Interstellar surfaces: from Laboratory to Models

- Day 1
  - Introduction and overview
- Day 2
  - Surface Reactions
- Day 3
  - Desorption of ices
- Day 4
  - Photoprocessing of ices
- Day 5
  - Experimental techniques

Grand Challenges

Things we can look back at in 5 years and say
"now we understand X much better"

- physisorption mobility (Day 2 + 5)
- Charge (Day 4)
- standard ice mixtures/porosity (Day 4)
- structural calculations

- need of stochastic methods (Day 1)
- 3 phase model (gas-surface-bulk) (Day 1)
- Modelling experiments (Day 2)
- Database? (citation) (Day 3)

Day 1: Overview and Introduction

- Xander Tielens “The Astronomical Context”
- Steve Charnley “Constructing surface reaction networks”
- Herma Cuppen “Microscopic simulations of grain surface chemistry
- Ingo Lohmar “Analytical and numerical studies of the simplest interstellar surface reaction”
- Anton Vasyunin “Study of stochastic effects in grain surface chemistry”

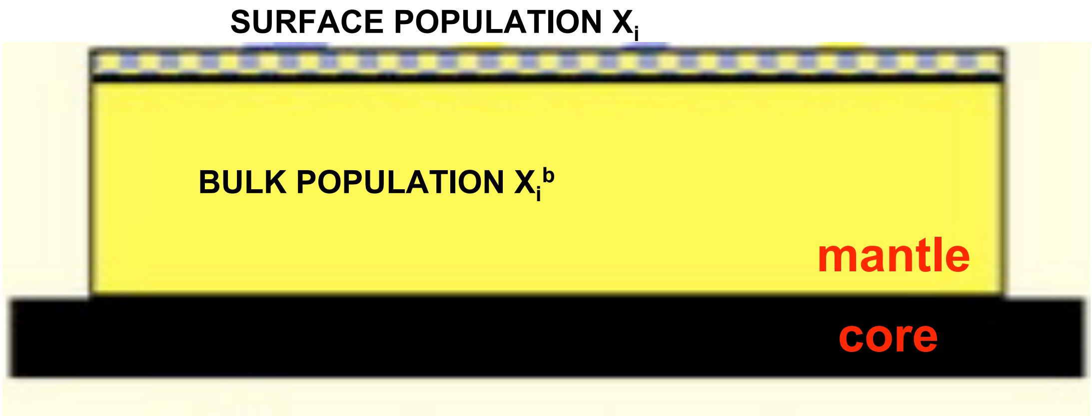
Steve Charnley

Surface Simulation Issues

- Gas and grain chemistries solved in tandem

- Surface vs. bulk population

- Max. ~ 10^6 particles on surface

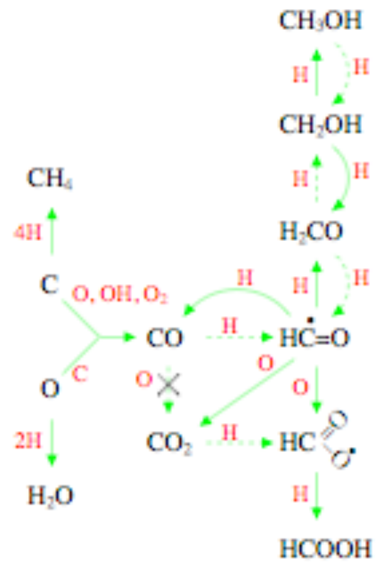


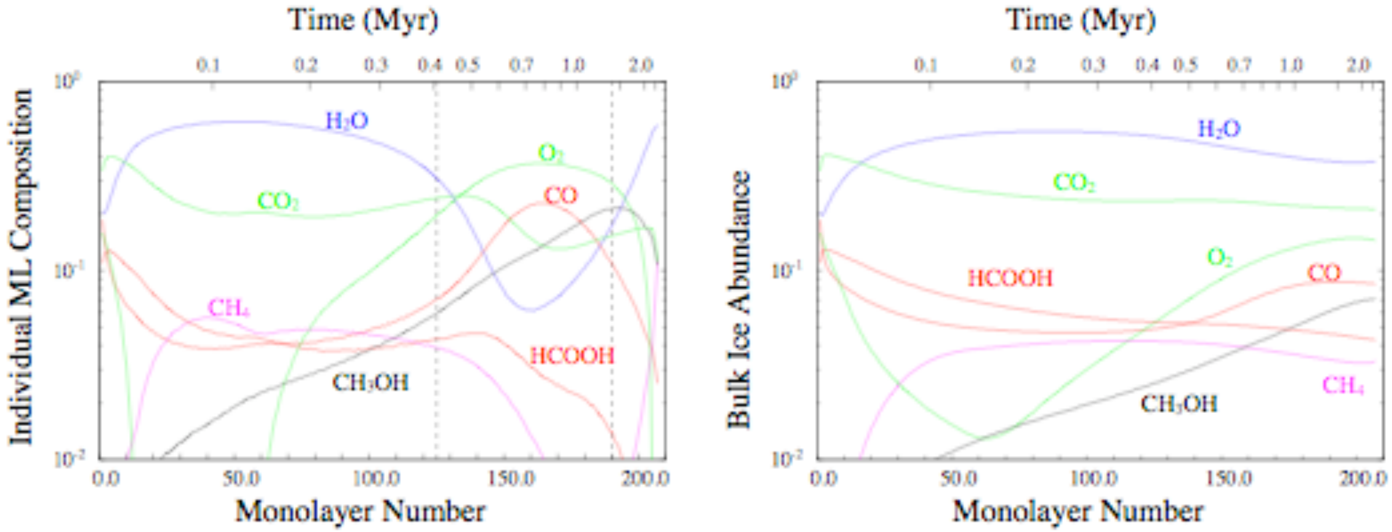
- Surface population changes by arrivals and reactions:

  i) particles are removed from the reactive population by arrivals

  ii) surface reactions uncover particles in the sub-surface monolayer and return them to the reactive population.

