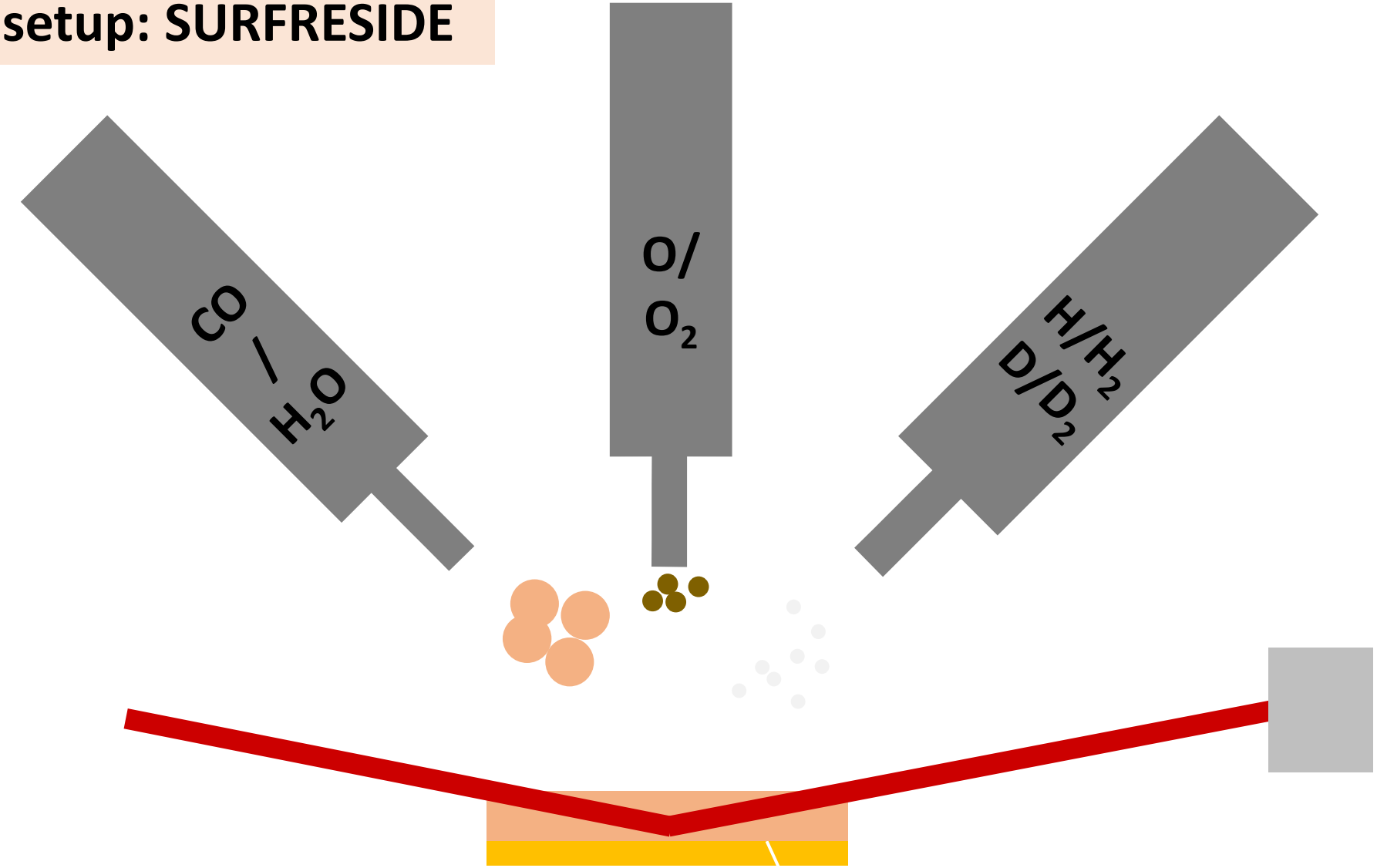


Laboratory for Astrophysics @ Leiden



Experimental setup: SURFRESIDE



Water reaction network

References:

Van de Hulst 1949

Tielens & Hagen 1982

Hiraoka et al. 1998

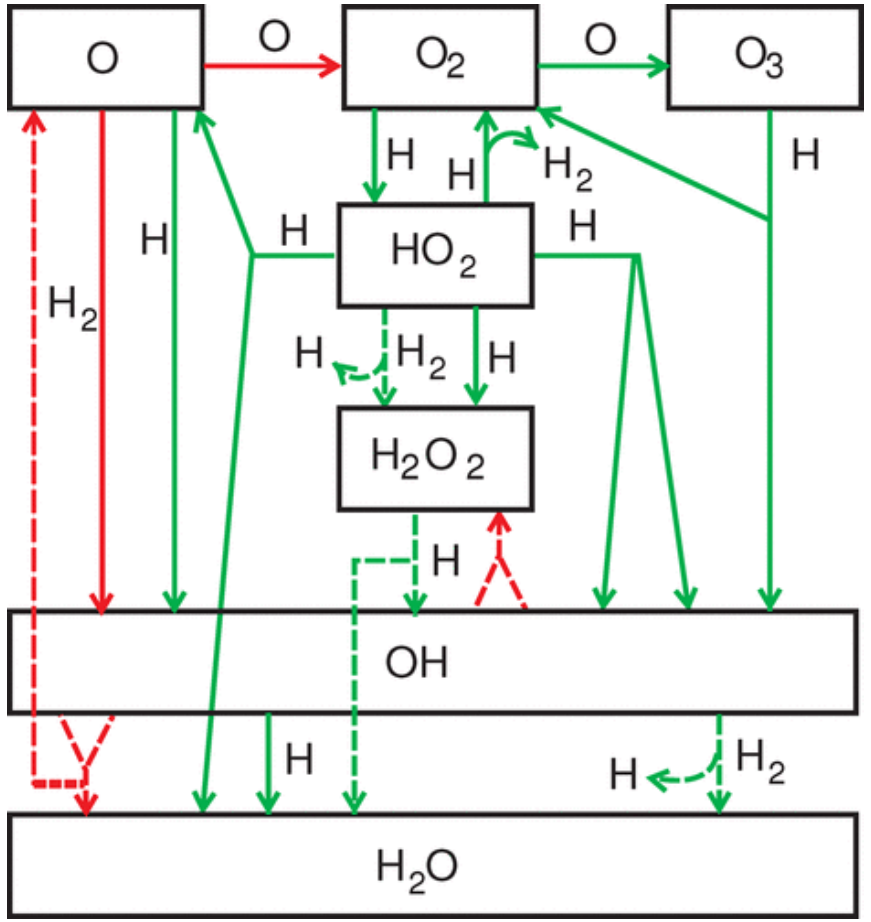
Ioppolo et al. 2008

Dulieu et al. 2010

Cuppen et al. 2010

Oba et al. 2012

Lamberts et al. 2017



Van Dishoeck et al. 2013

Theoretical work on water formation I

Kinetic Monte Carlo lattice-gas model

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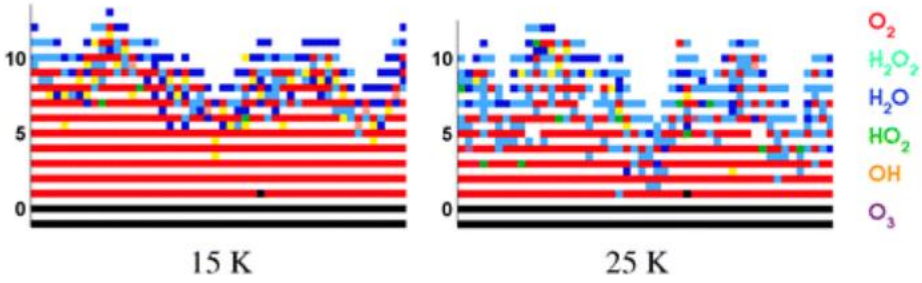
Water formation at low temperatures by surface O_2 hydrogenation III: Monte Carlo simulation

Cite this: *Phys. Chem. Chem. Phys.*, 2013, **15**, 8287

Thanja Lamberts,*[ab] Herma M. Cuppen,[b] Sergio Ioppolo†[a] and Harold Linnartz[a]



Faraday Discussions

Cite this: *Faraday Discuss.*, 2014, **168**, 327

PAPER

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The formation of ice mantles on interstellar grains revisited – the effect of exothermicity

