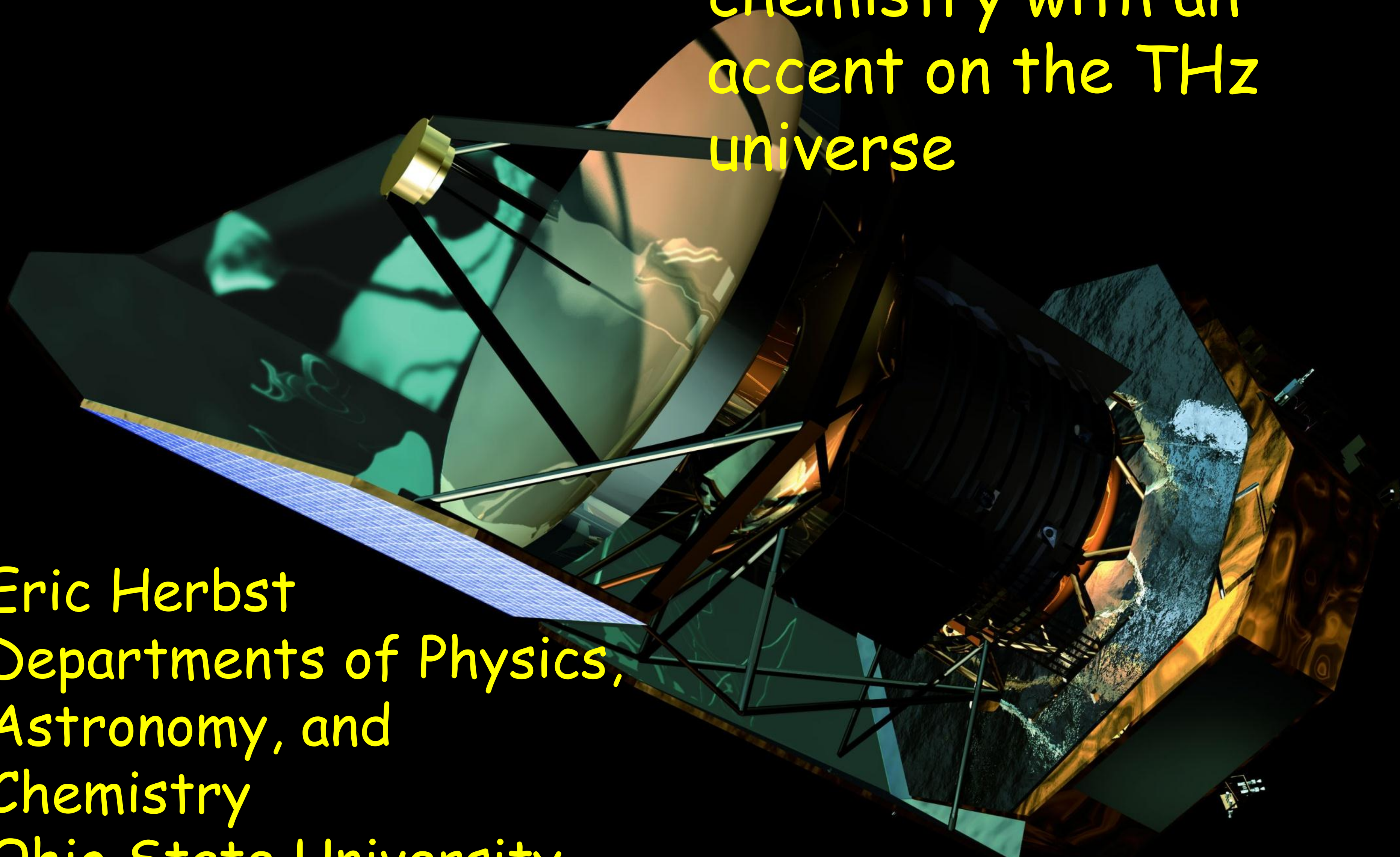
# Gas and grain-surface chemistry with an accent on the THz universe



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And coming shortly…


Results to yield many new challenges to modelers!

