Monte Carlo Simulations of Water Ice

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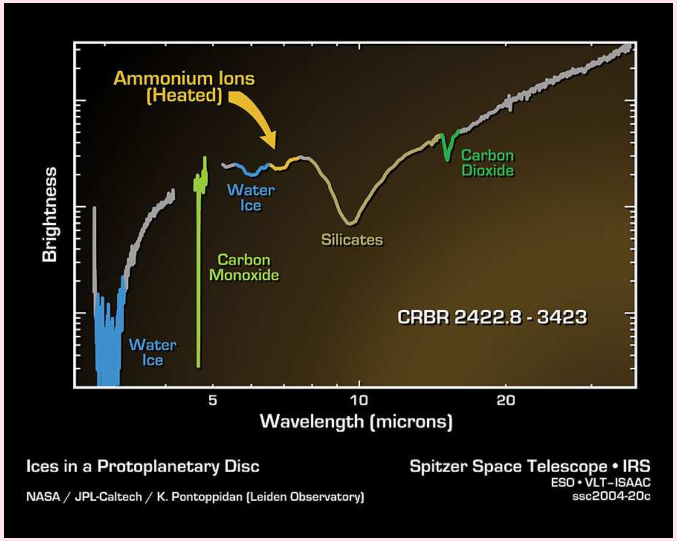
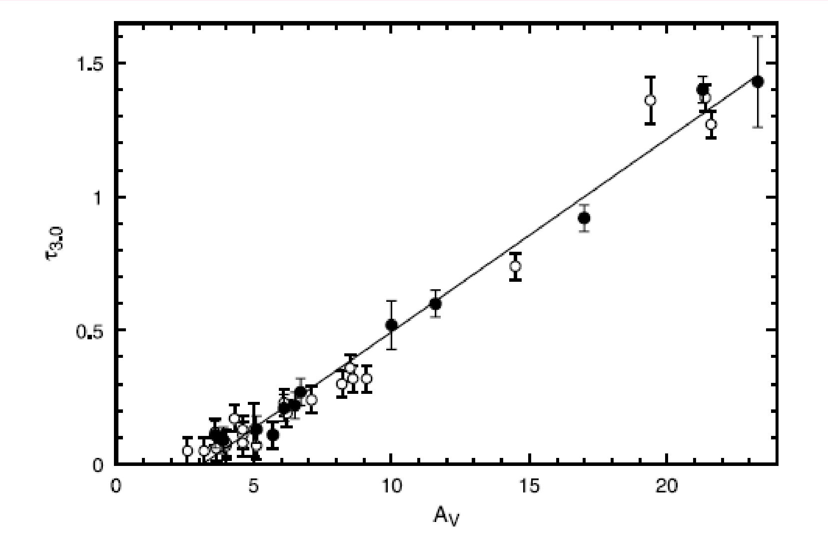
Water ice in Molecular Clouds





Whittet, ApJ (2001) 547, 872

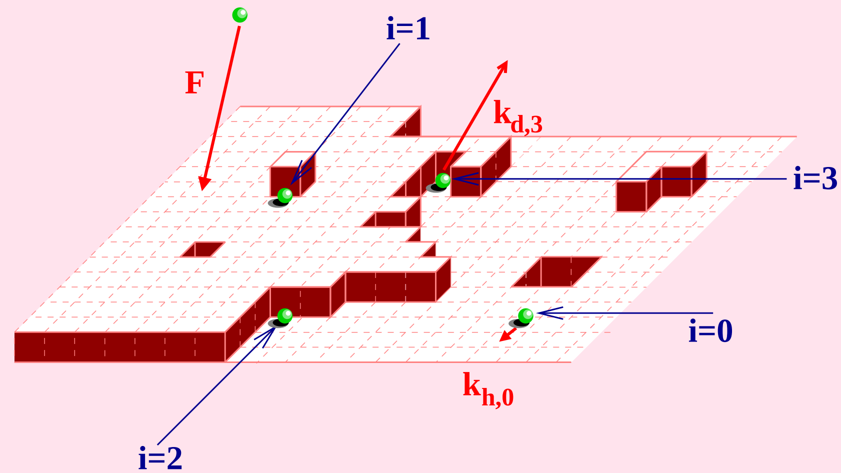
Threshold value of $A_V = 3$

Contents

- CTRW-Monte Carlo technique
- Water ice formation
  - ⋆ Morphologies
  - ⋆ Temperature regimes
  - ⋆ Time evolution
- Water ice desorption
  - ⋆ Theory
  - ⋆ Experiments
  - ⋆ MONTY
  - ⋆ Simulations results

Monte Carlo simulations

- START
- Choose surface structure and possible reactions
- Determine all possible events and probabilities
- Calculate a time for each new event (t = ln[X/R])
- Determine first event
- Evaluate event and update time
- t > t(end) ?
  - no → Determine new possible events and probabilities → Calculate a time for each new event
  - yes → STOP

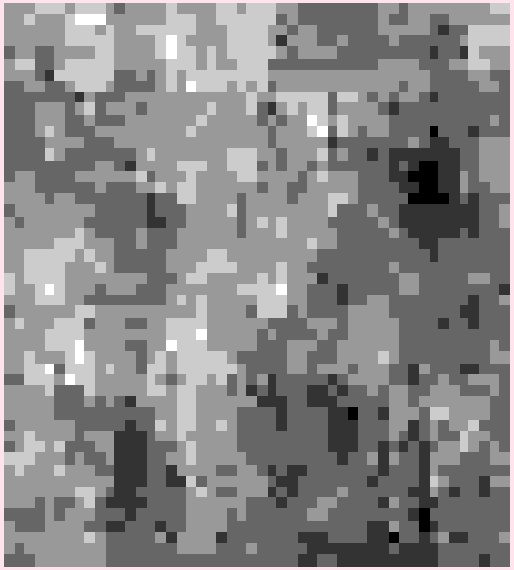


$$R_{hop} = \nu \exp\left(-\frac{E_b(i)}{kT}\right)$$

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

Monte Carlo simulations

Monte Carlo simulations

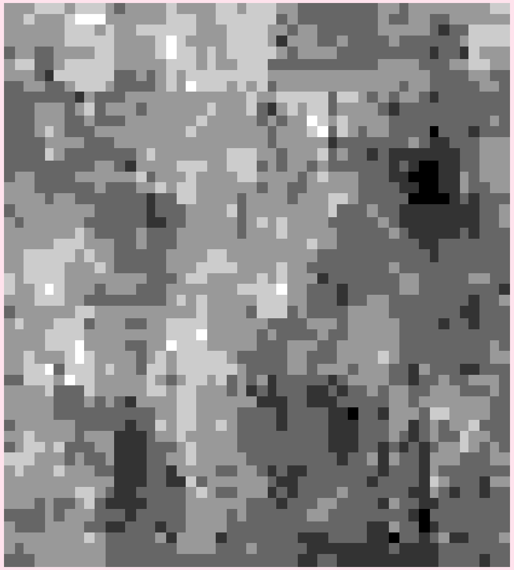


- Surface structure can be included
- Individual atoms can be followed
- Topological effect can be taken into account
- High demand of cpu

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
- 0.9% of products desorb upon reaction (Andersson et al. (2006))

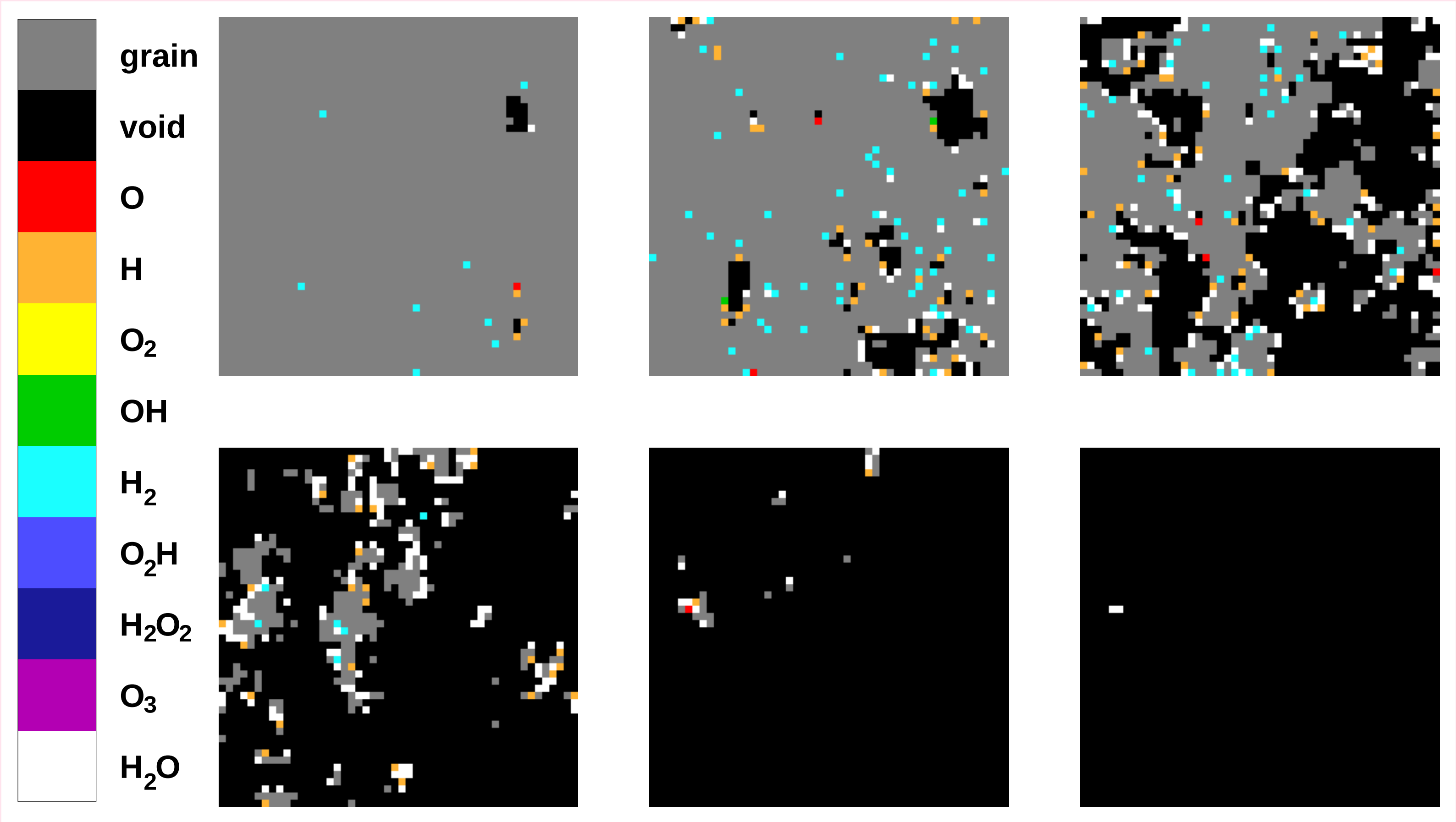
Surface



$$k^{\mathsf{A}}_{hop} = \nu \exp\left(-\frac{0.5E^{\mathsf{A}} + \alpha i_c E^{\mathsf{A}}_c + \alpha i_{\mathsf{H_2O}} E^{\mathsf{A}}_{\mathsf{H_2O}}}{kT}\right)$$

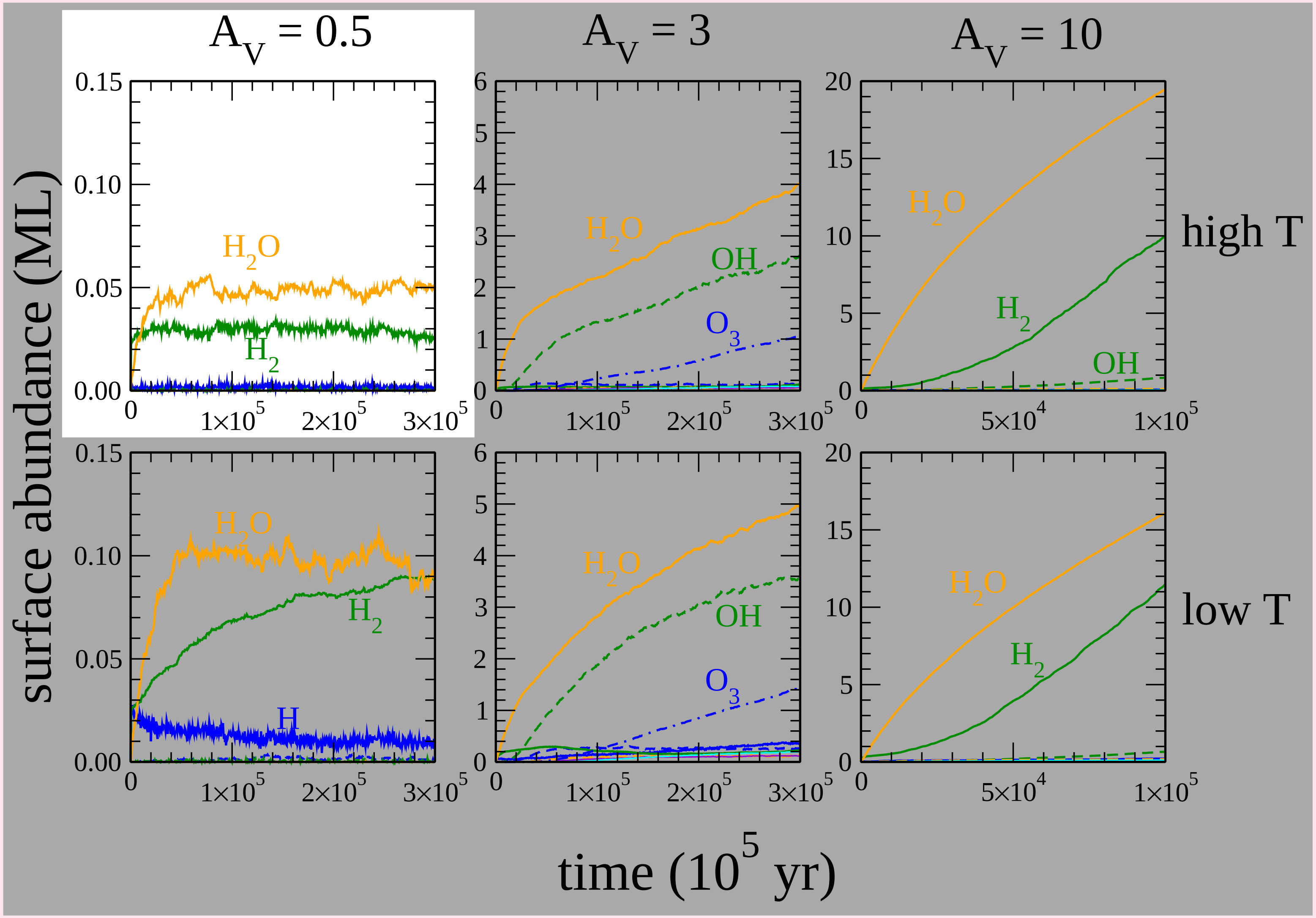
$$k^{\mathsf{A}}_{eva} = \nu \exp\left(-\frac{E^{\mathsf{A}} + \alpha i_c E^{\mathsf{A}}_c + \alpha i_{\mathsf{H_2O}} E^{\mathsf{A}}_{\mathsf{H_2O}}}{kT}\right)$$

