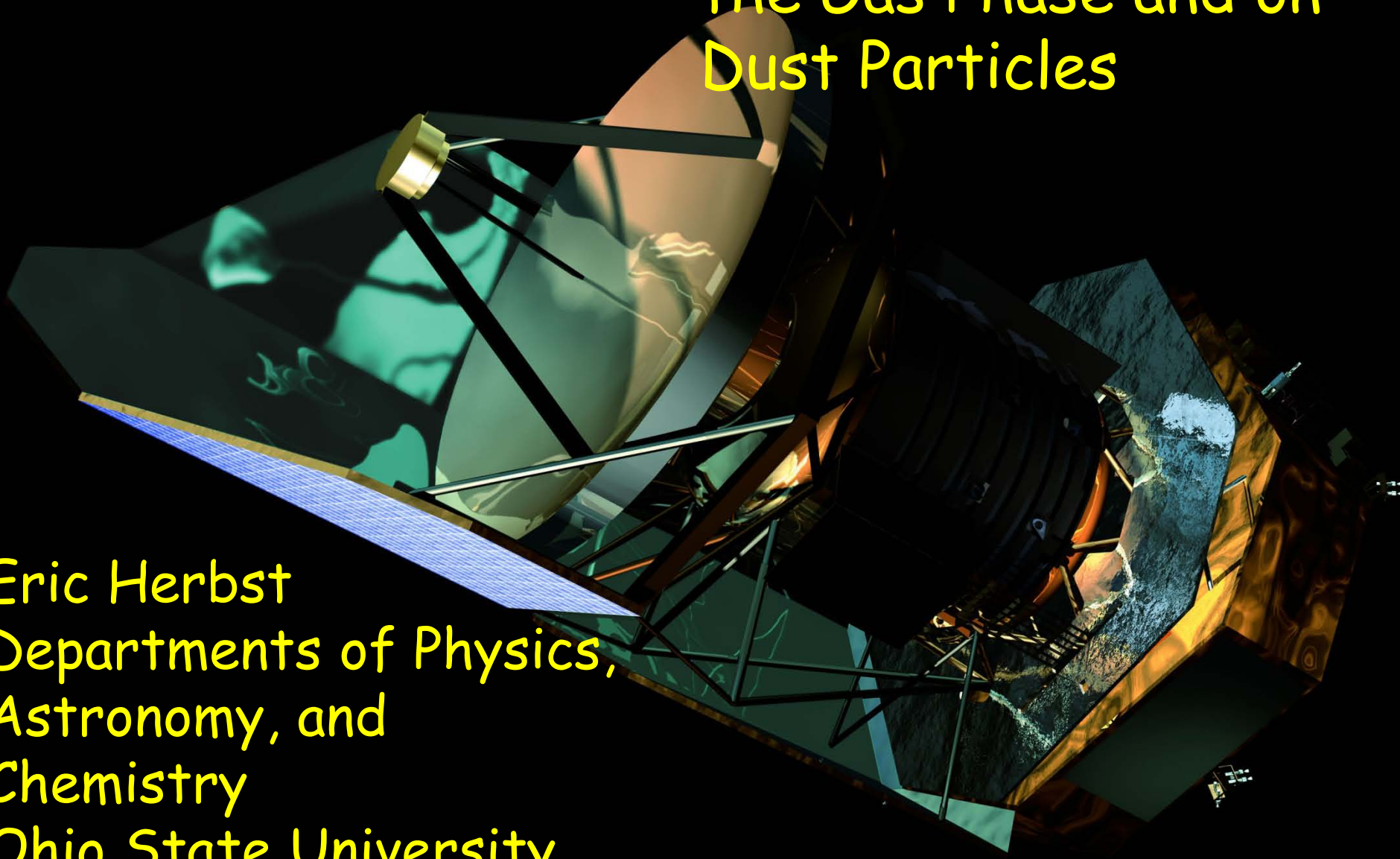
Molecular Processes in the Gas Phase and on Dust Particles