# Chemical Models

**Gas-phase reactions**

**Grain-surface reactions**

Abundances, columns, spectra, **uncertainties**

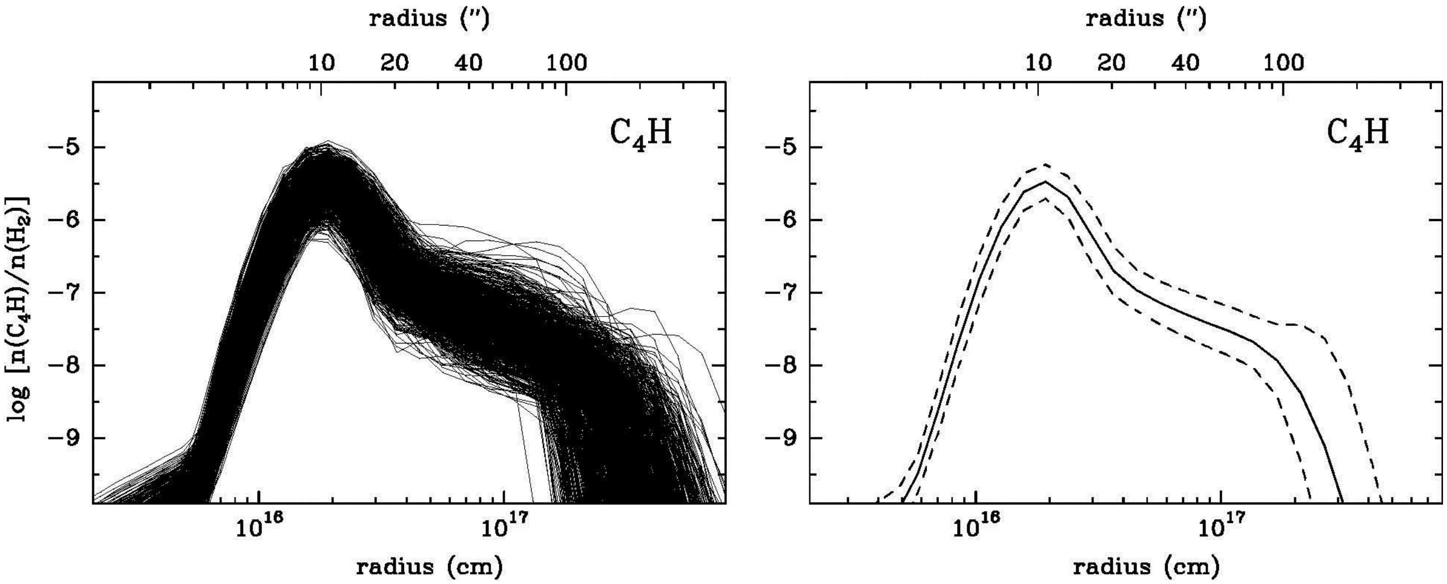
Observations

Physical conditions, history

Limited by chemical knowledge

# Uncertainty &Sensitivity Methods

Help to determine which reactions to study in the lab or theoretically




Wakelam et al. 2010

# Sources Modeled

- Diffuse clouds
- Cold dense cores
- Pre-stellar cores
- Hot Cores
- Outflows
- Shocks
- Protoplanetary disks
- PDR's; XDR's
- Circumstellar envelopes
- Protoplanetary nebulae
- Planetary nebulae
- AGN disks
- Exo-planetary atmospheres

# Dynamics/Heterogeneity

- Static shell/zone model (pre-stellar cores; PDR's)
- Homogeneous warm-up model (hot cores, environment surrounding hot cores)
- Shock model (formation of dense cores while chemistry occurs)
- 1-D hydrodynamic model (prestellar core collapse, prestellar → protostellar collapse)

# Gas-phase Chemical Networks

Biased towards low temperature, but very few measurements at 10 K

Two major networks: udfa.net, osu

Cosmic ray ionization
Photoionization/dissociation
Ion-molecule reactions
**Radical-neutral reactions**
**Dissociative recombination**
Radiative association
Electron attachment
+ ion - - ion neutralization
Dissociative attachment

