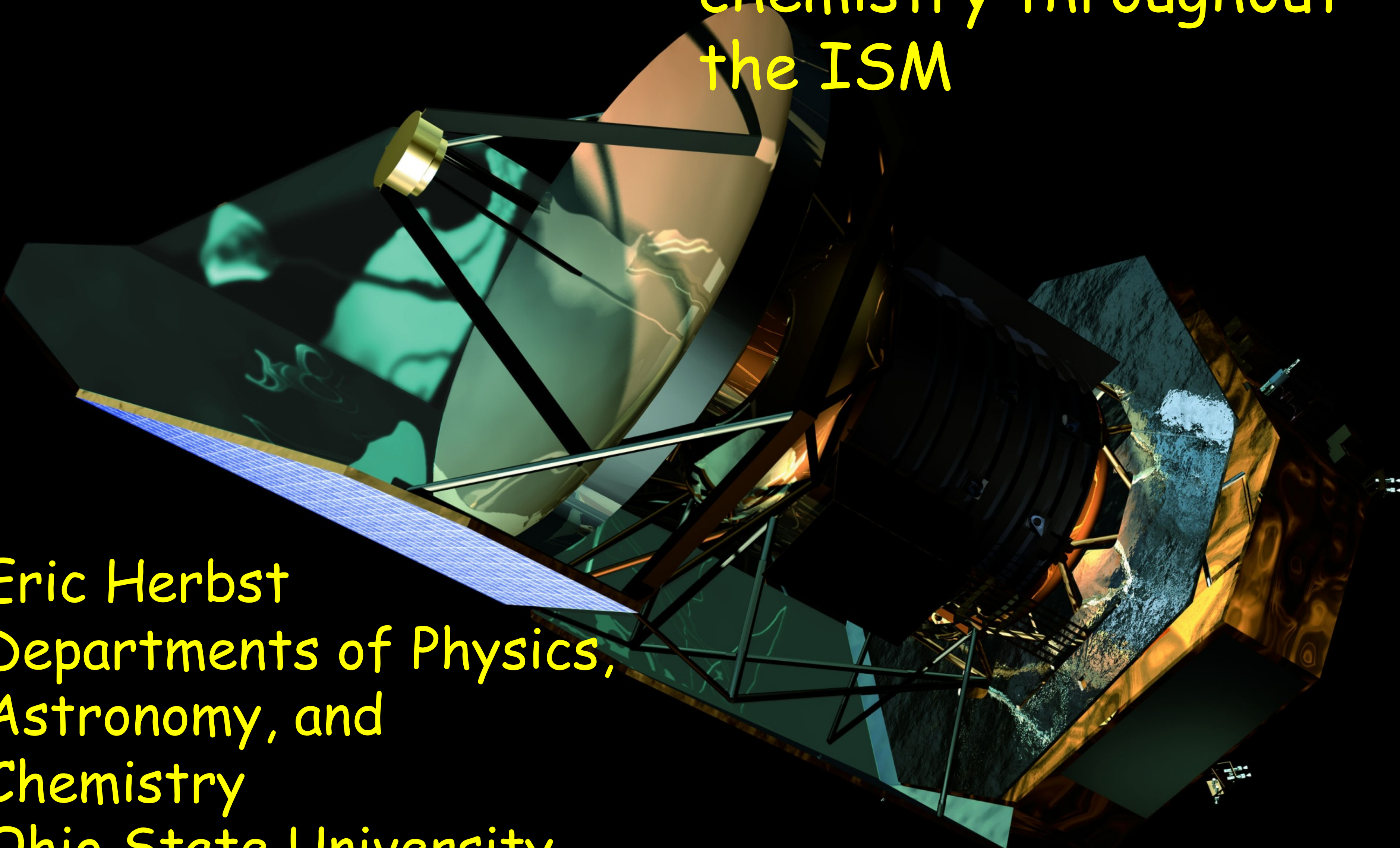
Gas and grain-surface chemistry throughout the ISM



