Uncertainties in stochastic simulations

Herma Cuppen

Sackler Laboratory of Astrophysics, Leiden Observatory

Why a theoretical study of ices?

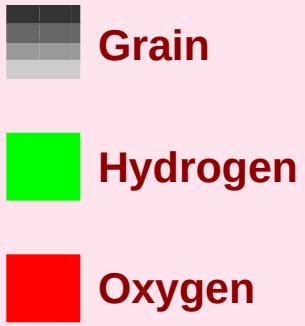
- Vary one parameter at the time
- Switch off certain processes
- Large range of timescales and fluxes
- Complementary to experiments

Monte Carlo simulations

Sequence of processes is chosen using random numbers according to transition probabilities

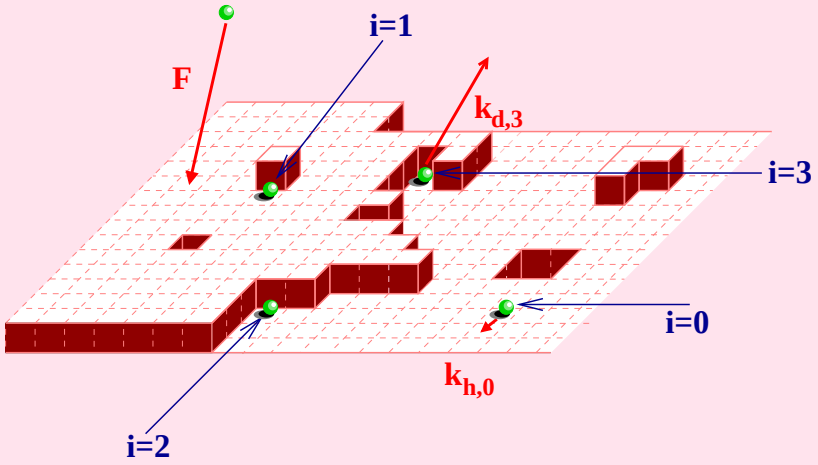
Free parameters

- temperature
- flux
- surface
- energy barriers



Top view of the surface

Monte Carlo simulations



$$R_{hop} = \nu \exp\left(-\frac{E_b(i)}{kT}\right)$$

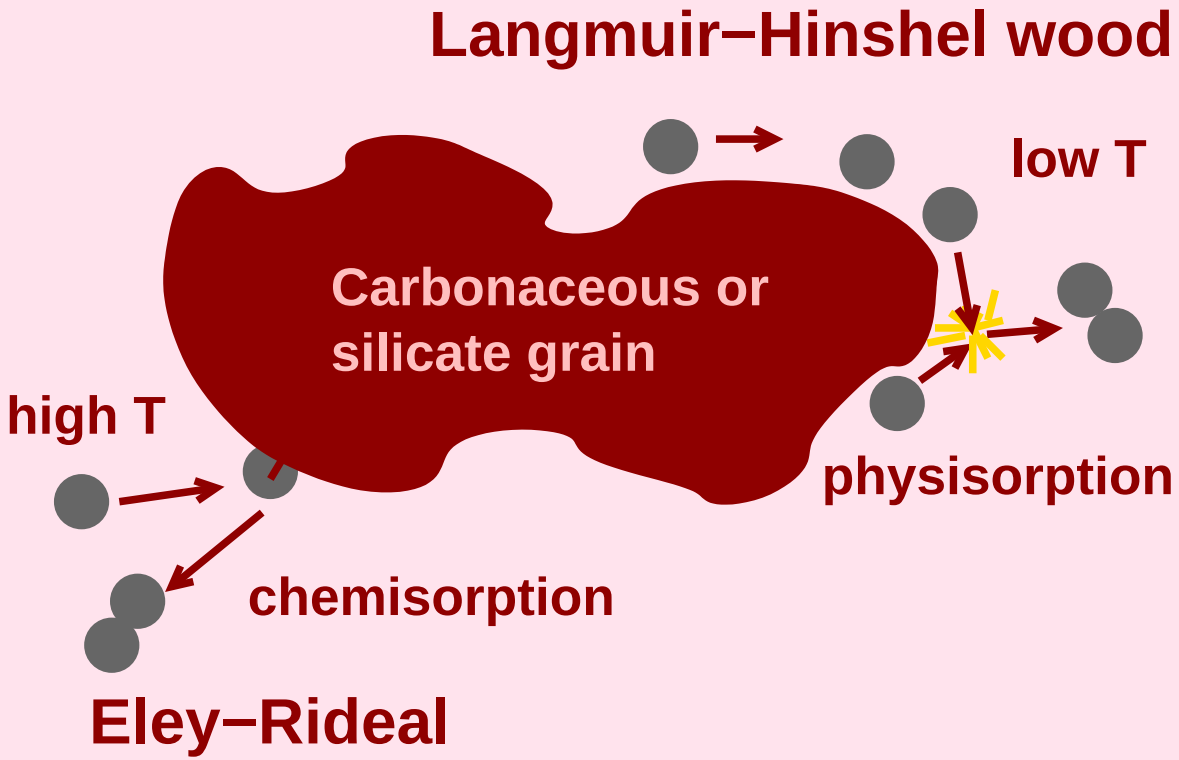
$$R_{eva} = \nu \exp\left(-\frac{E_D(i)}{kT}\right)$$

+ Surface structure can be included
+ Individual atoms can be followed
+ Laboratory and interstellar fluxes can be used
± All energy barriers have to be provided
- High demand of cpu
- No dynamical and structural information

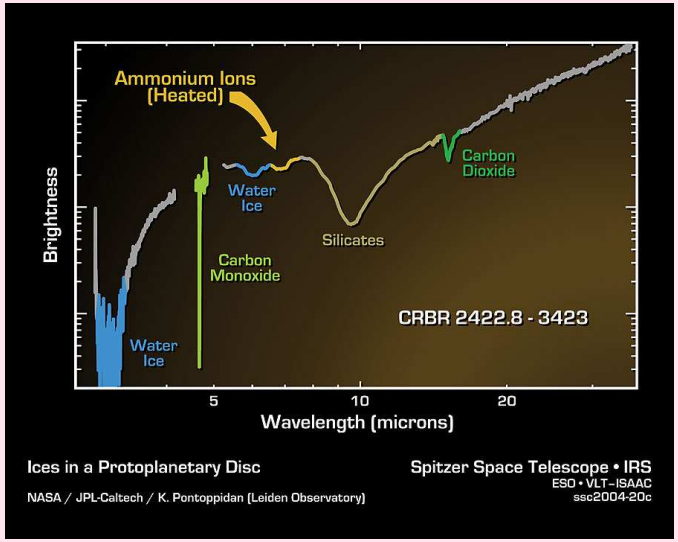
Contents

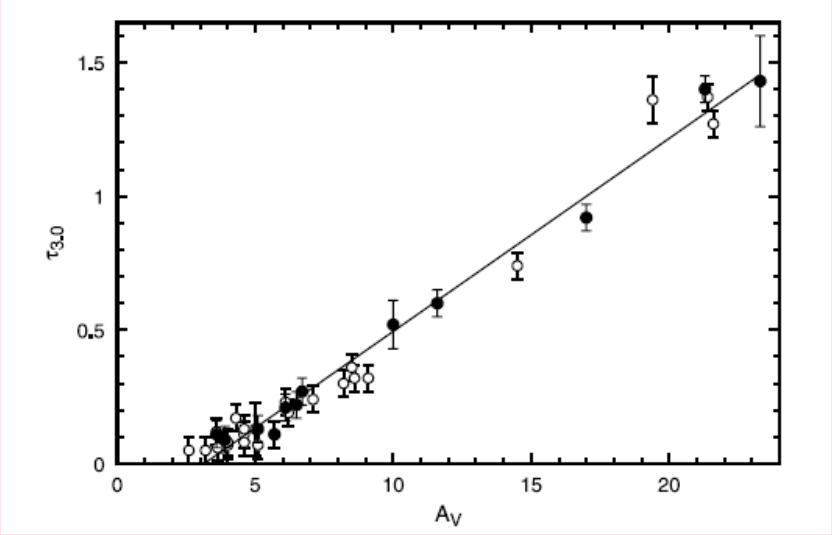
Uncertainties in model parameters using two examples

- Ice formation for different extinctions
- Molecular hydrogen formation on graphite