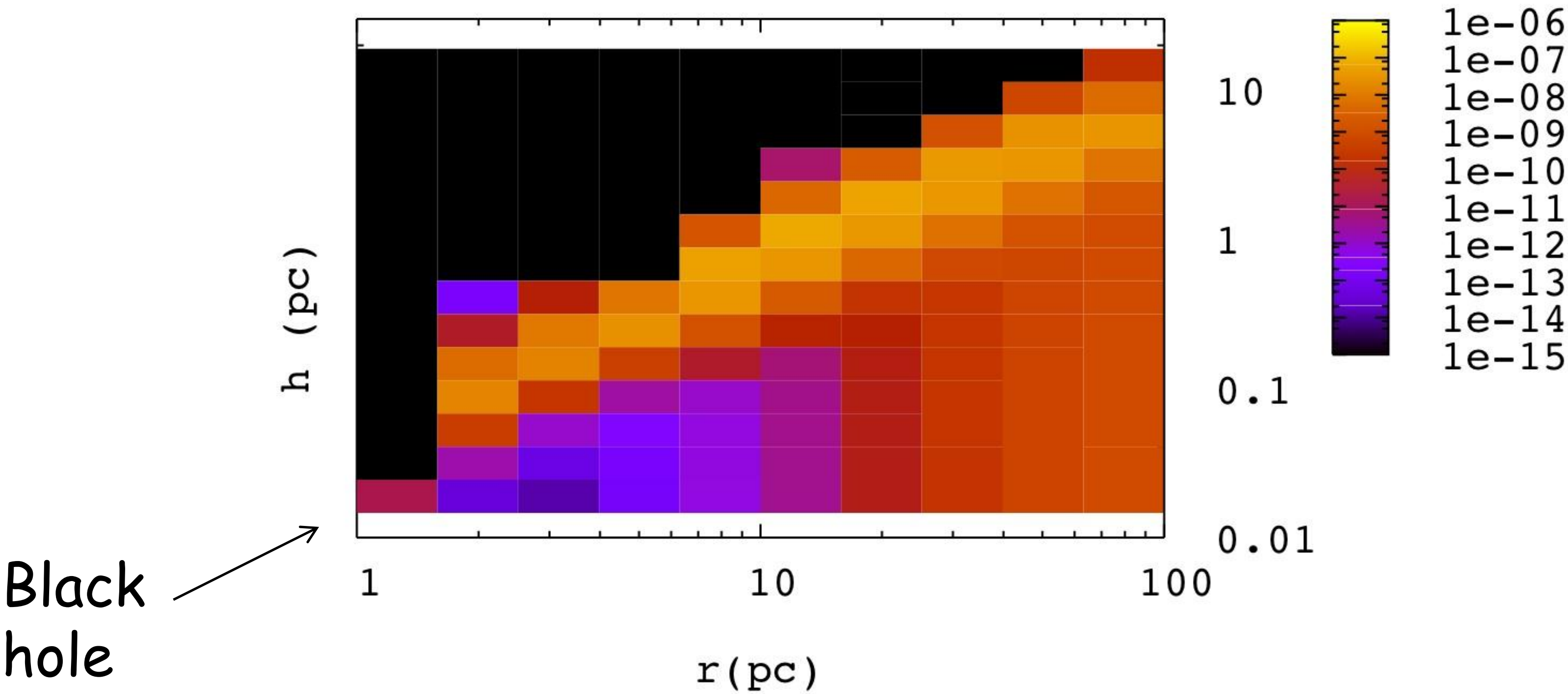
# High Temperature Network

- Should work up to 800 K (limited mainly by formation of H2 on dust)

Classes of reactions added/improved:

1. ion-polar neutral reactions
2. Reactions with barriers, especially involving H2.
3. Reverse endothermic reactions
4. Proton and charge exchange

# Model of AGN Disk (Harada et al. 2010) for NGC 1068

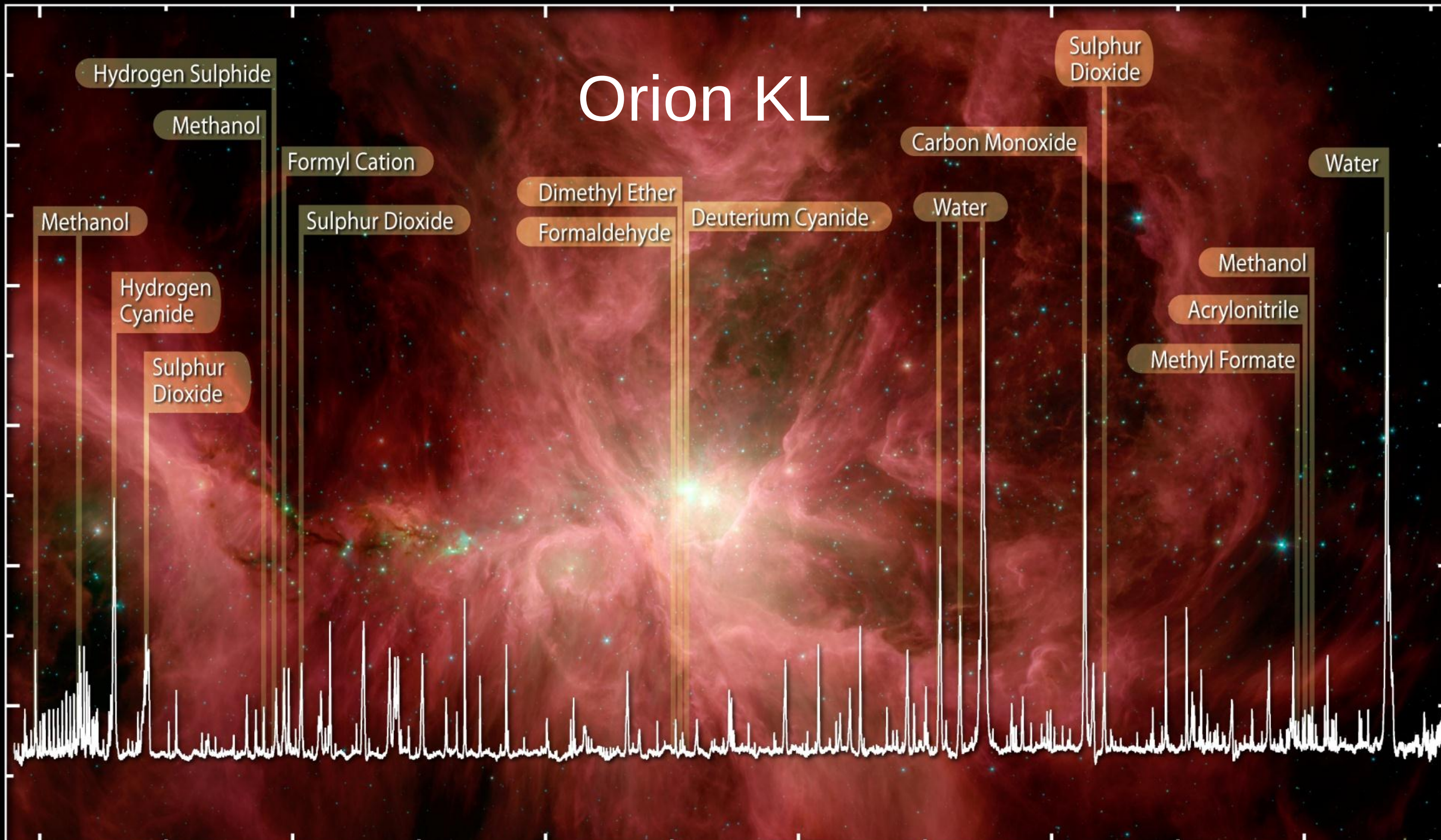



$HCO^+$ fractional abundance as a function of h and r calculated with new OSU high-temperature gas network and physical model.

