Forming Complex Molecules in Early Stages of Star Formation

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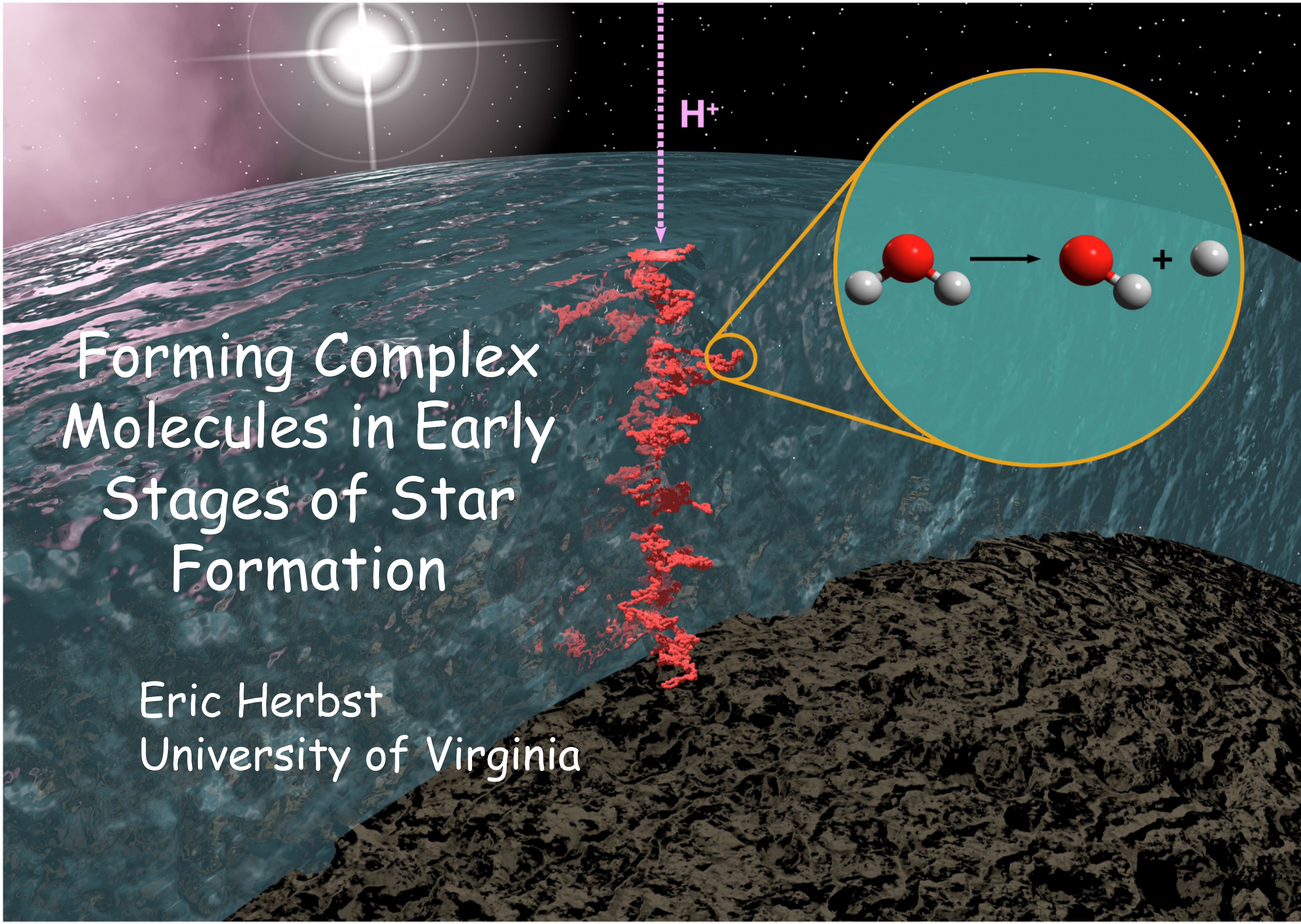
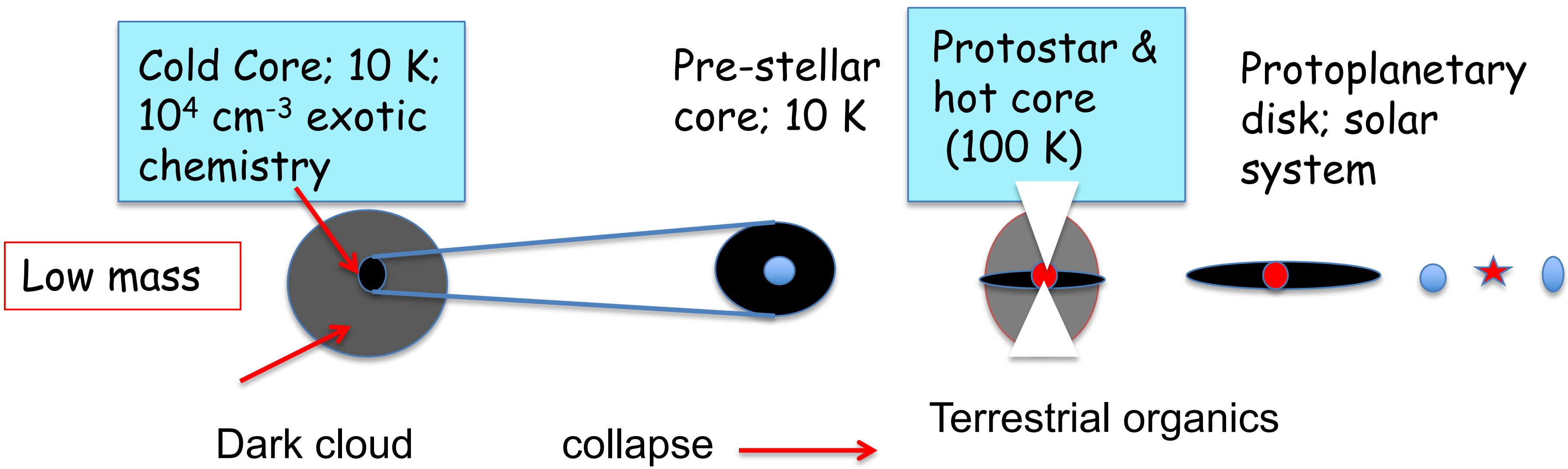