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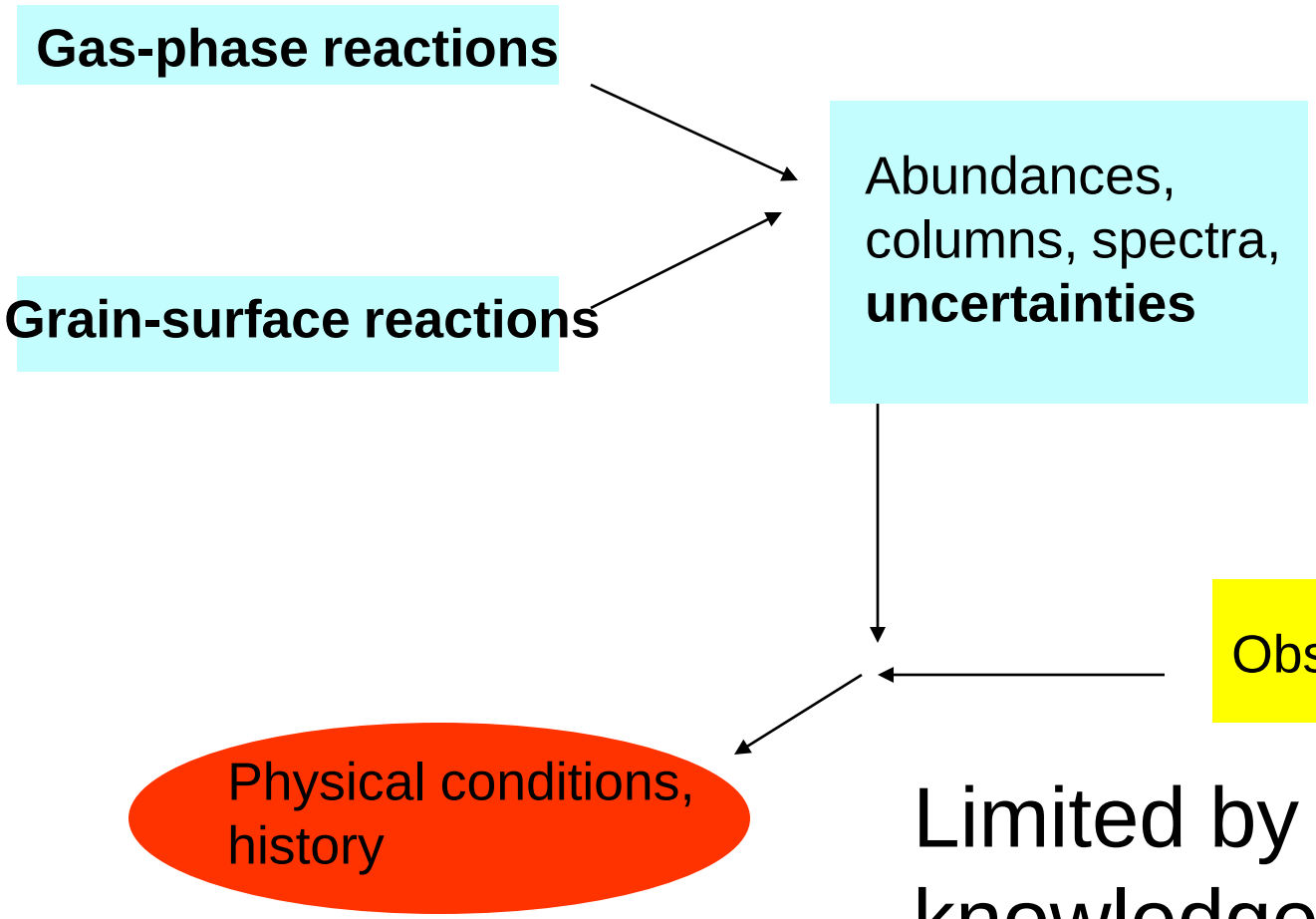
NASA-supported missions:

Herschel/HIFI
SOFIA
JWST

Results to yield many new challenges to modelers!