# Additional Networks

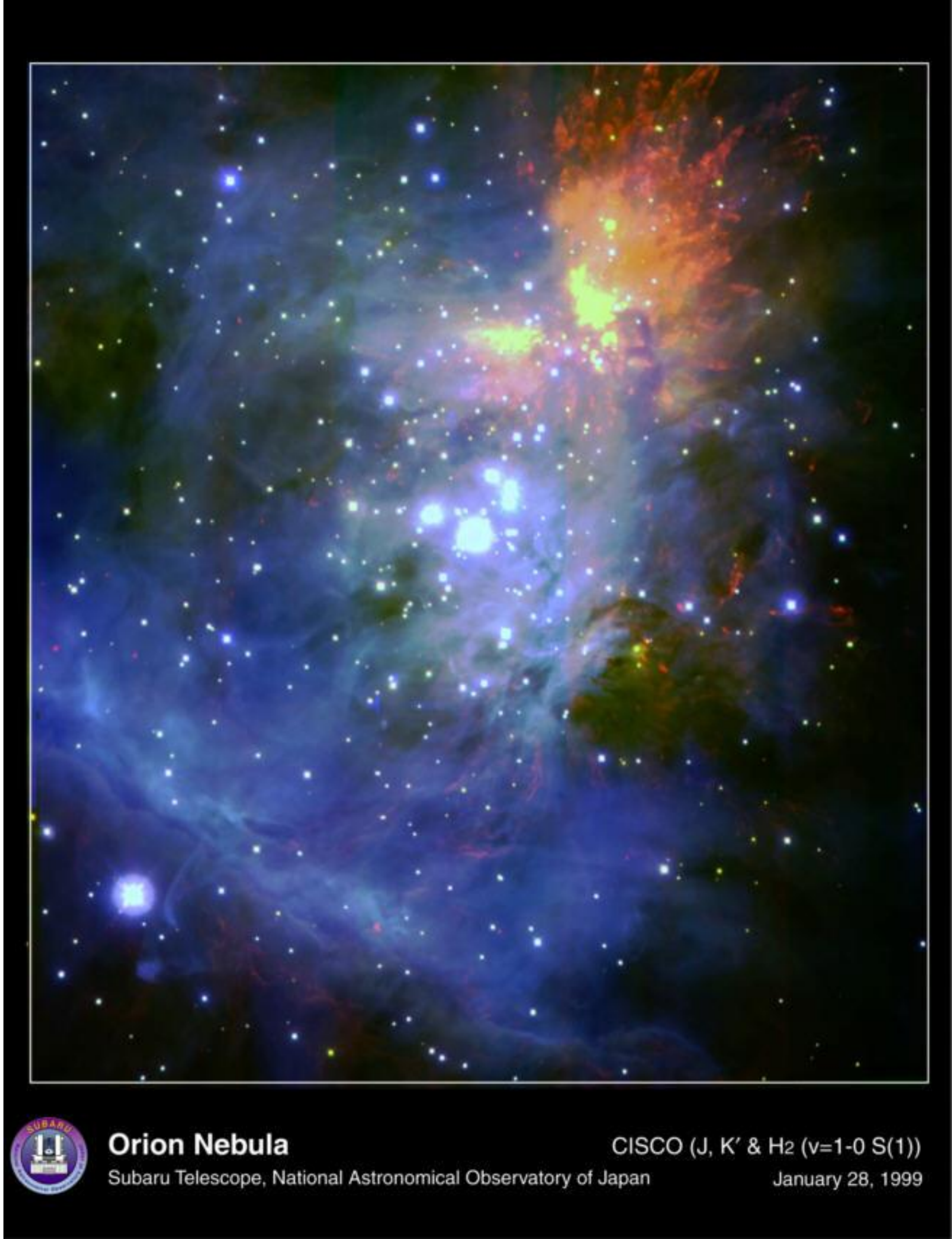
- *Shocks* (brief periods up to 4000 K)
- *Carbon-rich regions* (IRC+10216)
- *Isotopic fractionation* (D, 13C, 15N)
  - Details of synthesis, including gas-phase vs surface, and specific gas-phase processes. $^{13}CCH$ vs $C^{13}CH$; $^{13}CH_3OH/^{12}CH_3OH$
- *ortho-para conversion*
  - Handle on physical conditions and evolution