Water ice in Molecular Clouds





Whittet, ApJ (2001) 547, 872

Threshold value of $A_V = 3$

Ice simulations

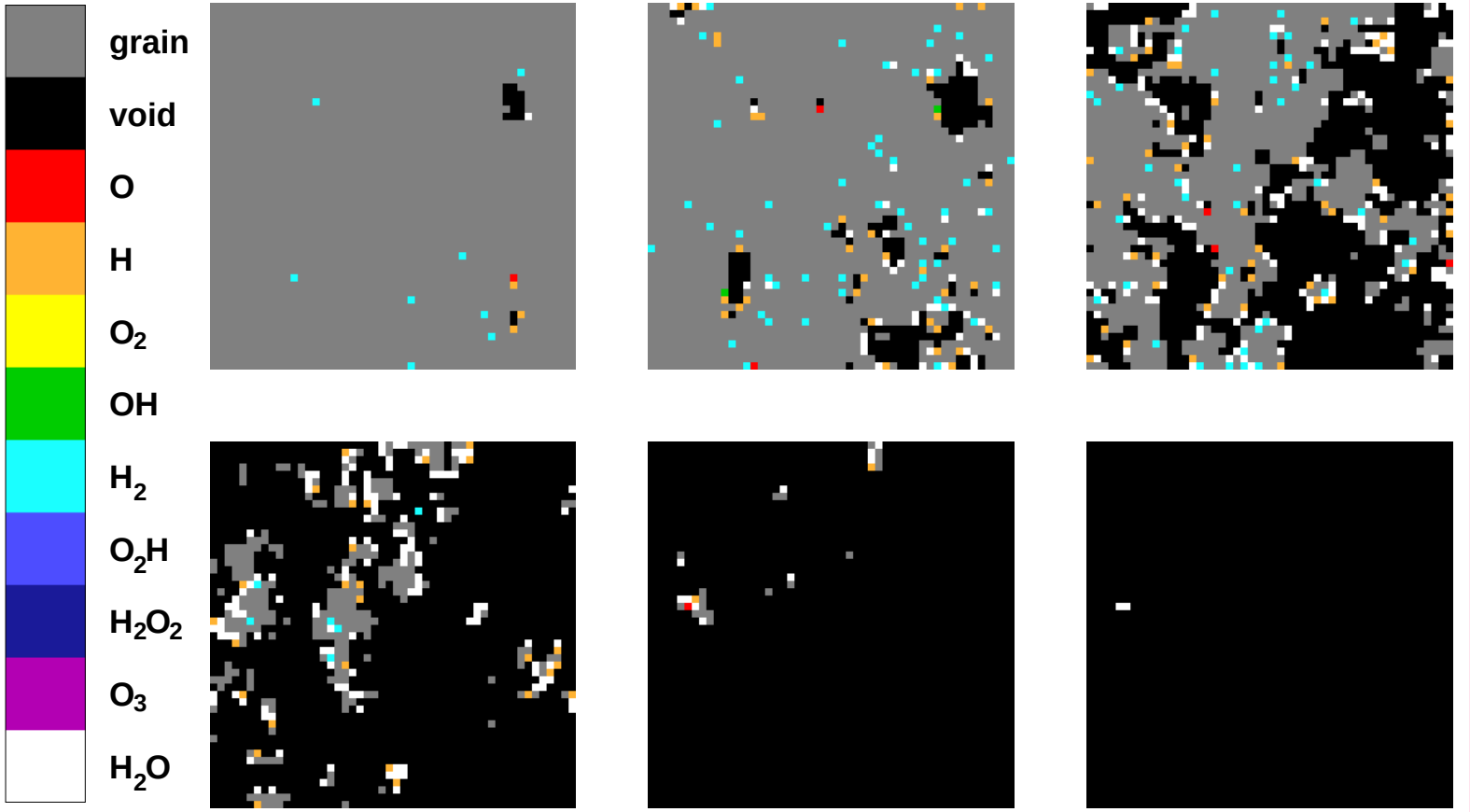
- Oxygen and hydrogen deposition
- 10 surface reactions
- 7 dissociation reactions (UV photons, CR-induced photons)
- Different extinctions
- 3 different temperatures, 2 densities per extinction

Model parameters

- Desorption
  - ⋆ Mixtures (mostly for pure species)
  - ⋆ Structure (porosity/co-desorption)
  - ⋆ Radicals (hardly any information)
- Diffusion
  - ⋆ Similar for all species?
  - ⋆ Structure
- Reactions
  - ⋆ Energy barrier
  - ⋆ Temperature dependence
  - ⋆ Excess energy (desorption/re-structuring/grain heating)

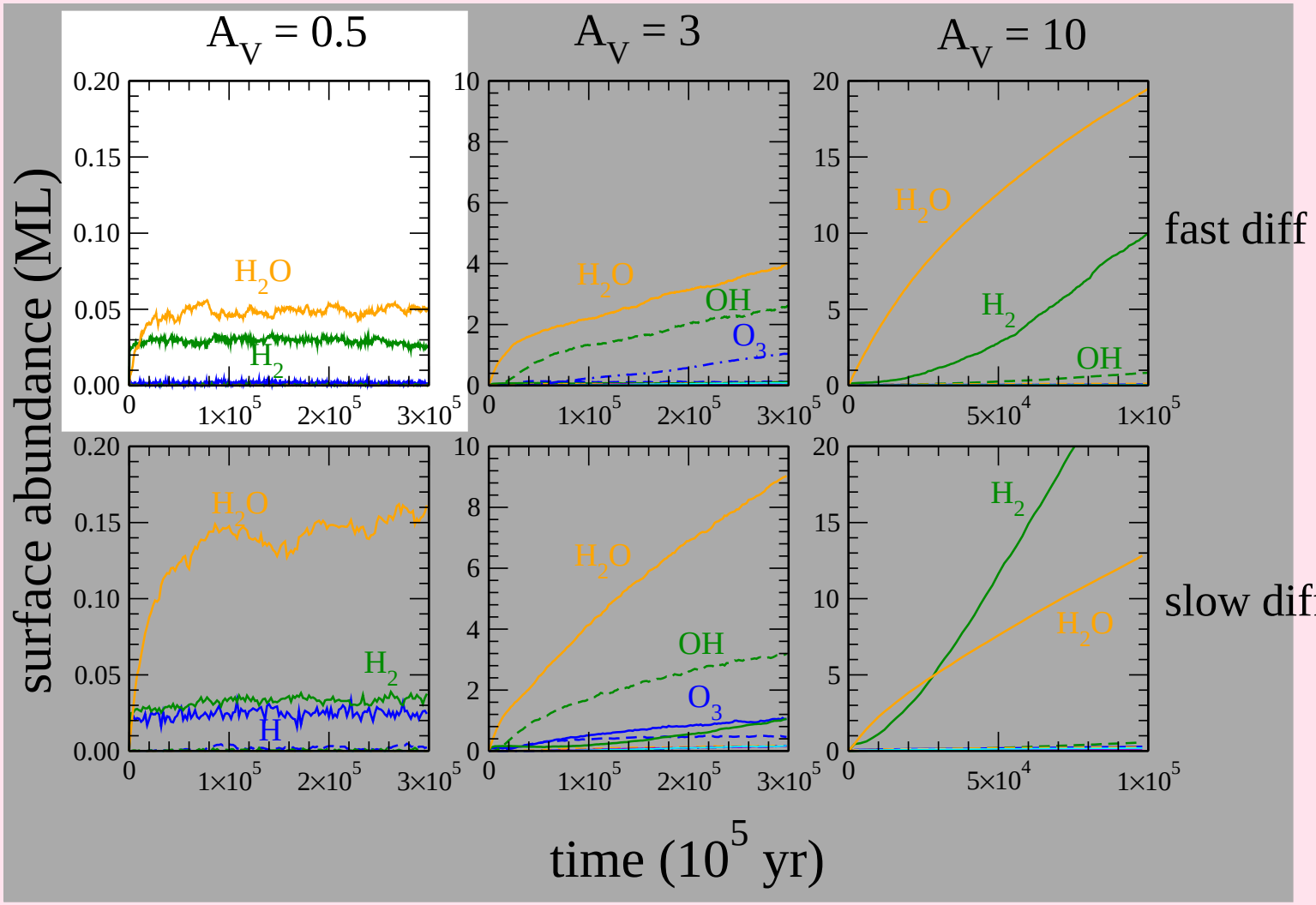
Very little known and often in wrong format