Low Mass Star Formation



We know accurately only when we know little, with knowledge doubt increases.

Johann Wolfgang von Goethe

“Complex” Organic Molecules (COMs)

- Definition: 6 or more atoms; can include unsaturated carbon chains (HC_9N) and more terrestrial species ($HCOOCH_3$). In reality 6-13 atoms; upper limit has stayed constant, roughly.
- Sources: most star-forming regions

- Cold cores: exotic molecules (ions, radicals, carbon chains) *and most recently some terrestrial COMs* ($HCOOCH_3$, CH_3OCH_3, CH_3CHO, C_6H_5CN)
- Hot cores: rich spectra of terrestrial COMs
- Protoplanetary disks: a few COMs recently detected in the gas (CH_3CN, CH_3OH)
- Exoplanets: not yet

Mechanisms for Formation of COMs (LAMs?)

- 1) Low-temperature gas-phase syntheses: **ion-molecule chemistry,** neutral-neutral chemistry
- 2) Low-temperature grain syntheses: **addition of atoms and molecules to heavier species at low temperatures**; non-thermal desorption needed to produce gas.
- 3) Warm-up gas-phase & grain syntheses: **photon-assisted radical-radical additions in warming sources (hot cores) followed by desorption.**
- 4) Other possibilities: grain bombardment**,** top-down??