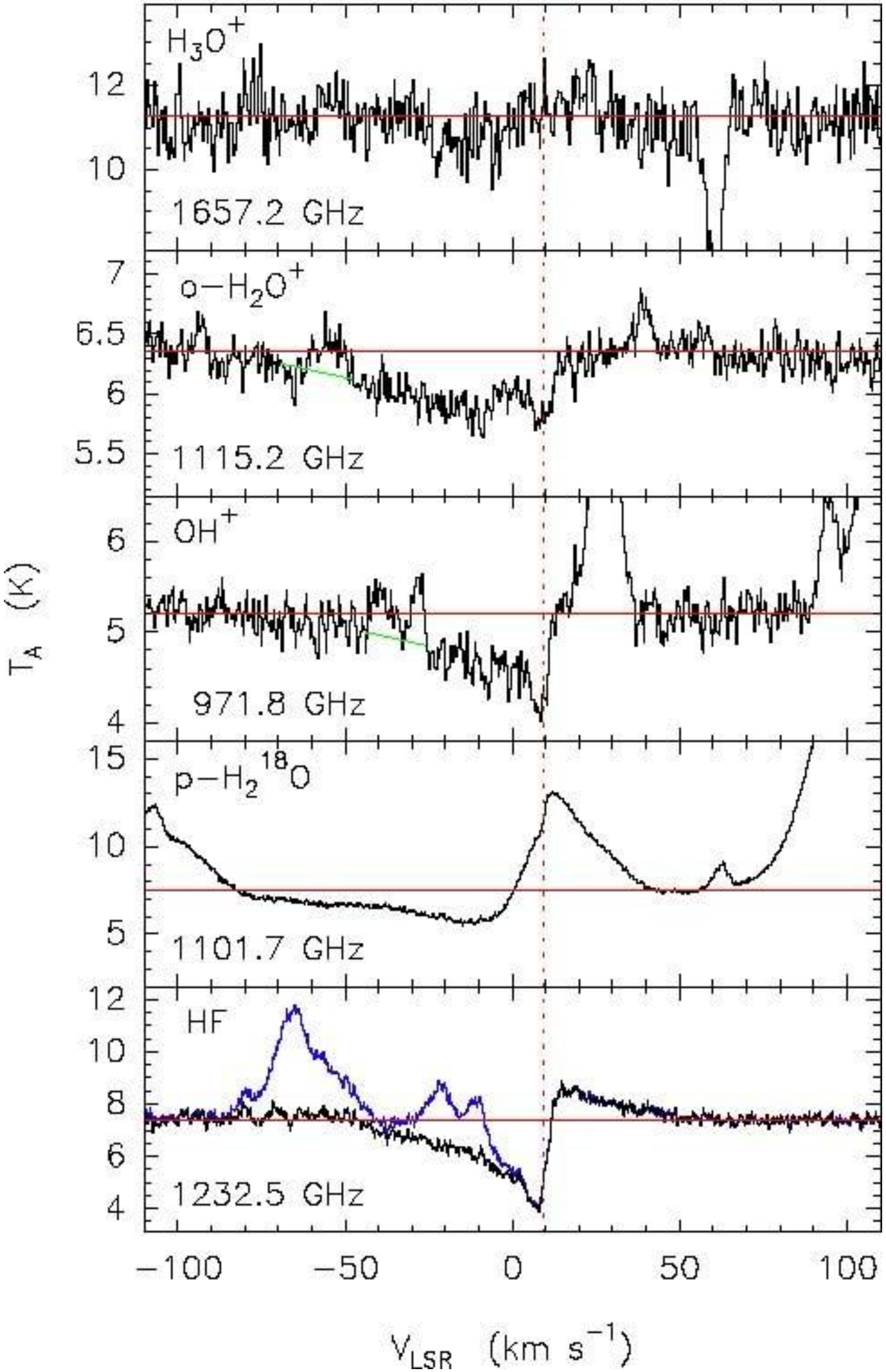
$$H_2 + H_3^+ \Leftrightarrow H_3^+ + H_2$$




HIFI Spectrum of Water and Organics in the Orion Nebula

Herschel is showing us absorption spectra of the outer regions of THz sources.






# Orion KL Outflow (0 to −50 km/s)

(Herschel/HIFI/HEXOS)