Snapshot of ice mantles

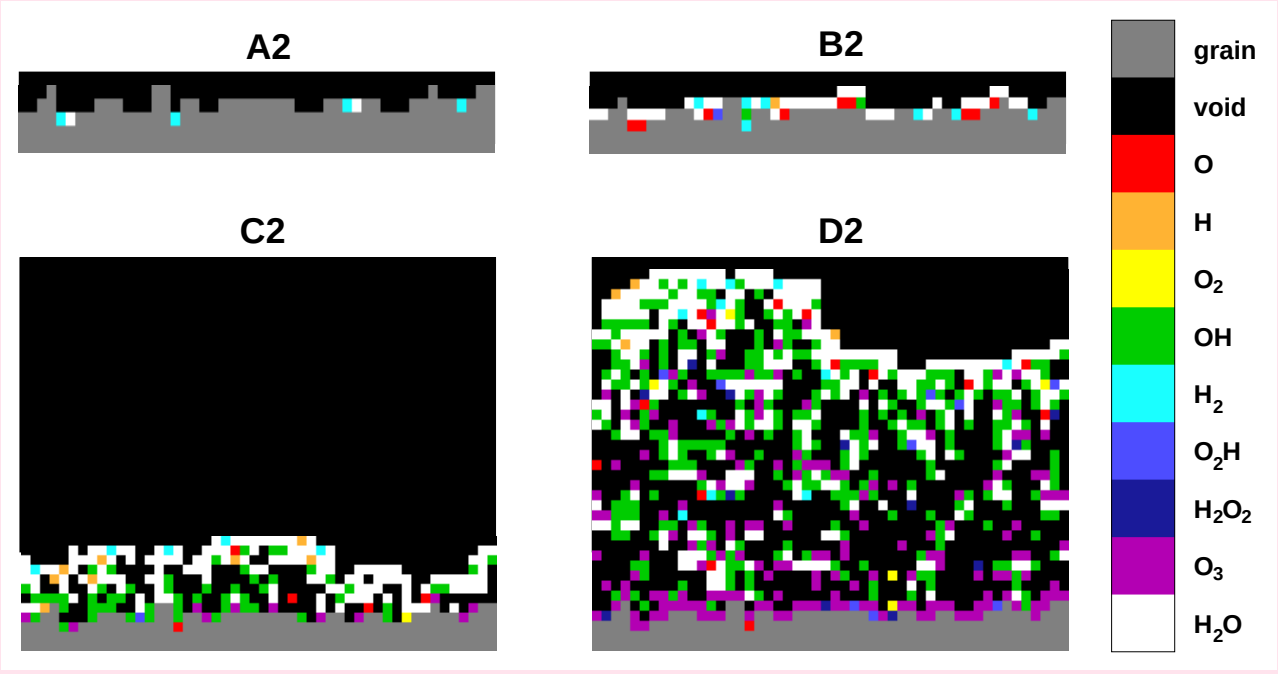


A_V	T_{grain}	T_{gas}	n(H)	form of H
0.5	18	80	1.0(2)	H

Surface Abundance

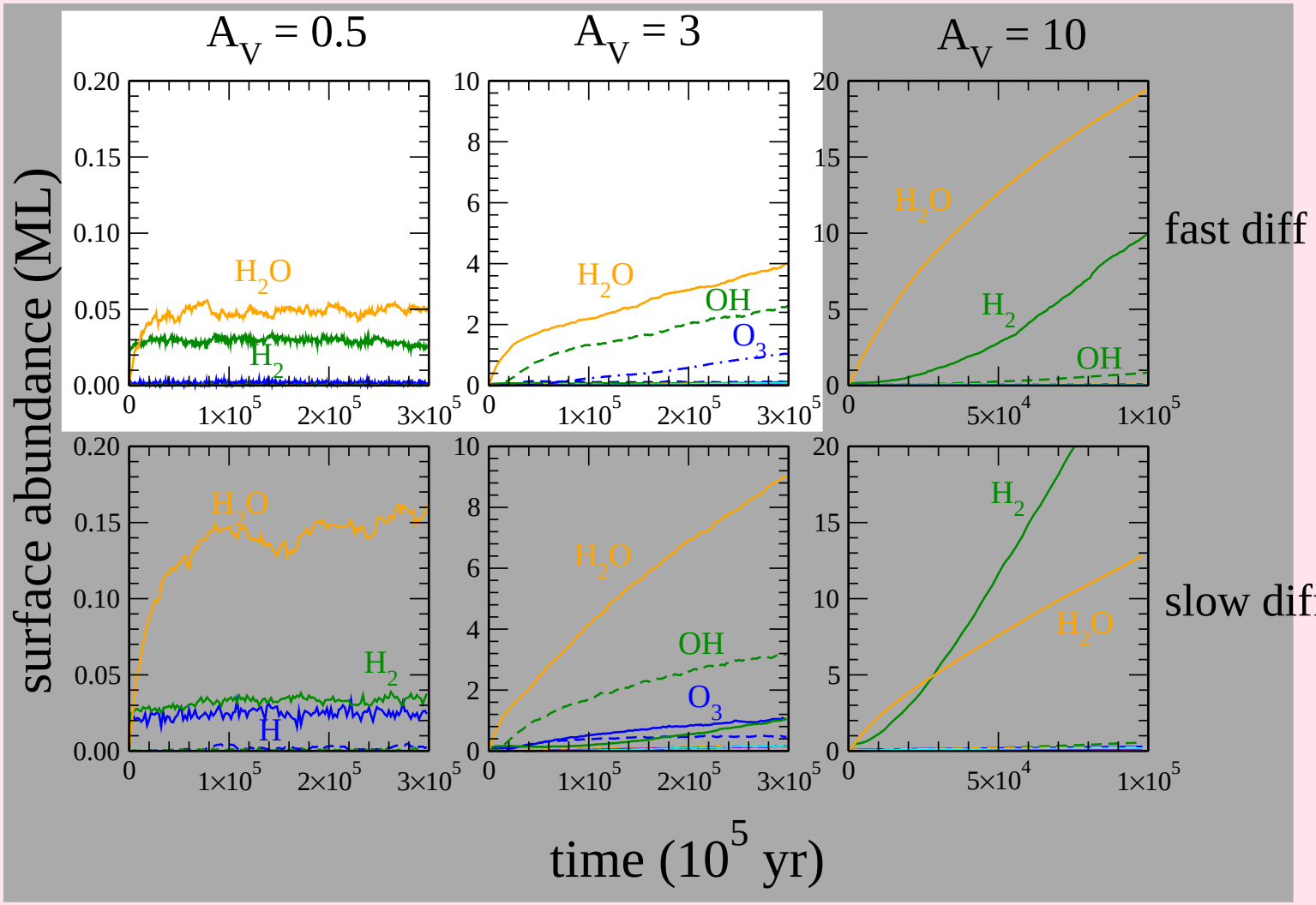


Snapshot of ice mantles

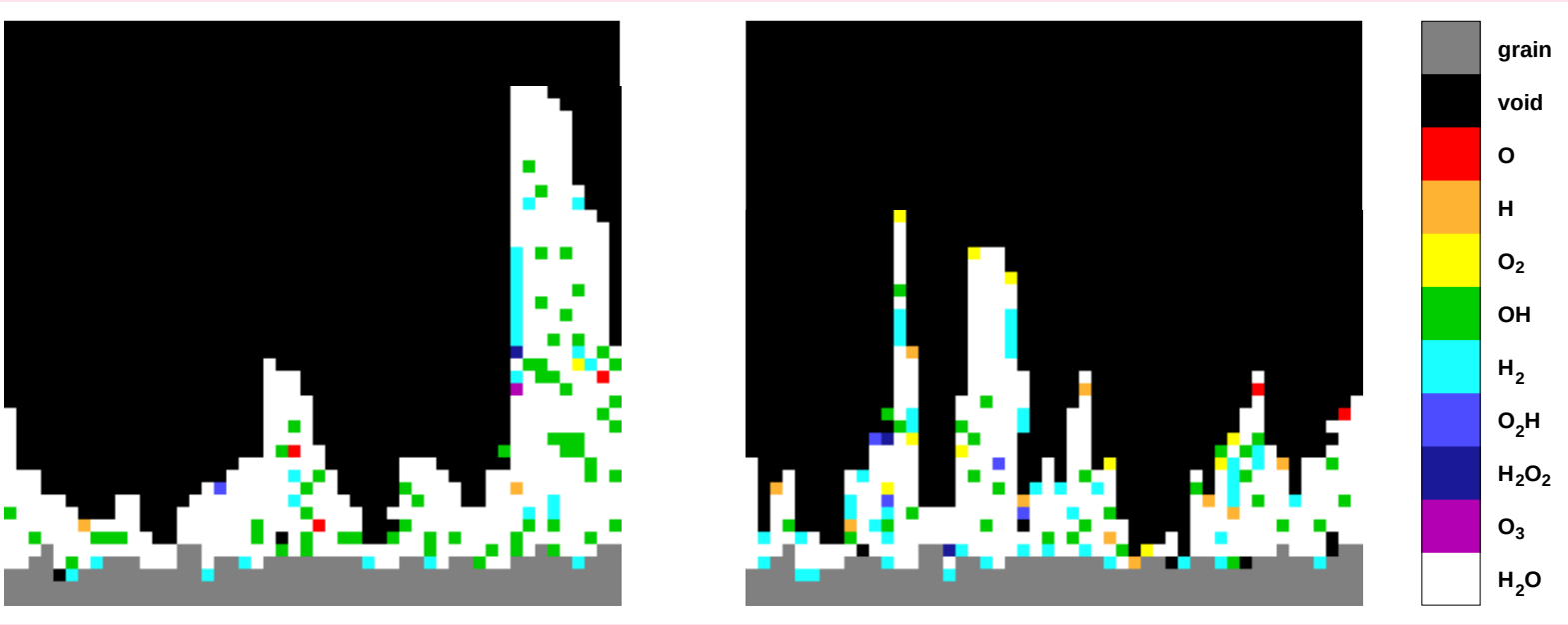