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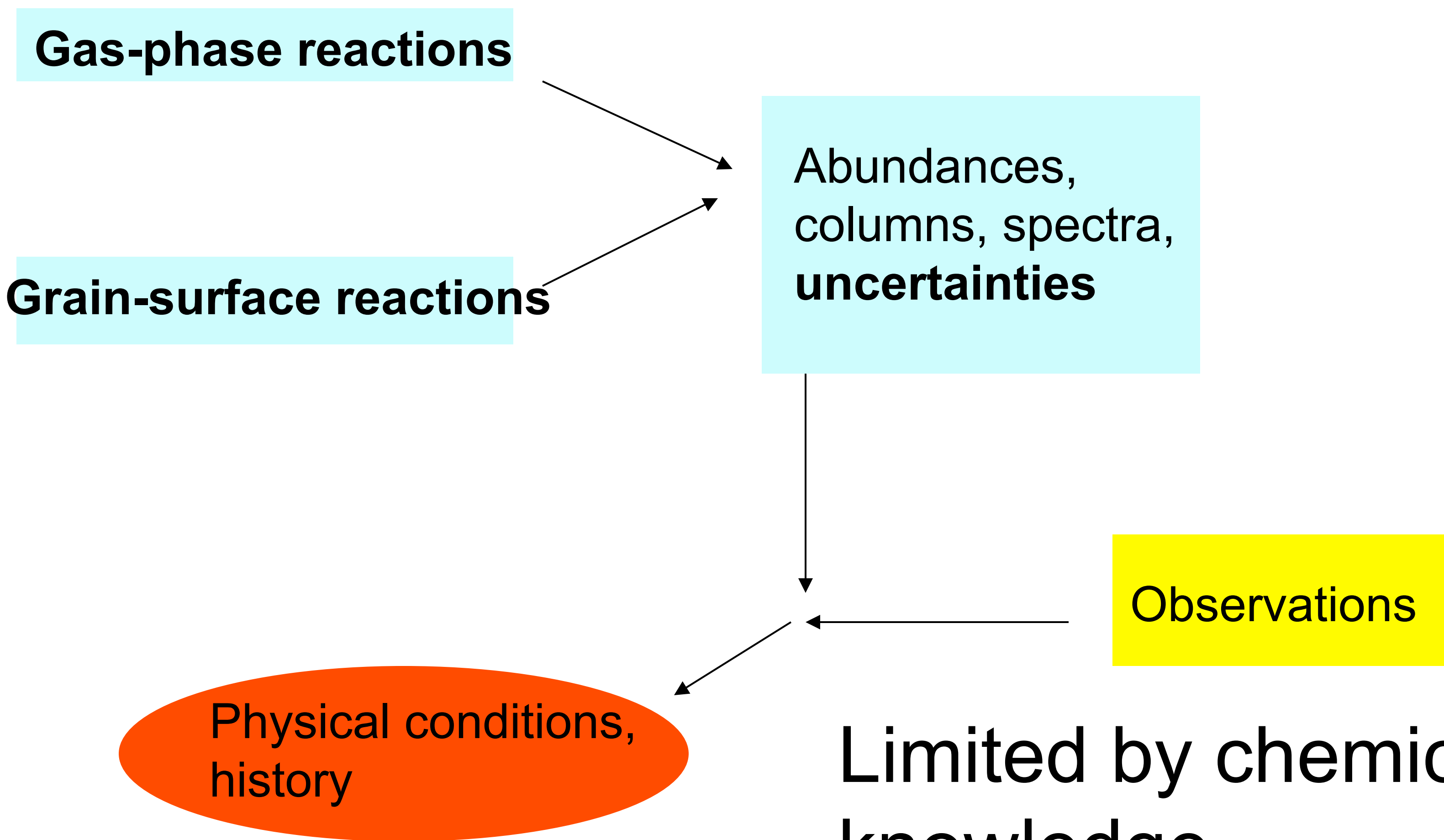