A violent place, rich in strange ions - OH+, H2O+ - that react with H2

$OH^+ \approx 2 \times H_2O^+ \gg H_3O^+$

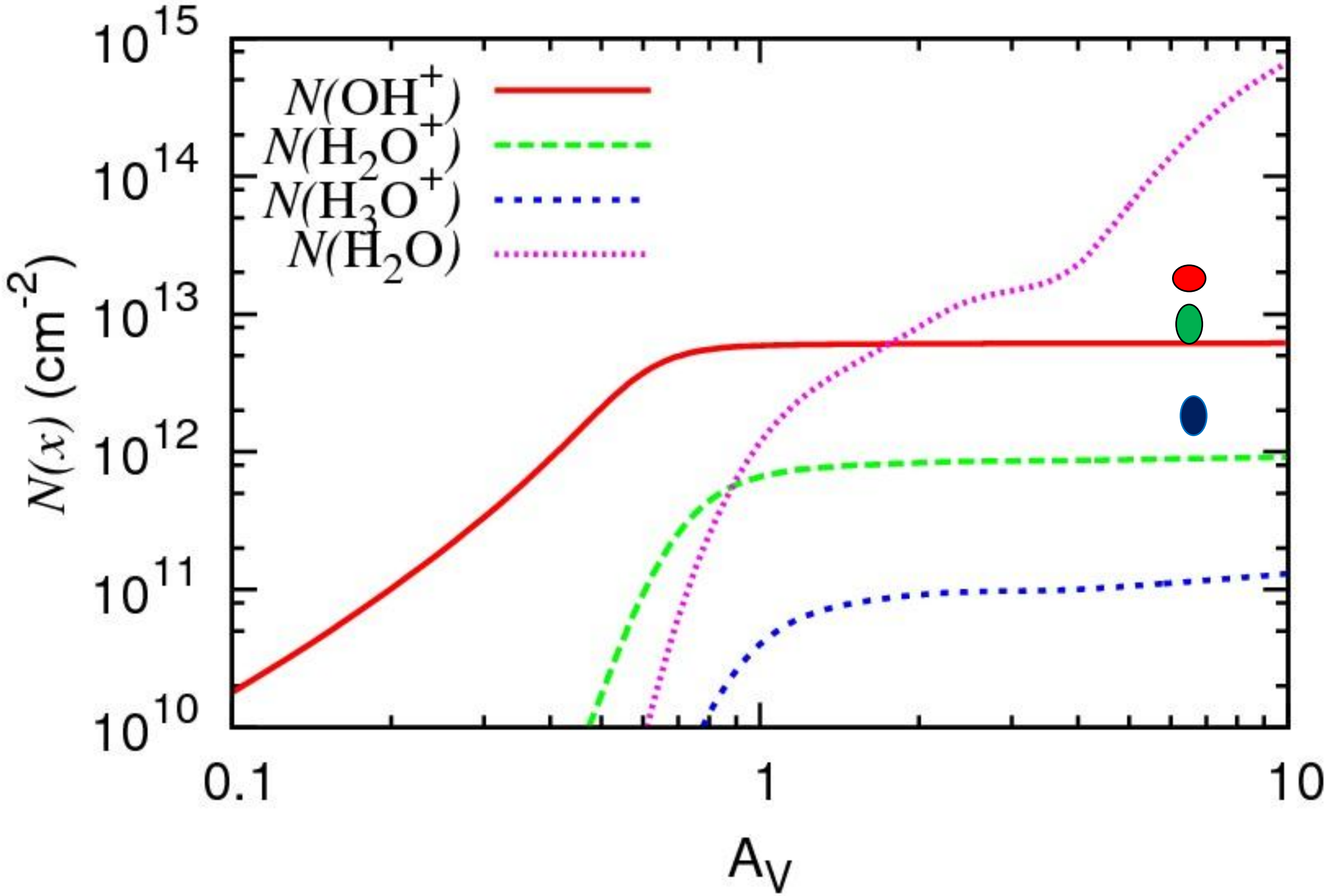
Gupta et al. (2010)

# Chemistry of $OH^+$, $H_2O^+$, $H_3O^+$, $H_2O$

- $OH^+ + e \longrightarrow O + H$
- $OH^+ + H_2 \longrightarrow H_2O^+ + H$
- $H_2O^+ + e \longrightarrow OH + H$; $O + H_2$
- $H_2O^+ + e \longrightarrow O + H + H$
- $H_2O^+ + H_2 \longrightarrow H_3O^+ + H$
- $H_3O^+ + e \longrightarrow H_2O + H$; $OH + H_2$, $OH + 2H$
- $H_2O + h\nu \longrightarrow H_2O^+ + e$
- $OH + h\nu \longrightarrow OH^+ + e$
- $H + CRP \longrightarrow H^+ + e$
- $H^+ + H_2O \longrightarrow H + H_2O^+$

- "PDR" models with high $\zeta$, $\chi$, and influx of water

Model of Orion Outflow Rimmer et al.