INITIAL FORMATION OF CARBON CHAINS

$H_3^+ + C \rightarrow CH^+ + H_2$

$CH_n^+ + H_2 \rightarrow CH_{n+1}^+ + H$; $n=1,2$

$CH_3^+ + H_2 \rightarrow CH_5^+ + h\upsilon$

$CH_5^+ + e \rightarrow CH_4 + H$ (5%)

$\rightarrow CH_3 + 2H$ (70%)

$C^+ + CH_4 \rightarrow C_2H_3^+ + H$

$C_2H_3^+ + e \rightarrow C_2H_2 + H$

$CH_3^+ + C_2H_4 \rightarrow C_3H_5^+ + H_2$

Dissociative recombination – limiting step

$CH_3OHCH_3^+ + e \rightarrow CH_3 + CH_3OH$ 49%
$\rightarrow O + CH_3 + CH_4$ 44%
$\rightarrow CH_3OCH_3 + H$ 7%

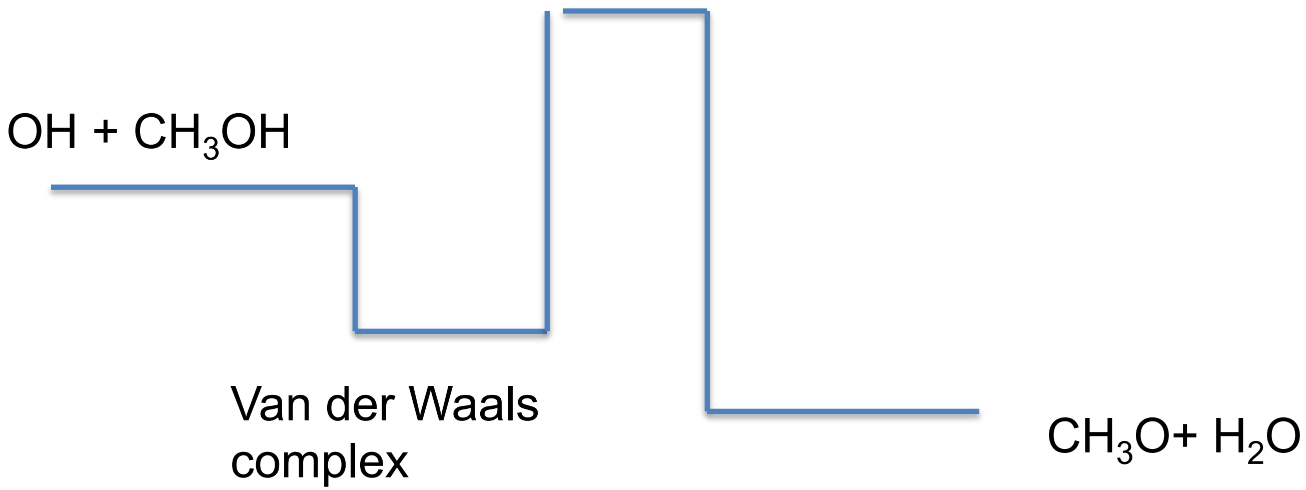
Situation can be helped if lots of ammonia around:
$CH_3OHCH_3^+ + NH_3 \rightarrow CH_3OCH_3 + NH_4^+$

Neutral-Neutral Reactions

- Husain, Rowe, Smith, Sims, Heard, Canosa, etc. have shown that many neutral-neutral reactions occur without barriers and can even have a slight inverse temperature dependence; e.g.,