Snapshot of ice mantles

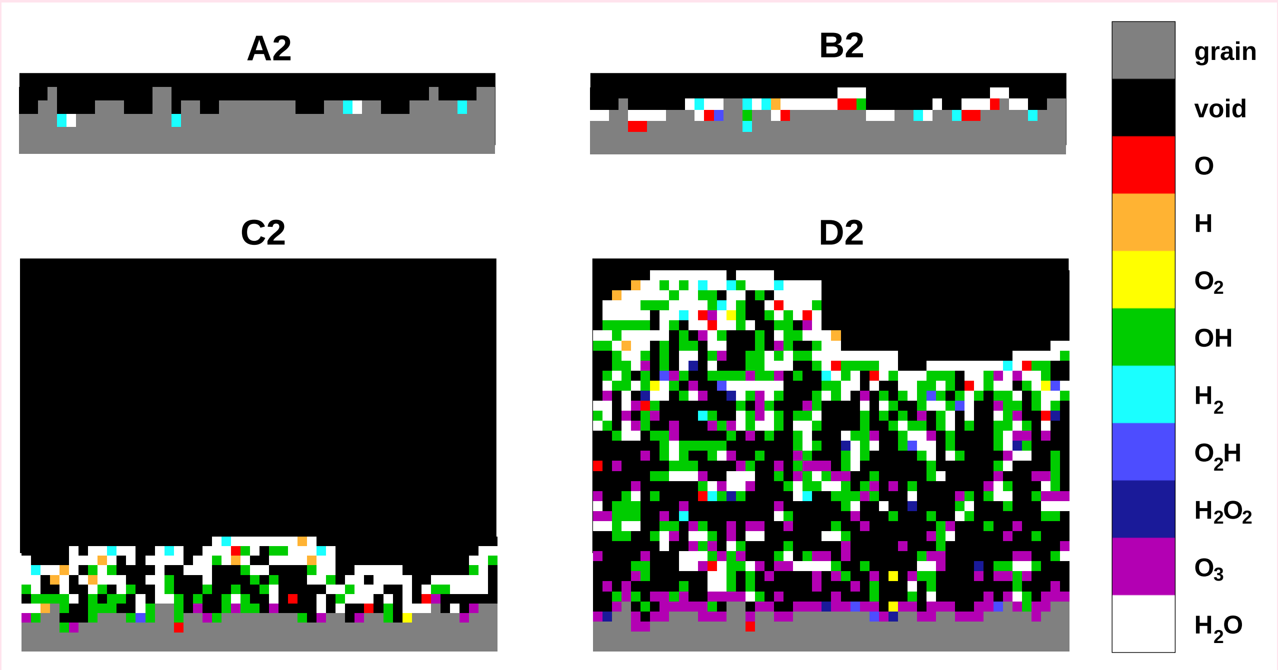


A_V	T_{grain}	T_{gas}	n(H)	form of H
0.5	18	80	1.0(2)	H

Surface Abundance

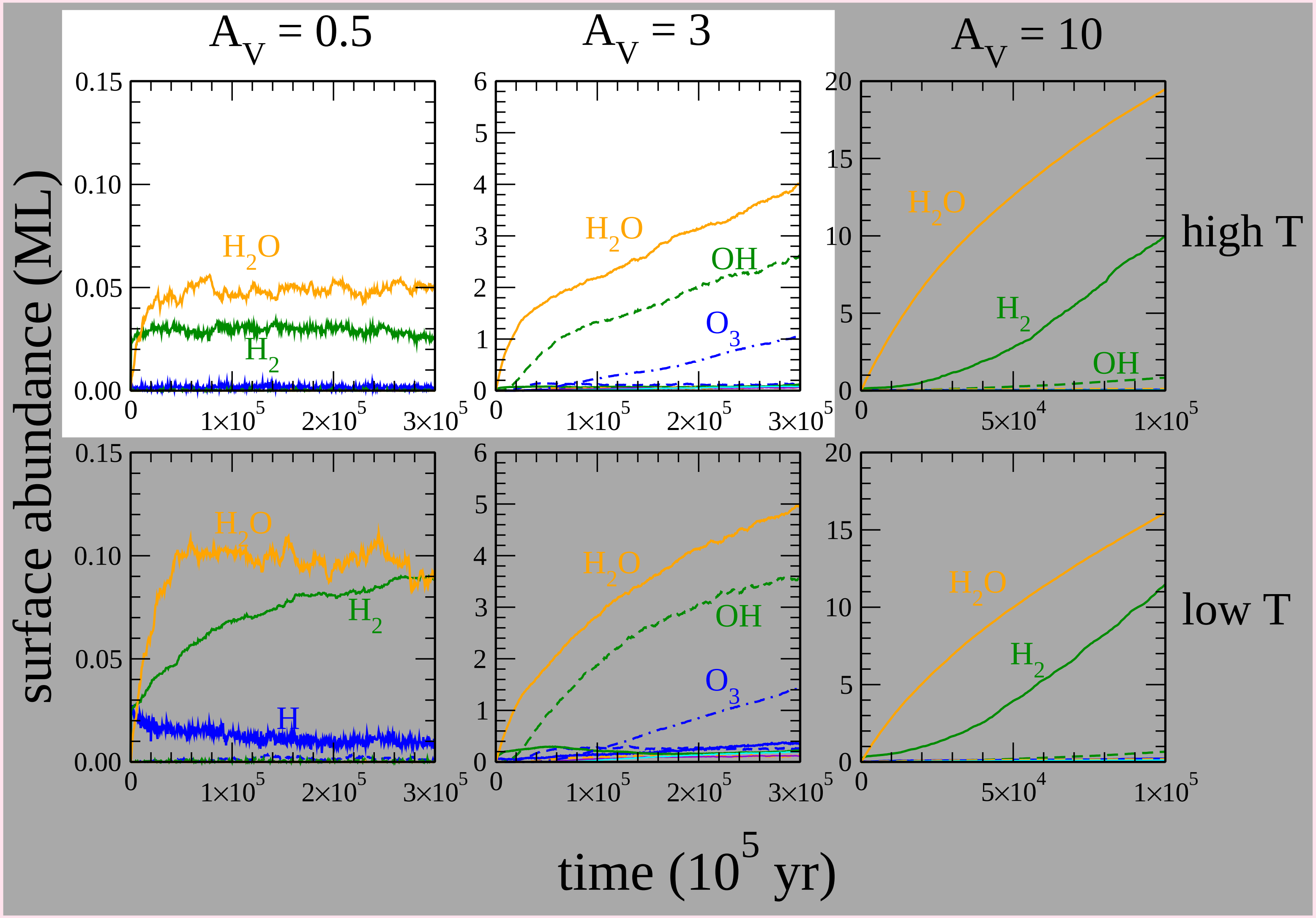


Snapshot of ice mantles

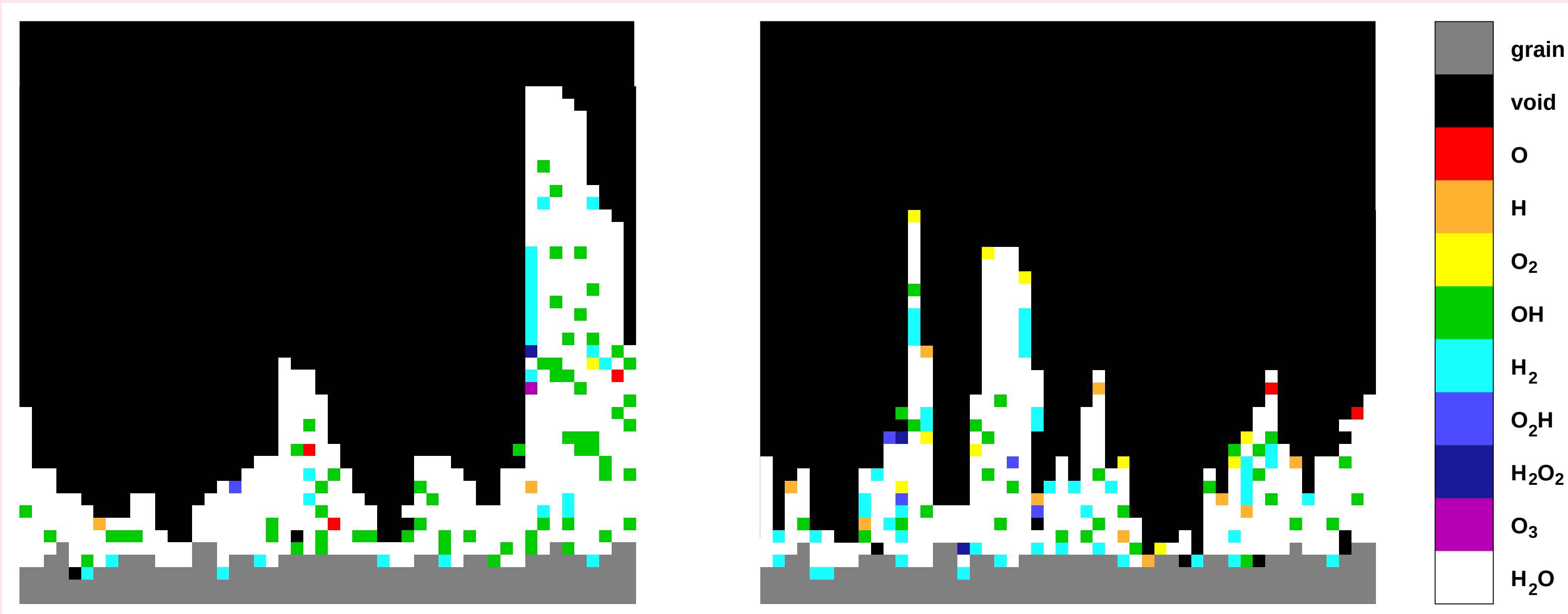


#	A_V	T_{grain}	T_{gas}	n(H)	form of H
A2	0.5	18	80	1.0(2)	H
B2	1	16	60	2.5(2)	H
C2	2	15	50	5.0(2)	H
D2	3	14	40	1.0(3)	H

Surface Abundance

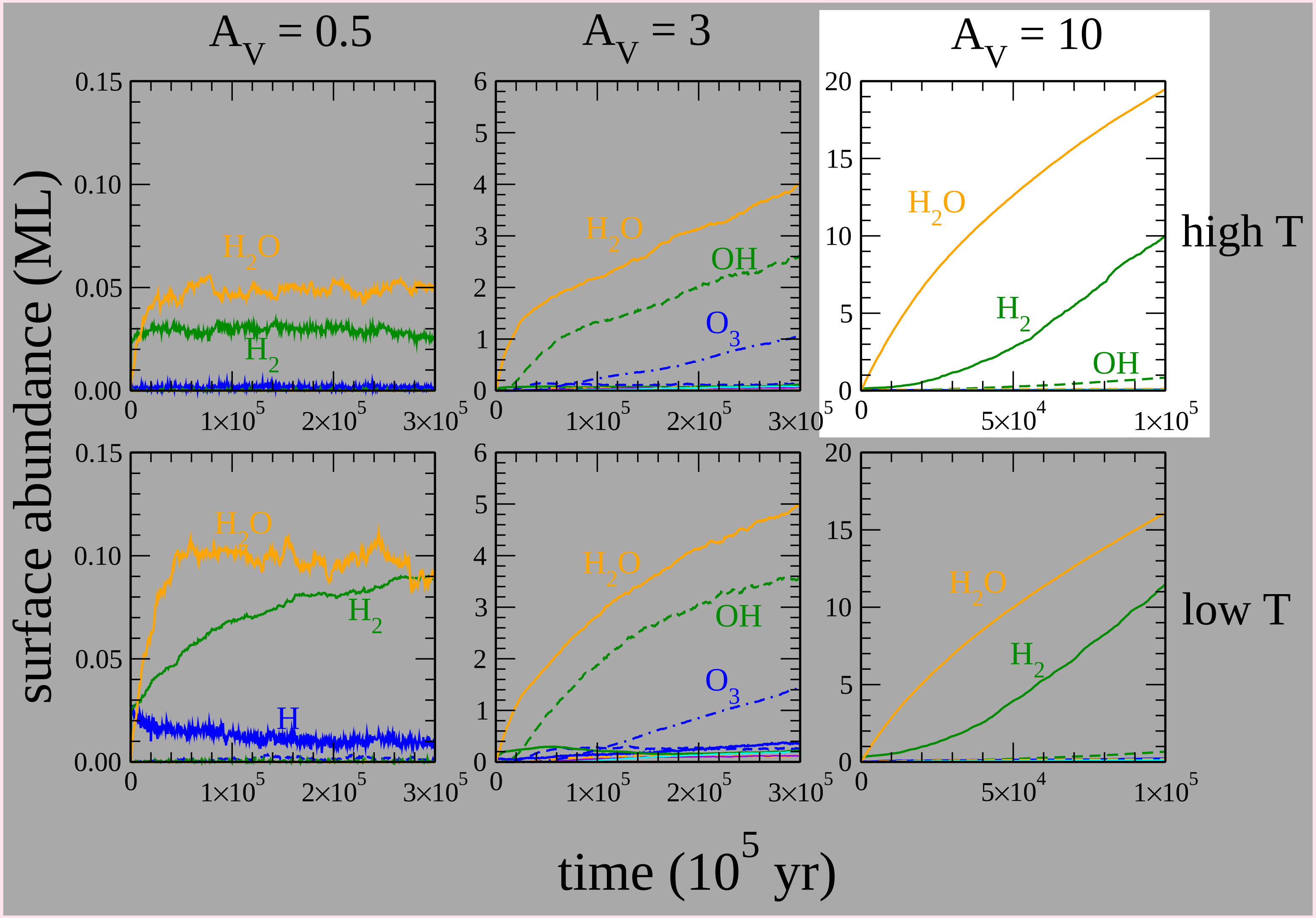


Snapshot of ice mantles

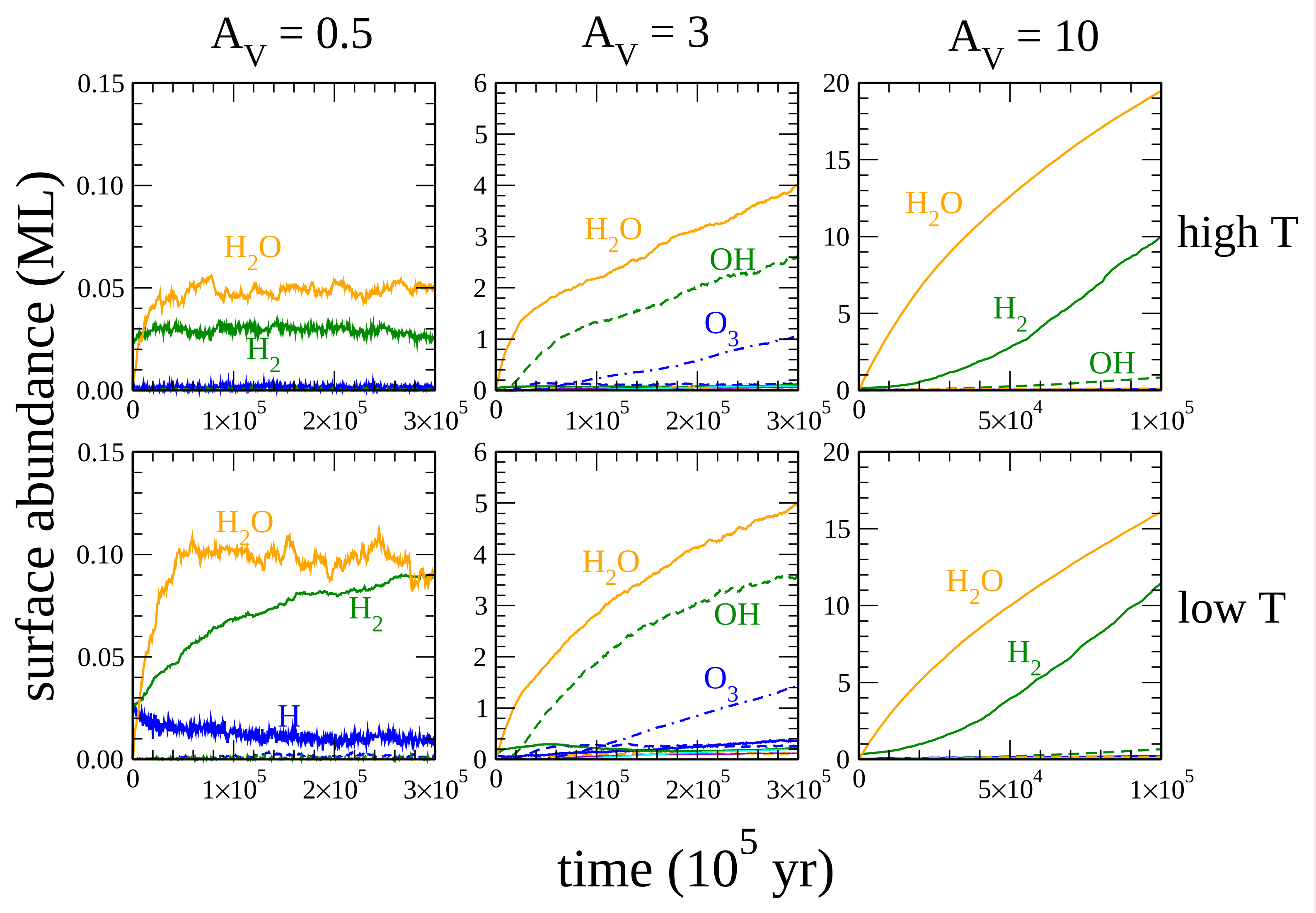


	A_V	T_{grain}	T_{gas}	n(H)	form of H
left	5	12	20	5.0(3)	H_2
right	10	10	10	2.0(4)	H_2