T. Lamberts,[ab] X. de Vries[a] and H. M. Cuppen*[a]

$H + HO_2 \rightarrow 2\ OH$

Theoretical work on water formation II

Reaction rate constants

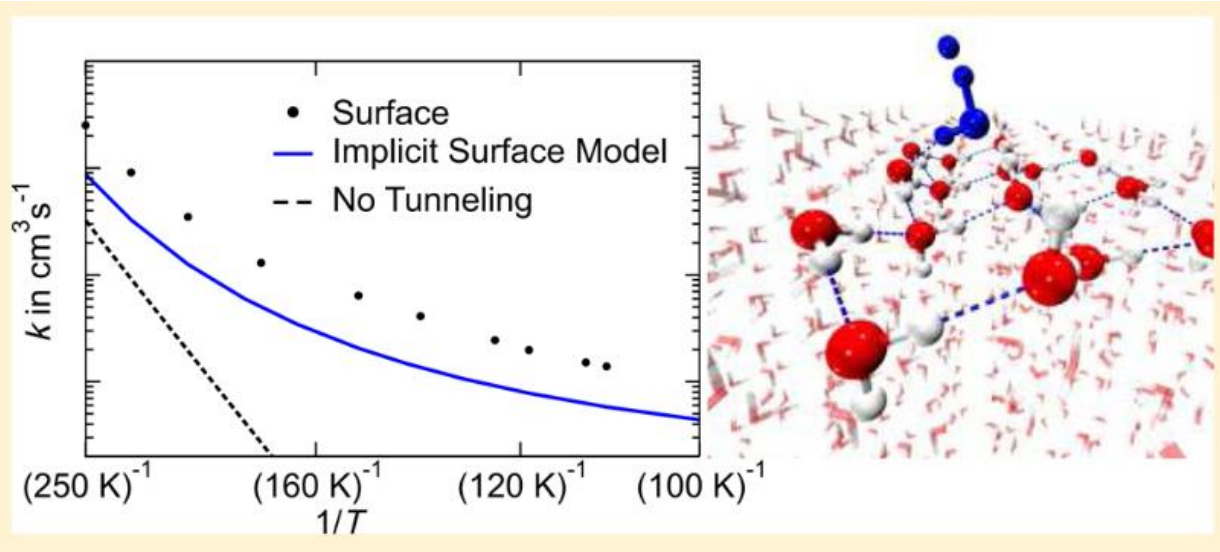
ACS EARTH AND SPACE CHEMISTRY

Article

http://pubs.acs.org/journal/aesccq

Atom Tunneling in the Water Formation Reaction $H_2 + OH \rightarrow H_2O + H$ on an Ice Surface

Jan Meisner, Thanja Lamberts, and Johannes Kästner*



Theoretical work on water formation II

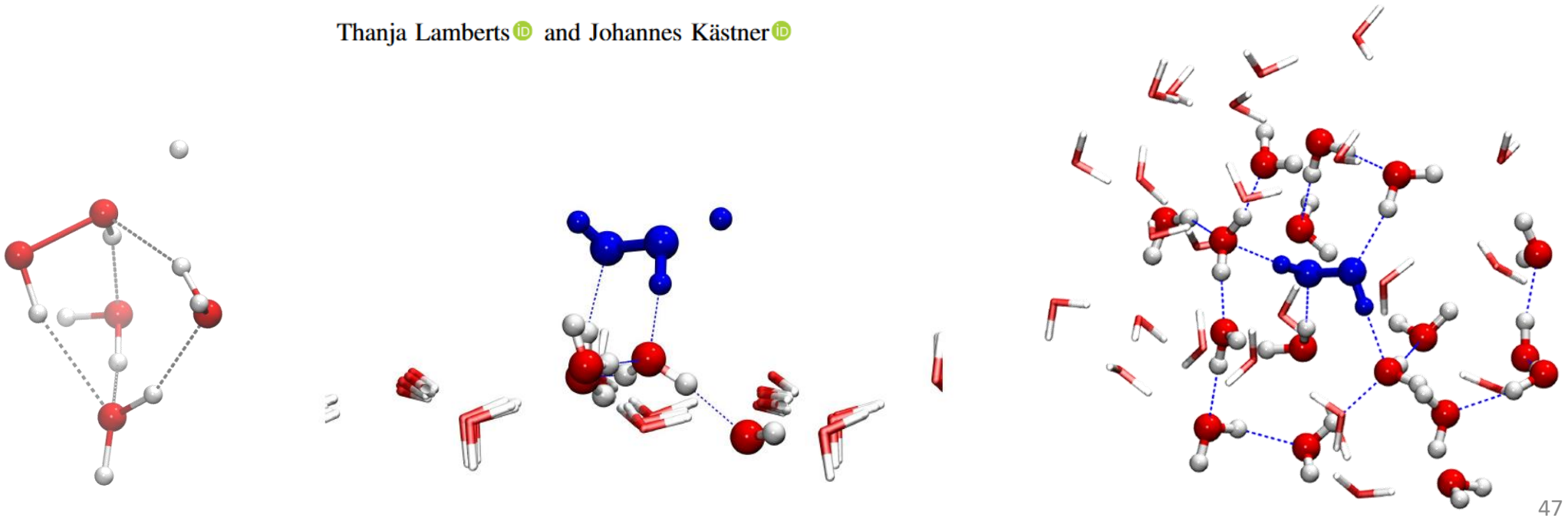
Reaction rate constants

THE ASTROPHYSICAL JOURNAL, 846:43 (7pp), 2017 September 1 https://doi.org/10.3847/1538-4357/aa8311

CrossMark

Influence of Surface and Bulk Water Ice on the Reactivity of a Water-forming Reaction