Calibration: Simulation of Gas-Grain Chemistry





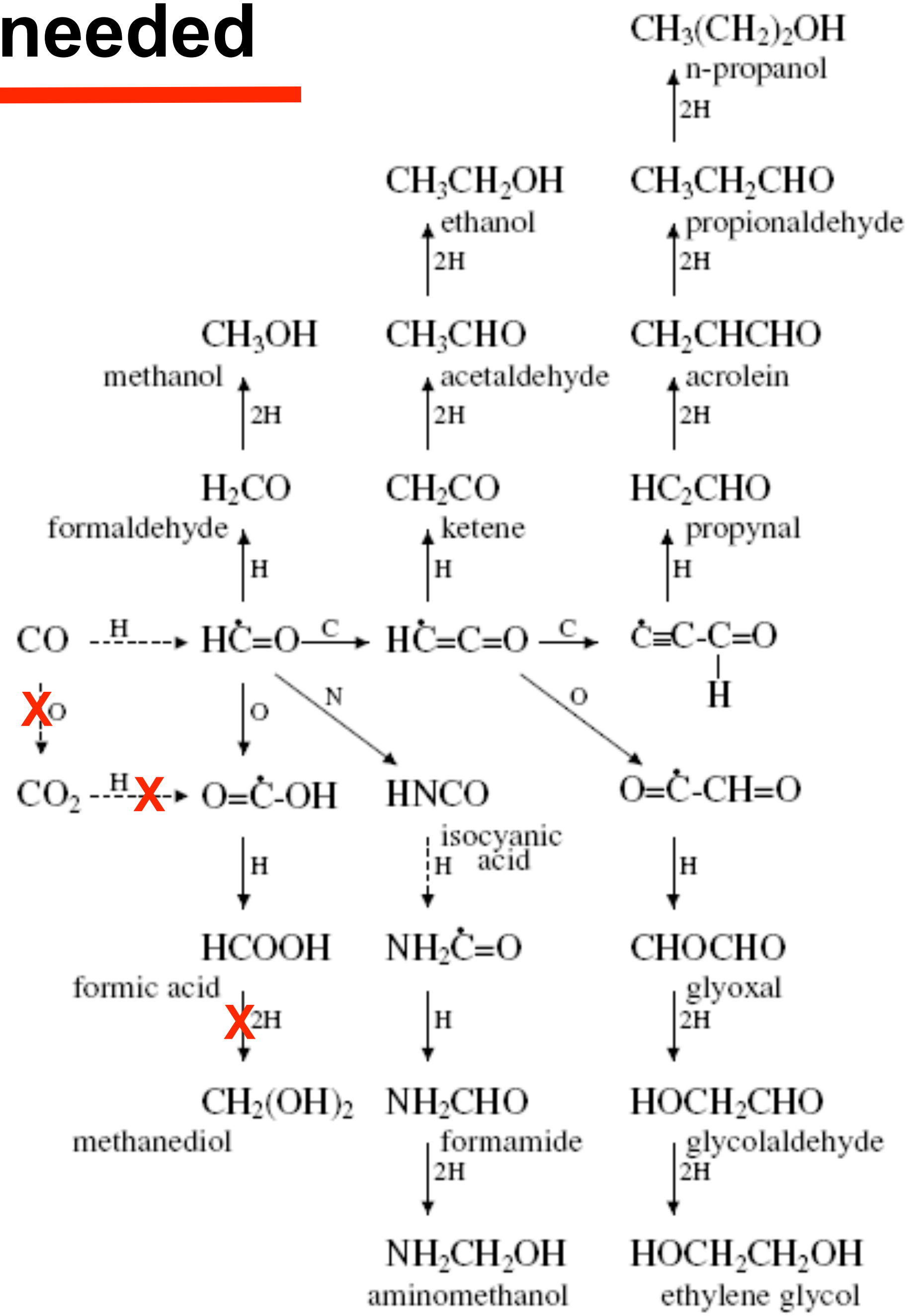
Rodgers & Charnley (2008)

But … revisions needed

$$O_2 \xrightarrow{H} HO_2 \xrightarrow{H} H_2O$$

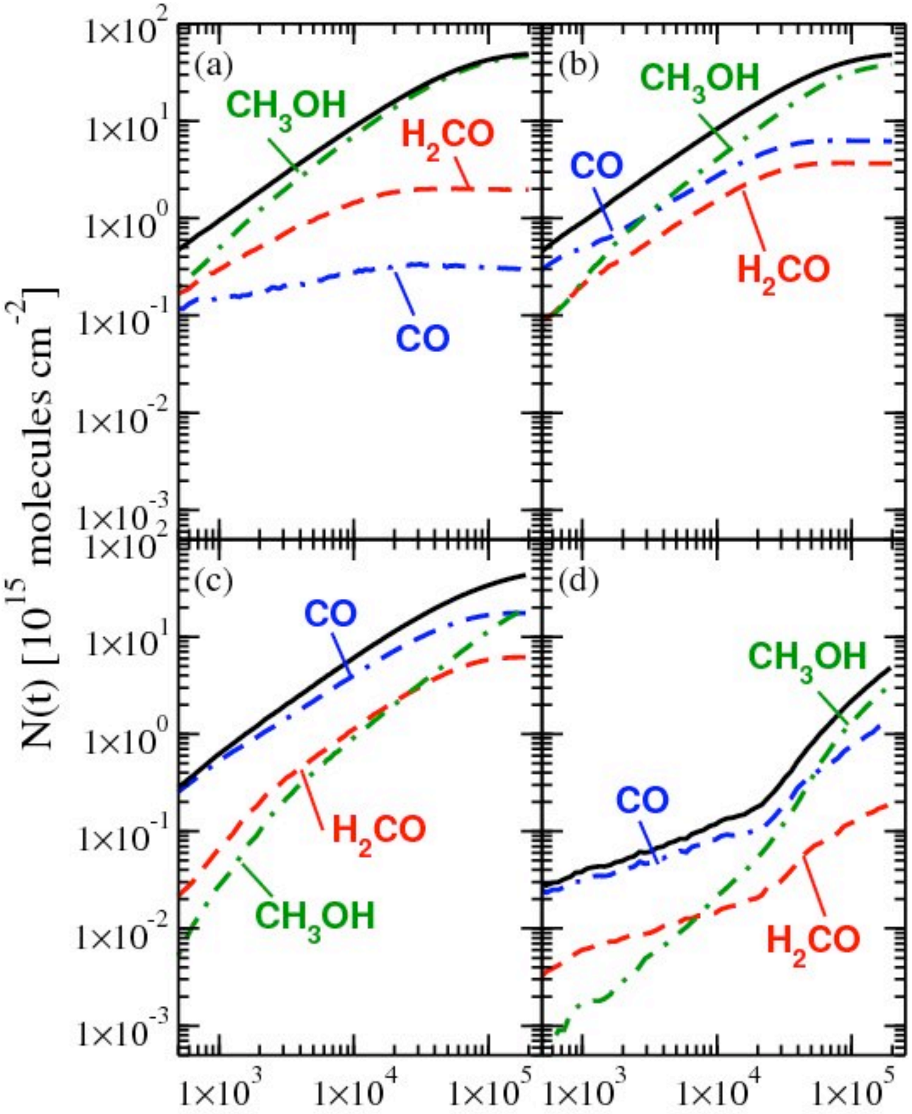
Miyauchi et al. (2008)
Ioppolo et al. (2008)

Bisschop et al. (2007)

