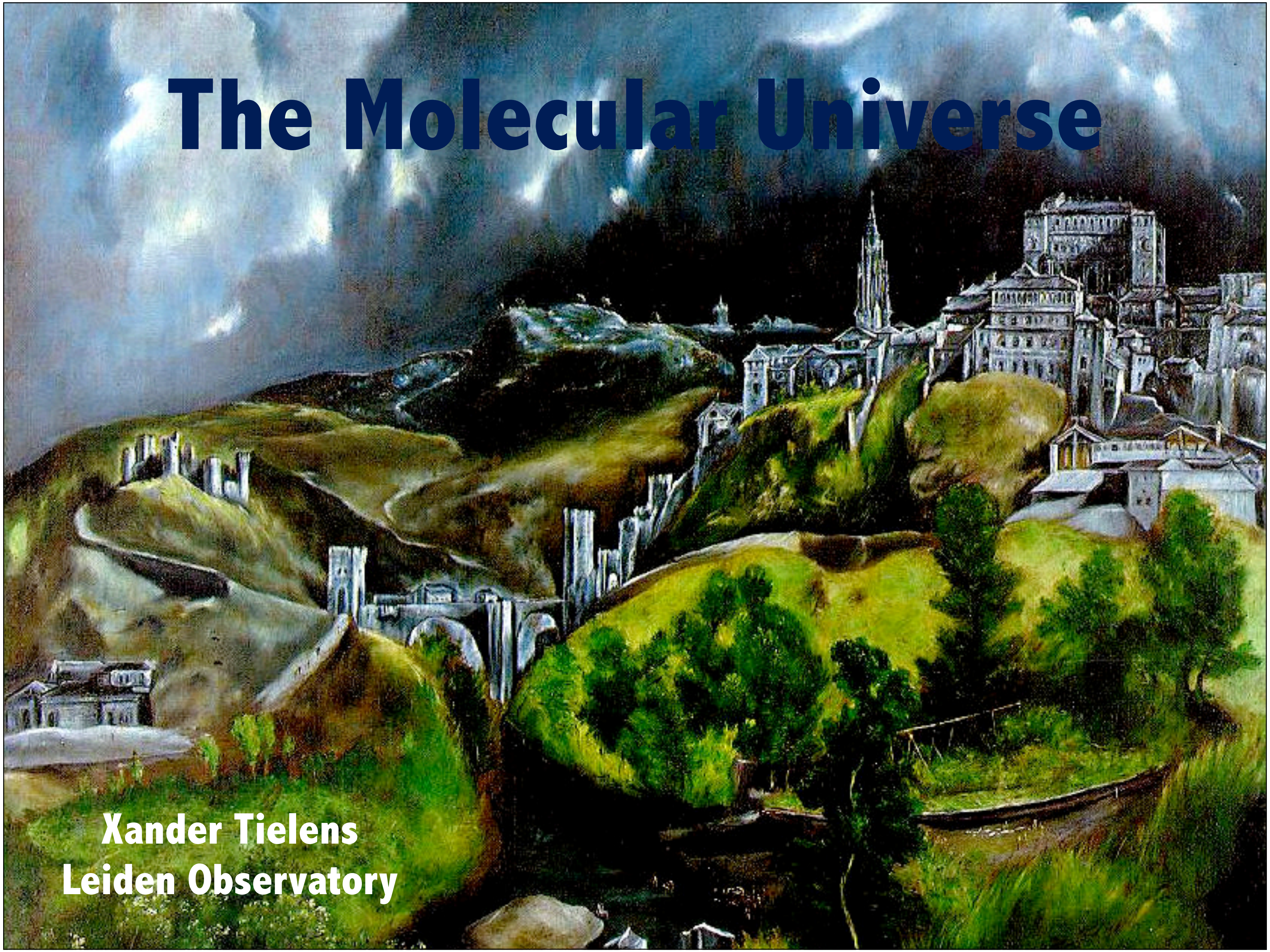
The Molecular Universe

Xander Tielens
Leiden Observatory



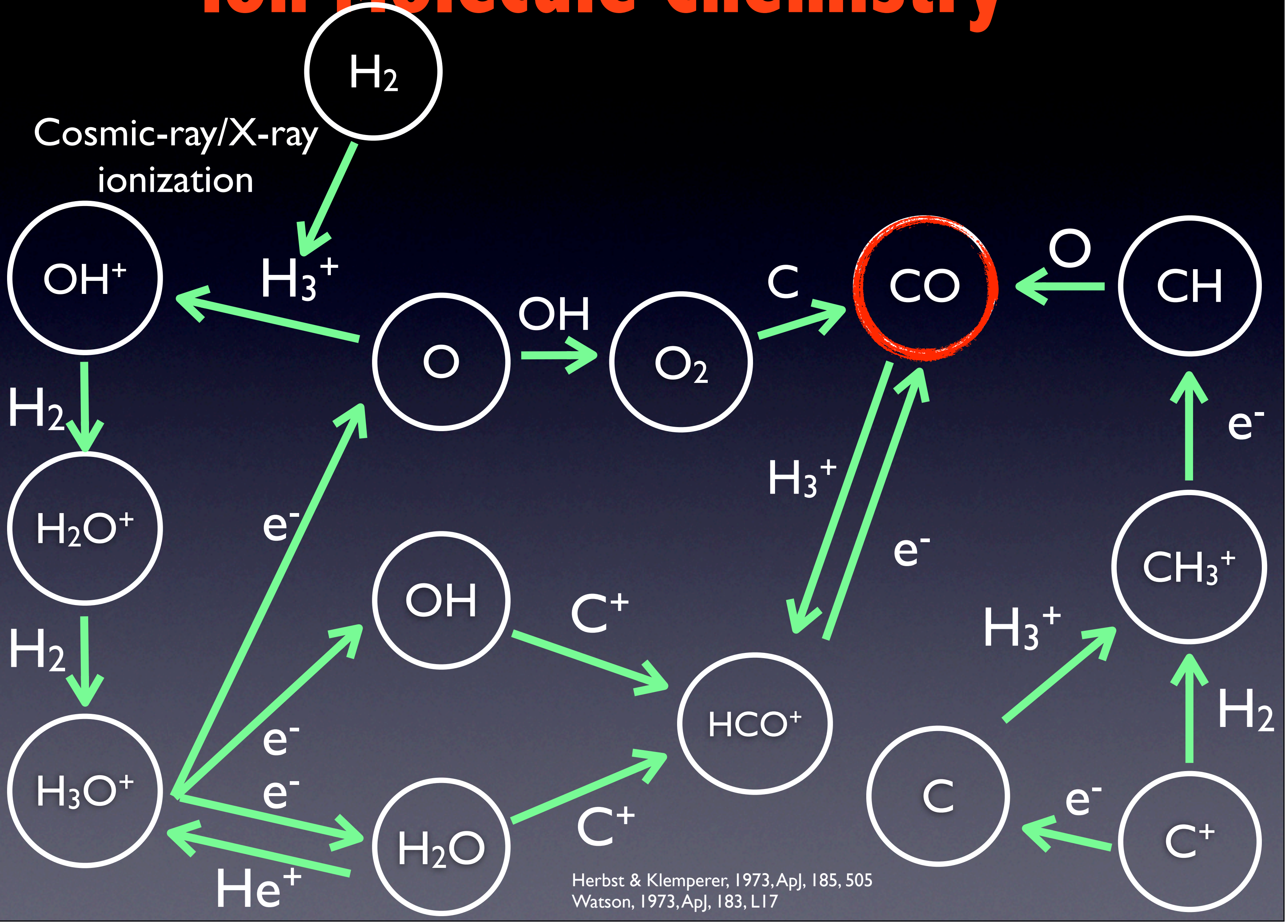
The Grand Challenges of Astrochemistry

- What is the organic inventory of space, in particular in regions of star and planet formation and how does that relate to the prebiotic origin of life ?
- What is the role of molecules in the evolution of the Universe ?
- How can we use molecules to study the Universe ?

Theme of this Talk

- What is the organic inventory of regions of planet formation ?

Ion Molecule Chemistry



Herbst & Klemperer, 1973, ApJ, 185, 505
Watson, 1973, ApJ, 183, L17

Ion Molecule Chemistry II

- Cosmic ray ionization
- Reaction network converts O/C/C+ into CO and traces of hydrocarbons