Thanja Lamberts and Johannes Kästner



Theoretical work on water formation III

Diffusion parameters

THE JOURNAL OF PHYSICAL CHEMISTRY Letters

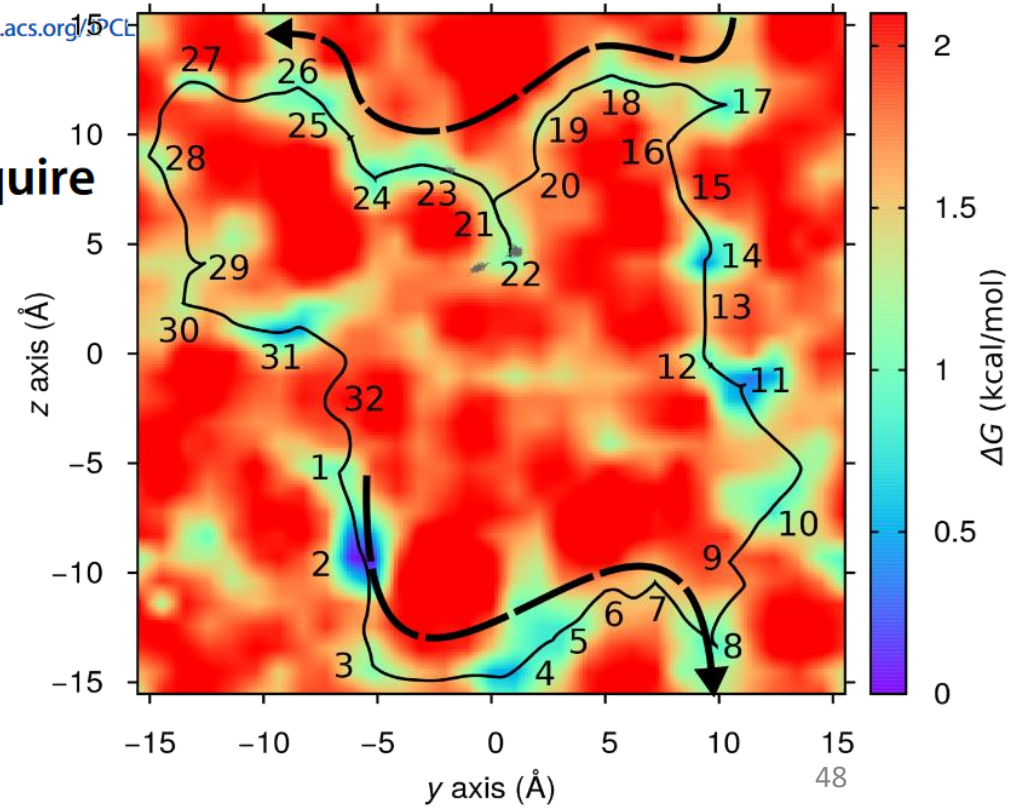
Letter

Cite This: J. Phys. Chem. Lett. 2018, 9, 1822−1826

pubs.acs.org/JPCL

Molecular Oxygen Formation in Interstellar Ices Does Not Require Tunneling

Marco Pezzella, Oliver T. Unke, and Markus Meuwly*



Theoretical work on water formation IV

Diffusion parameters

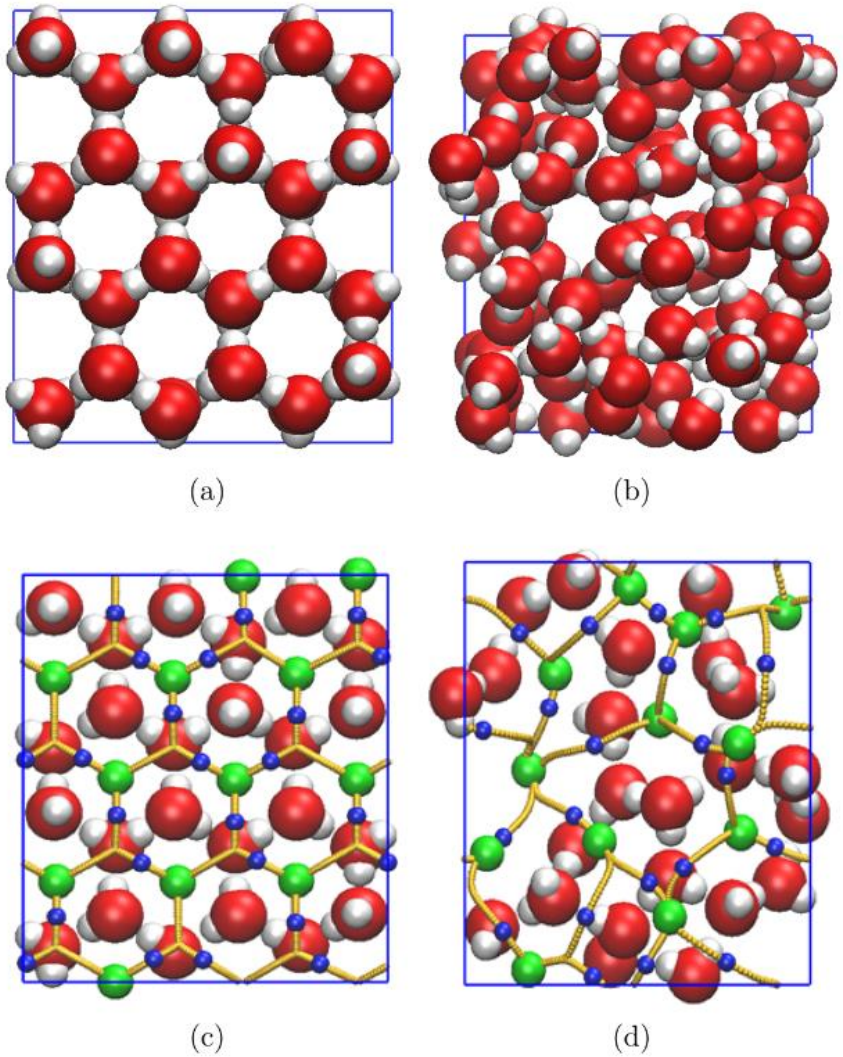
THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