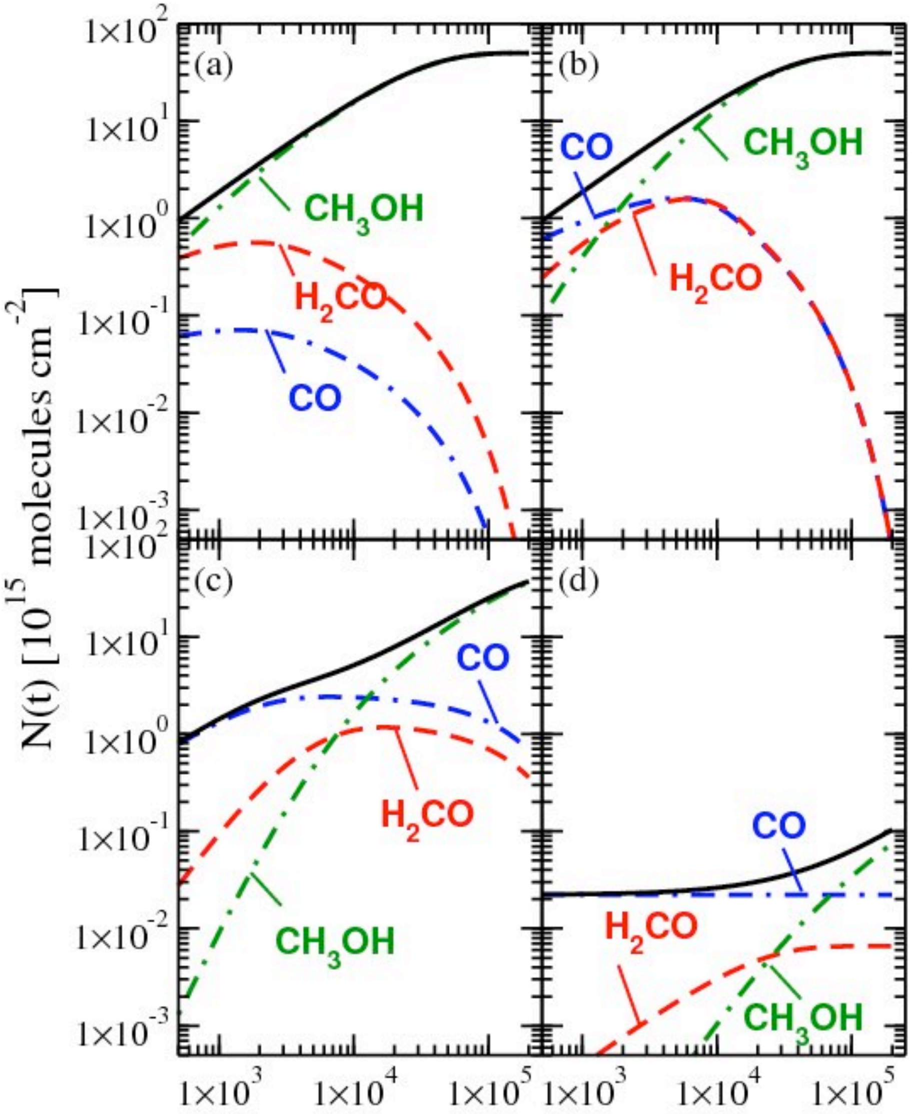


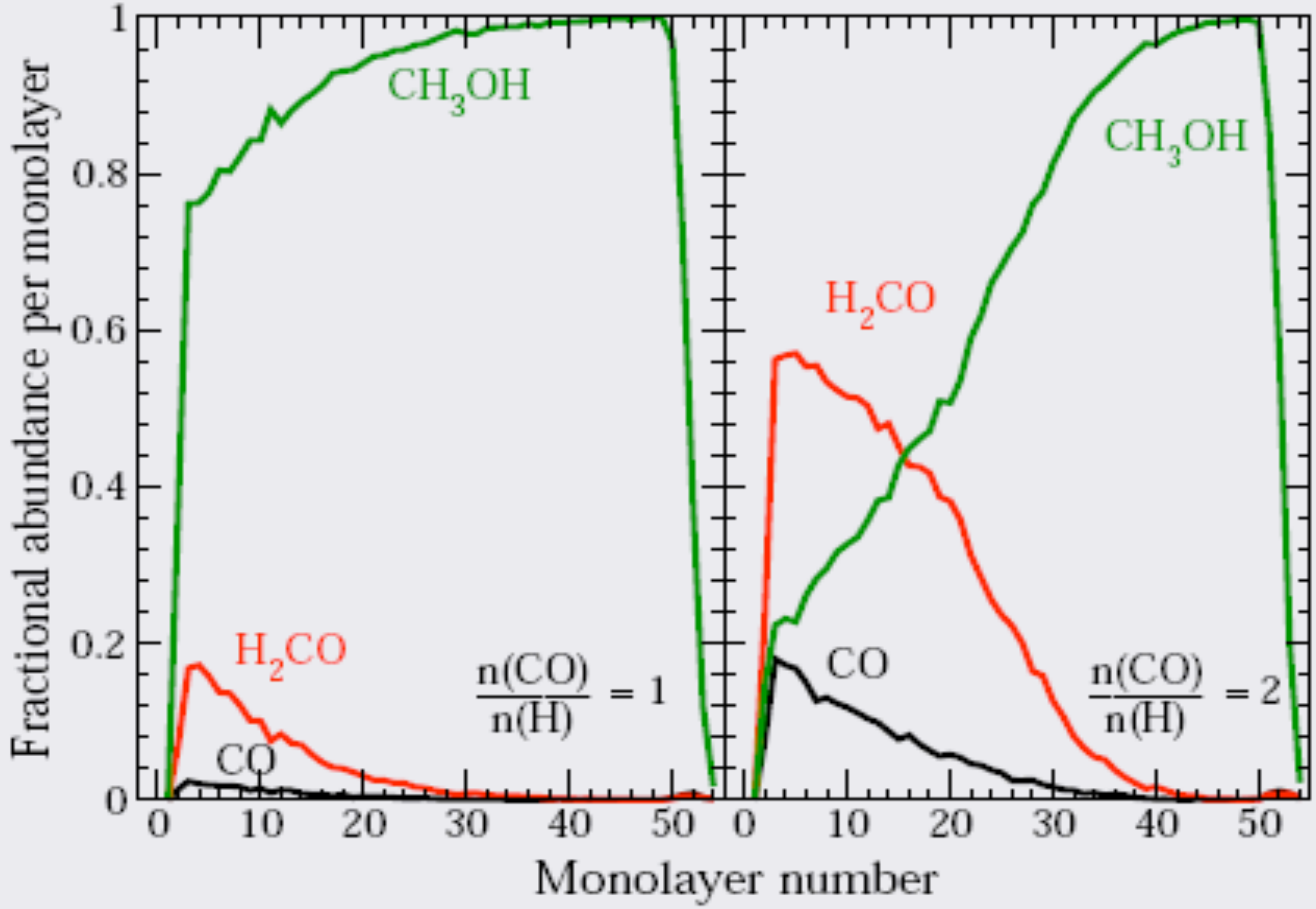
Herma Cuppen

Monte Carlo



Rate equations





- H_2CO and CO locked up in lower layers
- $n(\mathrm{CO})/n(\mathrm{H})$ ratio determines CH_3OH and H_2CO formation

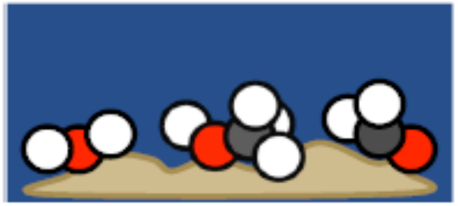
Day 2 Surface Reactions

- Naoki Watanabe (Hydrogenation/deuteration)
- Sergio Ioppolo (CO/O2 hydrogenation)
- Jean-Louis Lemaire (H2 formation)
- Farahjabeen Islam (Formation pumping of H2)
- Rob Garrod (Gas-grain model)
- Maria Elisabetta Palumbo (Ion irradiation)

Rob Garrod

Model Summary:
Timeline of Complex Molecule Formation in Hot Cores

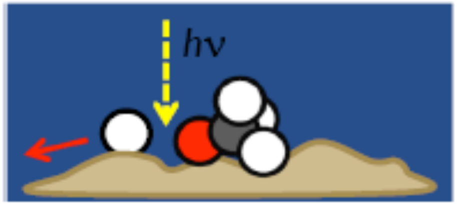
1) Ices: Store of molecular material formed during collapse phase. (Hydrogenation)



2) Continuously (but slowly) broken down:

Cosmic-Ray-induced photodissociation

→ functional-group radicals

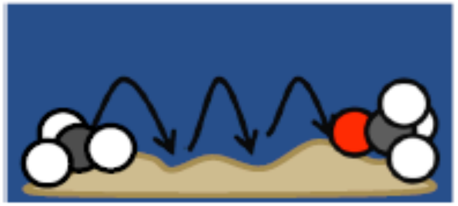


3) *Gradual* warm-up of hot core (10 - 200K)

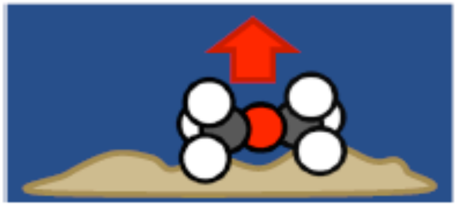
(not the old step-function)

4) Increased mobility

→ addition of functional-group radicals



5) Evaporation at varying temperatures



Lab data is crucial

- Surface chemical routes to complex molecules require accurate data:
  - Large molecules' desorption energies
  - Functional-group radical mobilities

- Photodissociation branching channels of methanol ice (and others)

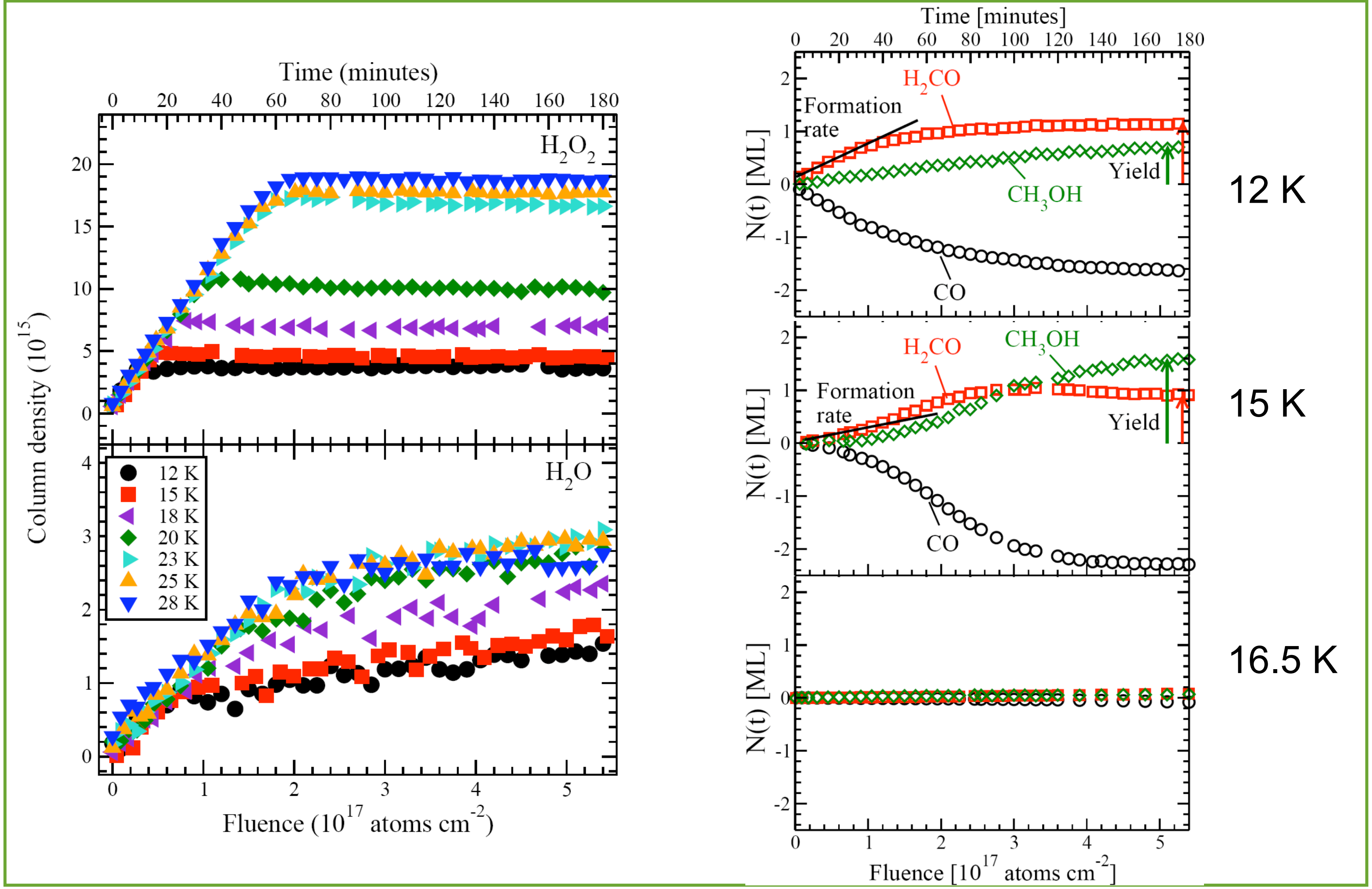
  $\Rightarrow$ IS ratios of the most complex molecules

- Need to test new surface mechanisms in the lab

- Need to model lab results with models *directly* applicable to ISM

Sergio Ioppolo

O_2 vs CO



12 K

15 K

16.5 K

Naoki Watanabe

What we can know from our experiments

What we can do

measurements of H (D) atom flux and column densities of parent & product molecules on the surfaces.

What we can not do

measurements of number density of H atoms on the surfaces and migration rate.

↑ sticking coefficient, recombination rate, desorption rate

☺ Very high flux (deposition rate) enables:

- atoms to encounter a reactant without long-distance migration.
- us to obtain the significant amount of products.

☺ Our experiments provide effective reaction rates.