Chemical Models



Limited by chemical knowledge

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

New Review/Critical Database

- Wakelam et al. (2011) "Reaction Networks for Interstellar Chemical Modelling: Improvements and Challenges (Space Science Reviews, in press)

- KIDA (Kinetic Database for Astrochemistry; http://kida.obs.-ubordeaux1.fr/)

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

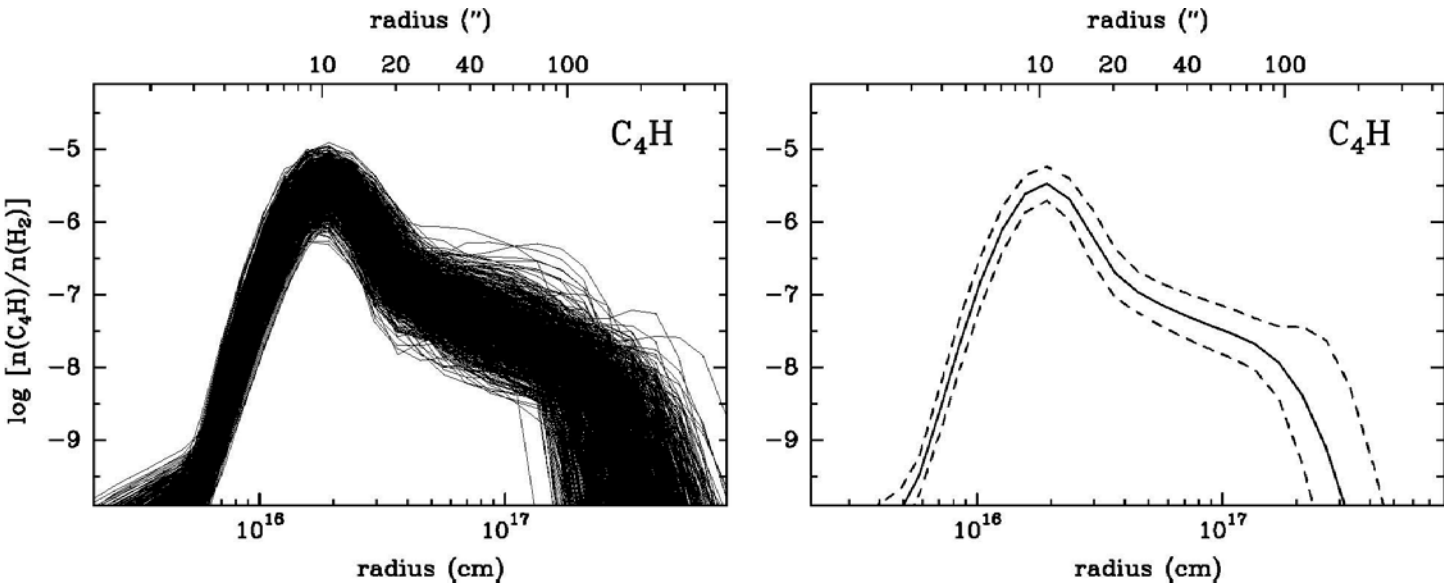
Additional Networks

- *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

$$H_2 + H_3^+ \square \quad H_3^+ + H_2$$

Uncertainty &Sensitivity Methods

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



Wakelam et al. 2010

Desperate Cases

Poorly understood classes of reactions

Radiative Association

$$A^+ + B \rightarrow AB^+ + h\upsilon$$

Few laboratory studies; mainly theoretical kinetics using statistical ideas such as phase space theory.

System proceeds through complex, which can redissociate or be radiatively stabilized (IR photons)

$$k(T) \propto T^{-r/2}$$

Dependent on size, bond energy

Negative Ions in Clouds

- Herbst (1981) considered the possible formation of anions in cold regions of the ISM based on radiative attachment:
- $A + e \rightarrow A^- + h\nu$

  and estimated the rate coefficients by a statistical technique, which predicts the process to be rapid for species with large electron affinities and at least 4-5 atoms (namely, radicals). Very few studies and none on the anions of interstellar interest: $C_{2n}\tilde{H}$. Destruction pathways also need work.