Long-Time Scale Simulations of Tunneling-Assisted Diffusion of Hydrogen on Ice Surfaces at Low Temperature

V. Ásgeirsson,[†,‡] H. Jónsson,[§] and K. T. Wikfeldt*[,†]

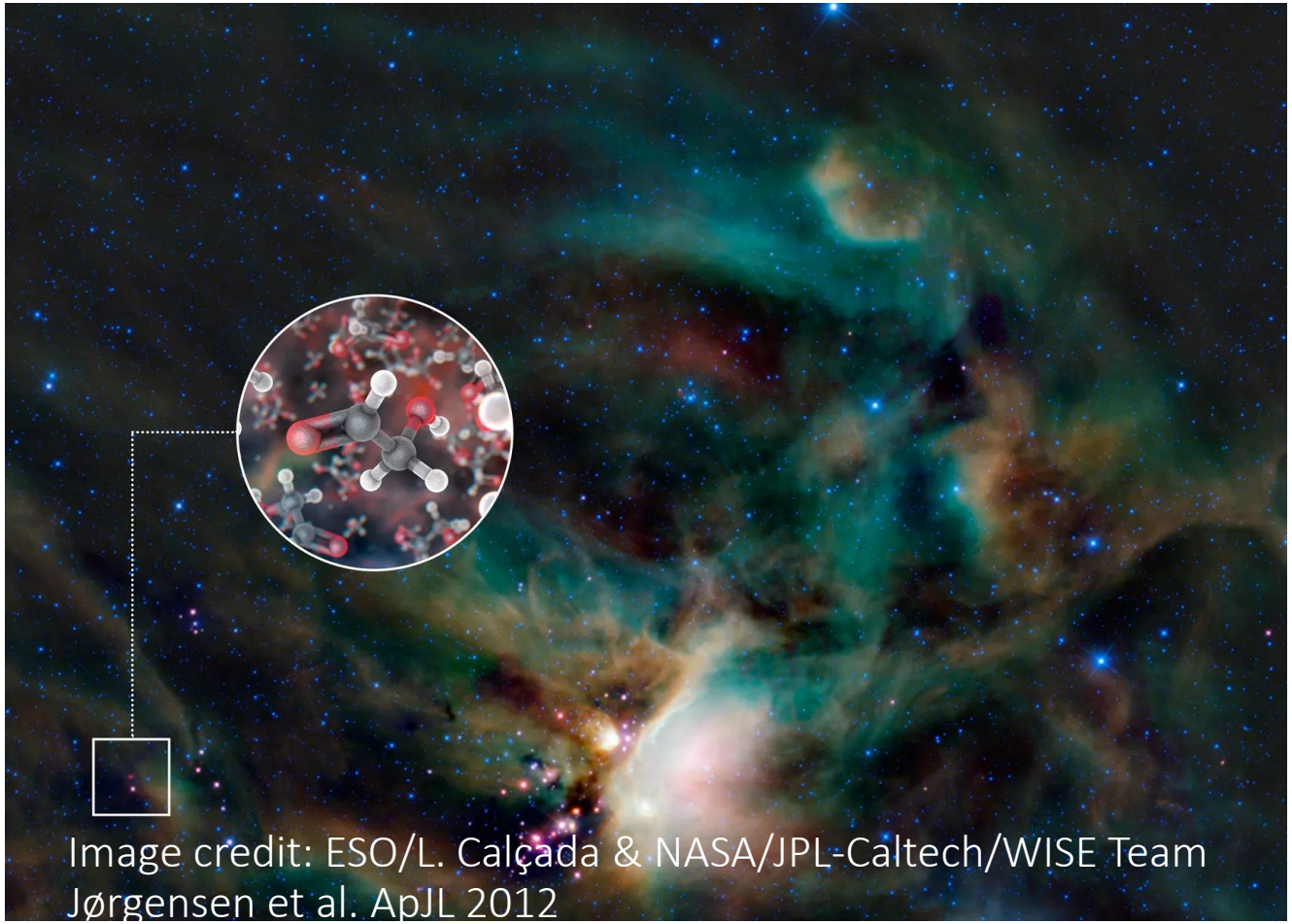


Great, H_2O! But… what about biomolecules?