#	A_V	T_{grain}	T_{gas}	n(H)	form of H
A2	0.5	18	80	1.0(2)	H
B2	1	16	60	2.5(2)	H
C2	2	15	50	5.0(2)	H
D2	3	14	40	1.0(3)	H

Surface Abundance

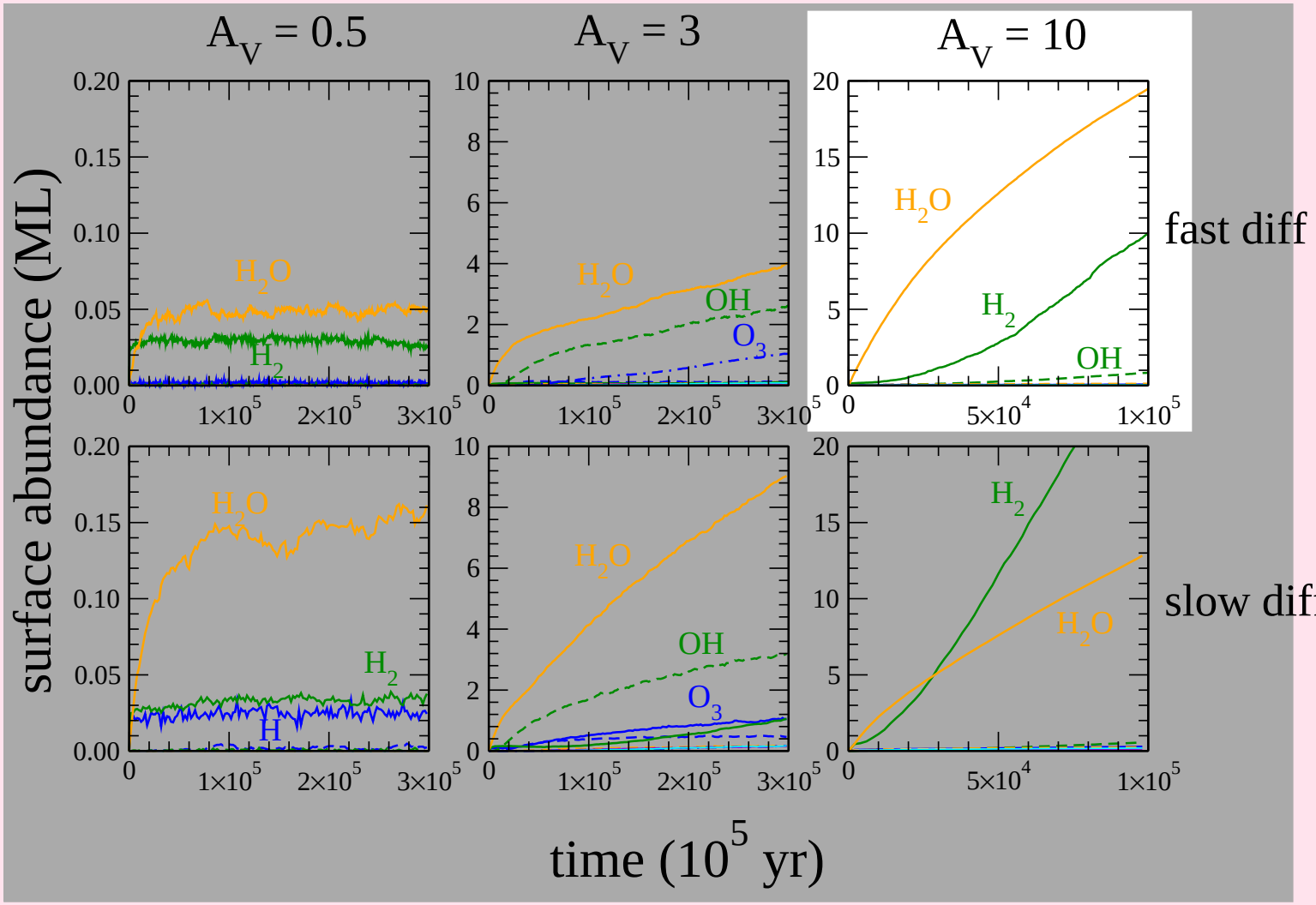


Snapshot of ice mantles



	A_V	T_{grain}	T_{gas}	n(H)	form of H
left	5	12	20	5.0(3)	H_2
right	10	10	10	2.0(4)	H_2