- Good agreement with species observed & their abundances (with "qualifications")

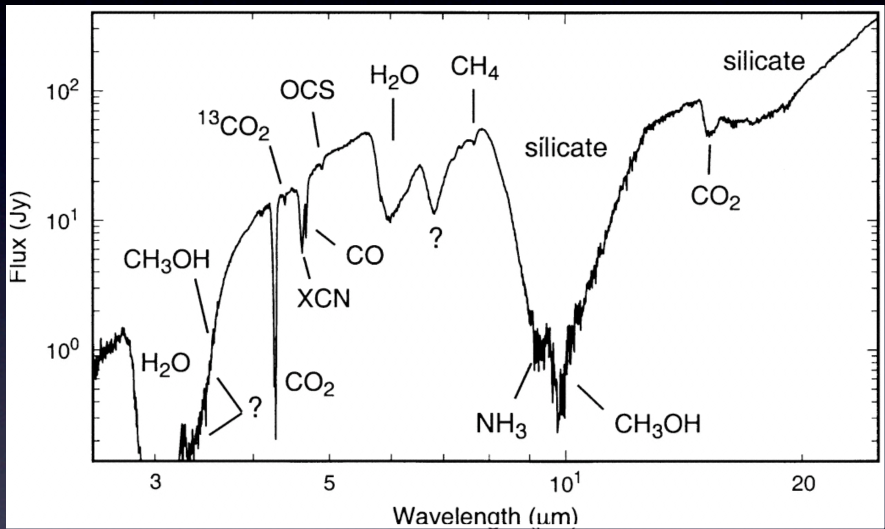
Herbst, 2006, AIPC 855, 260
Millar, 2005, Asilomar conference
Wakelam et al, 2010, SSR, 156, 13

Gas Phase Dead End

- Observed
  - hydrocarbons/CO $<10^{-3}$
  - Some variations (TMC1/L134N)
- Theory: Formation requires a source of C
  - Early time
  - Shocks/turbulence
  - Cosmic ray produced UV photons
- Complex organic inventory is limited

Grain Surface Chemistry

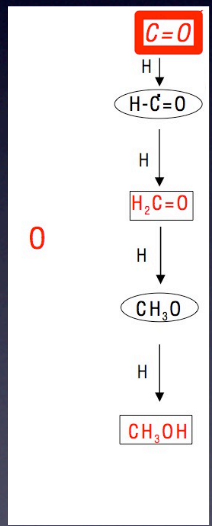
- Hydrogenation and oxidation reactions
- Simple saturated species: H_2O, CO, CO_2, CH_3OH, CH_4, NH_3, ...
- Good agreement with species observed and their abundances (with "qualifications")