↓

Good ! reaction channels, relative rates, activation barrier for reaction

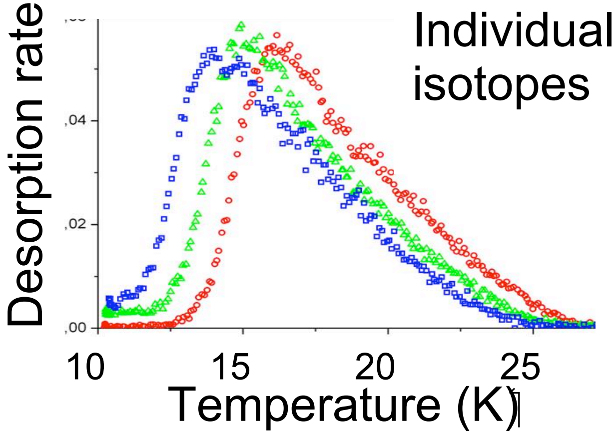
Poor migration

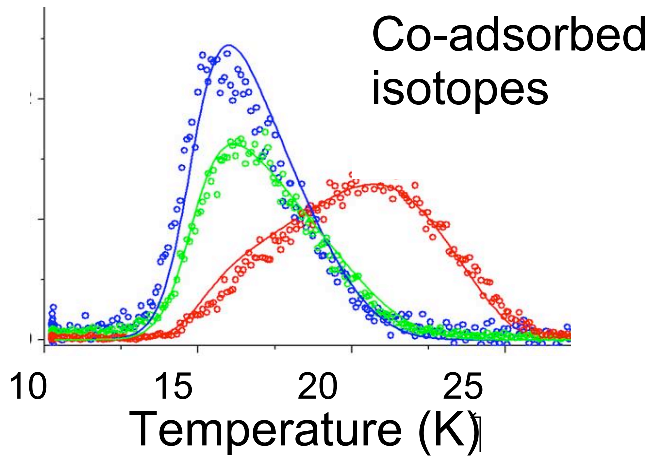
Jean-Louis Lemaire

Desorption of molecular hydrogen on grains

Isotopic segregation H_2, HD, D_2

enhance presence of D_2, and D

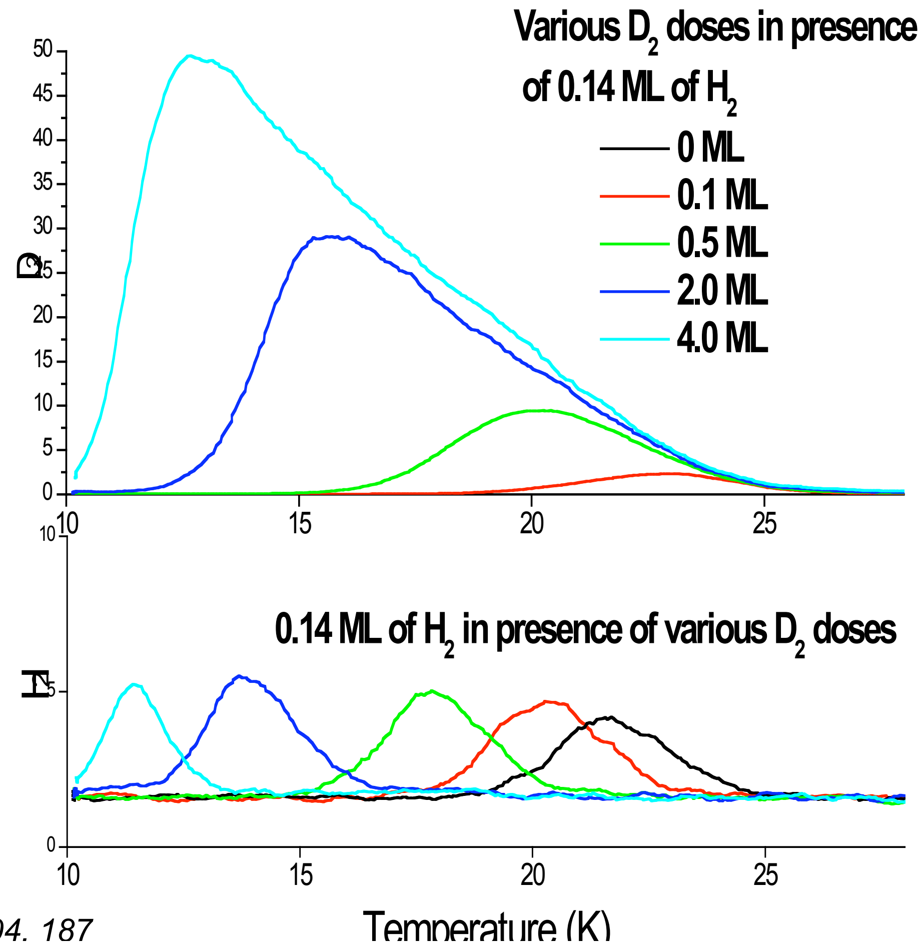




Dulieu. Amiaud. Baouche. Momeni. Fillion. Lemaire. 2005. CPL. 404. 187

Influence of already absorbed molecules on:

- Sticking
- Desorption
- Formation rate

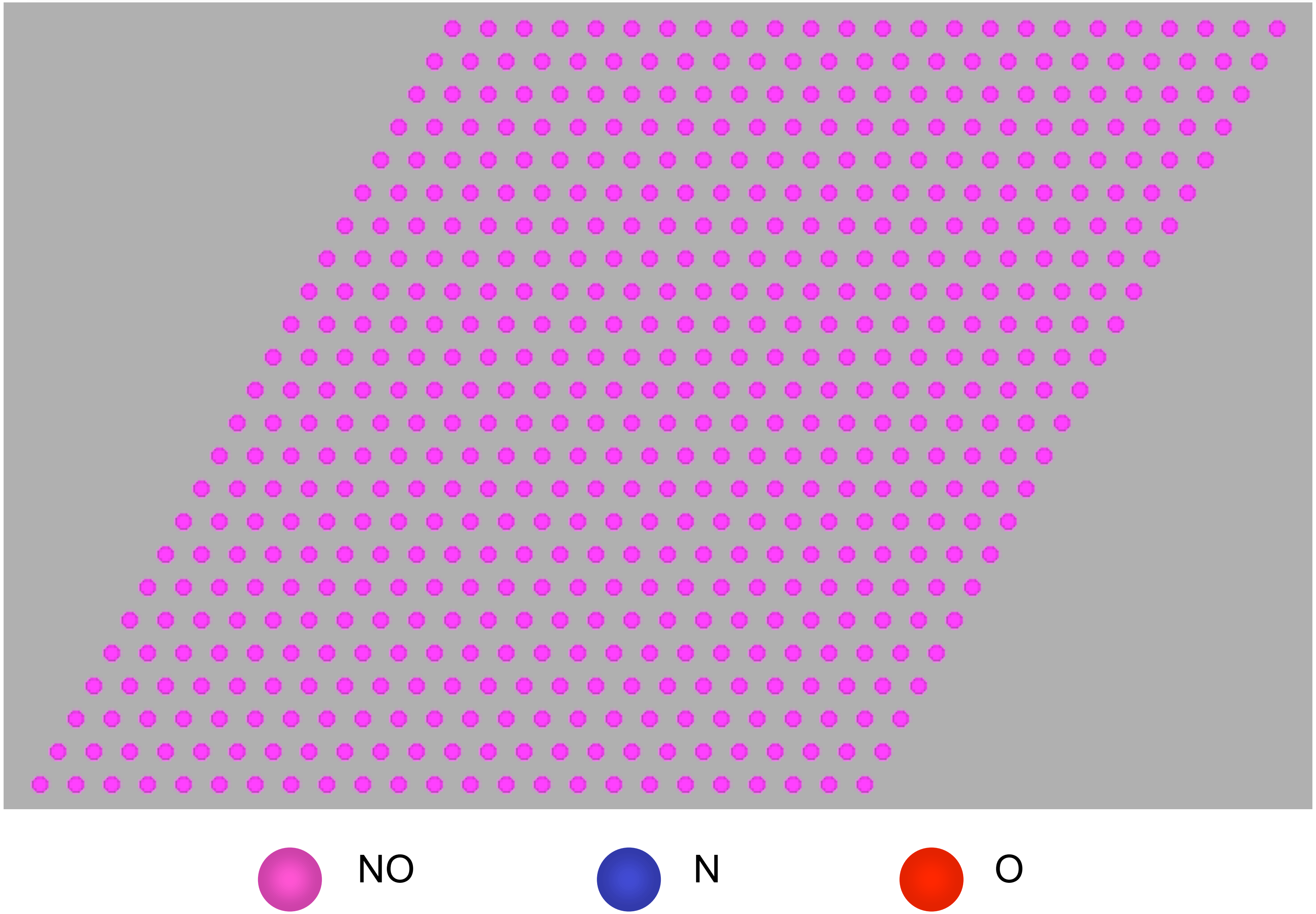


Day 3: Desorption of Ices

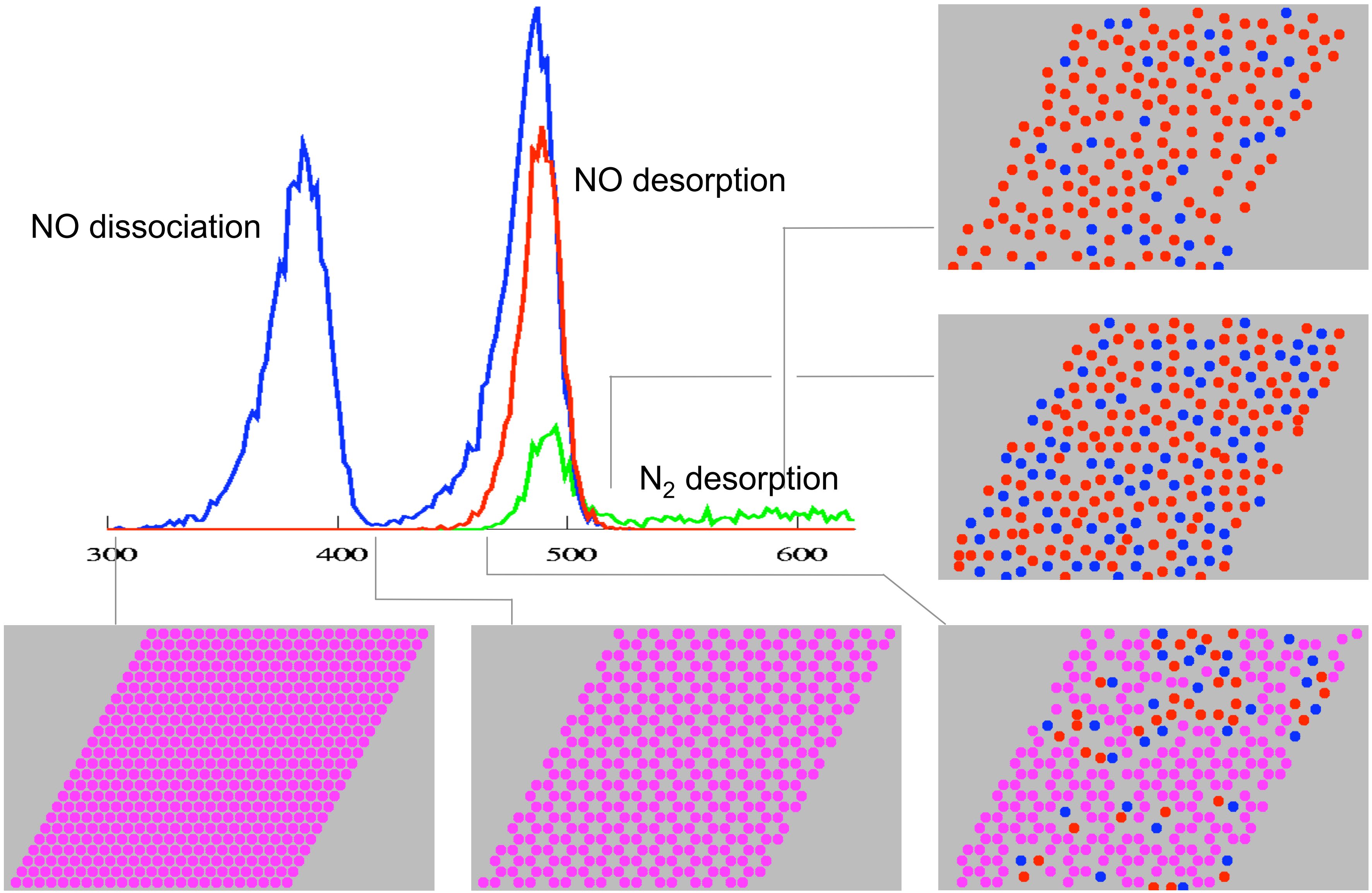
- Tonek Jansen kMC simulations of TPD
- Karin Oberg Segregation and desorption of mixed ices
- Martin McCoustra Interpreting Laboratory Desorption Data in an Interstellar Framework
- Zainab Awad Mantle Desorption and Chemical Evolution in Warm Cores around Solar-like stars

Tonek Jansen

Simulation 3-site model (high θ)