Surface Abundance

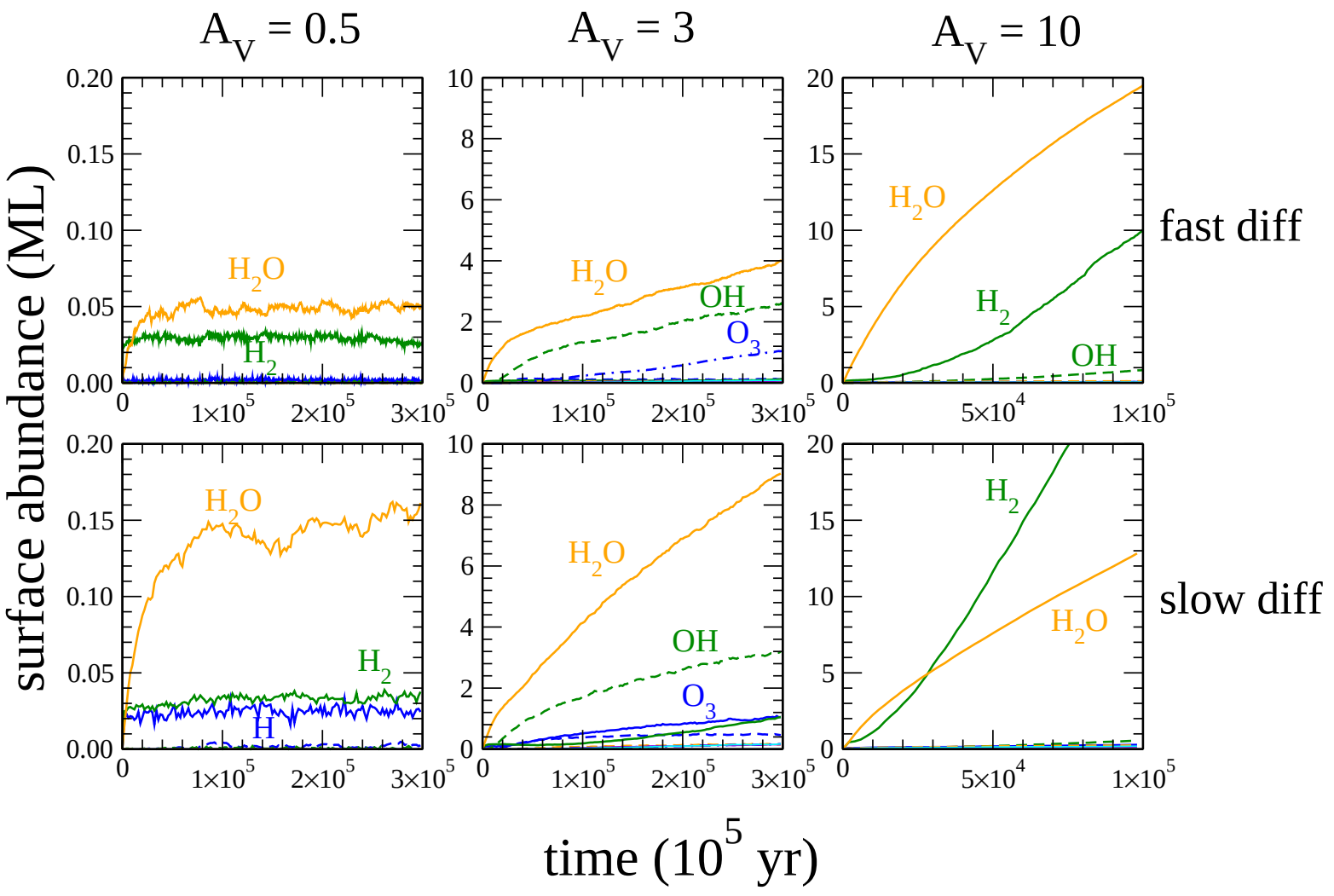


Desorption

Exact desorption energy only important for species with desorption temperature around simulated temperature. For ice formation only H and H_2.

Structure and porosity much more important.

Diffusion



Diffusion makes more compact ice. Formation increases for slow diffusion.

Surface reactions

Reaction	E_a (K)
$H + H \rightarrow H_2$	0
$H + O \rightarrow OH$	0
$H + OH \rightarrow H_2O$	0
$O + O \rightarrow O_2$	0
$H + O_2 \rightarrow O_2H$	1200[1]
$H + O_2H \rightarrow H_2O_2$	0
$H + O_3 \rightarrow O_2 + OH$	450[2]
$H + H_2O_2 \rightarrow H_2O + OH$	1400[3]
$H_2 + OH \rightarrow H_2O + H$	2600[4]
$O + O_2 \rightarrow O_3$	0

[1] Melius & Blint (1979) [2] Klemm et al. (1975) [3] Lee et al. (1978) [4] Schiff (1973)

Formation Reactions

Different physical conditions

		1			2			3			4	
H rich	A	99.9	0.0	0.1	99.6	0.0	0.4	95.9	0.0	4.2	99.5	0.0	0.5
	B	99.5	0.0	0.5	98.3	0.0	1.7	96.4	0.0	3.6	98.5	0.1	1.4
	C	98.4	0.5	1.1	97.1	0.8	2.0	93.1	1.0	5.9	95.9	1.3	2.9
	D	97.6	1.4	1.0	93.4	1.4	5.2	90.5	1.6	7.9	93.2	0.9	5.9
H_2 rich	E	14.3	21.0	64.7	11.6	19.3	69.1	7.0	16.7	76.3	9.7	18.3	72.0
	F	10.1	18.7	71.2	6.5	16.7	76.8	6.2	16.5	77.2	6.7	16.2	77.1

diffuse

translucent

dense

Note. — From left to right: $H + OH \rightarrow H_2O$, $H + H_2O_2 \rightarrow H_2O + OH$, and $H_2 + OH \rightarrow H_2O + H$.

Cuppen & Herbst, ApJ, 668 (2007) 294

Surface reactions

Reaction			E_a (K)
H + H	$\rightarrow H_2$		0
H + O	$\rightarrow$ OH		0
H + OH	$\rightarrow H_2O$		0
O + O	$\rightarrow O_2$		0
H + O_2	$\rightarrow O_2H$		1200[1]
H + O_2H	$\rightarrow H_2O_2$		0
H + O_3	$\rightarrow O_2$	+ OH	450[2]
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O + O_2	$\rightarrow O_3$		0

[1] Melius & Blint (1979) [2] Klemm et al. (1975) [3] Lee et al. (1978) [4] Schiff (1973)

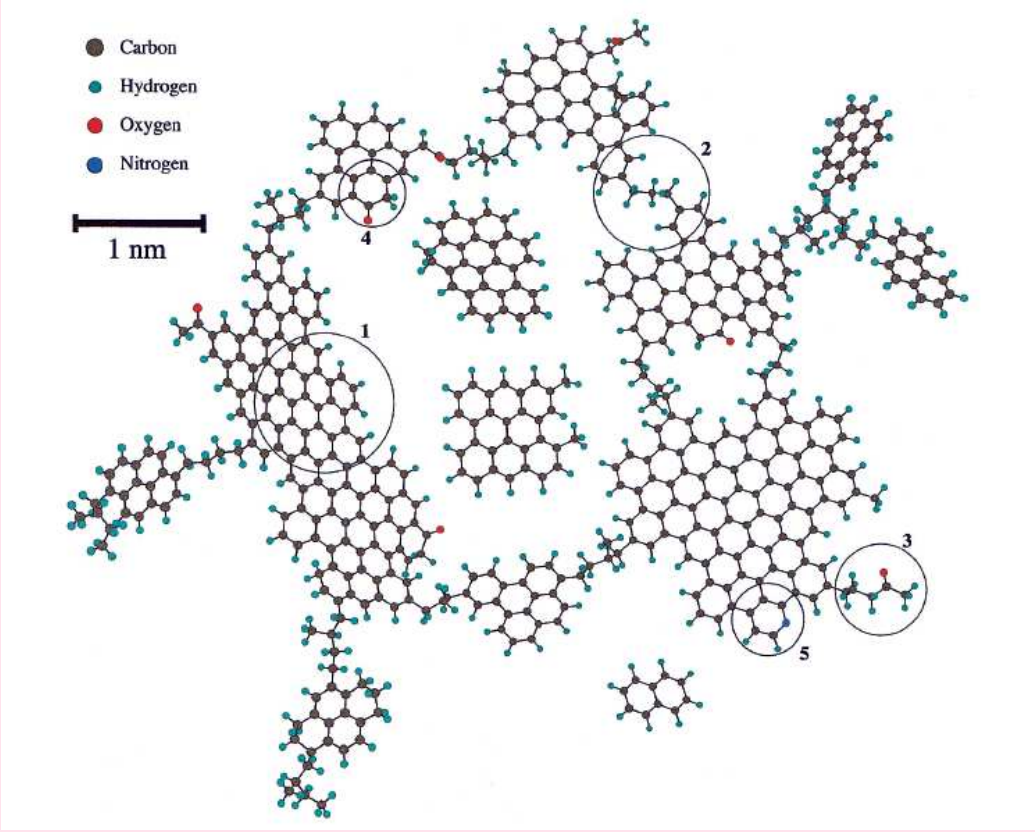
$O_2 + H$

- Water is formed
- H_2O_2 is intermediate
- Very strong temperature dependence with peak at 25 K