$\zeta$= 2.5(-15) s-1; $\chi$= 10(4); n = 1(04) cm-3

# $H_2O^+$ $(X\ ^2B_1)$

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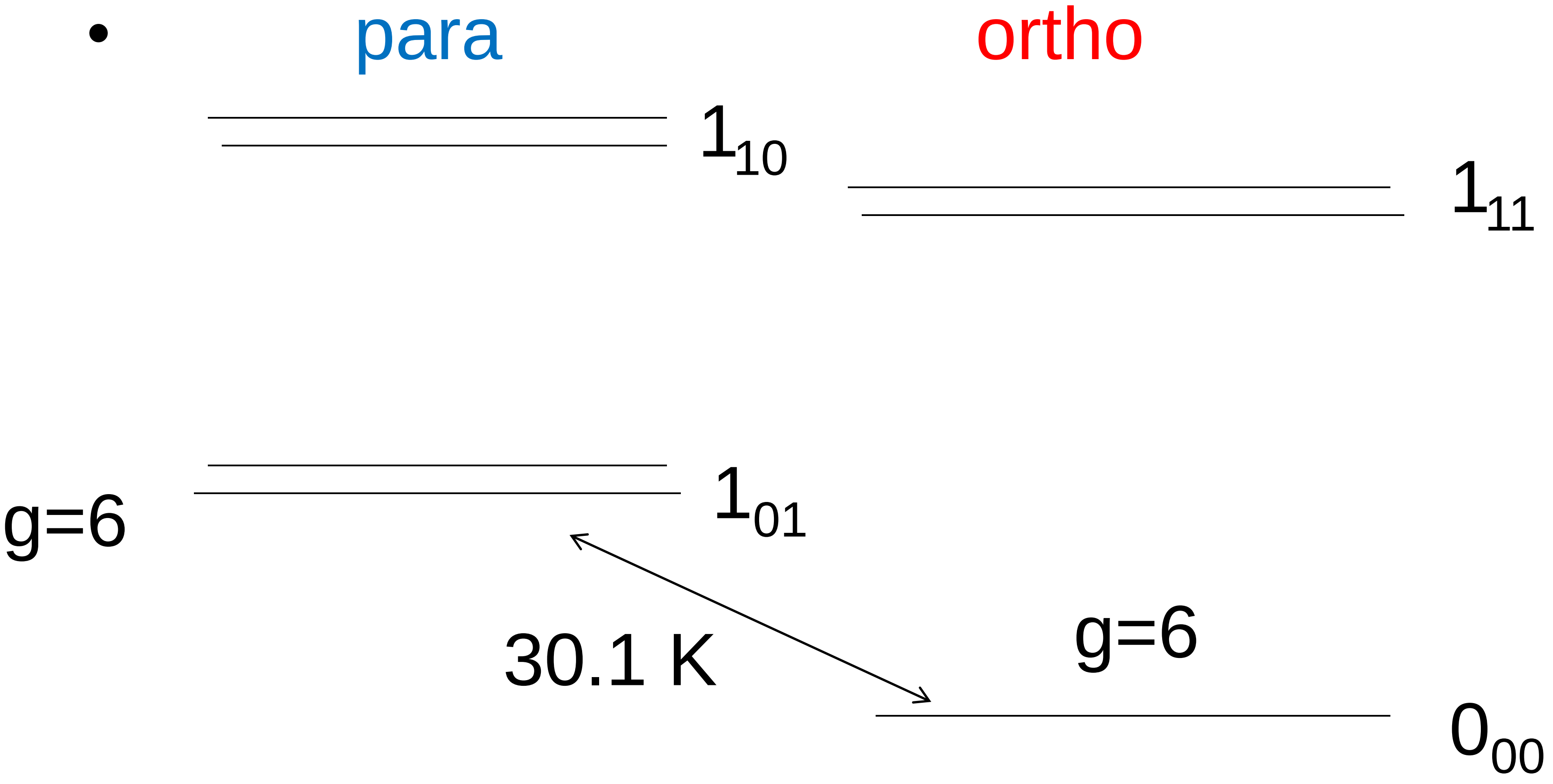



$T \to 0$ K OPR $\to \infty$ $\to$ $\to$

# A "Simple" Model for H2O+ (o,p) In Diffuse Clouds (Neufeld & Herbst)

- OH+ + H2 $\longrightarrow$ p-H2O+ + H   ($f_p$) hopping or
- $\longrightarrow$ o-H2O+ + H ($f_o$)   complex
- p-H2O+ + H $\longleftrightarrow$ o-H2O+ + H ($k_f$, $k_r$)
- (equilibration towards some $T_{spin,rot}$ which must be determined)
- H2O+ + e $\longrightarrow$ Products  ($k_{dr}$)

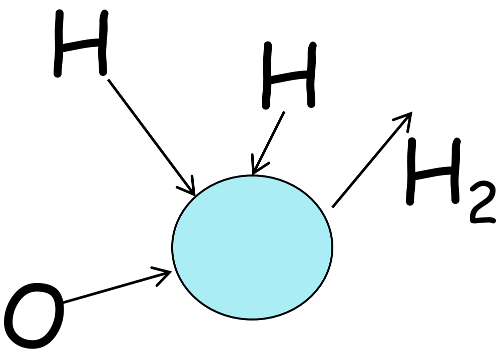
- OPR  = 4.8:1 must be reproduced

# Gas-grain Chemical Networks

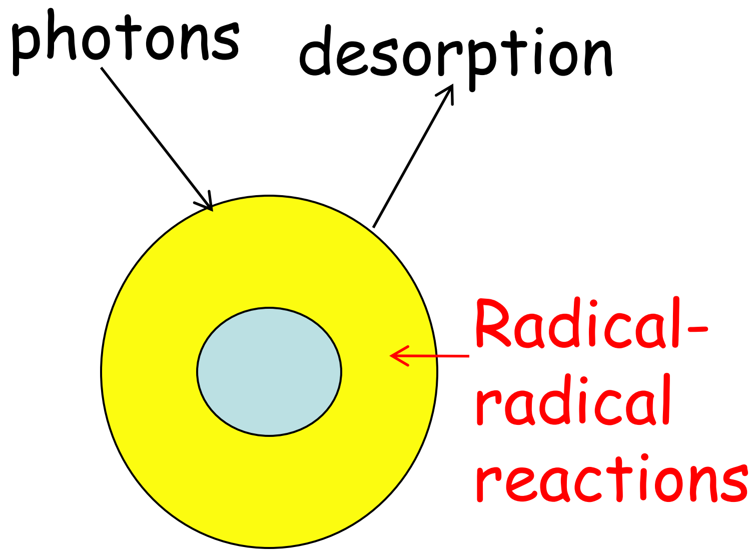
Designed in our group, starting from Hasegawa et al. (1992) and now used by a few others.