Tielens & Hagen, 1982, A&A, 114, 245
Gibb et al, 2004, ApJS, 151, 35

Grain Surface Chemistry II

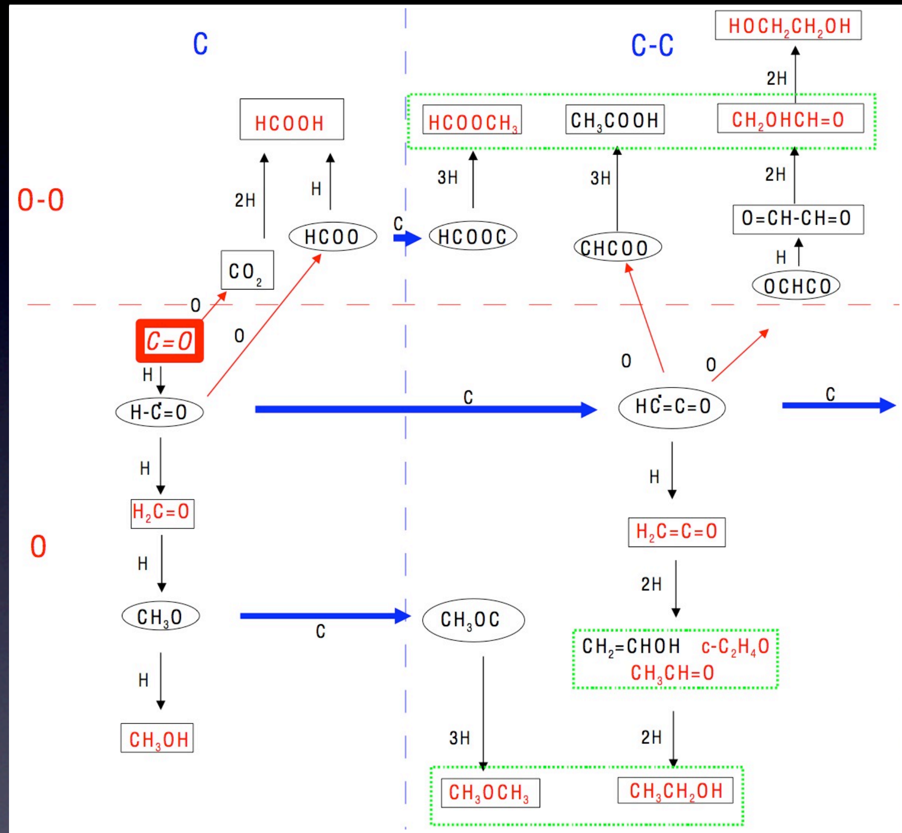
- CO is "activated" through H-addition reaction
- Chemical routes are now tested in the lab
- Complex organic inventory is limited by C-accretion



Tielens & Hagen, 1982, A&A, 114, 245
Hiraoka et al, 1998, ApJ, 498, 710
Hidaka et al, 2004, ApJ, 614, 1124
Fuchs et al, 2009, A&A, 505, 629
Ioppolo et al, 2008, ApJ, 686, 1474

Grain Surface Chemistry II

- CO is "activated" through H-addition reaction
- Chemical routes are now tested in the lab
- Complex organic inventory is limited by C-accretion
- Potentially more efficient route towards complexity
- Chemical specificity
- Issues: observations of trace species



Tielens & Hagen, 1982, A&A, 114, 245
Hiraoka et al, 1998, ApJ, 498, 710
Hidaka et al, 2004, ApJ, 614, 1124
Fuchs et al, 2009, A&A, 505, 629
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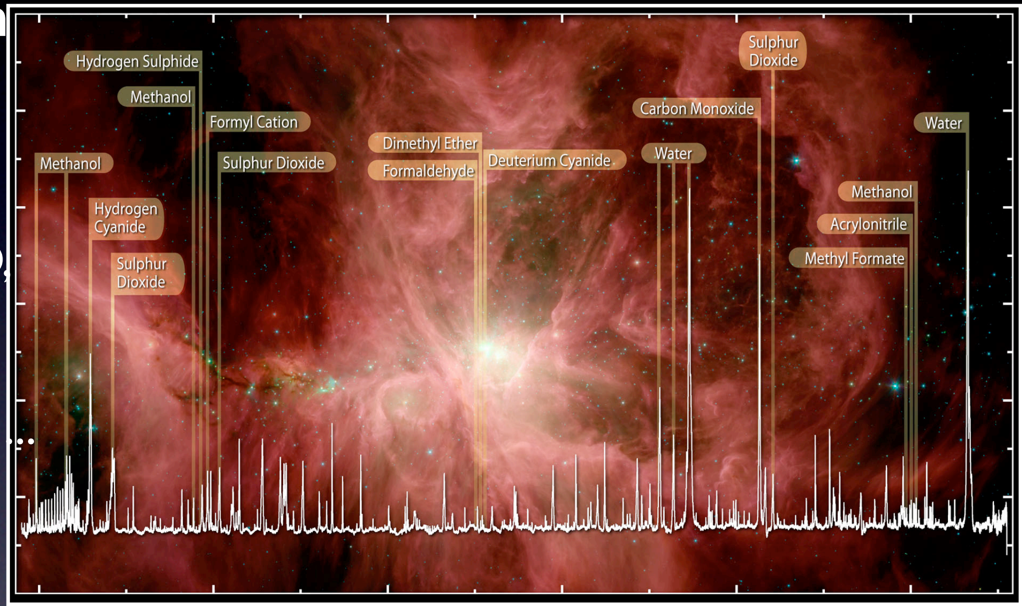
Hot Cores/Corinos

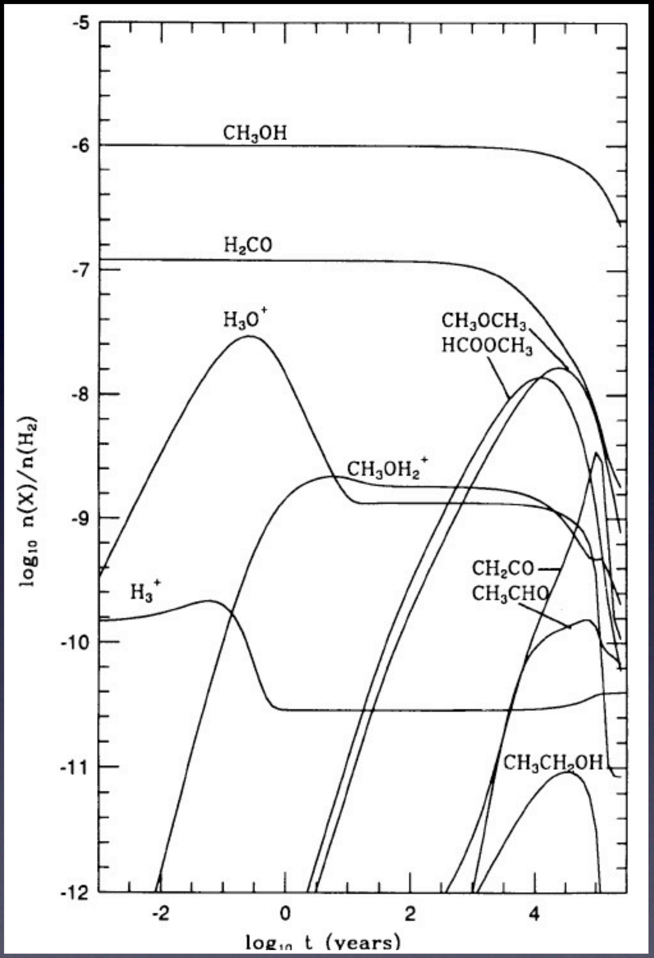
- Warm dense gas with rich organic inventory:
  - CH_3OH, CH_3CH_2OH, CH_3OCH_3, H_2CO, CH_3CHO, HCOOH, NH_2CHO, ...
  - HCN, CH_3CN, CH_3CH_2CN, ...
- Large deuterium fractionations
- Driven by evaporation of ice mantles formed in cold phase