H_2 formation in warm regions

H atom is chemically bonded to the grain and does not diffuse

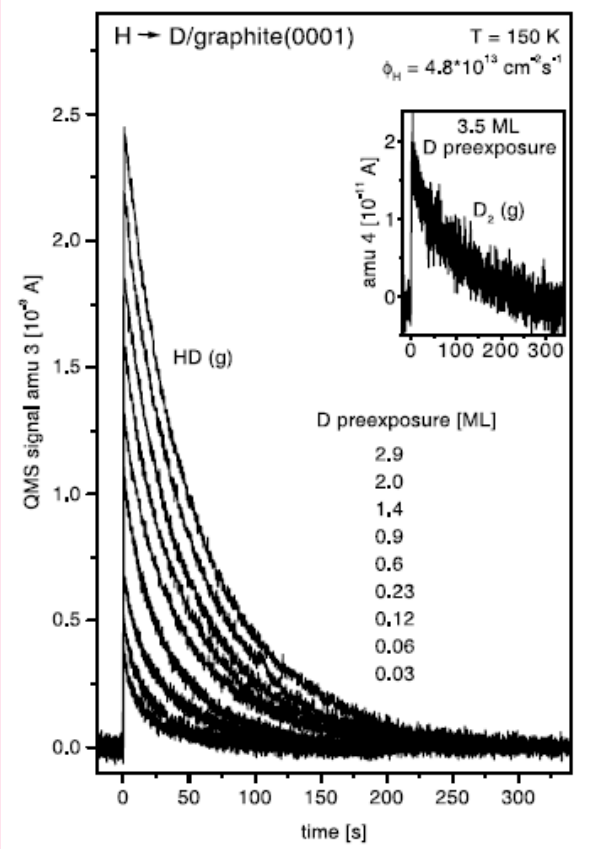
Graphite + H is model system



Pendleton & Allamandola, ApJ 135 (2002) 75

Hydrogen abstraction

Known D coverage exposed to H forming HD



Hydrogen abstraction

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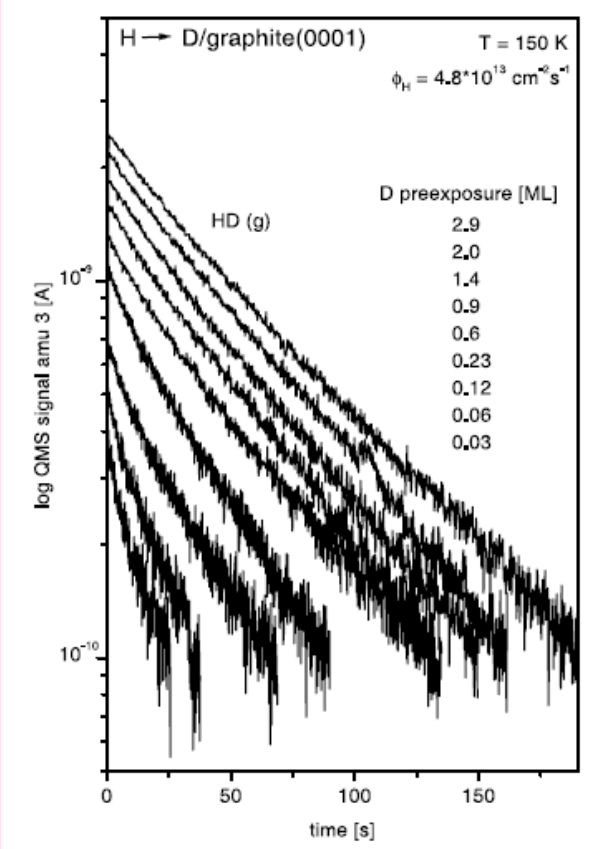


$$\frac{\mathrm{d}[\mathrm{HD}]}{\mathrm{d}t} = \sigma\Phi[\mathrm{D}]_0 \exp\left(-\sigma\Phi t\right)$$

$\frac{\mathrm{d}[\mathrm{HD}]}{\mathrm{d}t}$:HD formation rate

σ :cross section

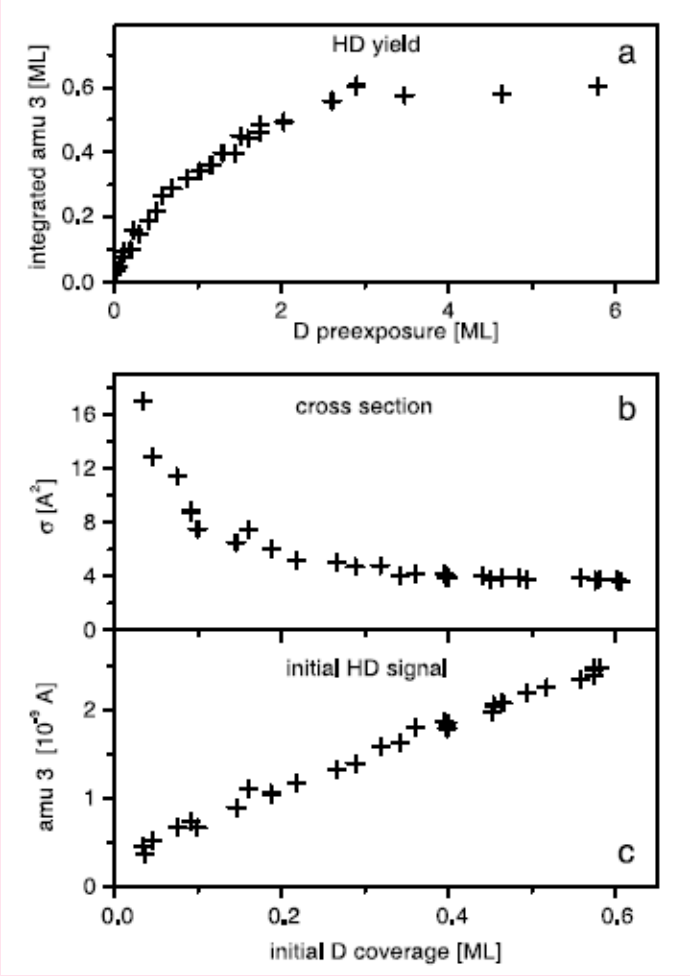
Φ :flux

$[\mathrm{D}]_0$:initial D coverage

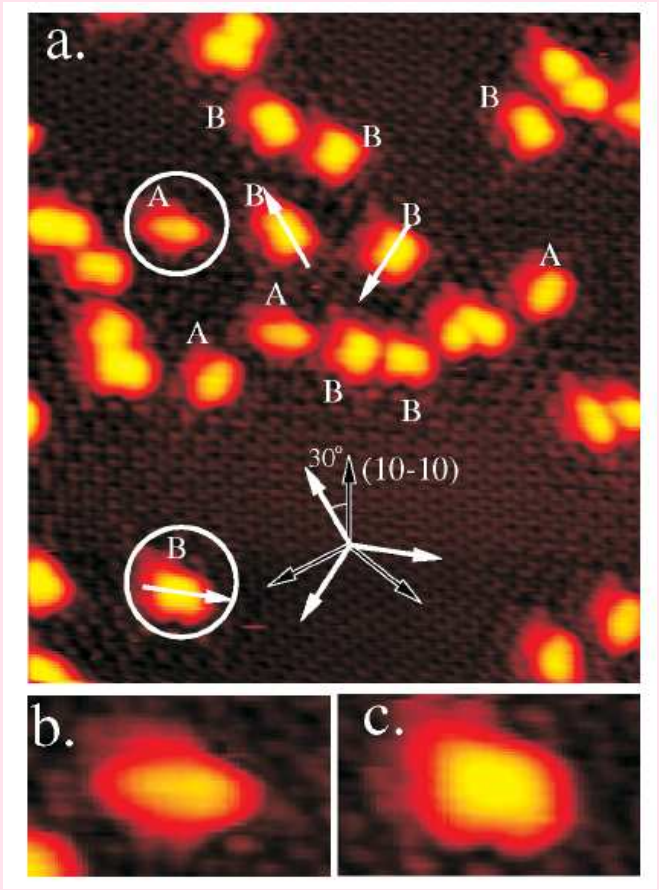
HD formation rate as a function of time

Zecho et al, Chem Phys Lett, 366 (2002) 188

Hydrogen abstraction



Zecho et al, Chem Phys Lett, 366 (2002) 188

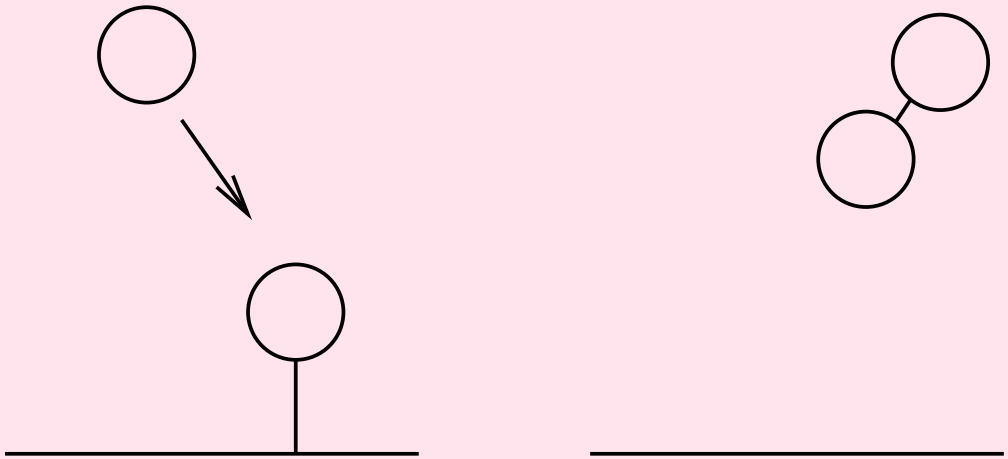


~85 % of atoms in dimer conf. at 0.01 ML

Hornekær et al. PRL 96, 156104 (2006)