Gas-phase and grain-surface reactions are coupled by accretion and desorption, both thermal and non-thermal (e.g. photodesorption).

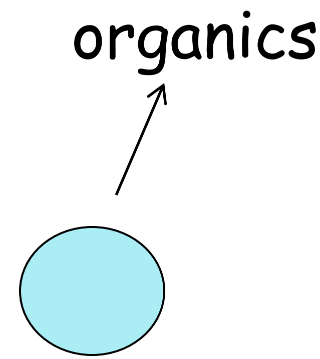
# Evolution of surface processes




Diffusion on bare dust particles leads to:




Build up of ice mantles, mainly H2O, CO, CO2, methanol, leads to:




Thermal evaporation during heat-up; or sputtering

# Surface Chemistry in Spiral Arm Diffuse Clouds

Possibly dominant in formation of water, ammonia, NH2, but need desorption mechanism (e.g. reactions or photodesorption)

Dominant in formation of H2

# Hot Core Chemistry: gas-grain model

100-300 K

desorption

10 K

Cold phase +accretion + surface chemistry (H-rich) leads to saturated ices

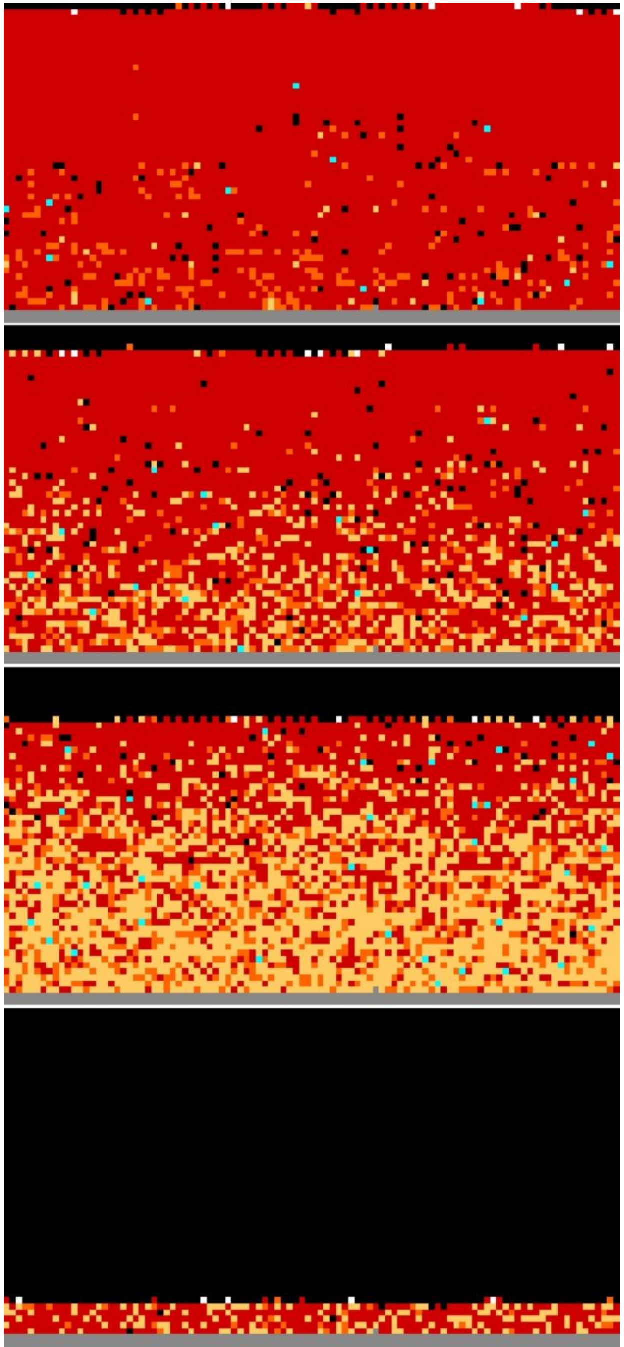
Surface chemistry (H-poor) involving radicals (formed by photolysis)

Saturated organic molecules such as ethers, alcohols

Garrod & Herbst (2006)
Garrod et al. (2008)

# Methods for Surface Chemistry

- Rate equations (as in gas)
- Modified rate equations
- Macroscopic stochastic methods (Monte Carlo, direct master equation, method of moments)
- Microscopic stochastic methods; aka kinetic Monte Carlo approaches



# Interstellar Simulation based on Lab Simulation

Hydrogenation of CO into methanol at temperatures of (top to bottom) 12.0 K, 13.5 K, 15.0 K, and 16.5 K

Cuppen et al. 2009

2 x $10^5$ yr cold core

# New Gas-Grain Network Improvements

- 1. High temperature version (up to 800 K) for gas-phase network, with lower dust temperatures.
- 2. Grain size distribution, with growth over time.

# Conclusions

- 1. Stochastic methods are needed to make surface chemistry more robust; progress is being made but we are still not there.
- 2. We do not yet fully understand the chemistry of some environments detected by Herschel and to be detected by SOFIA and ALMA.
- 3. Heterogeneity and dynamics will play an exceedingly important role in the next decade.