Simplest sugar: $CHOCH_2OH$

Ingredients: CO and H

We will look at molecules that can be formed with CO and H in the exercise



Sneak-peak at the molecular scales

- Introduction Astrochemistry

- Surface processes & Timescales
  - Dissipation (3rd body)
  - Adsorption
  - Desorption
  - Diffusion
  - Reaction
    - Energetics of a chemical reaction
    - Surface reaction mechanisms

- **Energetic Processing & Non-thermal Desorption**

Energetic Processing

Different sources of radiation:

- UV
- X-Rays
- Cosmic Rays

Leads to:

- Excitation of molecules
- Dissociation of molecules
- Secondary electron generation
- UV generated radiation

Recent advances: cosmic ray impact

A&A 671, A156 (2023)
https://doi.org/10.1051/0004-6361/202245383

Astronomy & Astrophysics

Cosmic-ray sputtering of interstellar ices in the electronic regime

A compendium of selected literature yields

E. Dartois[1], M. Chabot[2], C. A. P. da Costa[3], T. Nguyen[2], J. Rojas[2], J. Duprat[4], B. Augé[5], A. Domaracka[3], H. Rothard[3], and P. Boduch[3]

The Astrophysical Journal, 944:181 (12pp), 2023 February 20
https://doi.org/10.3847/1538-4357/acb545

CrossMark

Bombardment of CO Ice by Cosmic Rays. I. Experimental Insights into the Microphysics of Molecule Destruction and Sputtering

Alexei V. Ivlev[1], Barbara M. Giuliano[1], Zoltán Juhász[2], Péter Herczku[2], Béla Sulik[2], Duncan V. Mifsud[2,3], Sándor T. S. Kovács[2], K. K. Rahul[2], Richárd Rácz[2], Sándor Biri[2], István Rajta[2], István Vajda[2], Nigel J. Mason[2,3], Sergio Ioppolo[4,5], and Paola Caselli[1]

Non-thermal desorption

At 10 K it is unlikely that molecules can desorb “thermally”

Alternative mechanisms that are proposed are:

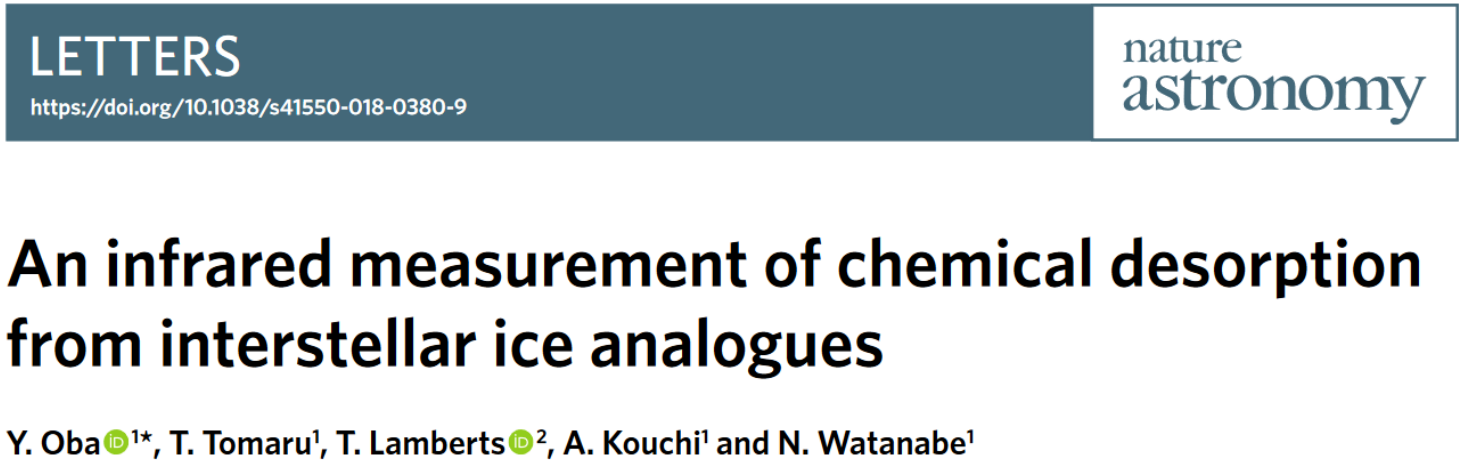
- Desorption induced by energetic radiation
  - Problem: what about dissociation?
- Desorption induced by the excess energy of a chemical reaction
  - Problem: what about dissipation?