Role of PAH's

- Allowing generic chemical reactions such as
- $PAH + \tilde{e} \rightarrow PAH^{-} + h\nu$
- $PAH^{-} + X^{+} \rightarrow PAH + X$

in models of cold cores can affect results in many ways depending upon abundance and size of PAH's. Most important: arbitrary low-metal abundances are not necessary (Wakelam & Herbst 2008)

Towards Complex Molecules

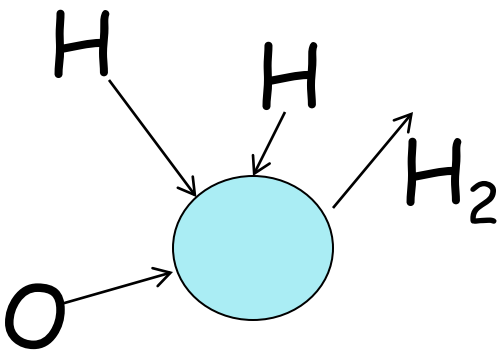
- Now that C_{60} has been detected, it might be interesting to determine how it is synthesized. A gas-phase synthesis was published by Bettens & Herbst in 1995; it is highly speculative and needs to be studied:
- Carbon chains → single rings → triple rings → fullerenes
- Reactions with C atoms and ions critical.

Gas-grain Chemical Networks

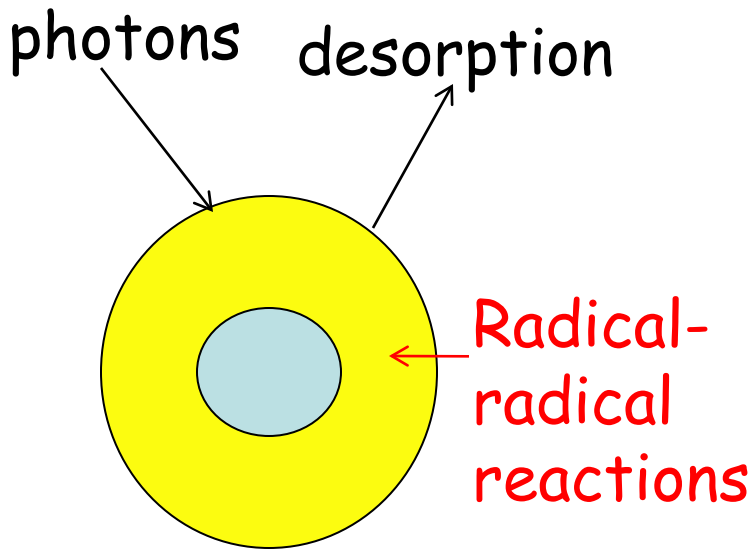
Designed in our group, starting from Hasegawa et al. (1992) and now used by a few others.

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

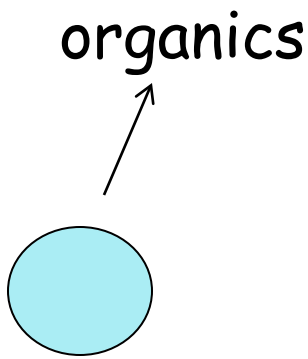
Evolution of surface processes



Diffusion on bare dust particles leads to:



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



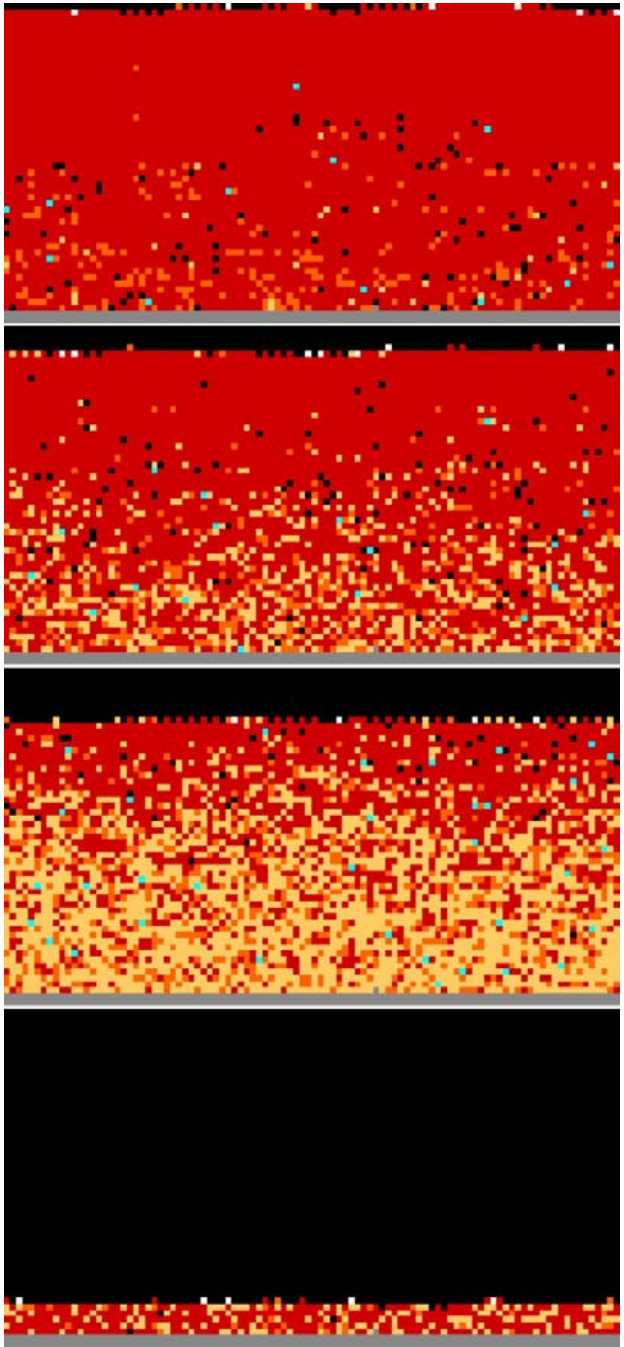
Thermal evaporation during heat-up

Laboratory Measurements

- H_2 formation on bare and icy surfaces
  Ice build-up leading to simple water, CO2, methanol studied at low temperatures
- Radical-radical photochemistry leading to complex molecules as temperature increases
- Photodesorption; thermal desorption

Problems with Measurements

- Not performed on tiny dust particles
- Not easy to convert lab rates to rate equations or stochastic methods used in chemical simulations.



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

2×10^5 yr cold core

Conclusions

- 1. Experiments are needed both for exotic gas-phase reactions at any temperature, many reactions at 10 K and many at 800 K. Sensitivity analyses can tell us specific reactions and classes. Some "basket cases":
- Radiative association, anion formation/destruction, ortho/para conversion

- 2. More work needed to convert experimental results in surface chemistry to suitable mathematical expressions needed in interstellar simulations. It would be nice if laboratory experiments could be run on particles!! Some work starting on support structures.