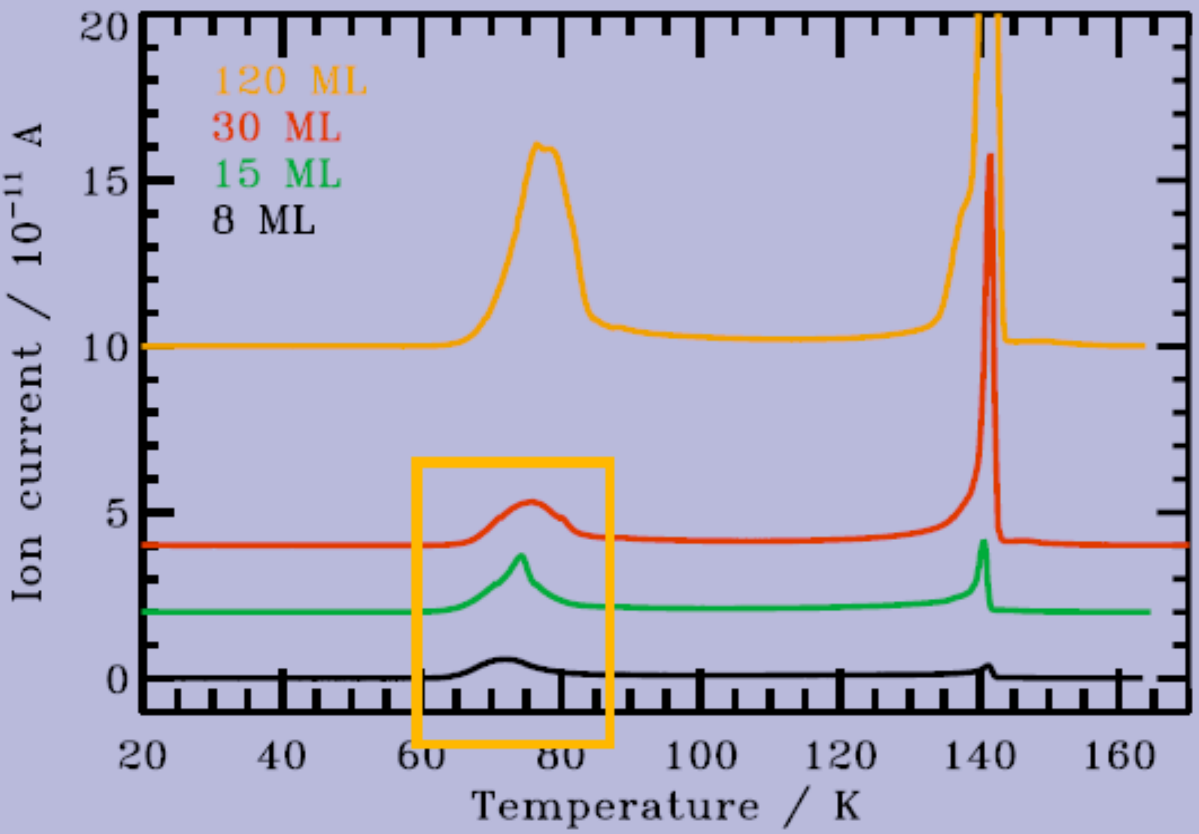


Rates and coverages



Karin Öberg

Surface segregation during desorption

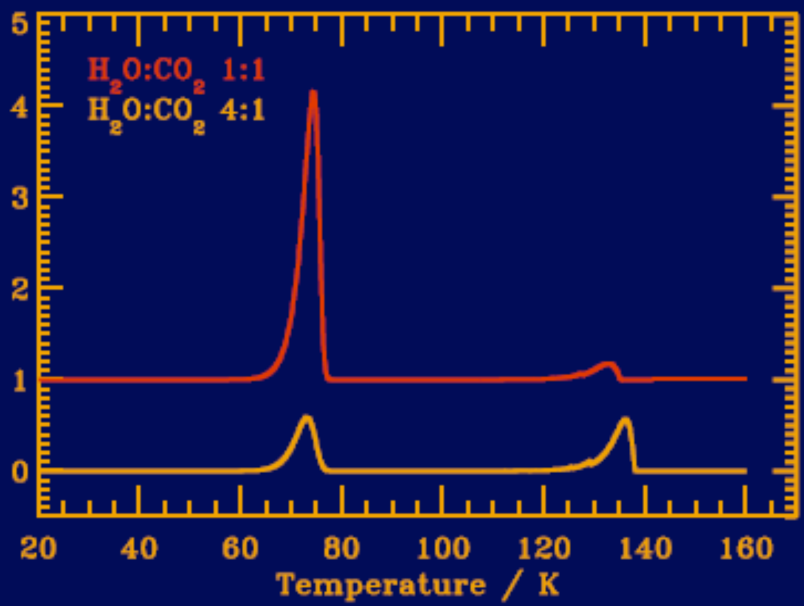


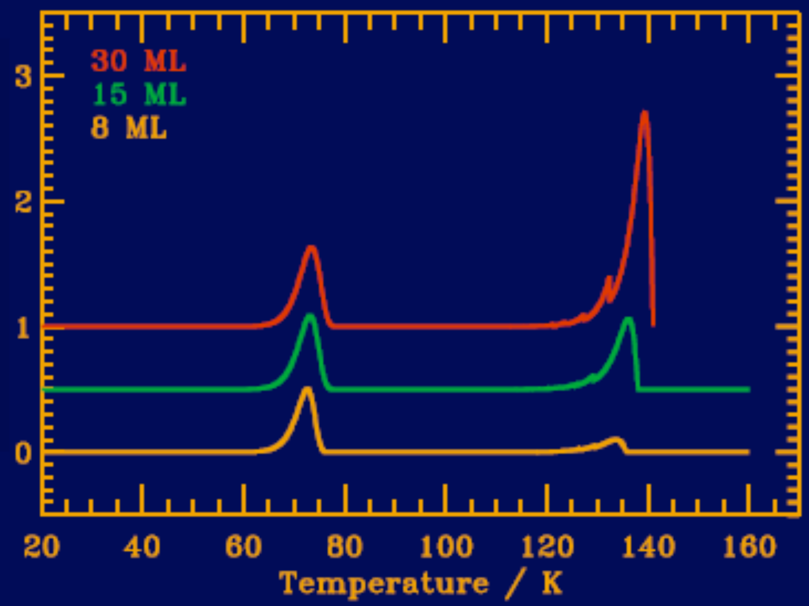
Desorption pattern explained by surface segregation before or during desorption for H_2O:CO_2 4:1 ices

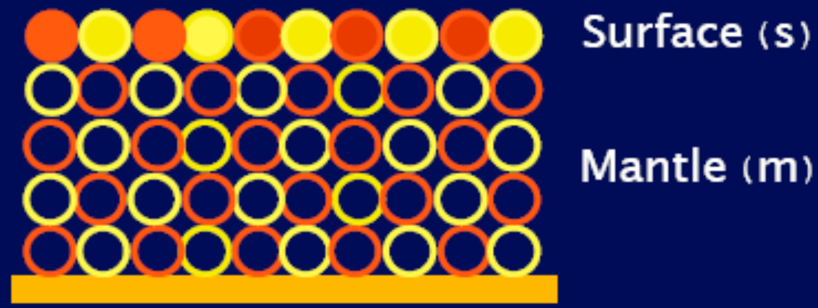
Qualitative model

$$\frac{dn_i^s(T,t)}{dt} = -R_i^{des} + \alpha R^{des}\frac{n_i^m}{n^m} \times \boxed{P_i} \qquad P_i \sim e^{-E_i^{dif}/T}$$

Need pure ice desorption barriers, CO_2 E^{dif}. Only fitting parameter is relative diffusion barrier $E_{CO2}/E_{H2O} \sim 0.81$







Day 4: Photoprocessing

- Lou Allamandola Ice grain photochemistry: It's worse than you think
- Stefan Andersson Photochemistry of water
- George Hassel Incorporating Laboratory Results into Gas-Grain Chemistry Models
- Dimtry Semenov Chemical evolution of Protoplanetary Disks

Lou Allamandola

RECOMMENDATION 1

Define several standard ices representative of different astronomical environments and study all processes on these standards

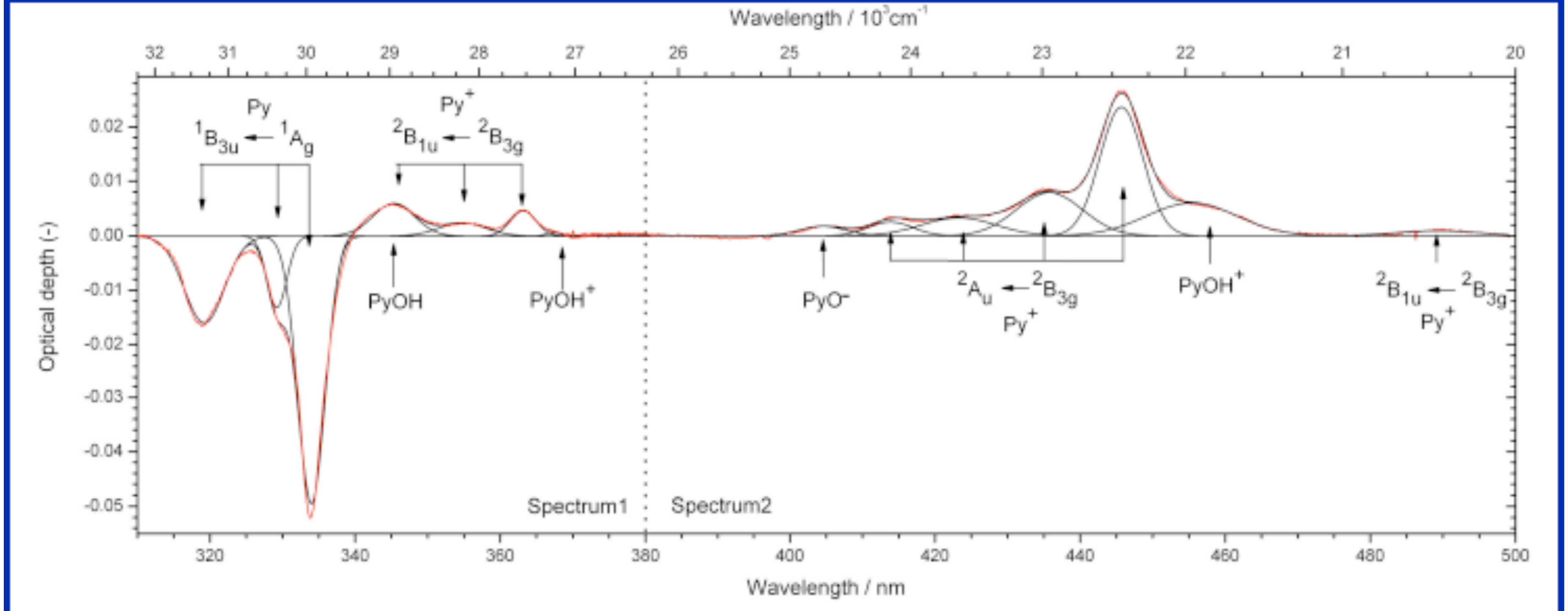
RECOMMENDATION 2

Simplify models at some point to paint big picture. Use the semi-empirical approach of the computational chemist rather than try to model every detail.