Example: Do reaction products evaporate?

How do vibrationally excited molecules dissipate their energy?

$H_{ads} + H_2S_{ads} \rightarrow HS_{ads} + H_2$?

$H_{ads} + HS_{ads} \rightarrow H_2S_{gas}$?



Example: Do reaction products evaporate?

How do vibrationally excited molecules dissipate their energy?

The Astrophysical Journal, 897:56 (13pp), 2020 July 1

https://doi.org/10.3847/1538-4357/ab8a4b

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namics

Chemical Desorption versus Energy Dissipation: Insights from Ab Initio Molecular Dynamics of HCO● Formation

Stefano Pantaleone[1], Joan Enrique-Romero[1,2], Cecilia Ceccarelli[1], Piero Ugliengo[3], Nadia Balucani[1,4,5], and Albert Rimola[2]

- Excitation by fixe
- Excitation into a
- Quantum effects

SPACE CHEMISTRY

http://pubs.acs.org/journal/aesccq

Article

Molecular Dynamics Simulations of Energy Dissipation on Amorphous Solid Water: Testing the Validity of Equipartition

Adrien Fredon, Gerrit C. Groenenboom, and Herma M. Cuppen*

Cite This: *ACS Earth Space Chem.* 2021, 5, 2032–2041

Read Online

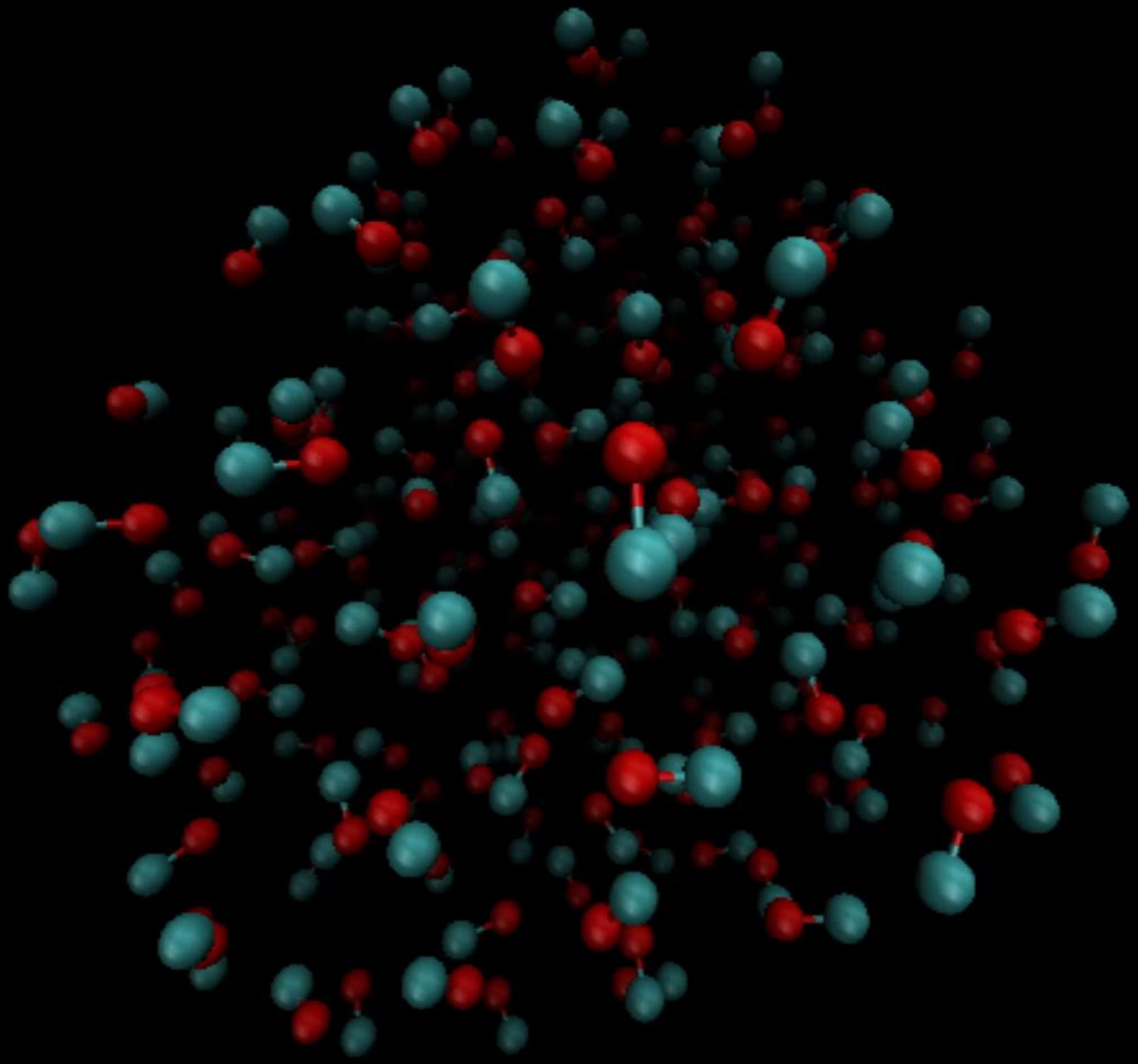

Figure courtesy: Brian C. Ferrari

Take Home Messages

- Ice surface chemistry leads to formation of (saturated) molecules
- Dust grains are pivotal in taking up excess energy of reactions
- There are various elementary surface processes at play
- Surface reactions can be barrierless or with a barrier
- There are thermal and non-thermal desorption mechanisms

Molecular complexity ?!

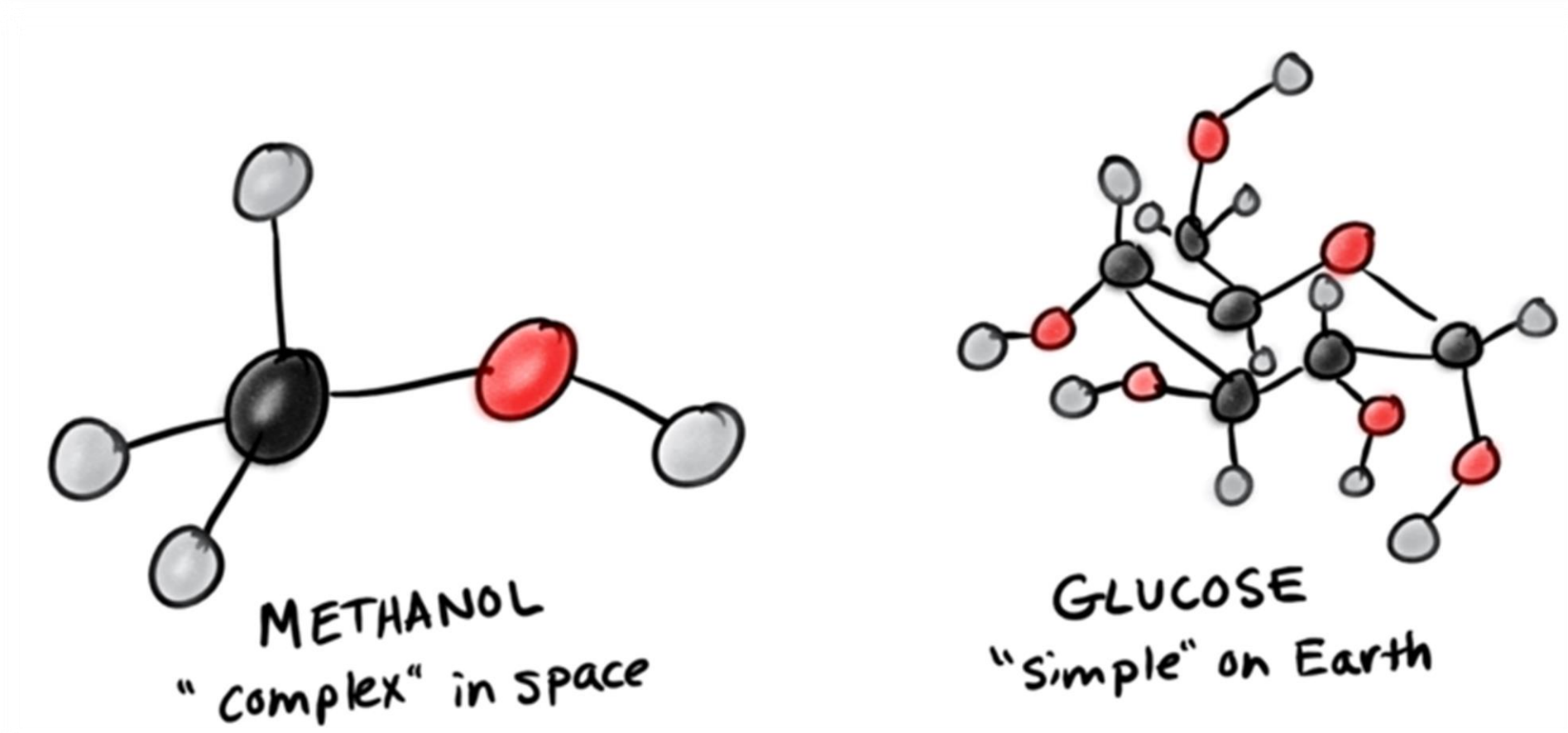

Figure courtesy: Olivia Harper Wilkins