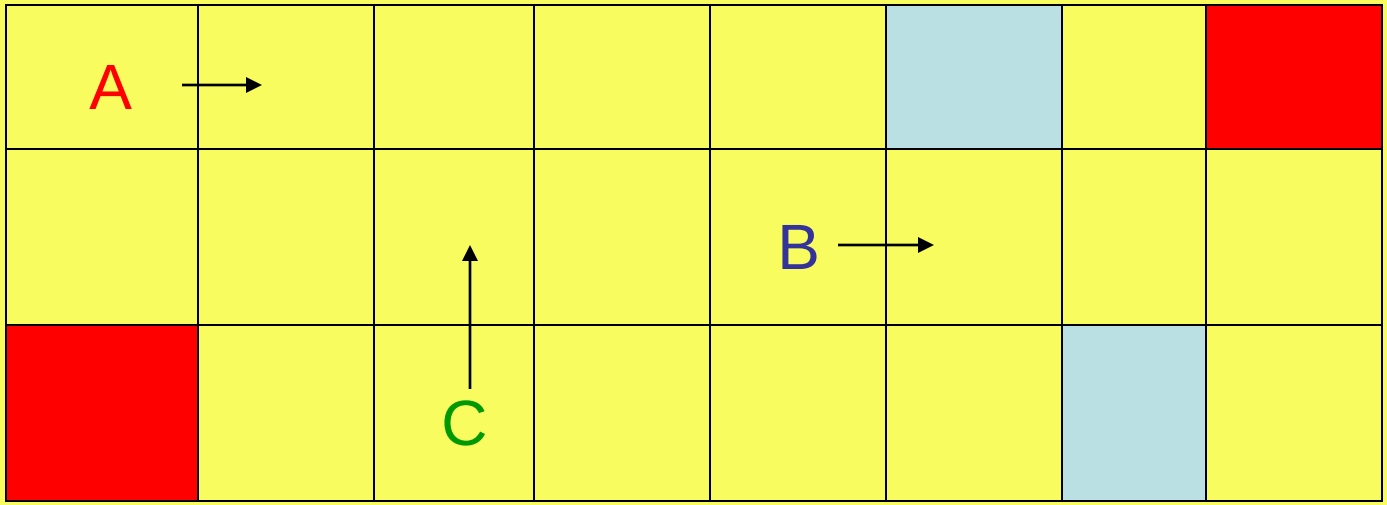
Acknowledgments

- NASA/JPL for $$$$$
- Graduate students and postdocs through the years!

KMC (MICROSCOPIC) APPROACH

Chang, Cuppen & Herbst (2005)

- A Monte Carlo approach in which the actual positions of individual species on a lattice are followed with time. Can use to follow reactions on and in mantle and show mantle build-up. Each lattice site can have different energy parameters.



Some Sensitive Examples

$$C^+ + H_2 \rightarrow CH_2^+ + h\nu$$ f = 2-10 (ion trap)

$$C + H_2 \rightarrow CH_2 + h\nu$$ 3 body?

$$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu$$ f ≥ 10

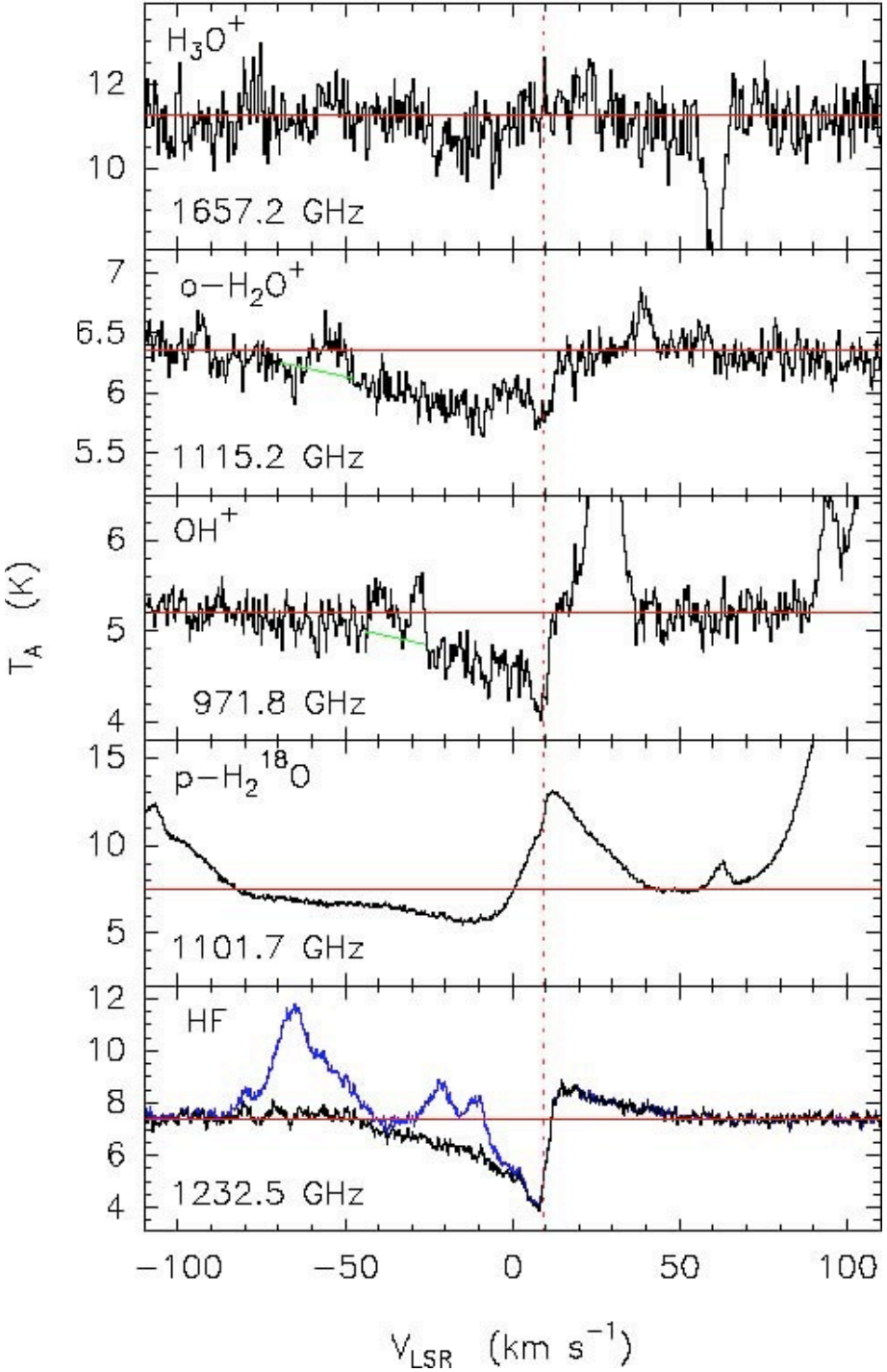
$$CH_3^+ + H_2O \rightarrow CH_3OH_2^+ + h\upsilon$$ f = 100?