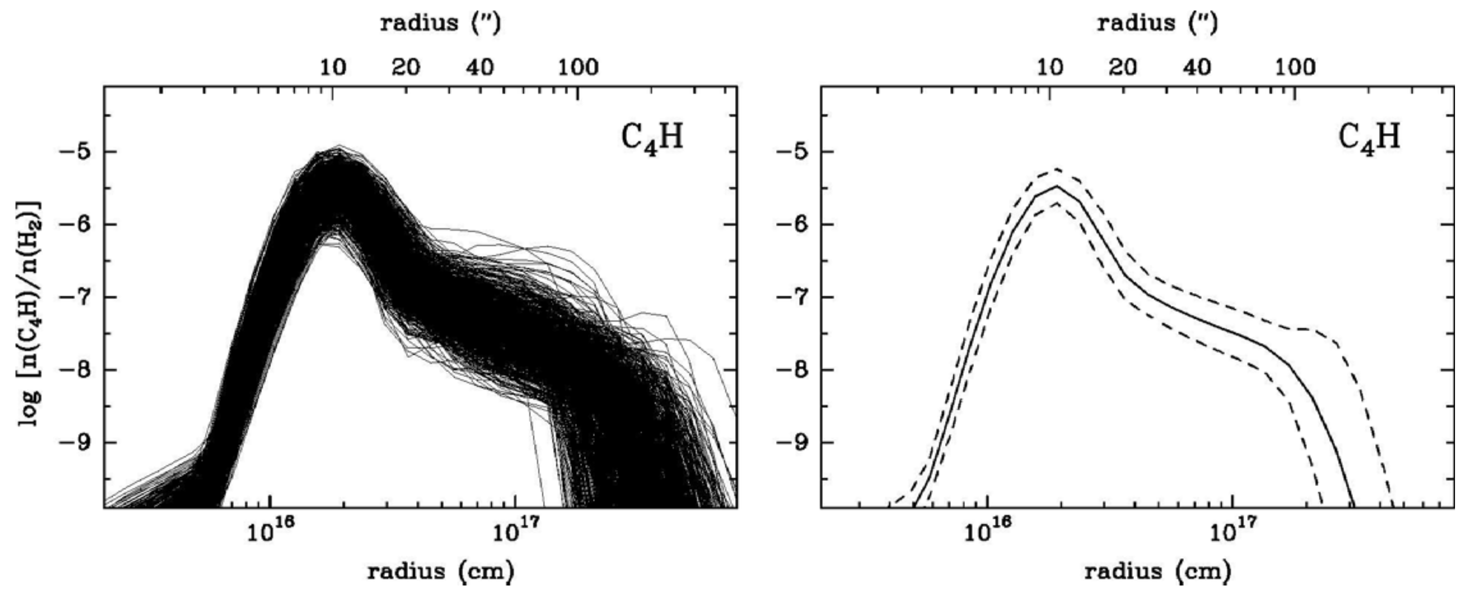
Chemical Models