Blake et al, 1987, ApJ, 315, 621
Ceccarelli et al, 2007, PPV, 47

Hot Core Chemistry

- Evaporating ice molecules drive rich chemistry
- Protonated methanol & methyl transfer
- Issues:
  - Experimental studies disagree
    - formation of intermediaries inhibited
    - Recombination leads to fragmentation
  - Chemical clock ~3x10^4 yr incompatible with hot corinos

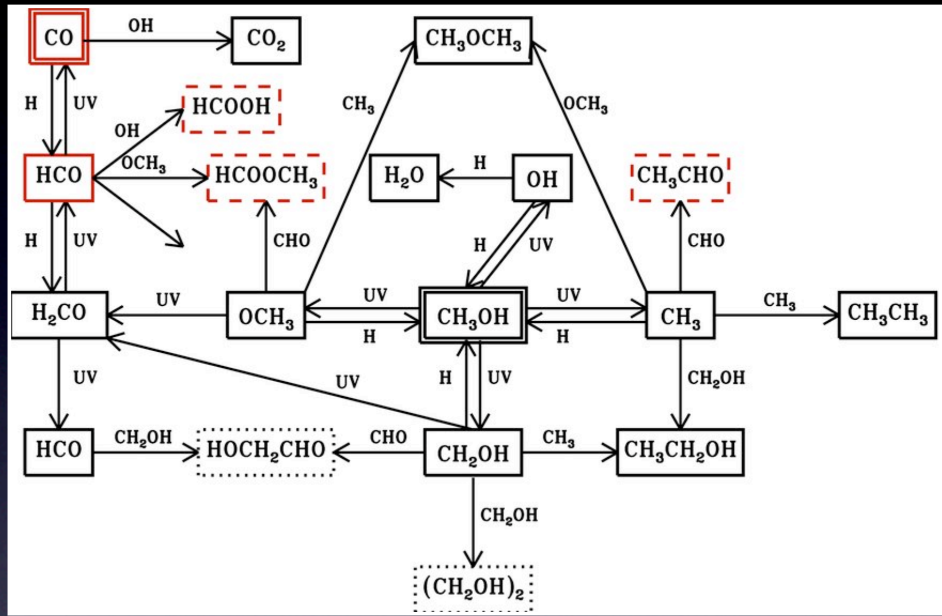


Charnley et al 1992, ApJ, 399, L71
Caselli et al, 1993, ApJ, 408, 538
Geppert et al, Faraday discussions, 133, 177
Horn et al, 2004, ApJ, 611, 605

Hot Core Chemistry II

UV photolysis/ion bombardment & warm up

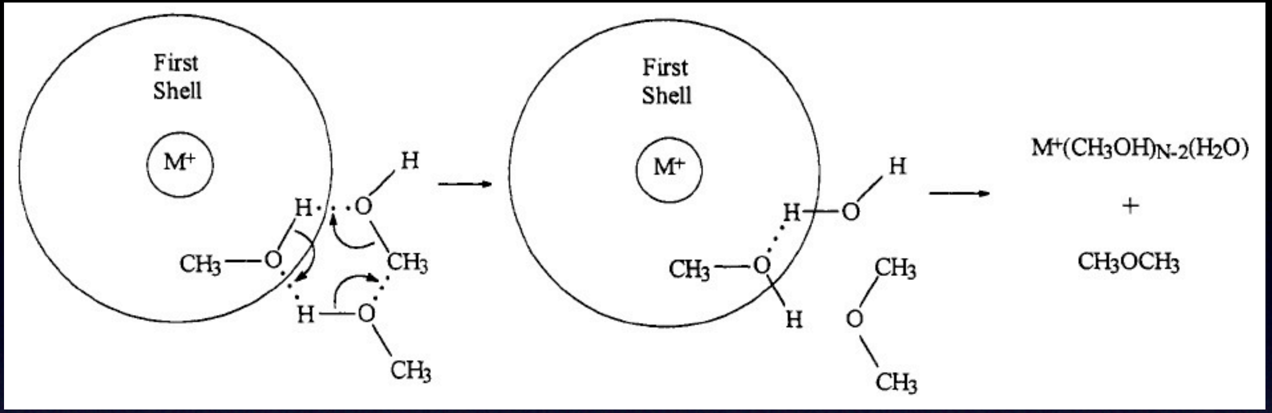
- Radical production (CH_3 & others)
- Recombination