No radiation ever detected!

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)
- $K = k_f/k_r$
- H2O+ + e $\longrightarrow$ Products (k_{dr})
- OPR = $\{k_f[H] + f_o k_{dr}[e]\}/\{k_r[H] + f_p k_{dr}[e]\}$
- □3:1 in all cases (model fails to reproduce OPR = 4.8:1 in spiral arm clouds)

Need larger network and/or state-to-state chemistry



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 x H_2O^+ >> H_3O^+

Gupta et al. (2010)

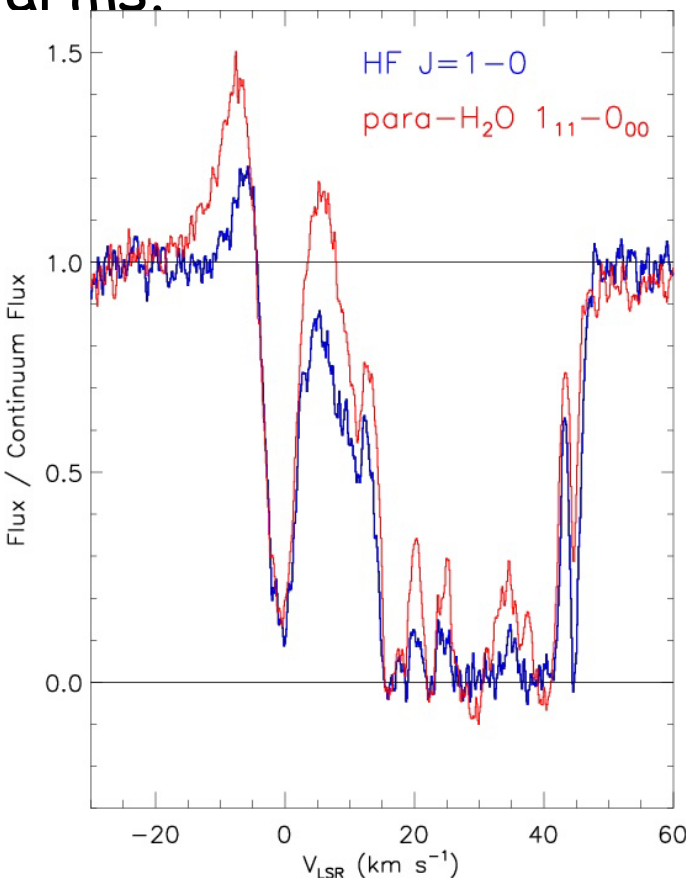
SPIRAL ARM DIFFUSE MATTER

- Neufeld et al. W31C (HERSCHEL/HIFI/PRISMAS)
- HF seen both in self-absorption around the continuum source and in partially resolved saturated absorption from diffuse matter in spiral arms.