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

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

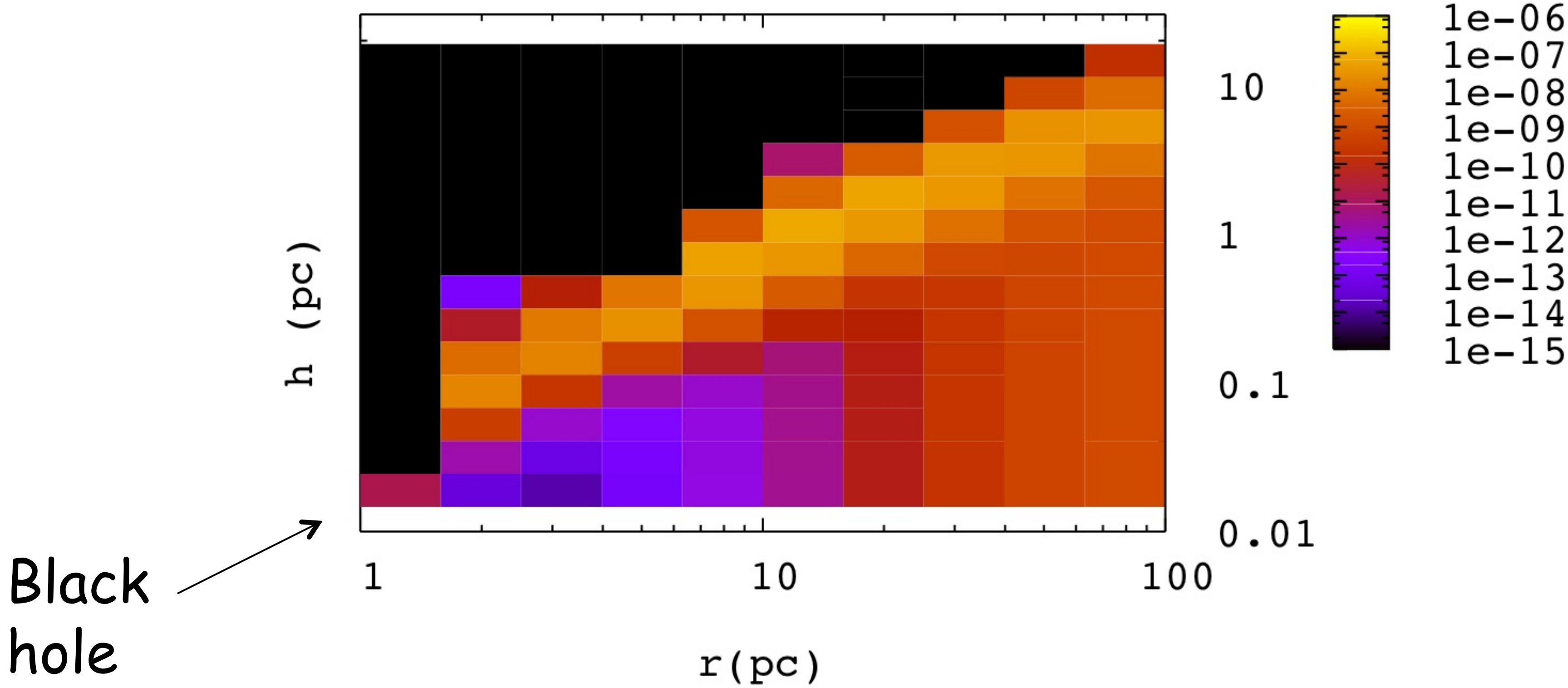
High Temperature Network

- Should work up to 800 K (limited mainly by formation of H_2 on dust)

Classes of reactions added/improved:

1. ion-polar neutral reactions
3. Reactions with barriers, especially involving H_2.
5. Reverse endothermic reactions
4. Proton and charge exchange