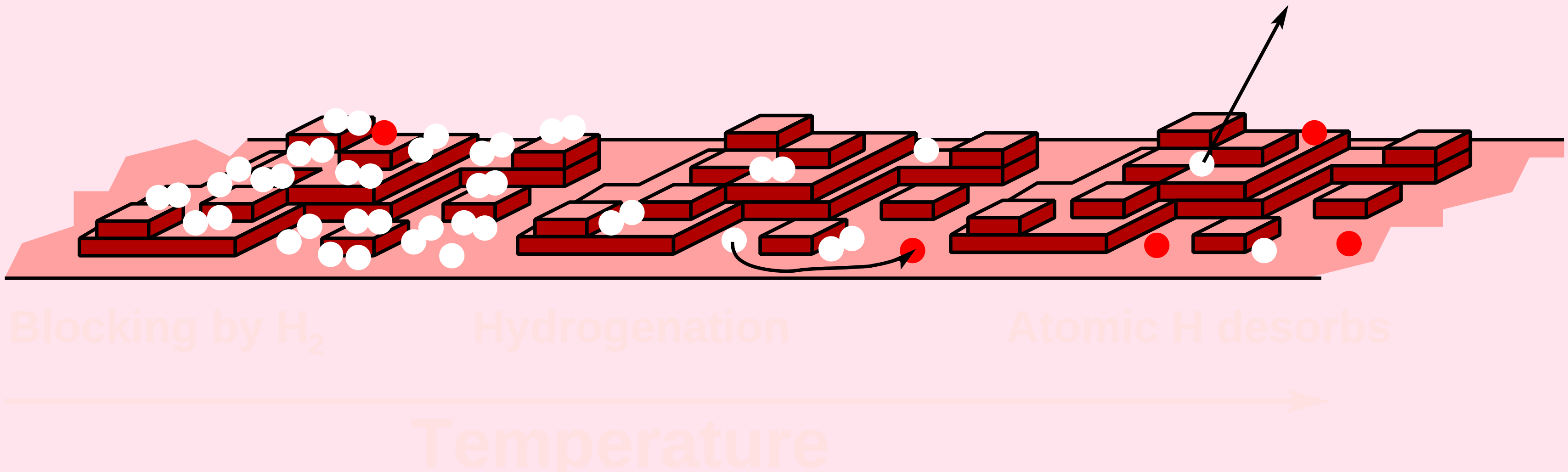
Surface Abundance



Surface Abundance

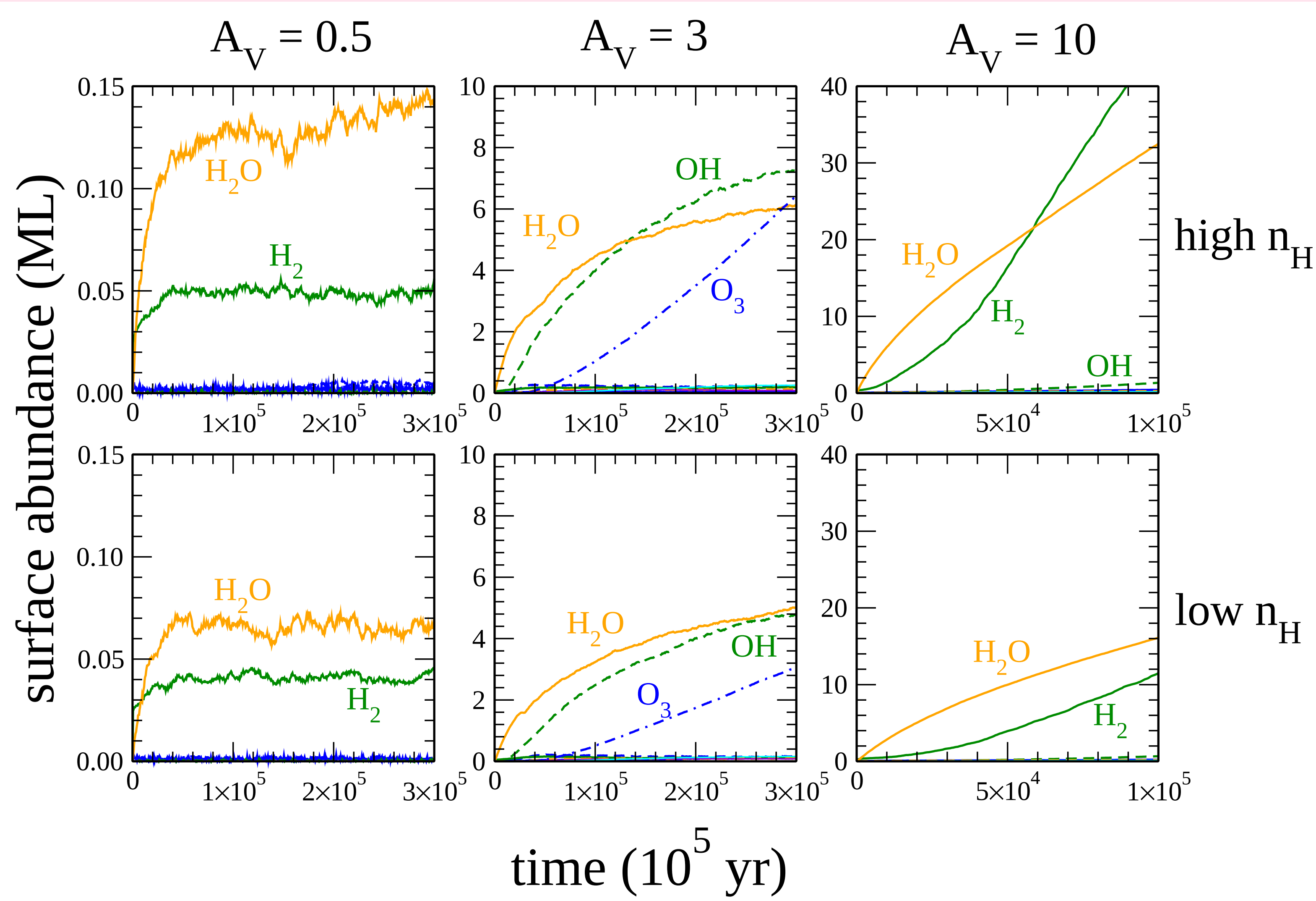


Temperature Dependence



Three regimes

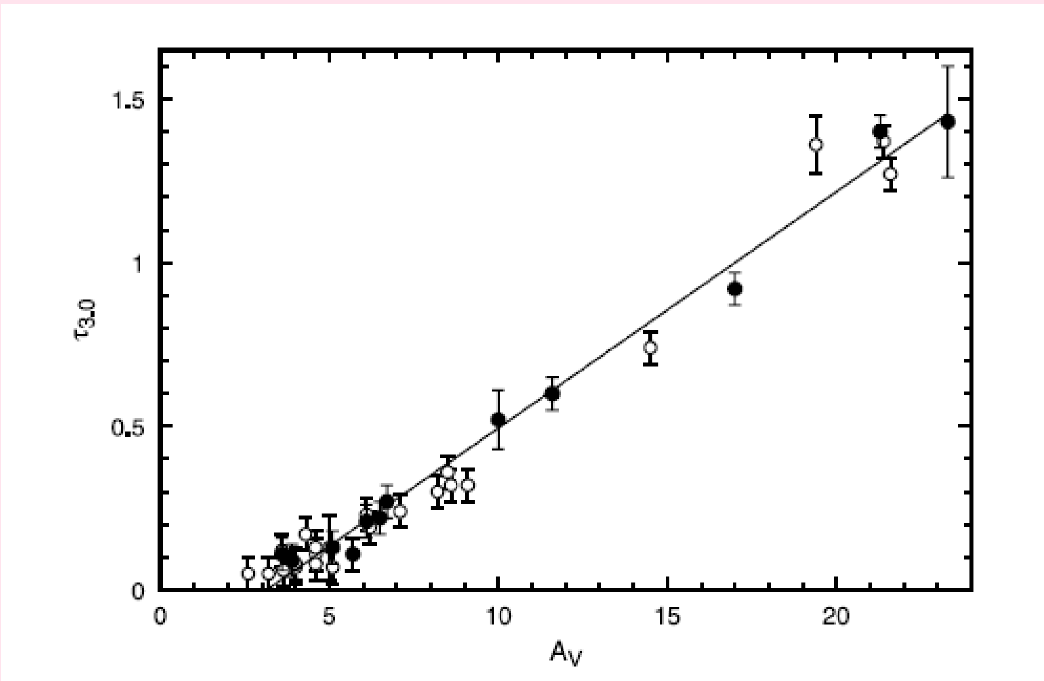
Density Dependence



Interstellar ice vs extinction

Whittet, ApJ (2001) 547, 872

Threshold value of $A_V = 3$



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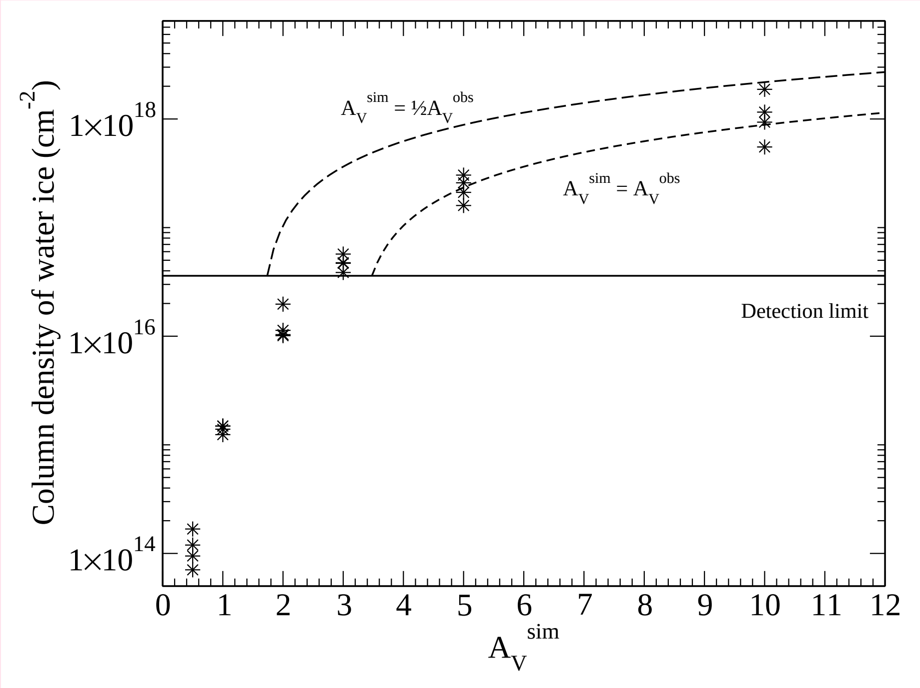

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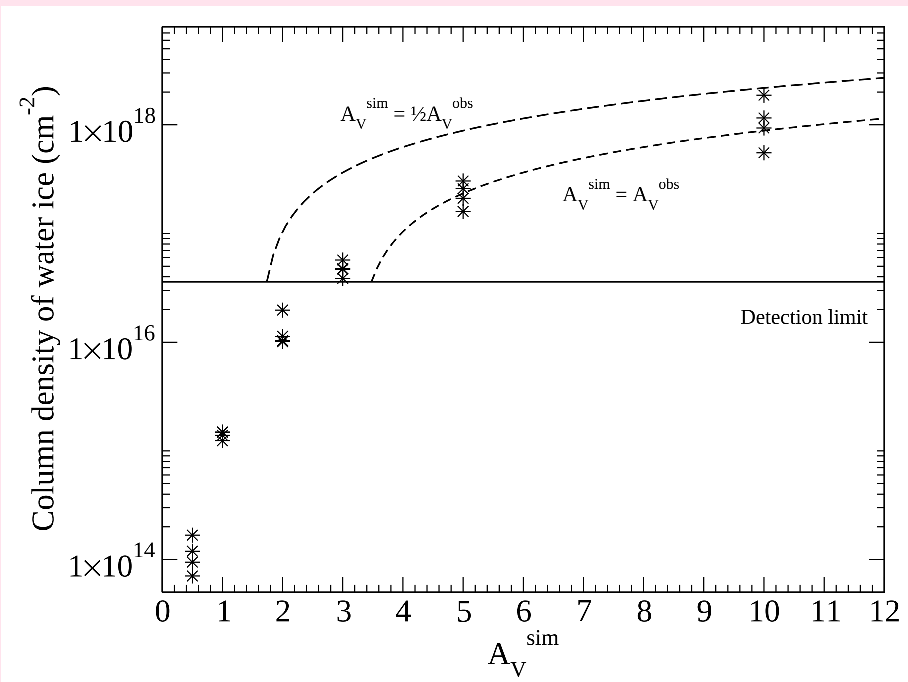
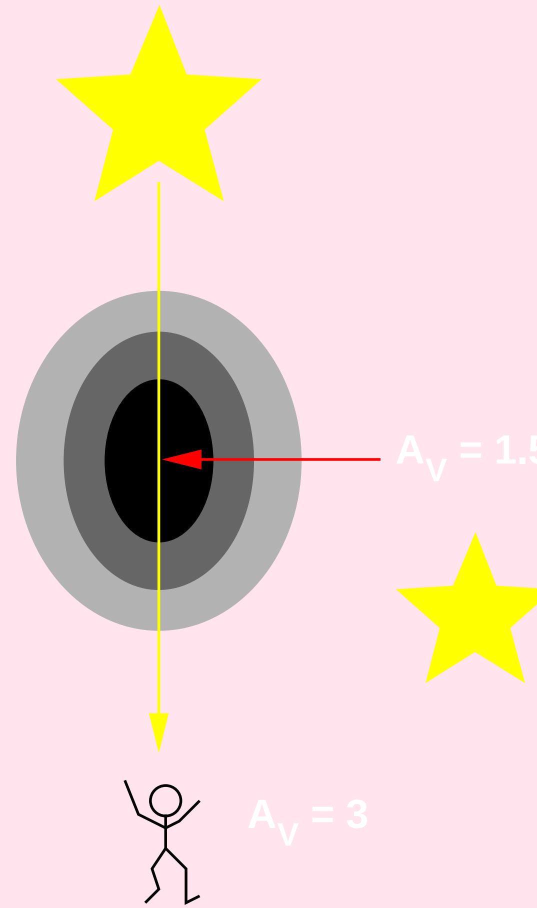




Surface reactions

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)

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

	1			2			3			4		
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
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