- Issues:
  - Chemical specificity
  - Polymerization

Garrod et al, 2008, ApJ, 682, 283
Oberg et al, 2010, ApJ, 718, 832

Hot Core Chemistry III



Ion-molecule Chemistry in Ices

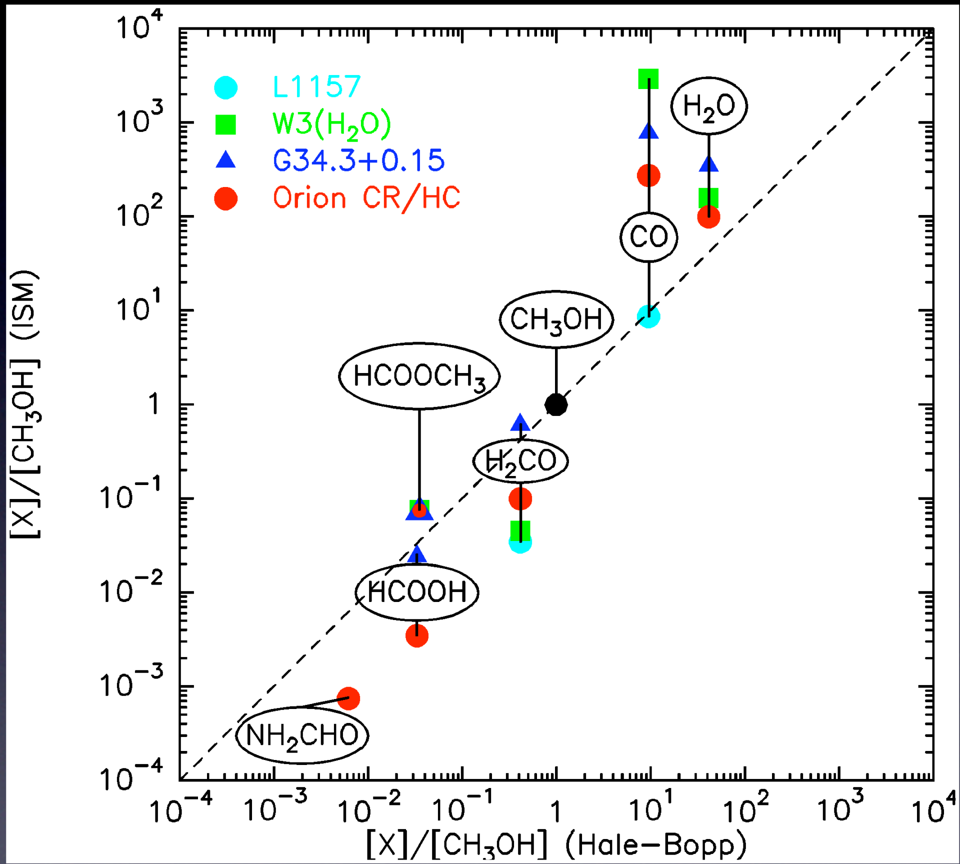
- Ices are charged & charges are localized:
  - Na, PAHs
  - OCN^-
  - Polarization charge
- Warm-up leads to segregation
- H-bonding
- Stereochemistry
- Methanol drives chemistry
- Near evaporation, "droplets" may conduce methyl transfer without fragmentation

charged ices: Bouwman et al, 2011, A&A, 529, 46; Schutte et al, 2003, 398, 1049; Demyk et al, 1998, A&A, 339, 553, Cassidy et al, this meeting

Hot Cores & Comets

Resemblance in organic inventory in composition and abundance

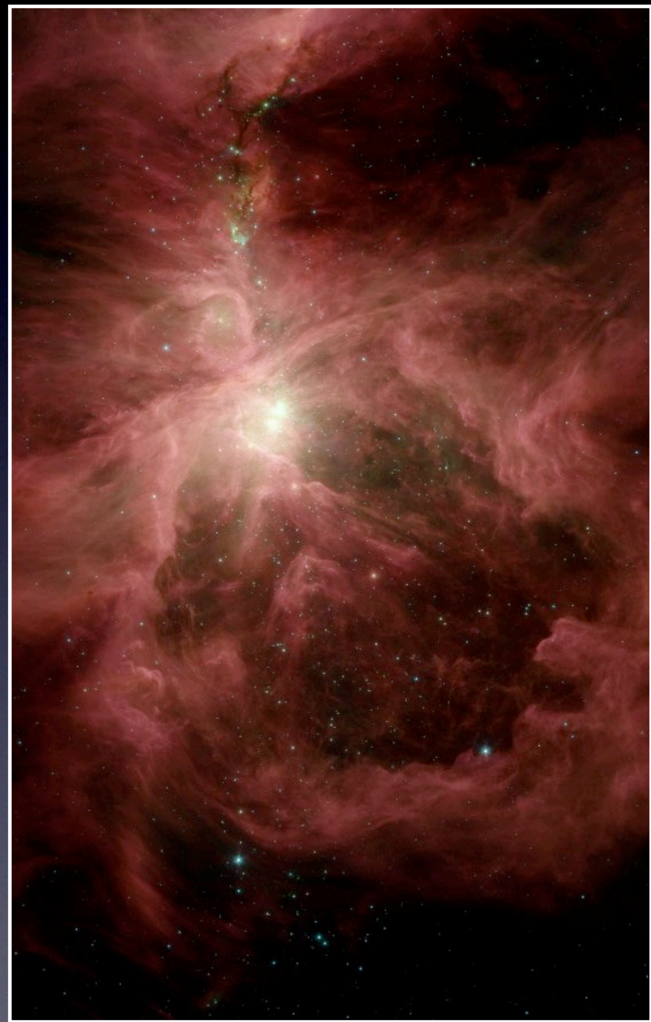
Chemistry in/on ices or cycling between gas and ice phases ?



Bockelee-Morvan et al, 2000, A&A, 353, 1101

Interstellar PAH Reservoir

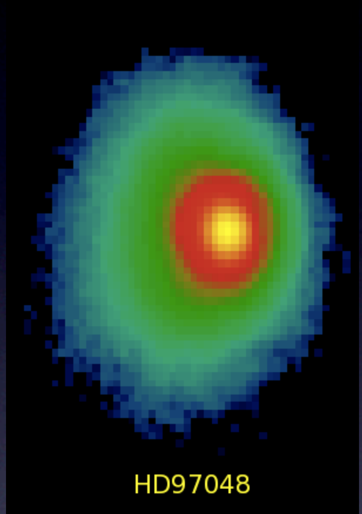
Large PAH molecules contain ~5% of the elemental C