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

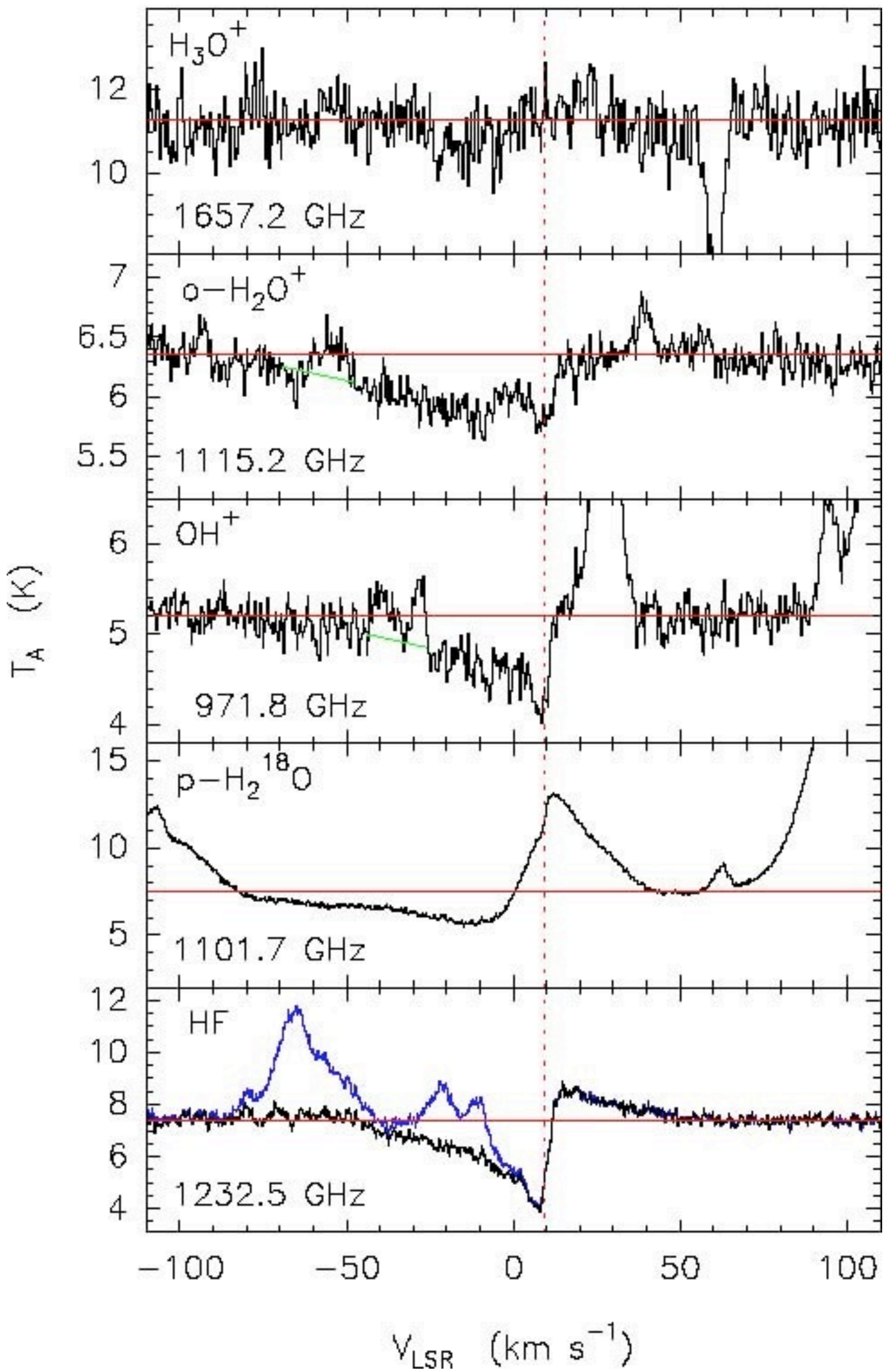


HCO^+ fractional abundance as a function of h and r calculated with new OSU high-temperature gas network and physical model.

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

$H_2 + H_3^+$ [illegible] $H_3^+ + H_2$



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

Gupta et al. (2010)

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

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

- "PDR" models with high ζ and influx of water

A "Simple" Model for H_2O^+ (o,p) In Diffuse Clouds (Neufeld & Herbst)

- $OH^+ + H_2 \rightarrow$ p-H_2O^+ + H (f_p) hopping or
- $\rightarrow$ o-H_2O^+ + H (f_o) complex
- p-H_2O^+ + H $\longleftrightarrow$ o-H_2O^+ + H (k_f, k_r)
- (equilibration towards some $T_{spin,rot}$ which must be determined)
- H_2O^+ + e $\longrightarrow$ Products (k_{dr})