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, in press

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)

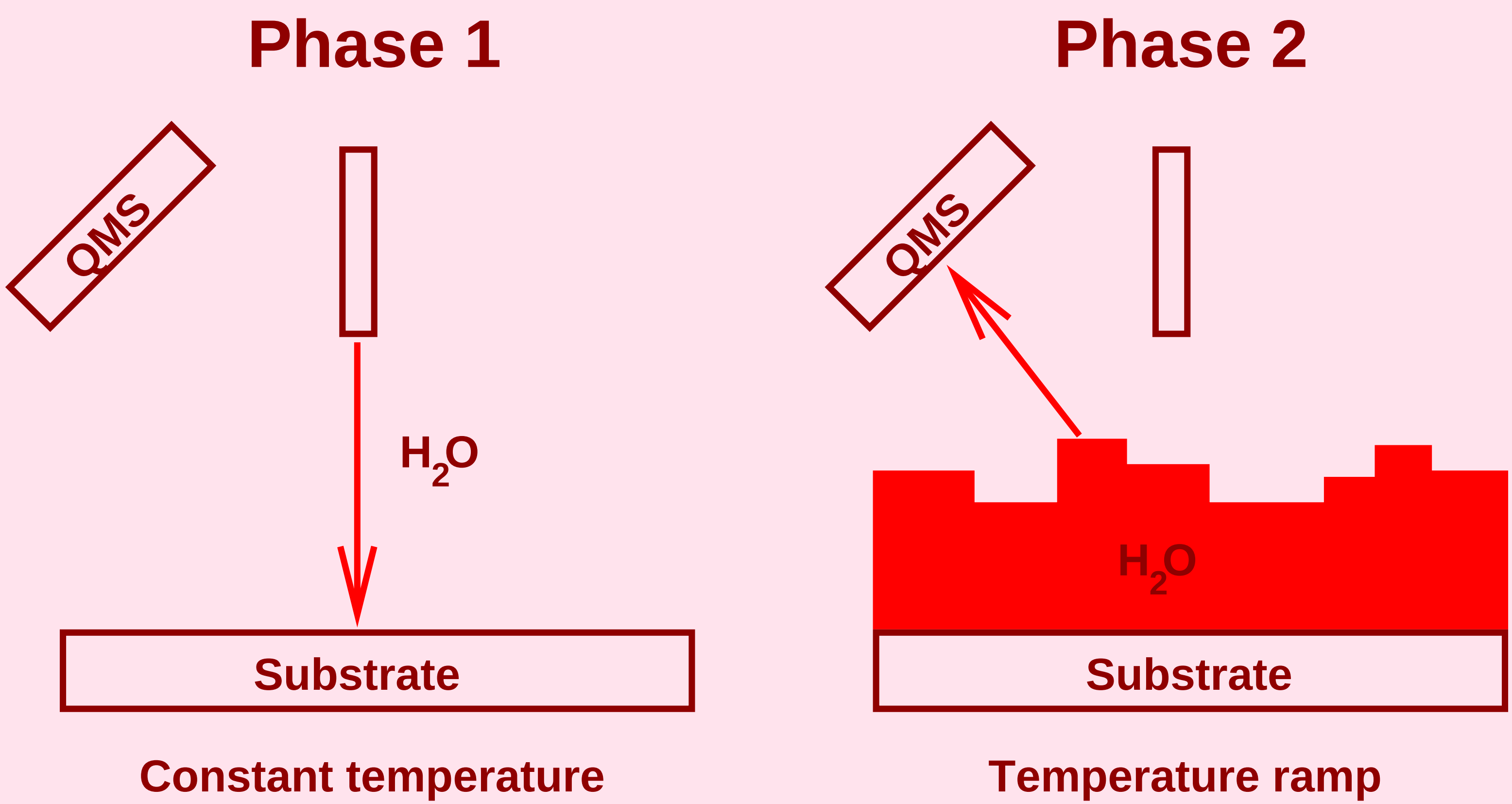
Formation Conclusions

- Small surface coverage of ice in diffuse areas, below detection limit
- Ice mainly forms at surface steps
- Simulations in qualitative agreement with observations
- Surface coverage by H_2 becomes important in dense clouds
- Formation route depends on the conditions
- Energy barriers are easier to overcome than in gas phase chemistry

Cuppen & Herbst, ApJ, in press

Water desorption

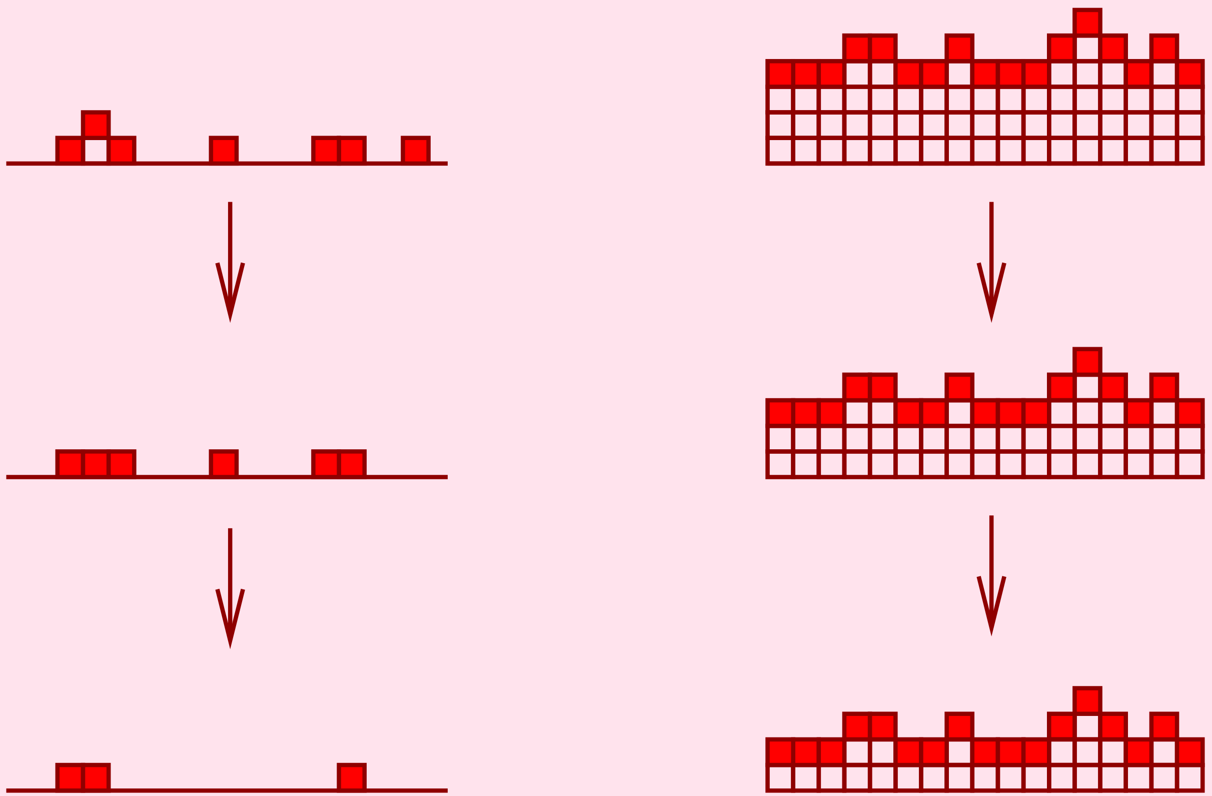
Temperature Programmed Desorption



Polanyi-Wigner equation

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = \nu_n \theta^n \exp\left(-\frac{E_{des}}{kT}\right)$$