RECOMMENDATION 3

Consider Charged interstellar ices

Loss of neutral pyrene (Py) and growth of Py^+ PyOH, $PyOH^+$, and possibly PyO^- upon VUV irradiation of H_2O/Py (~1000/1) ice at 10K



Spectrum after 1200s of VUV radiation

Bouwman et al. ApJL, submitted

Stefan Andersson

What is the influence on the solid-phase chemistry?

- "High-energy" H atoms
  - $H + H_2O \rightarrow OH + H_2$
  - H + other species in ice (CO, ...)

- OH radicals
  - $OH + CO \rightarrow H + CO_2$

- Vibrationally excited H_2O?

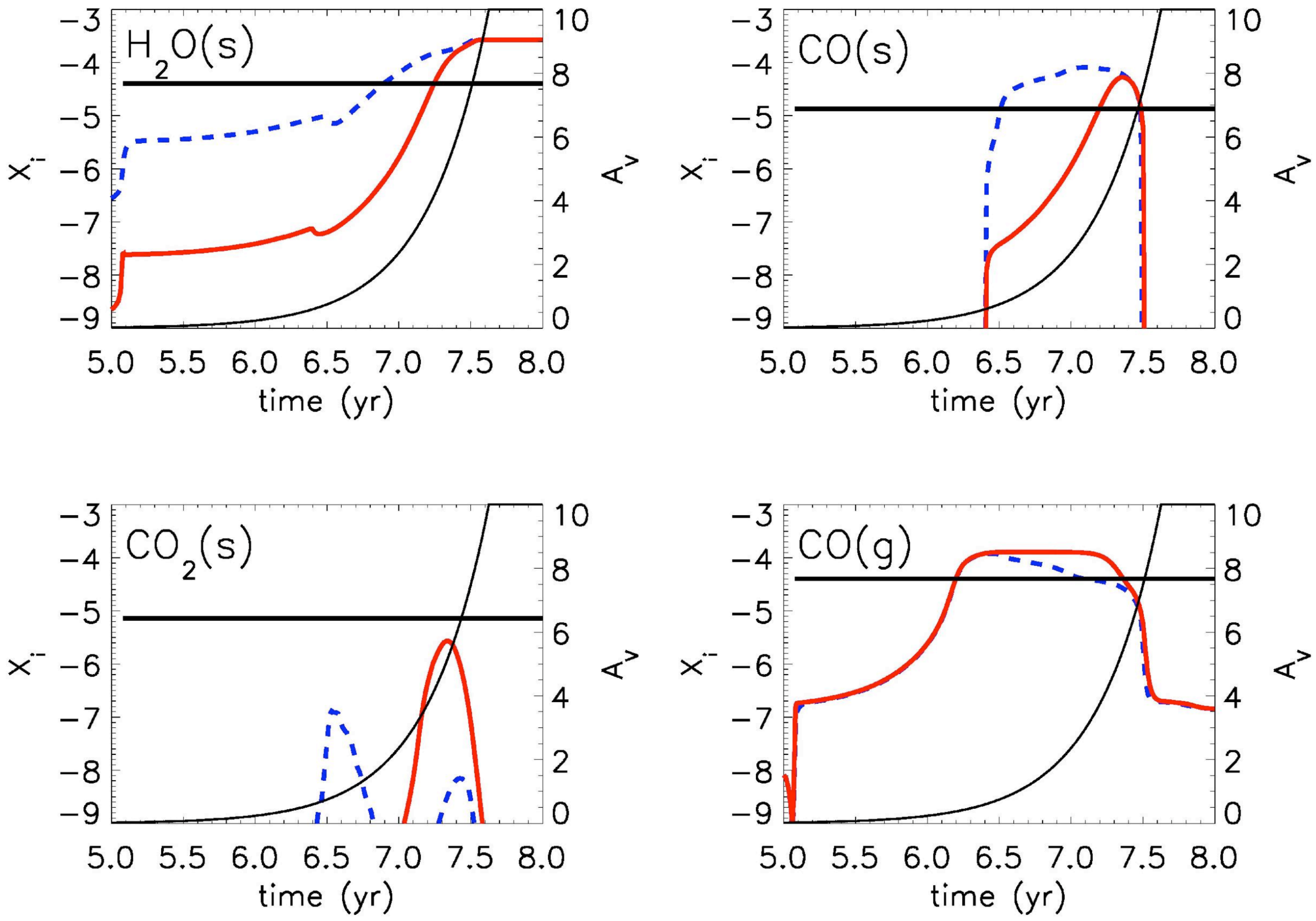
- Local heating?

What is the influence of photodesorbed species on the gas-phase chemistry?

- "High-energy" H atoms
- Vibrationally excited H_2O?
- OH radicals

George Hassel

Ice – Photodesorption



Day 5: Experimental techniques

- Liv Hornekaer Insights gained from complimentary experimental techniques in laboratory studies of surface reactions of interstellar relevance
- Elias Vlieg Determining interface structures using microscopy and X-ray diffraction
- Harold Linnartz Laboratory astrochemistry: problems, solutions, and problems to be solved

Experimental challenges

Mobility of physisorbed species

Complexity

-To what level of detail do we need to understand interstellar surface reactions?

Influence of grain size

- to which extend may we simplify (i.e. work under laboratory controlled conditions) ?
- to which extend may we cheat (i.e. use higher fluxes / densities, worse vacuum) ?
- to which extend may we extrapolate (3 hr laboratory experiment to 10^6 yrs) ?
- to which extend do we **<u>really</u>** know where we are talking about ?

Scientific challenges

More data on well characterized samples

- Two lab data
- Internal state distributions (less important)
- TPD's over a wider temperature interval
- More "realistic samples"
  - -influence of small size
  - -Role of small grains/PAHs
  - -extrapolation issues

Reaction induced desorption

Complex molecule formation

Charge

How well can interstellar grains be characterized?

Overall summary of the meeting

- Adsorption and desorption relatively well understood with good parameters available for stable species.

- For surface reactions, we are getting there

- Charged species are not addressed yet

- Mobility of reactive species still hard to measure

- Gas phase and surface reactions are very different and need different modelling approaches

Overall summary of the meeting

- Adsorption and desorption relatively well understood with good parameters available for stable species.
- For surface reactions, we are getting there
- Charged species are not addressed yet
- Mobility of reactive species still hard to measure
- Gas phase and surface reactions are very different and need different modelling approaches
- Don't be afraid!!! There are ways around this and to couple them.