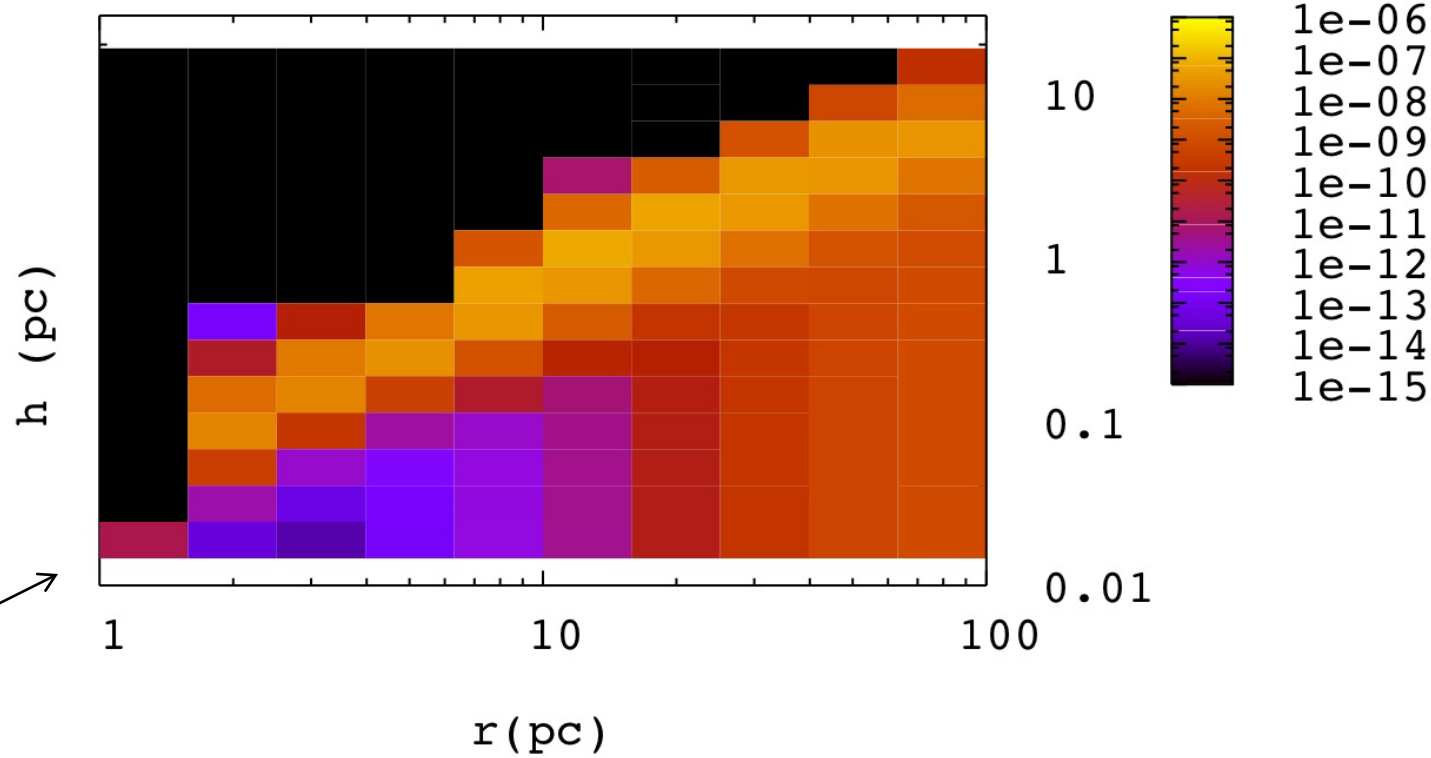
- $F + H2 \longrightarrow HF + H$
- (barrier but exoergic)

HF most of fluorine in diffuse sources with T high enough for reaction above; tracer of H_2

How distinguish diffuse spiral arm sources?



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



Black hole

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

Methods for Surface Chemistry

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

Dynamics/Heterogeneity

- Static shell/zone model (PDR)
- Homogeneous warm-up model (hot core)
- Shock model (dense cloud formation)
- 1-D hydrodynamic model (spherical collapse to form protostar)
- Turbulence model (diffuse cloud)

Herschel is showing us absorption spectra of the outer regions of THz sources and of diffuse spiral arm clouds