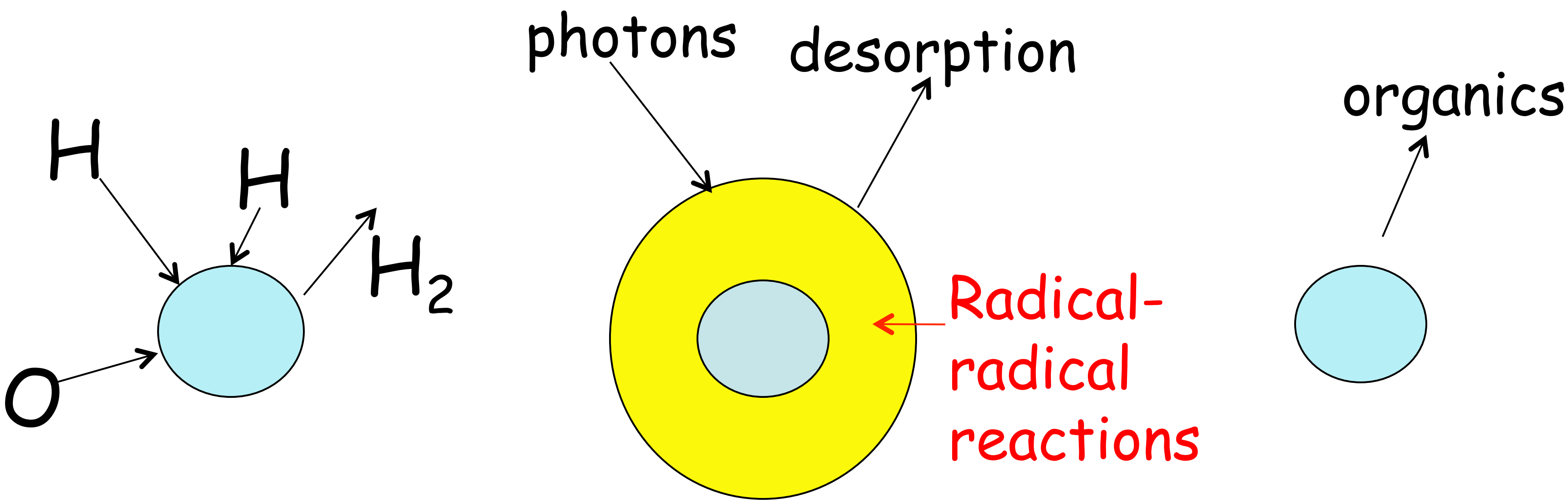
- OPR = 4.8:1 must be reproduced

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



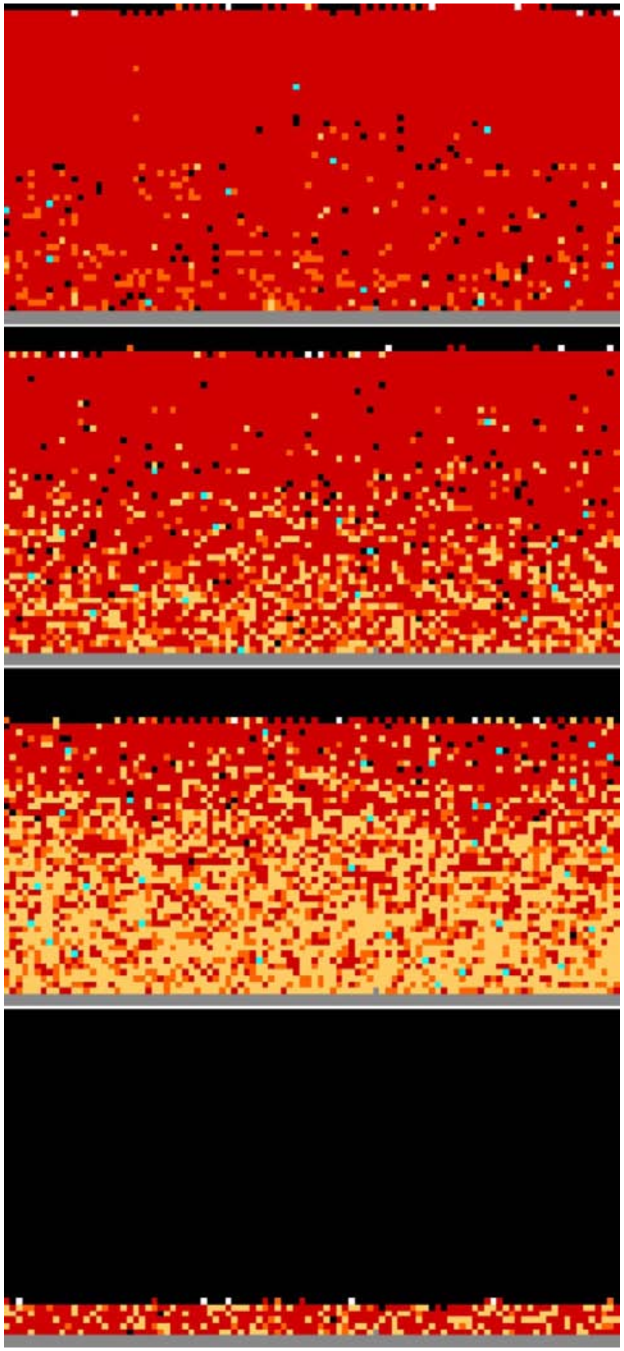
Diffusion on bare dust particles leads to:

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

Thermal evaporation during heat-up; or sputtering

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

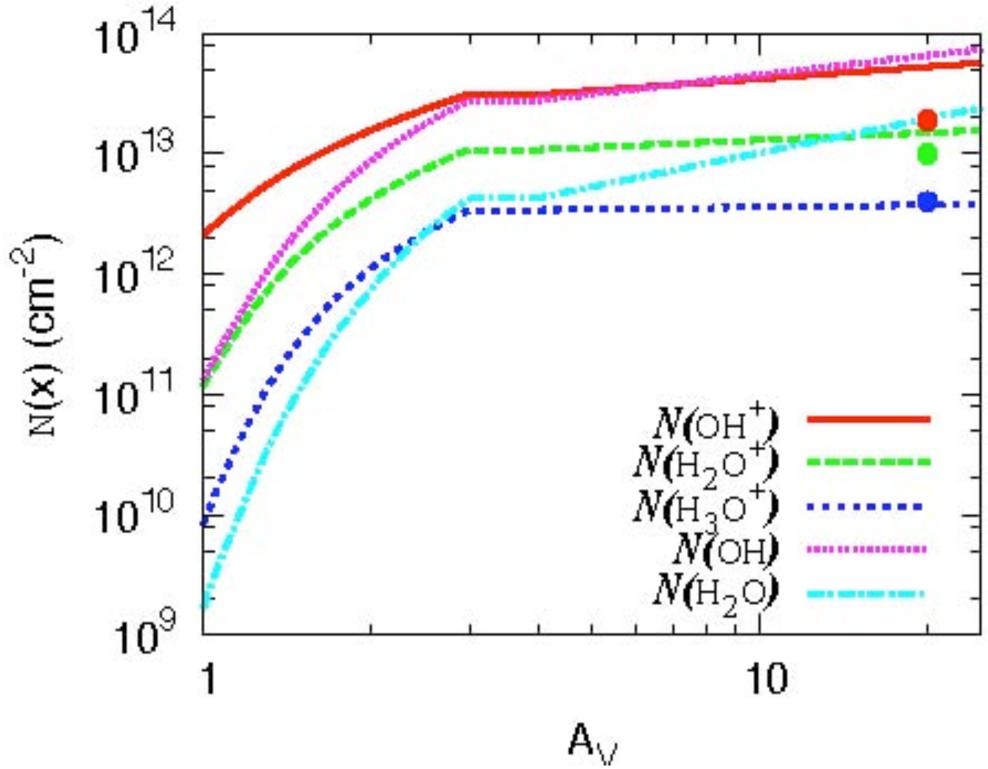
- 1. High temperature version (up to 800 K) for gas-phase network, with lower dust temperatures.
- 2. Grain size distribution, with growth over time.

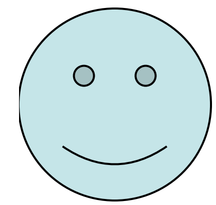
Conclusions

- 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 ALMA.
- 3. Heterogeneity and dynamics will play an exceedingly important role in the next decade.