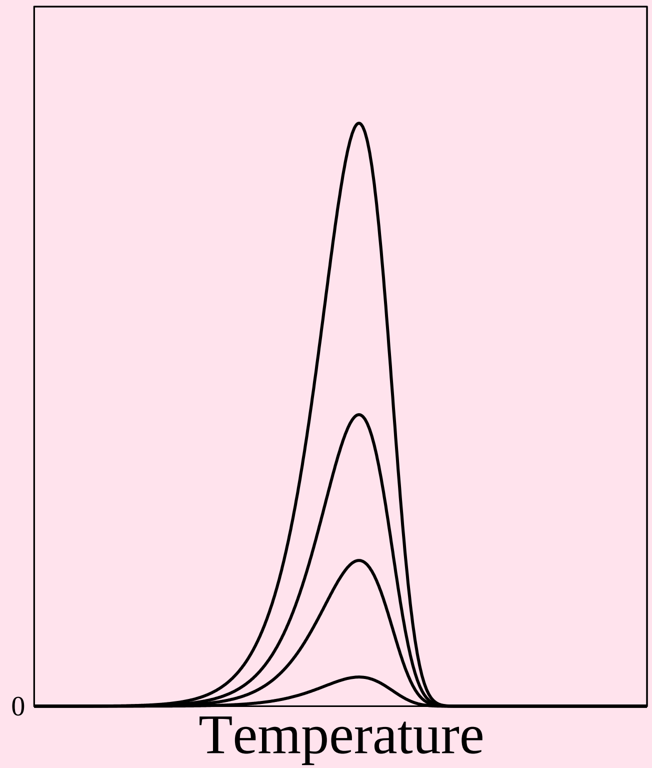
low coverage **high coverage**



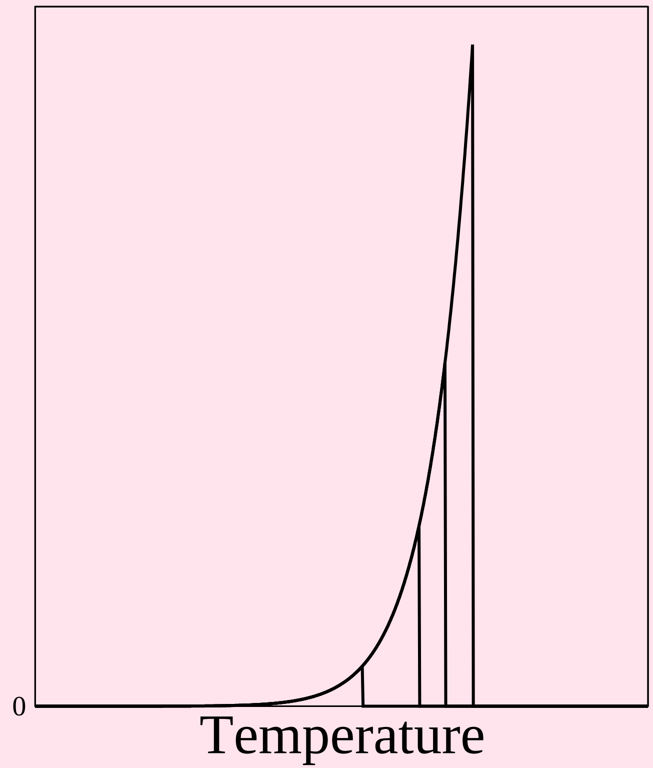
Polanyi-Wigner equation

$$\frac{\mathrm{d}\theta}{\mathrm{dt}} = \nu_n \theta^n \exp\left(-\frac{E_{des}}{kT}\right)$$

First order



Zeroth order



Water ice experiments

Fraser et al. MNRAS, 327, 1165 (2001)

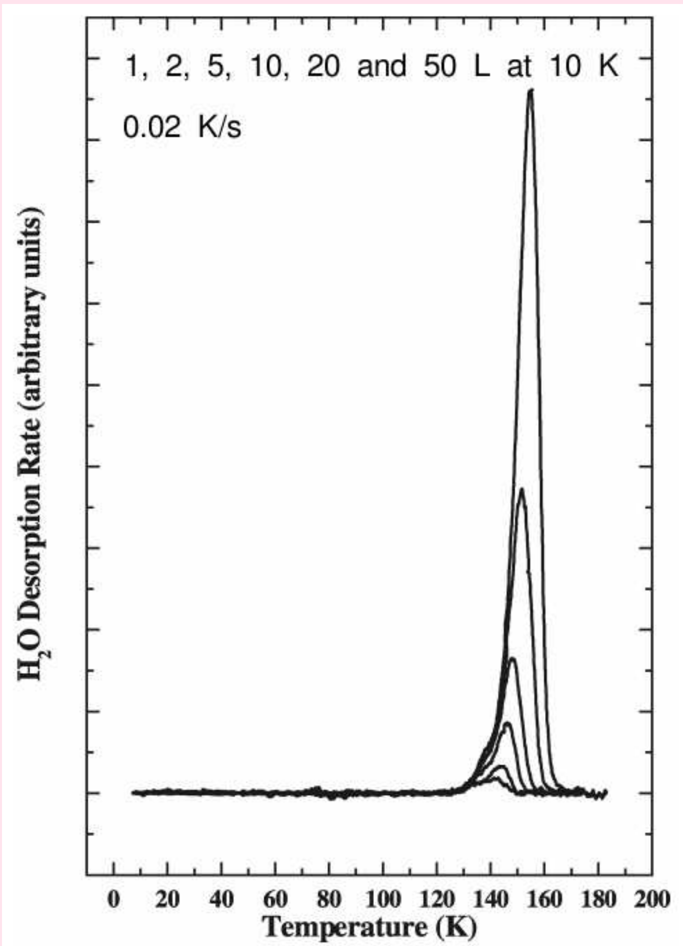


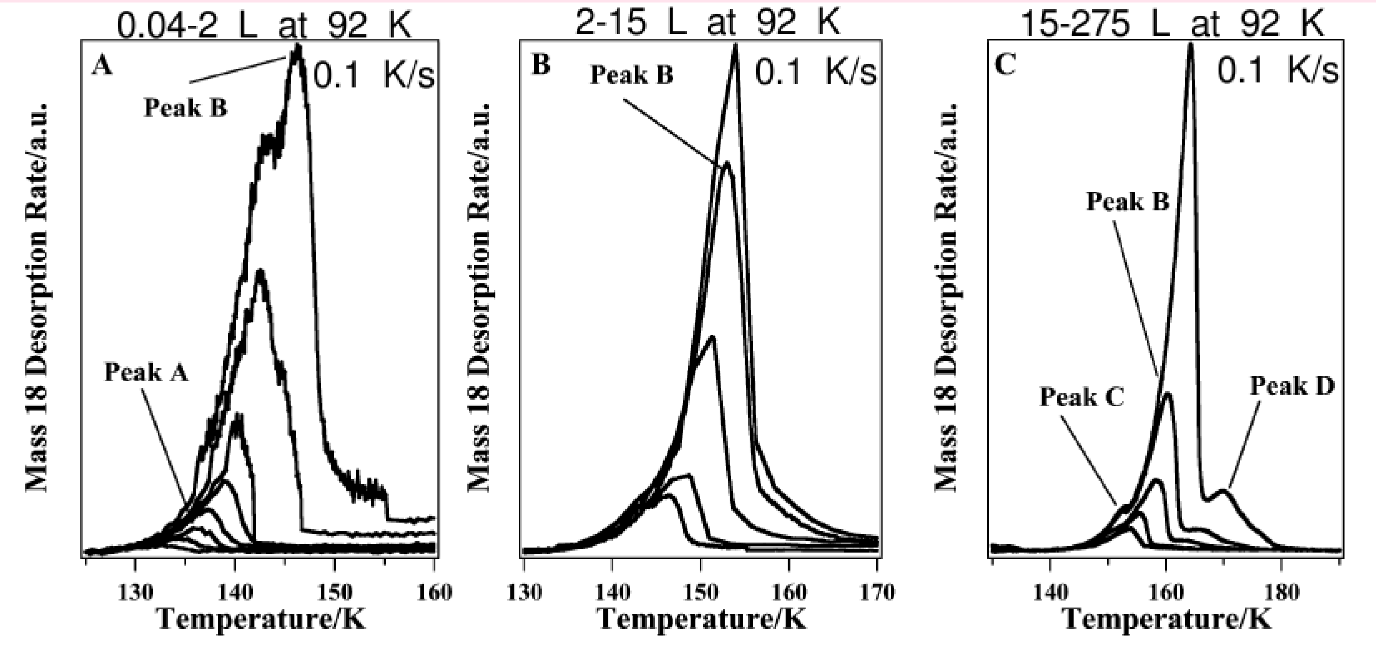
Table 1. A comparison of surface binding energy, E_{des}, and pre-exponential factor, A, measurements for (a) crystalline ice and (b) amorphous ice.

Substrate	Au[a]	Ru (001)/ Au (111)[b]	Sapphire[c]	CsI[d]
(a) Crystalline ice				
E_{des} (K)	5773 ± 60	5803 ± 96	5989	5070 ± 50
$A \times 10^{30}$ (molecules $cm^{-2} s^{-1}$)	1	4.58	2.8	$*2 \times 10^{12} s^{-1}$
m	0	0	0	1
(b) Amorphous ice				
E_{des} (K)	≈ 5600	5640 ± 96		4815 ± 15
$A \times 10^{30}$ (molecules $cm^{-2} s^{-1}$)	≈ 1	3.75		$*2 \times 10^{12} s^{-1}$
m	0	0		1

* Units of s^{-1}, not molecules $cm^{-2} s^{-1}$, as reaction was assumed to be first- and not zeroth-order.
References: [a]this work; [b]Speedy et al. (1996); [c]Haynes et al. (1992); [d]Sandford & Allamandola (1988).

Water ice experiments

Bolina et al. JPC B, 109, 16836 (2005)
Brown & Bolina MNRAS 374, 1006 (2007)

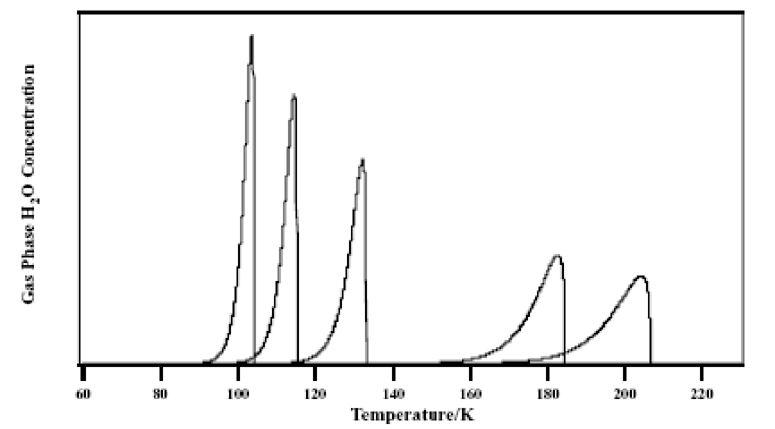


	Desorption order *n*	Desorption energy (K)	Pre-exponential factor[a] (molec m^{-2} s^{-1})
H_2O	0.26 ± 0.02	4799 ± 96	$1 \times 10^{27\pm1}$
NH_3	0.25 ± 0.05	2790 ± 144	$8 \pm 3 \times 10^{25}$
CH_3OH multilayer	0.35 ± 0.21	4931 ± 98	$6 \times 10^{25\pm3}$
CH_3OH monolayer	1.23 ± 0.14	5773 ± 95	$9 \times 10^{9\pm3 b}$

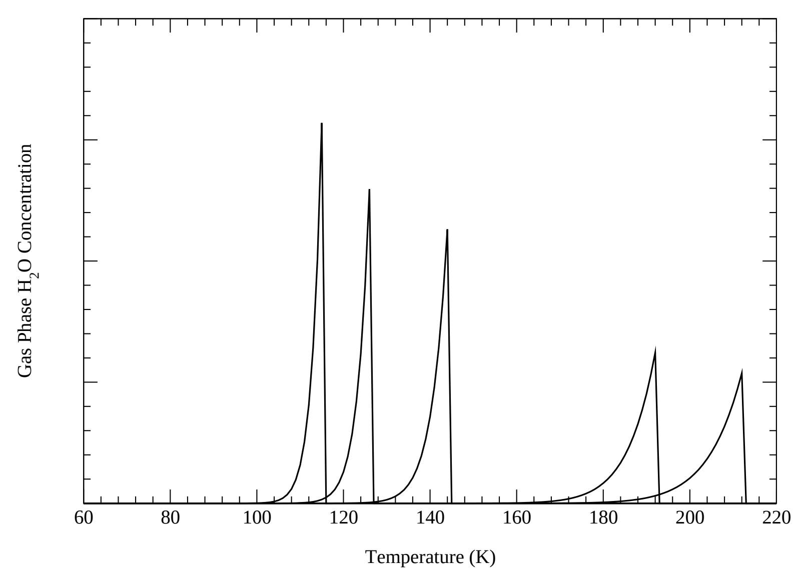
Experiments: a comparison

	Fraser et al.	Bolina et al.
Substrate	Au	HOPG
Dep. temp. (K)	10-130	92
Ramp (Ks^{-1})	0.1	0.02
Energy (K)	5773 ± 60	4799 ± 96
A (molec m^{-2}s^{-1})	1×10^{34}	$1 \times 10^{27 \pm 1}$
Order	0	0.26 ± 0.02

Desorption in the ISM



Brown & Bolina MNRAS 374, 1006 (2007)



Based on Fraser et al.