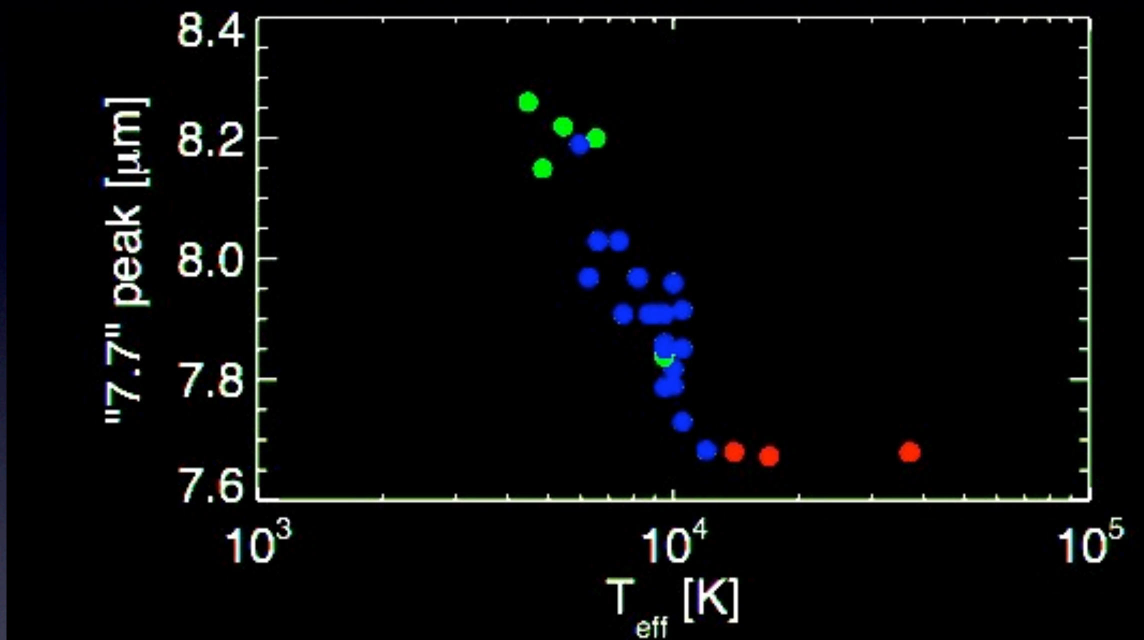


Tielens, 2008, ARAA, 46, 289

PAH Chemistry

PAHs in disks





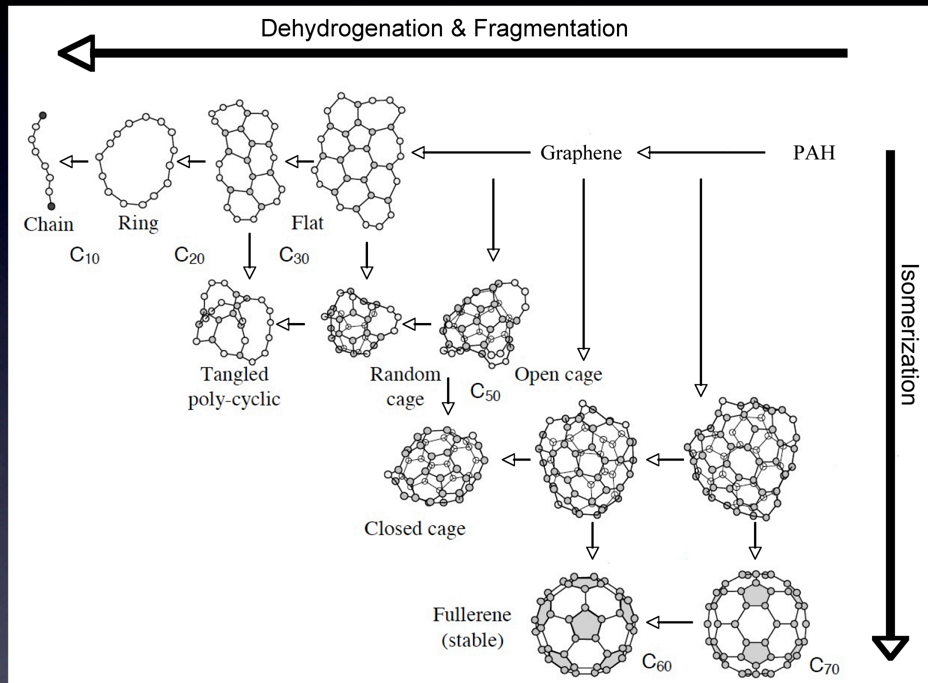
Active chemistry in regions of planet formation

- UV & X-ray photochemistry
- Radical chemistry in warm gas

Doucet et al, 2007, A&A, 470, 625
Sloan et al, 2007, ApJ, 664, 1144
Keller et al, 2008, ApJ, 684, 411
Boersma et al, 2009, ApJ, 502, 175