Strong PDR Model of Orion KL Outflow

CR, X-ray,
UV





T = 400 K at
edge
At Av=3, H = H2
& e/n = 10(-4)

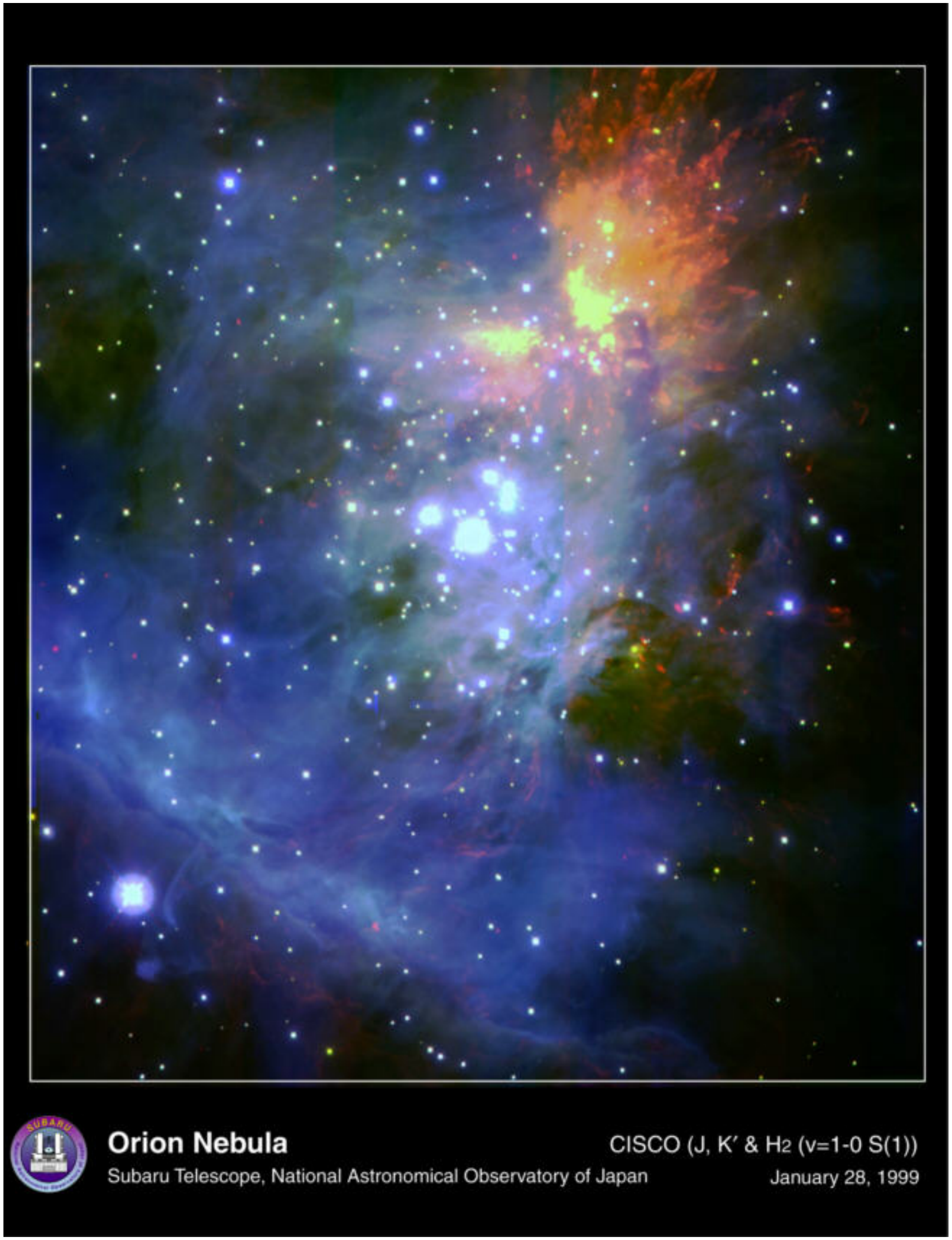
Filled in circles observed
values & limits

Rimmer et al. 2010

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 $\rightarrow$ protostellar collapse)

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



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)

Desperate Cases

Poorly understood classes of reaction

Acknowledgments

- NASA/JPL for $$$$$
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