MONTY simulation program

- MONTY can simulate any crystallographic orientation at different temperatures and supersaturations.
- 2D nucleation, spiral growth and stepflow are possible growth mechanisms.
- MONTY uses the crystal graph of a structure as input.

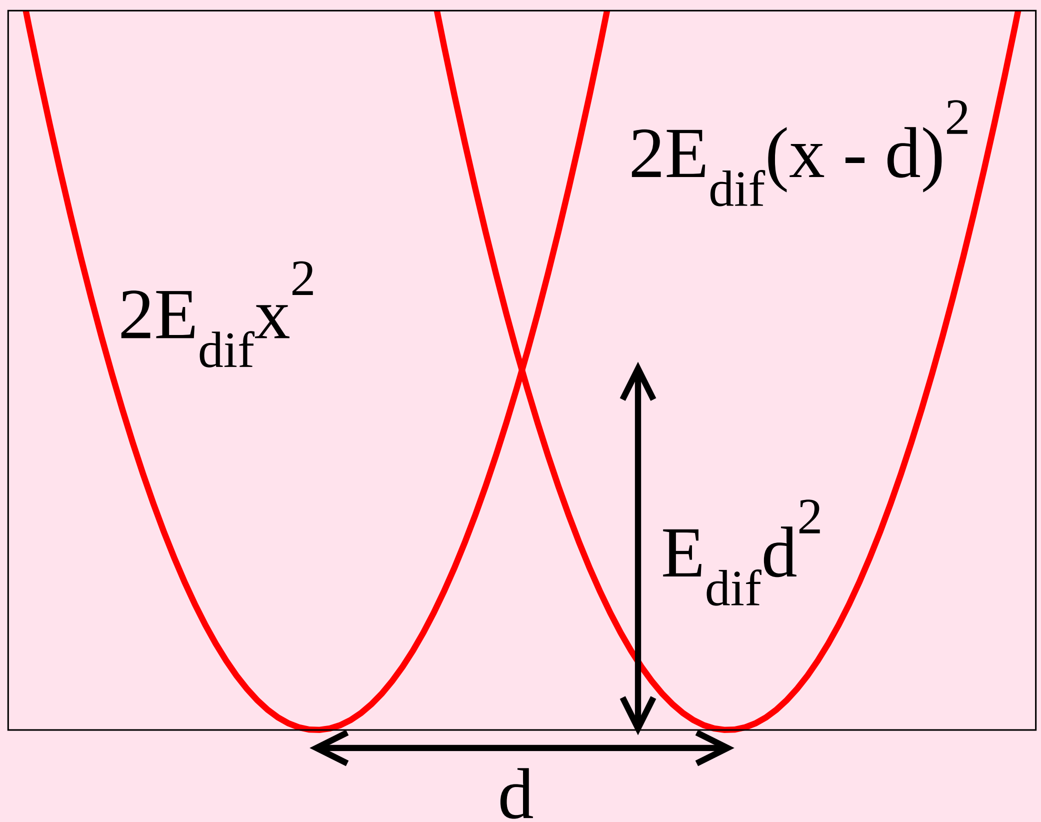
Changes to MONTY

- Deposition versus Solution Growth
- Temperature ramp
- Diffusion

MONTY

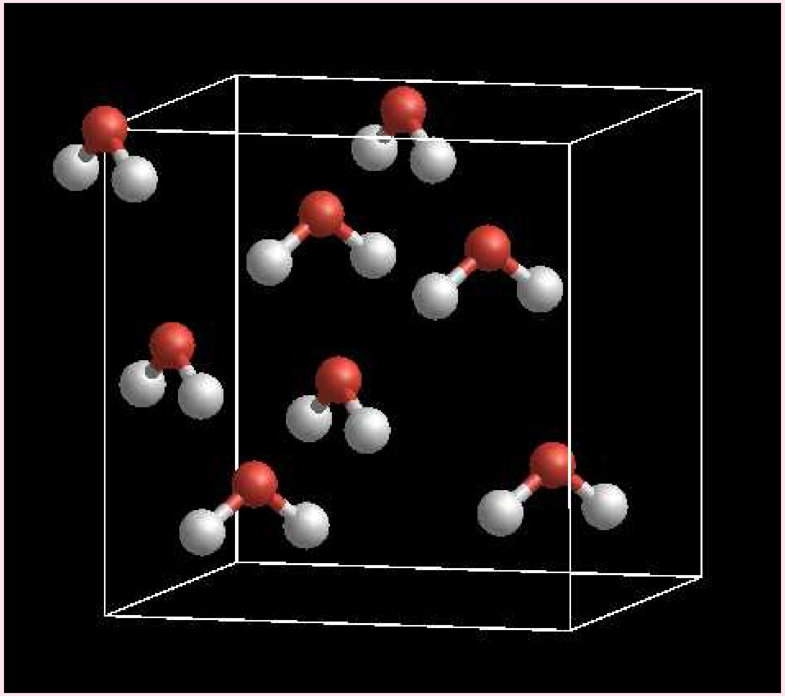
$$P_{\mathrm{desorb}} = \nu \exp\left(-\frac{E}{T}\right)$$

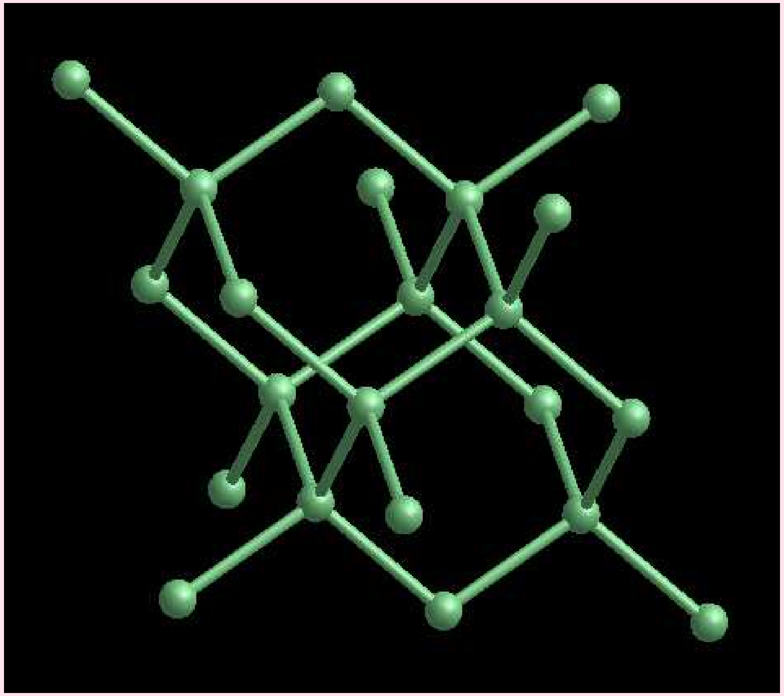
$$P^{i,j}_{\mathrm{diffuse}} = \nu \exp\left(-\frac{E_{\mathrm{dif}} d^2 + \frac{1}{2}\Delta E_{i,j}}{T}\right)$$



Desorption of H_2O

Cubic form of water ice

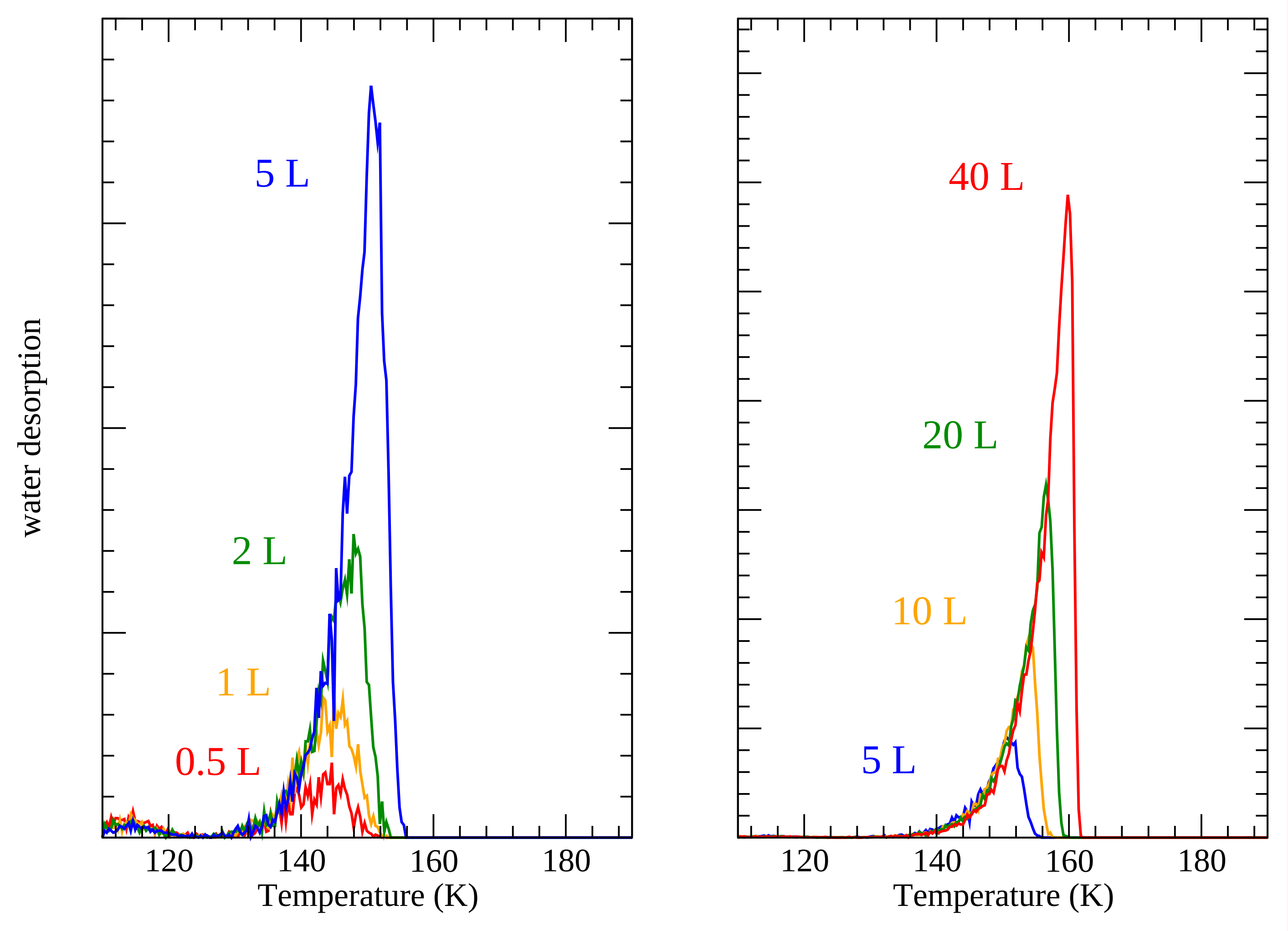




The crystal graph is a simplified representation of the crystal structure. All growth units, molecules, are represented by balls. The stick indicated the strongest intermolecular interactions.