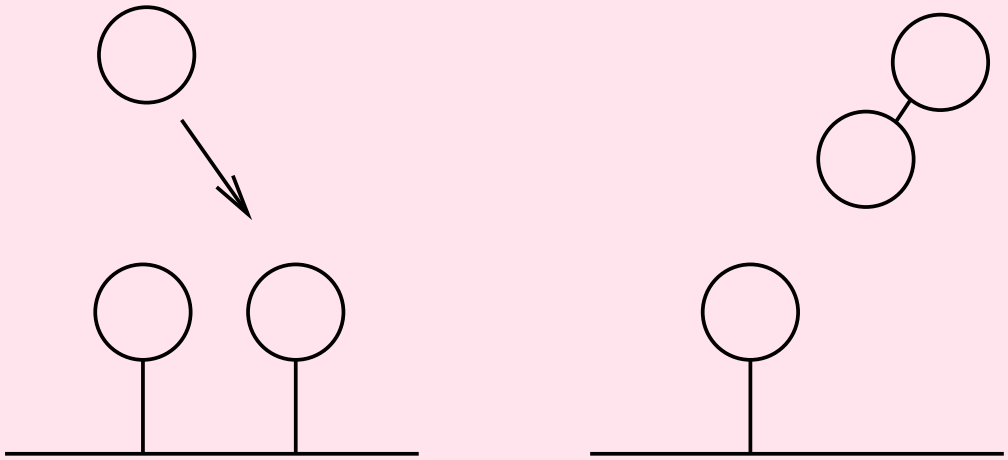
Mechanism 1

Direct Eley-Rideal



Mechanism 2

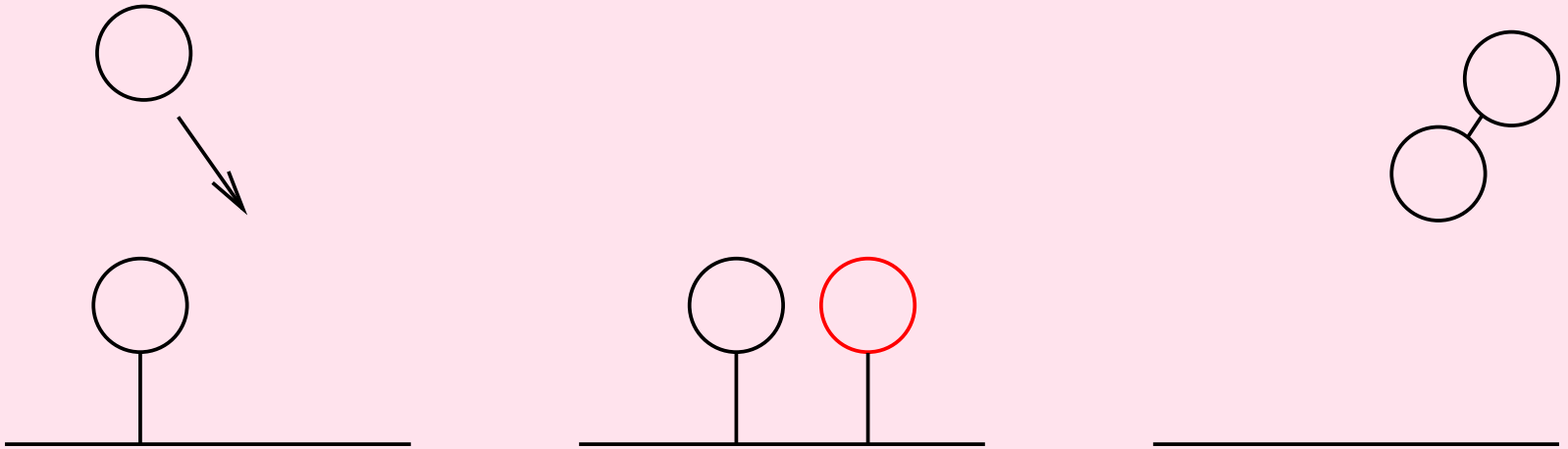
Dimer Eley-Rideal



Bachellerie et al., submitted to Chem. Phys. Lett.