PAH photolysis

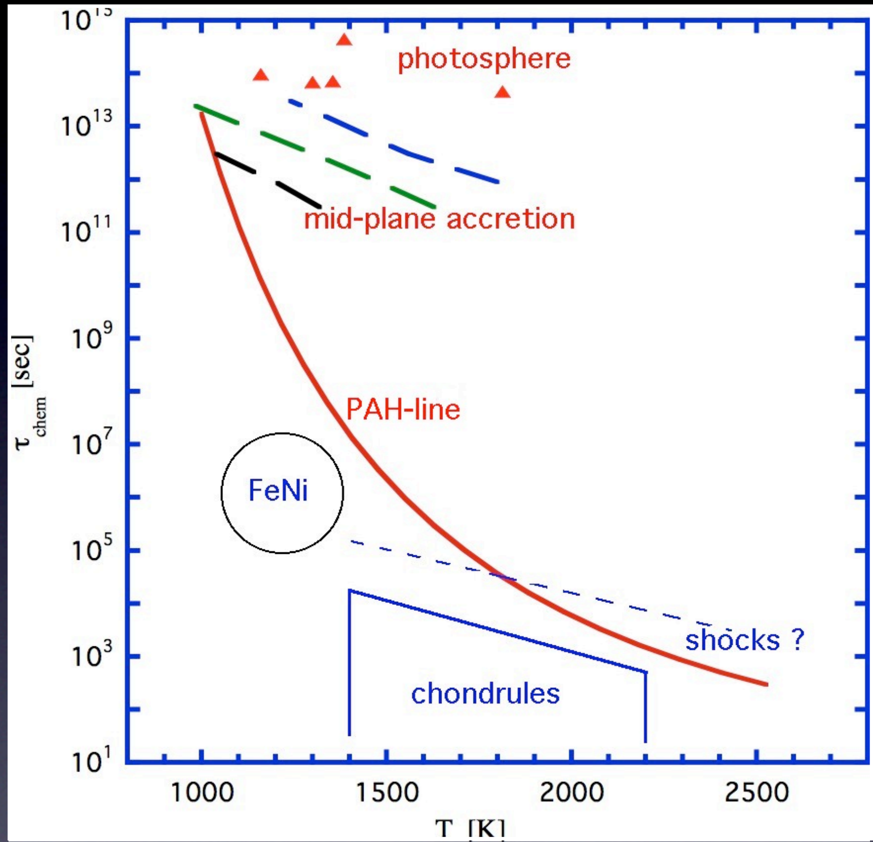
- Chemical routes are unclear
- Dehydrogenation & isomerization
- Stable intermediaries: cages & fullerenes
- Fragmentation products: hydrocarbon chains & radicals
- Relevant for hydrocarbon reservoir in PDRs ?



Tielens, 2011, Nature's nanostructures
Pety et al, 2005, A&A, 435, 885
Wehres et al, 2010, A&A, 518, 36

Soot Line

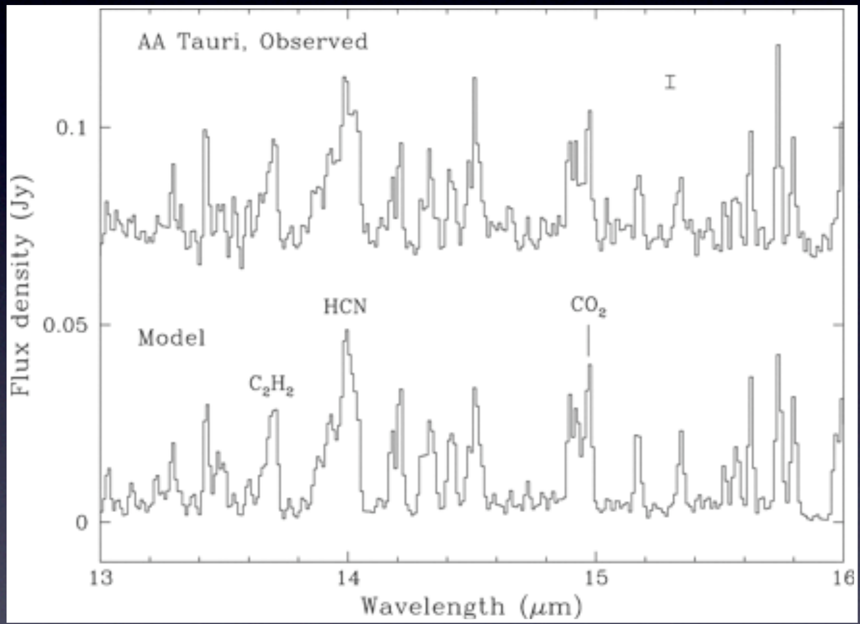
- H/OH attack on aromatic hydrocarbons at T>1000 K
- Formation of most stable PAHs
- Source of C_2H_2 (& HCN ?)
- Hydrocarbon radicals
- Turbulent diffusion: hydrocarbon chemistry throughout the nebula



Kress et al, 2010, Adv SR, 46, 44
see also: Nakano et al, 2003, ApJ, 592, 1252

Evidence for PAH chemistry

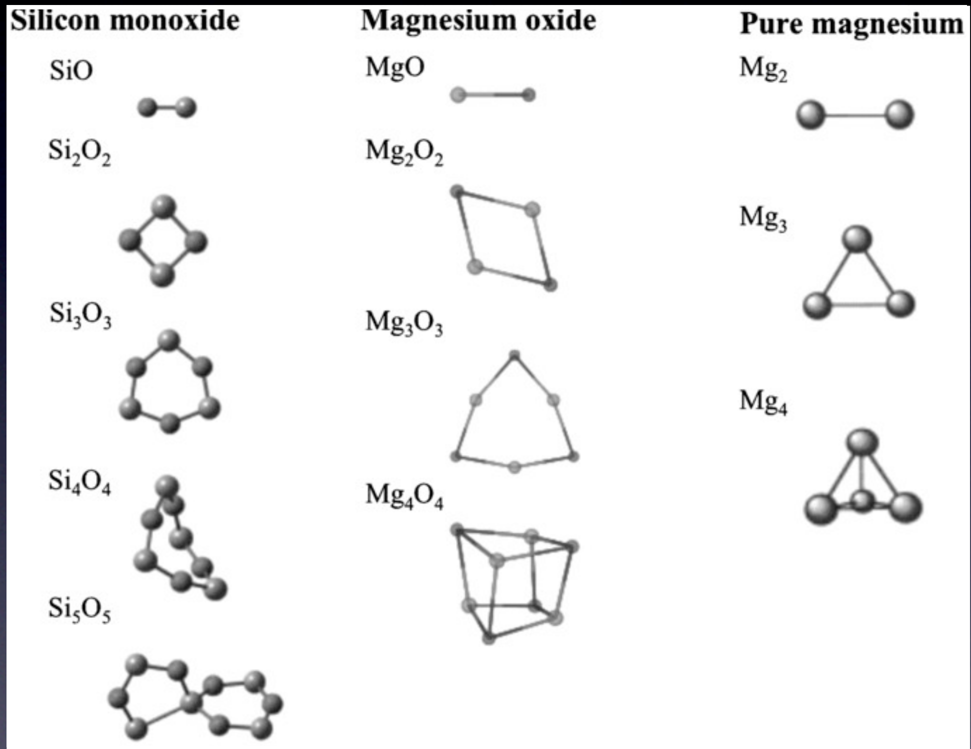
- Warm hydrocarbons in planetary disks & hot cores
- PAH spectral variations
- Alkanes/alkenes in Solar system comets