Desorption of H_2O

Simulation data

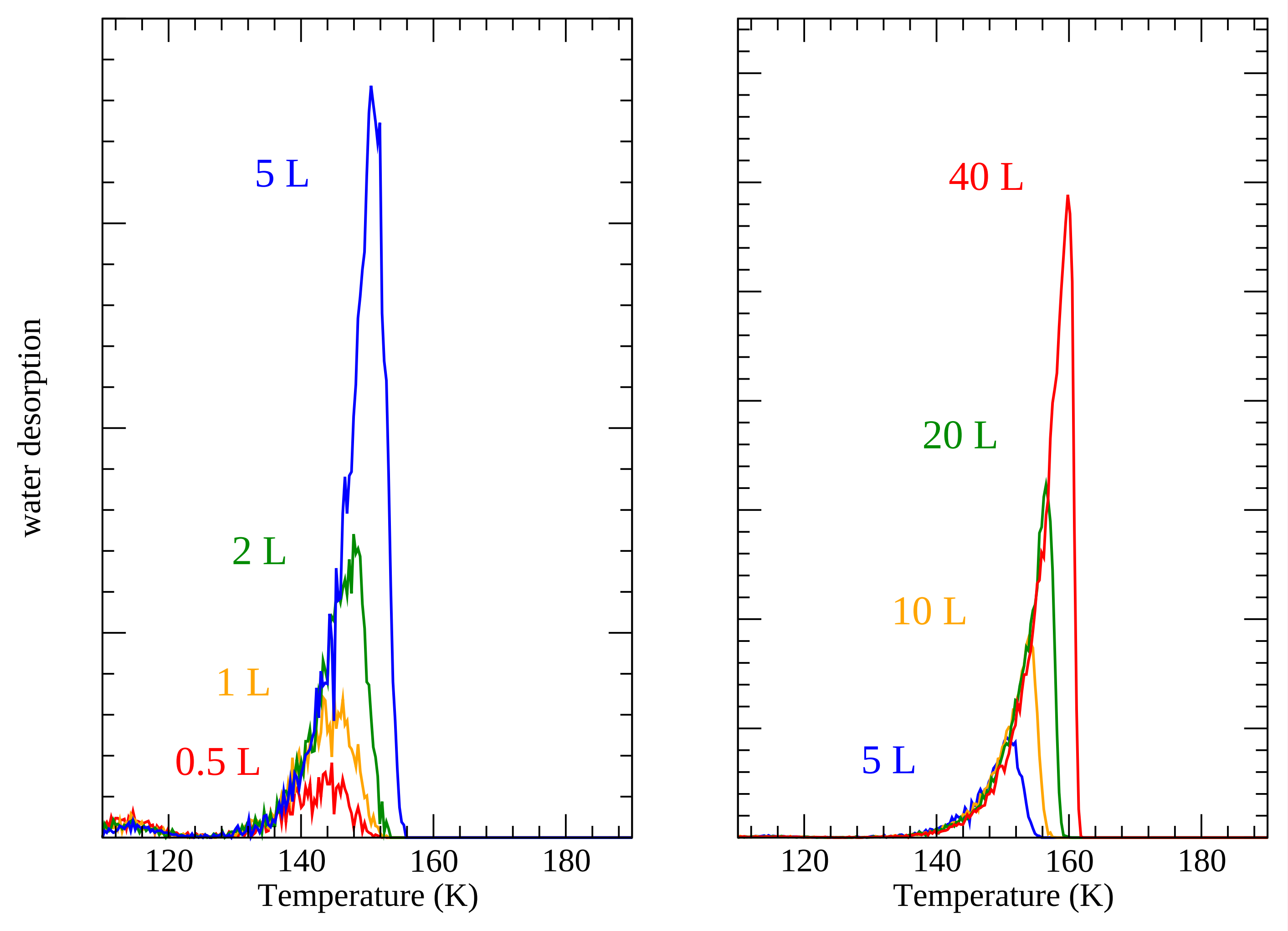


$E_{dif} = 3000$ K, $T_{dep} = 110$ K, Ramp = 2 K/min

Desorption of H_2O

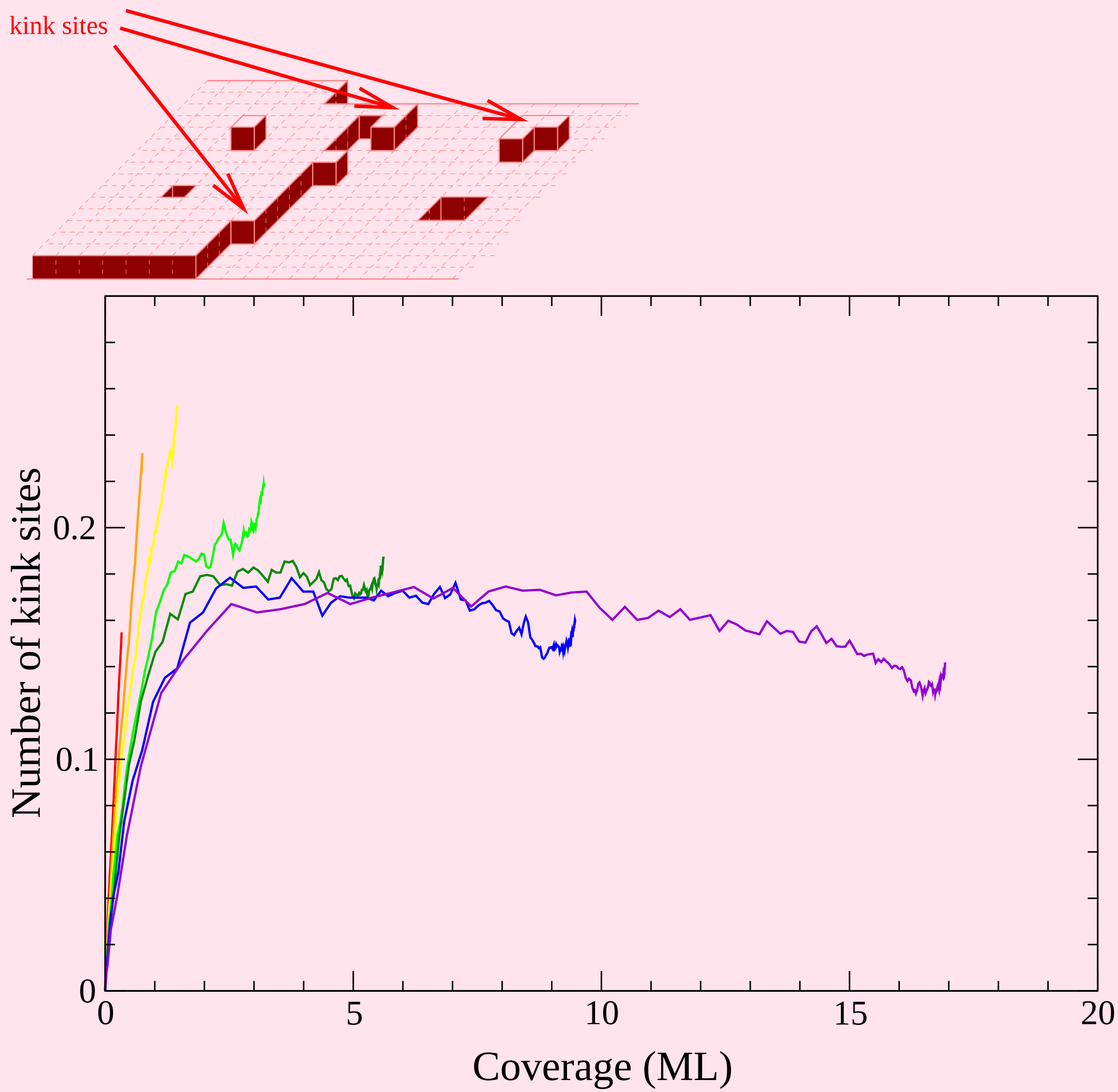
Desorption of H_2O

Simulation data

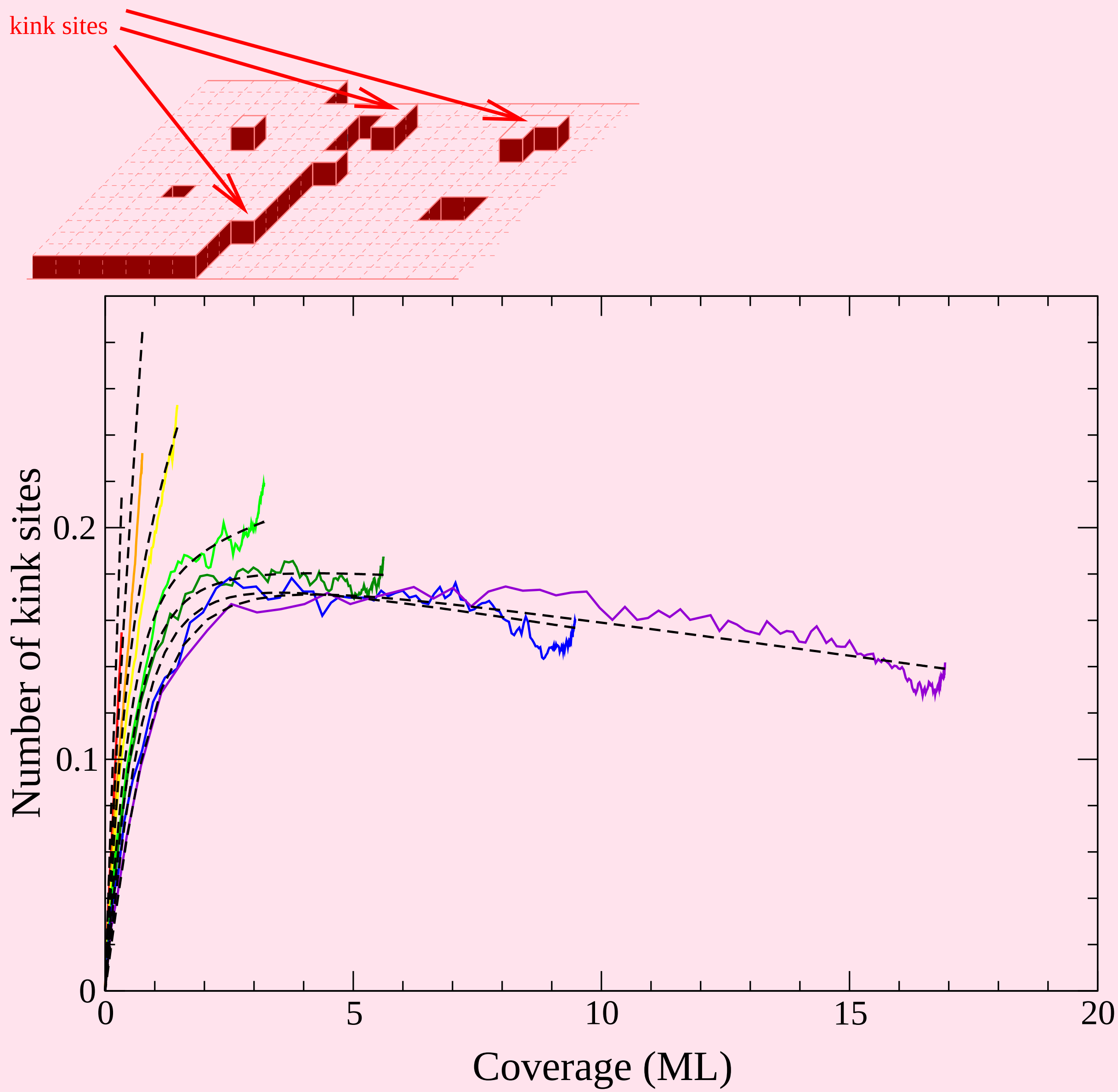


$E_{dif} = 3000$ K, $T_{dep} = 110$ K, Ramp = K/min

Kink sites vs. coverage

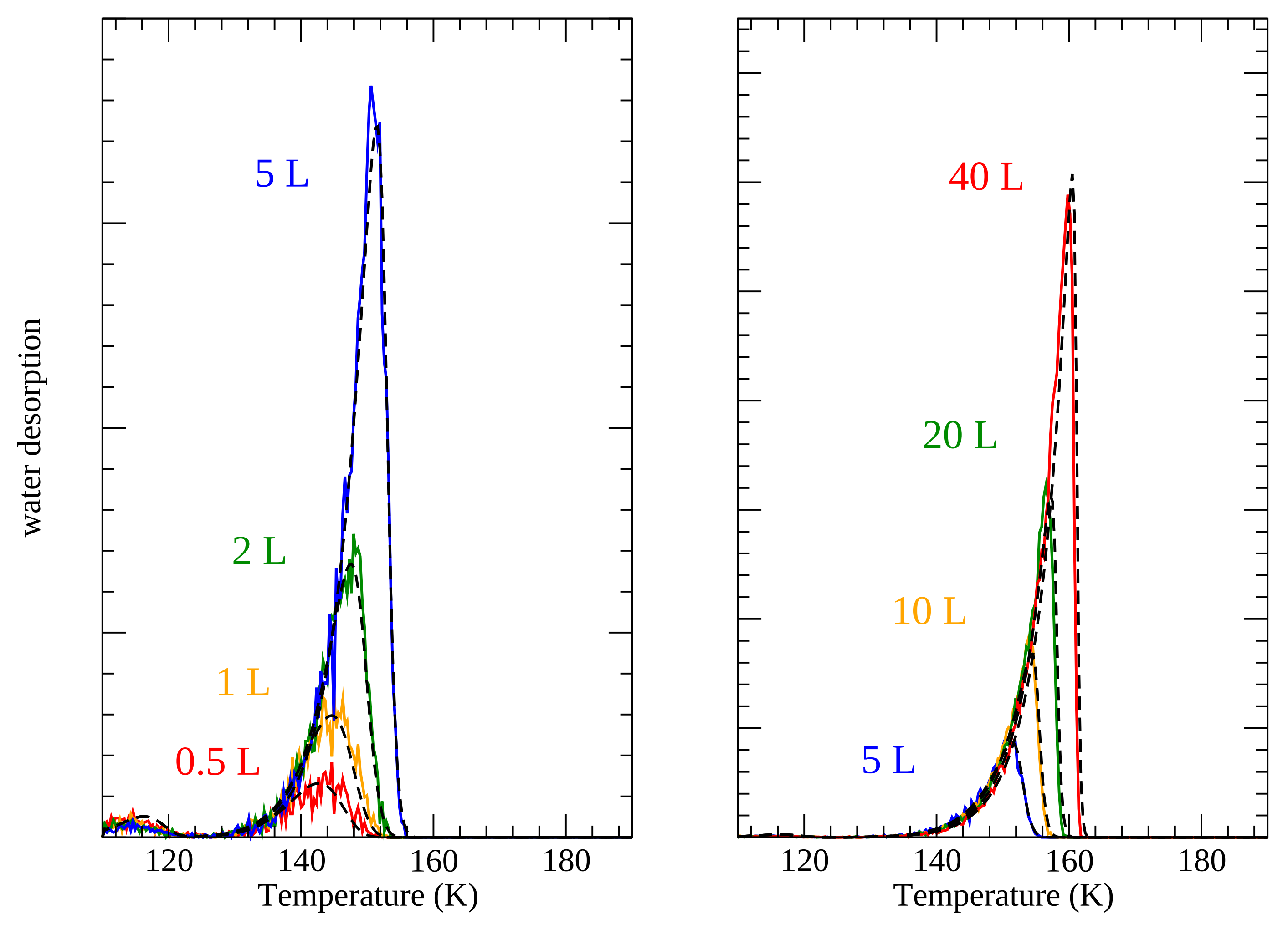


Kink sites vs. coverage



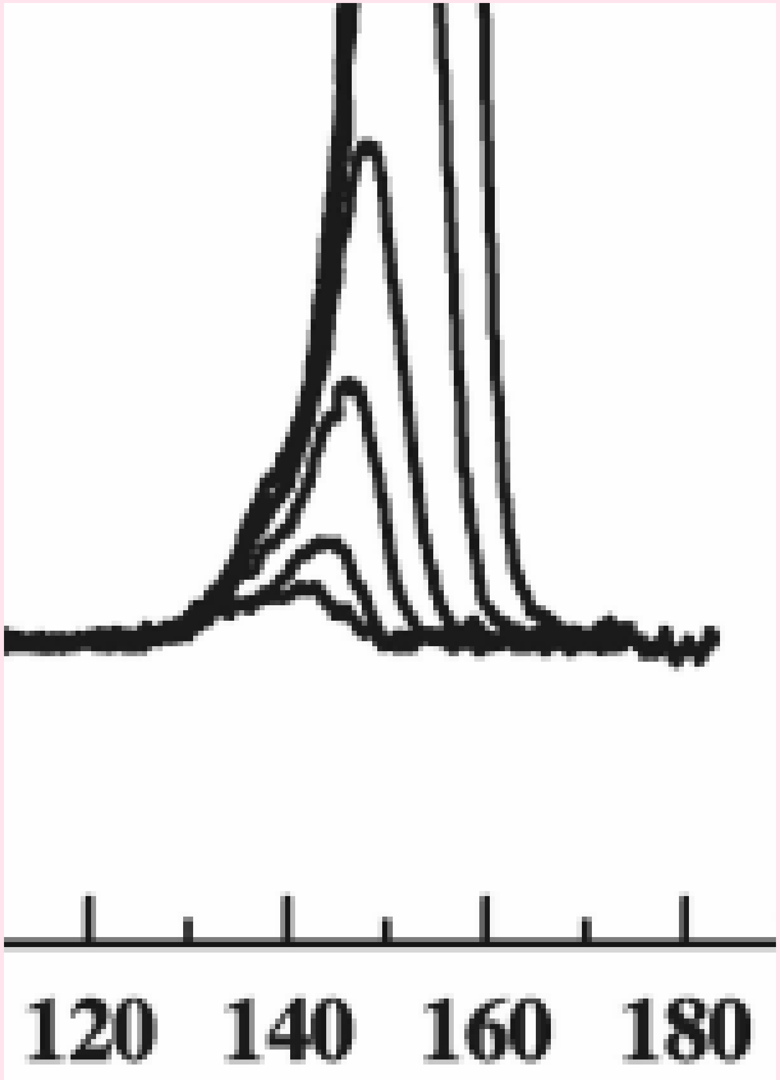
Desorption of H_2O (simulation)

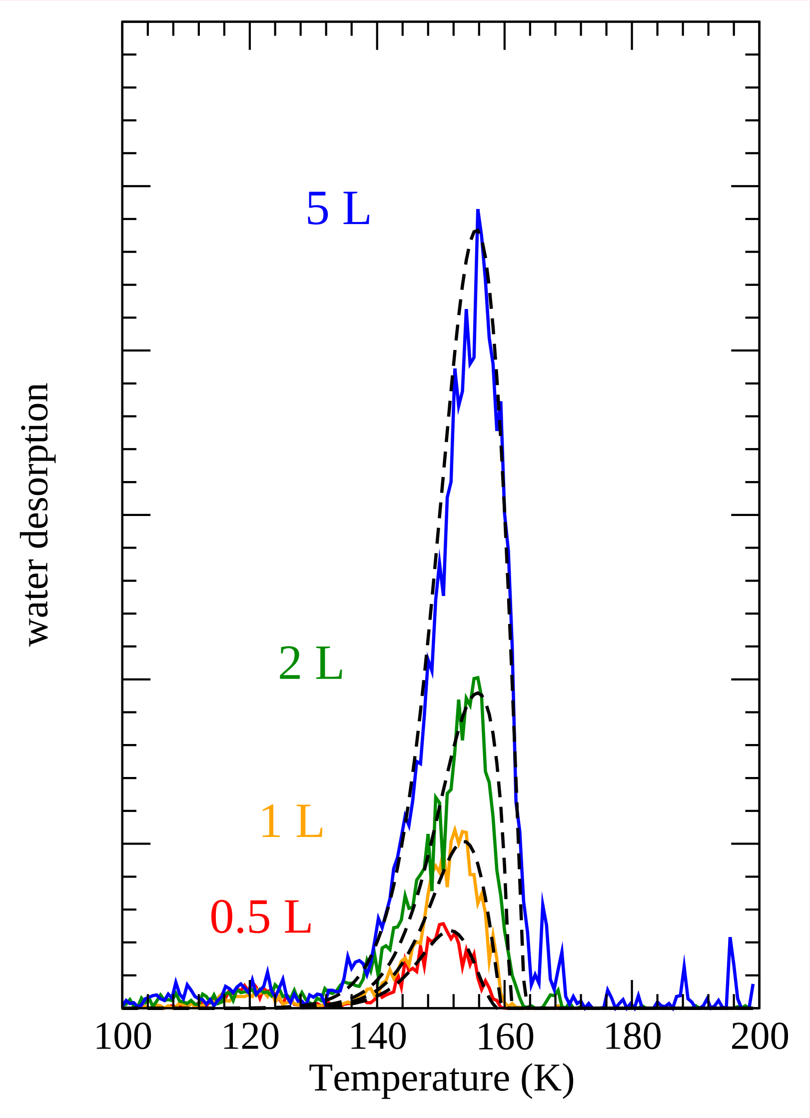
$$\frac{d\theta}{dt} = \nu_n \theta^{kink} \exp\left(-\frac{E_{kink}}{kT}\right)$$