Mechanism 3

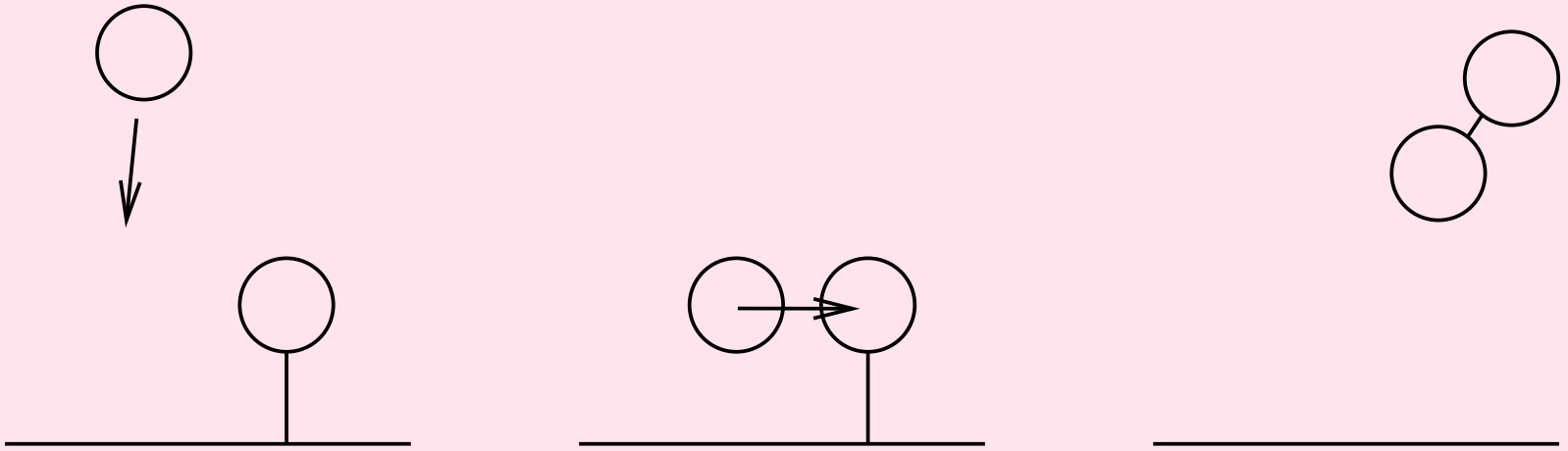
Dimer mediated abstraction



Cuppen & Hornekær, submitted to JCP

Mechanism 4

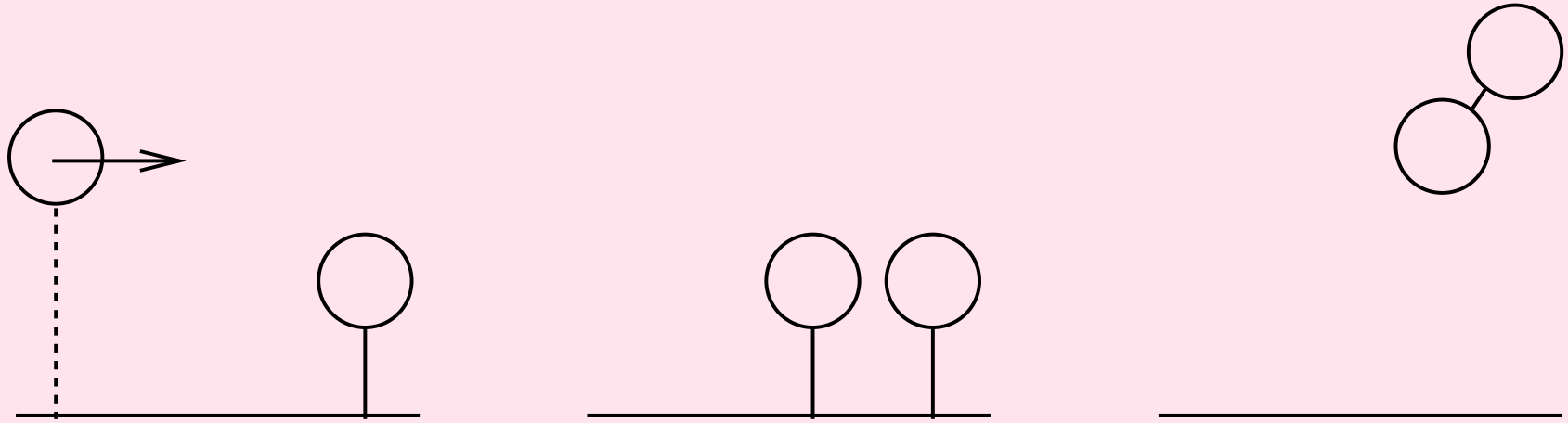
Eley-Rideal with steering



Sha & Jackson, Surf. Sci., 496 (2002) 318

Mechanism 5

Fast diffusion of physisorbed atoms in combination with direct Eley-Rideal

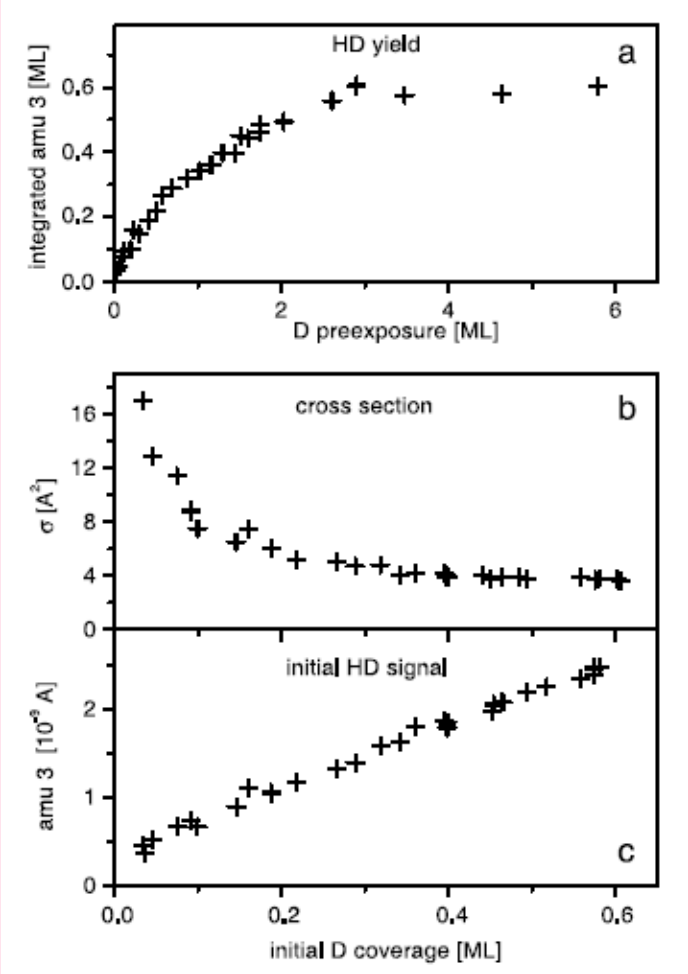


Bonfanti et al., JPC C, 111 (2007) 5825

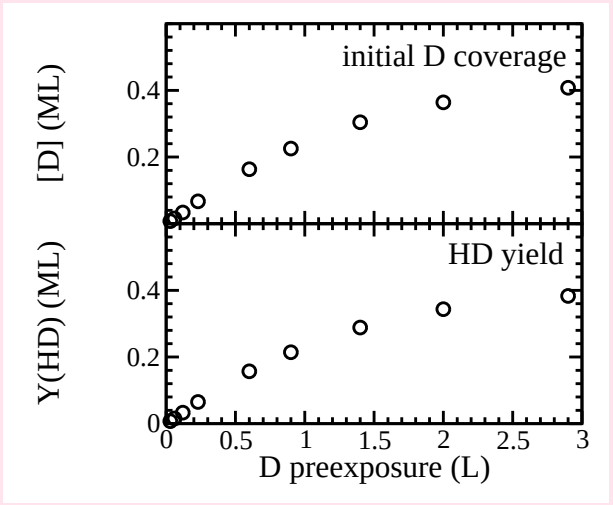
Results

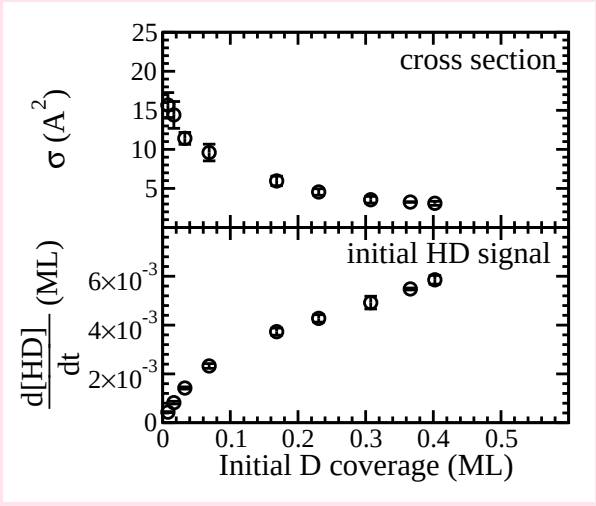
Mech.	E_{mono} (meV)	R_{hop} (s^{-1})	Cross section low $[D]_0$ (Å^2)	Cross section high $[D]_0$ (Å^2)	Correlation coefficient	$[D]_0$ (2.9 L) (ML)	Dimers %
1	9		4.3 ± 0.1	2.45 ± 0.12	0.999	0.48	13
	18		8.2 ± 0.4	2.62 ± 0.06	0.992	0.48	13
2			0.0 ± 0.0	2.58 ± 0.21	0.998	0.52	21
3			18.9 ± 5.6	1.68 ± 0.01	0.120	0.88	29
4	9		14.7 ± 1.4	11.38 ± 0.47	0.996	0.10	11
5	9	$1.3 \cdot 10^{13}$	12.0 ± 2.1	2.69 ± 0.03	0.977	0.46	32
	18	$1.3 \cdot 10^{13}$	9.2 ± 2.4	2.45 ± 0.02	0.989	0.47	32
	9	$5.0 \cdot 10^{13}$	9.7 ± 0.3	2.75 ± 0.03	0.984	0.46	52
	18	$5.0 \cdot 10^{13}$	6.4 ± 0.2	2.64 ± 0.01	0.982	0.47	53
1 + 2	9		6.1 ± 0.8	2.74 ± 0.12	0.999	0.47	21
1 + 3	9		11.7 ± 0.7	2.86 ± 0.12	0.986	0.41	30
3 + 4	9		16.5 ± 1.0	11.04 ± 0.44	0.994	0.08	27
3 + 5	9	$1.3 \cdot 10^{13}$	15.7 ± 2.4	3.05 ± 0.15	0.971	0.40	55
	18	$1.3 \cdot 10^{13}$	10.5 ± 1.9	2.72 ± 0.20	0.987	0.43	53
	9	$5.0 \cdot 10^{13}$	15.7 ± 1.6	3.09 ± 0.26	0.980	0.40	74
	18	$5.0 \cdot 10^{13}$	10.9 ± 0.7	2.77 ± 0.08	0.985	0.43	76
4 + 5	9	$1.3 \cdot 10^{13}$	14.9 ± 1.3	10.51 ± 0.20	0.998	0.12	30
	18	$1.3 \cdot 10^{13}$	11.6 ± 1.0	9.10 ± 0.19	0.996	0.13	30
	9	$5.0 \cdot 10^{13}$	12.9 ± 0.4	10.39 ± 0.32	0.997	0.13	50
	18	$5.0 \cdot 10^{13}$	11.3 ± 0.7	9.10 ± 0.41	0.997	0.14	51
Exp. (Zecho et al.)			17	4		0.4 ± 0.2	
Exp. (Hornekær et al.)							$\sim$85

Cross section



Zecho et al, Chem Phys Lett, 366 (2002) 188





Simulated Cuppen & Hornekær, JCP, submitted

Conclusions

- For surface modelling many parameters are still unknown, but with some reasonable assumptions useful results can be obtained.
- Diffusion is very important and should be studied in more detail.
- Not only parameters with uncertainties. Mechanisms sometimes not known.
- Modelling can help for interpretation of experimental results and finding underlying mechanisms.
- Hard to give simple temperature dependence of surface reaction rates. Many parameter problem.

Acknowledgments

- NSF, Leiden Observatory, and NWO for funding
- Sackler Laboratory in Leiden
- ... and you for your attention.