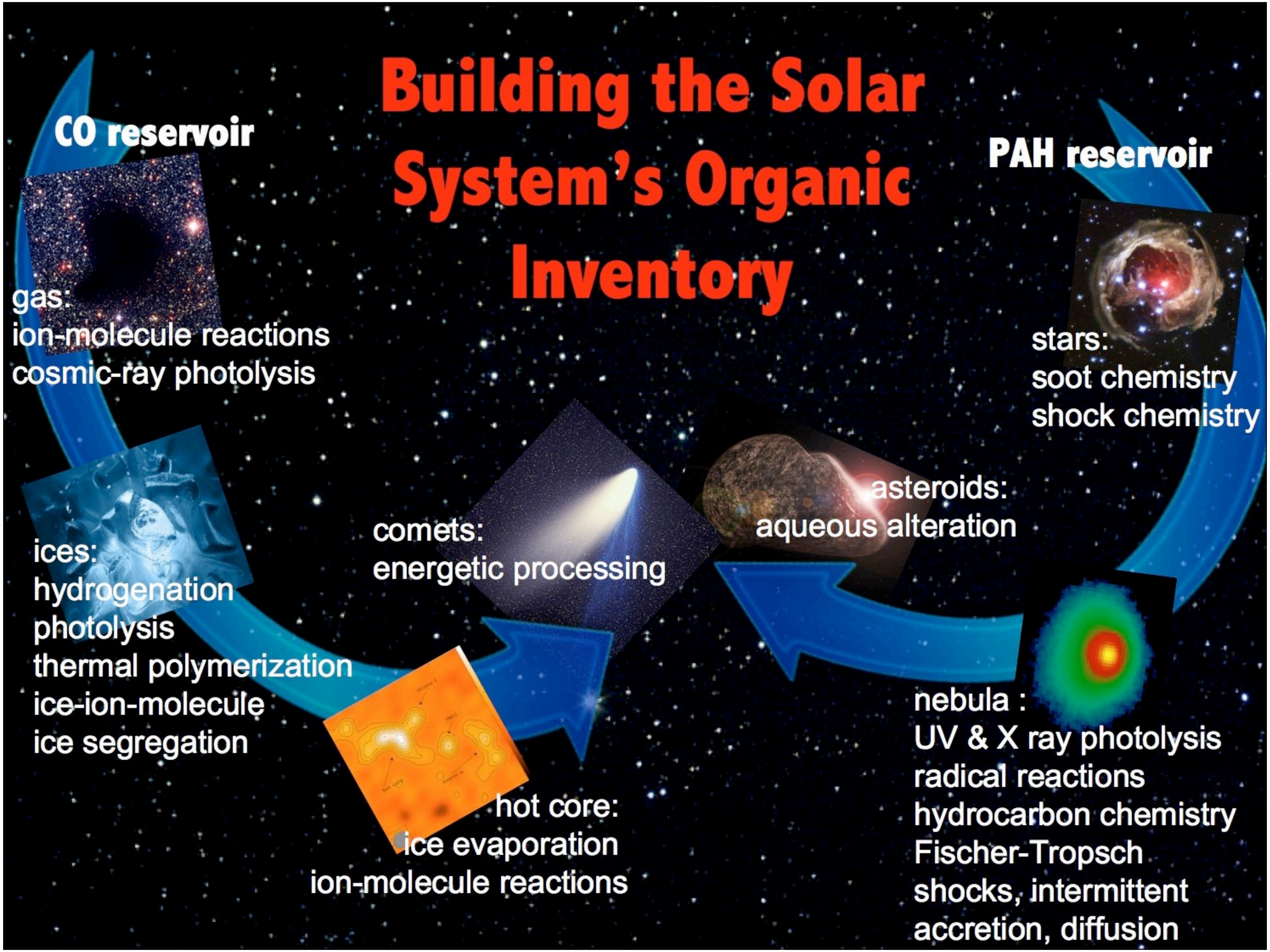
Najita et al, 2003, ApJ, 589, 931
Carr & Najita, 2011, ApJ, 733, 102
Lahuis et al, 2006, ApJ, 636, L145

Chemistry & Dust Evaporation Zone

- Dust is vaporized
- C may be released from CO
- Kinetics may drive an interesting organic chemistry



Cherchneff and Dwek, 2010, ApJ, 713, 1
Woods & Willacy,


Building the Solar System's Organic Inventory
CO reservoir
PAH reservoir
gas:
ion-molecule reactions
cosmic-ray photolysis
stars:
soot chemistry
shock chemistry
asteroids:
aqueous alteration
comets:
energetic processing
ices:
hydrogenation
photolysis
thermal polymerization
ice-ion-molecule
ice segregation
nebula :
UV & X ray photolysis
radical reactions
hydrocarbon chemistry
Fischer-Tropsch
shocks, intermittent
accretion, diffusion
hot core:
ice evaporation
ion-molecule reactions

Summary

- Organic reservoir of habitable zone reflects release of C from CO and PAHs
- CO: grain surface chemistry followed by ion-molecule chemistry or photolysis forms saturated organics
- PAHs: photolysis leads to fullerenes & hydrocarbon radicals
- PAHs: warm radical chemistry leads to acetylene, stable PAHs & unsaturated hydrocarbons

Future

- Herschel/HIFI: initiating ion-molecule chemistry
- Herschel/HIFI & ALMA: UV photolysis of PAHs & the hydrocarbon inventory in PDRs
- JWST & SOFIA: Hydrocarbon inventory (C_2H_2, CH_4, HCN, PAHs) on AU-scale-size
- ALMA: Hot corinos & protoplanetary systems

Molecular Universe

- Astrochemistry is highly interdisciplinary
  - Spectroscopy, molecular physics, chemical kinetics, surface sciences, quantum chemistry, astronomy
- Astrophysically relevant species/conditions
- Any process that can occur will occur !