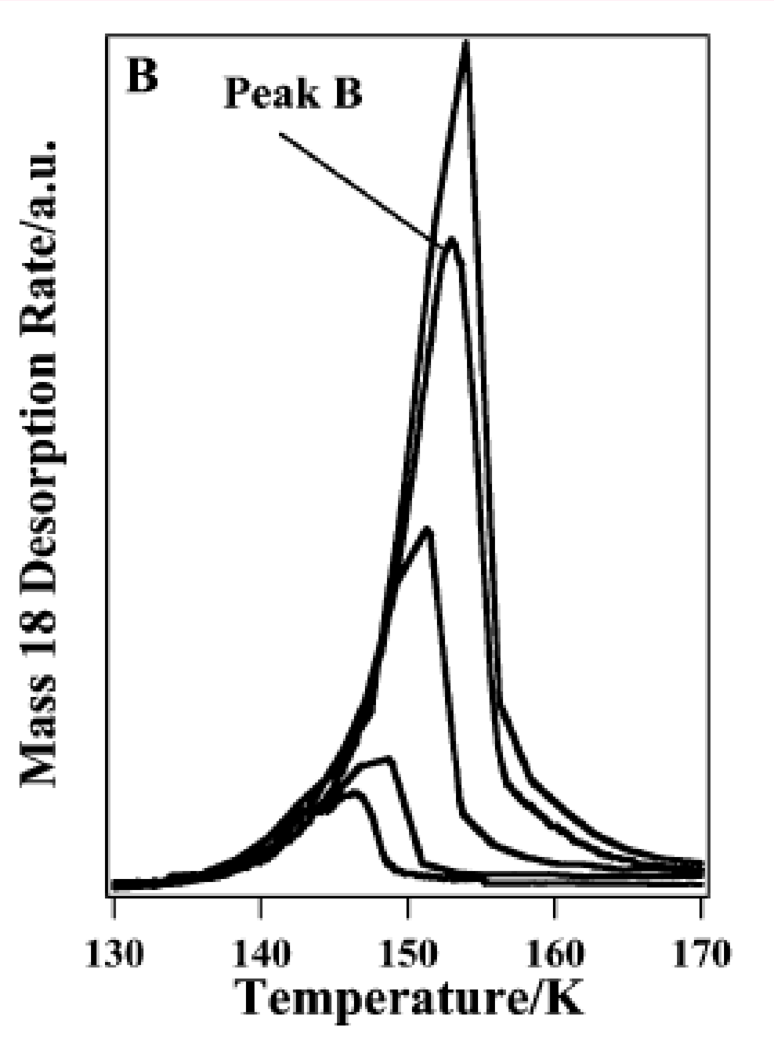
$E_{dif} = 3000$ K, $T_{dep} = 110$ K, Ramp = 2 K/min

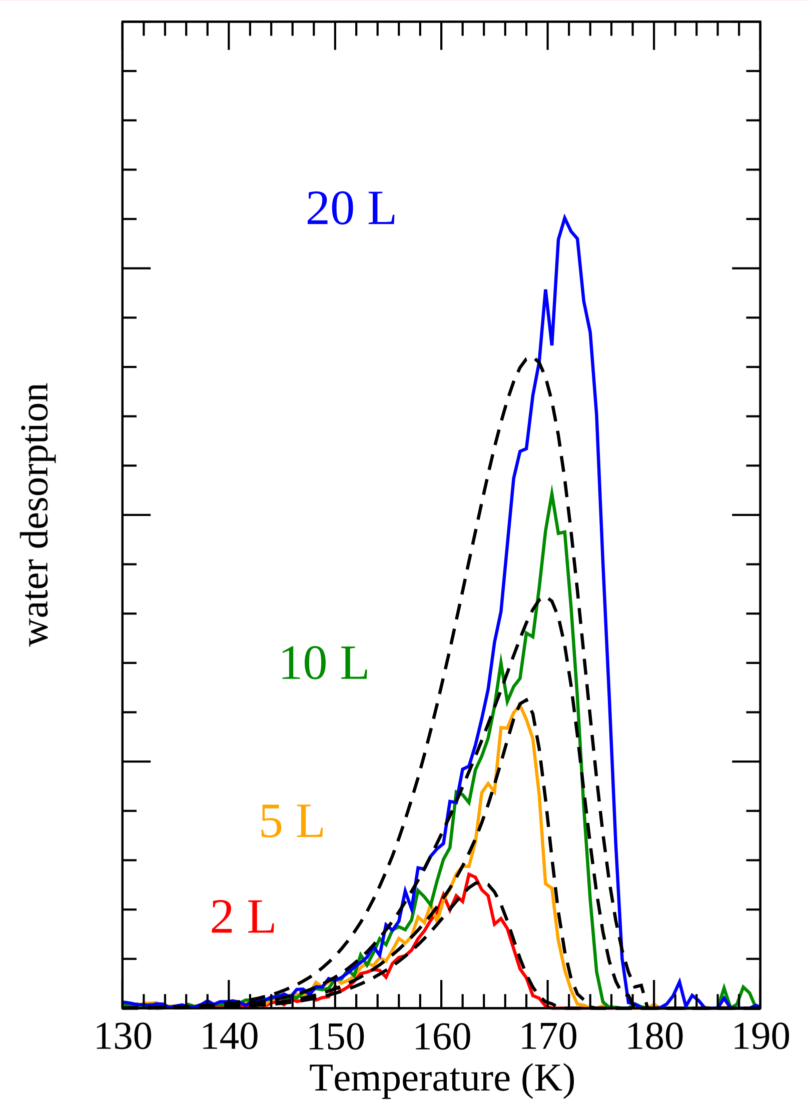
Fraser et al.


120
140
160
180


5 L
2 L
1 L
0.5 L
water desorption
100
120
140
160
180
200
Temperature (K)

Bolina and Brown





Conclusion

- Monte Carlo simulations are a powerful tool to study interstellar surface chemistry
  - ⋆ Translation of fluxes to study chemical reactions
  - ⋆ Study desorption processes: kink position very important
  - ⋆ Temperature ramp can be important

Acknowledgments

- NSF, Leiden Observatory, and NWO for funding
- AstroChem group in Leiden
- ... and you for your attention.