- $CN + C_2H_2 \rightarrow HC_3N + H$

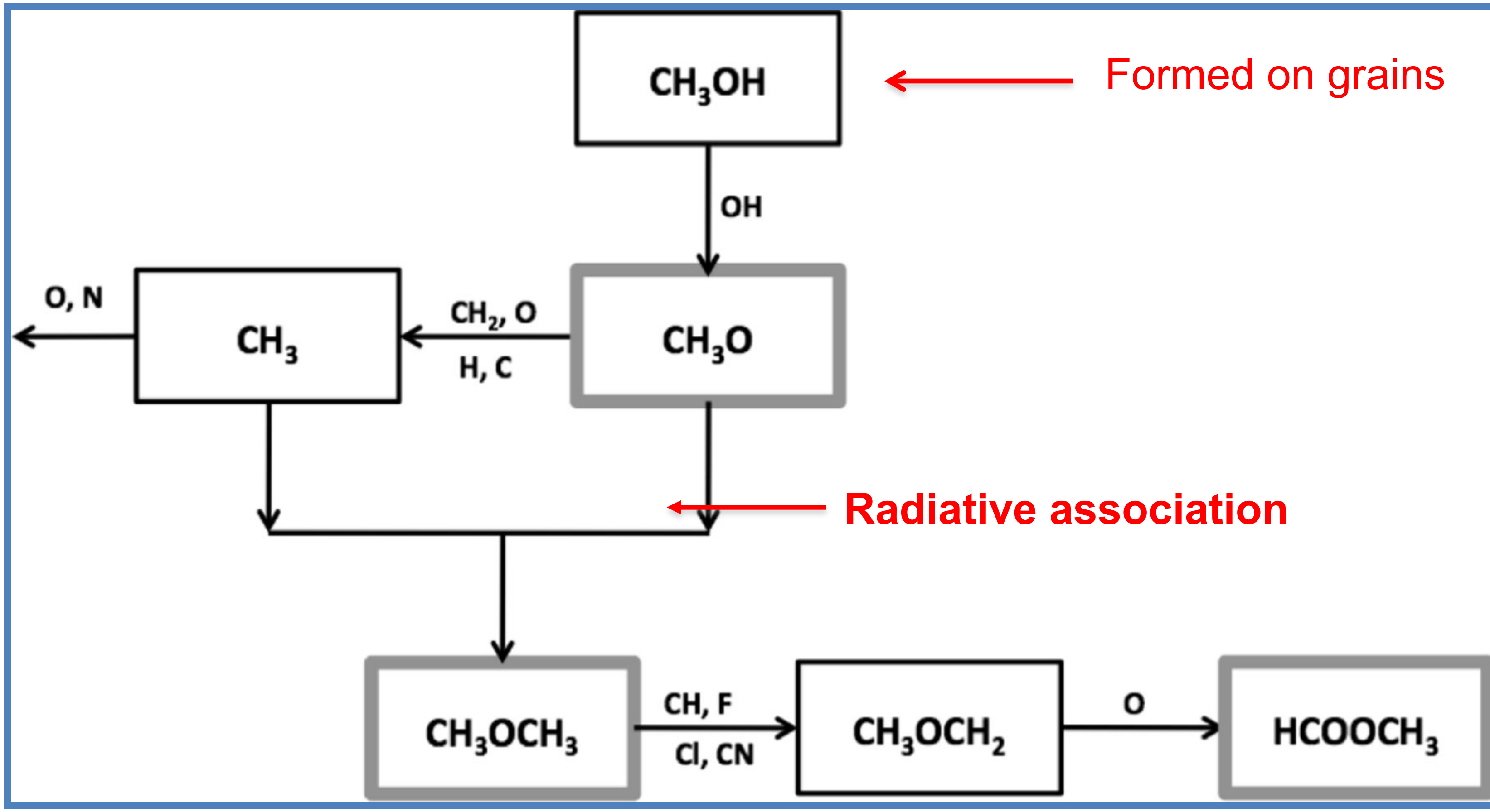
Barriered Radical-Neutral Reactions



Rate coefficient below room temperature is likely to increase as temperature declines due partially to a long-lived complex followed by tunneling.

Leeds group; Shannon, Heard, et al.

Neutral-Neutral Synthesis of Dimethyl ether and Methyl Formate at 10 K

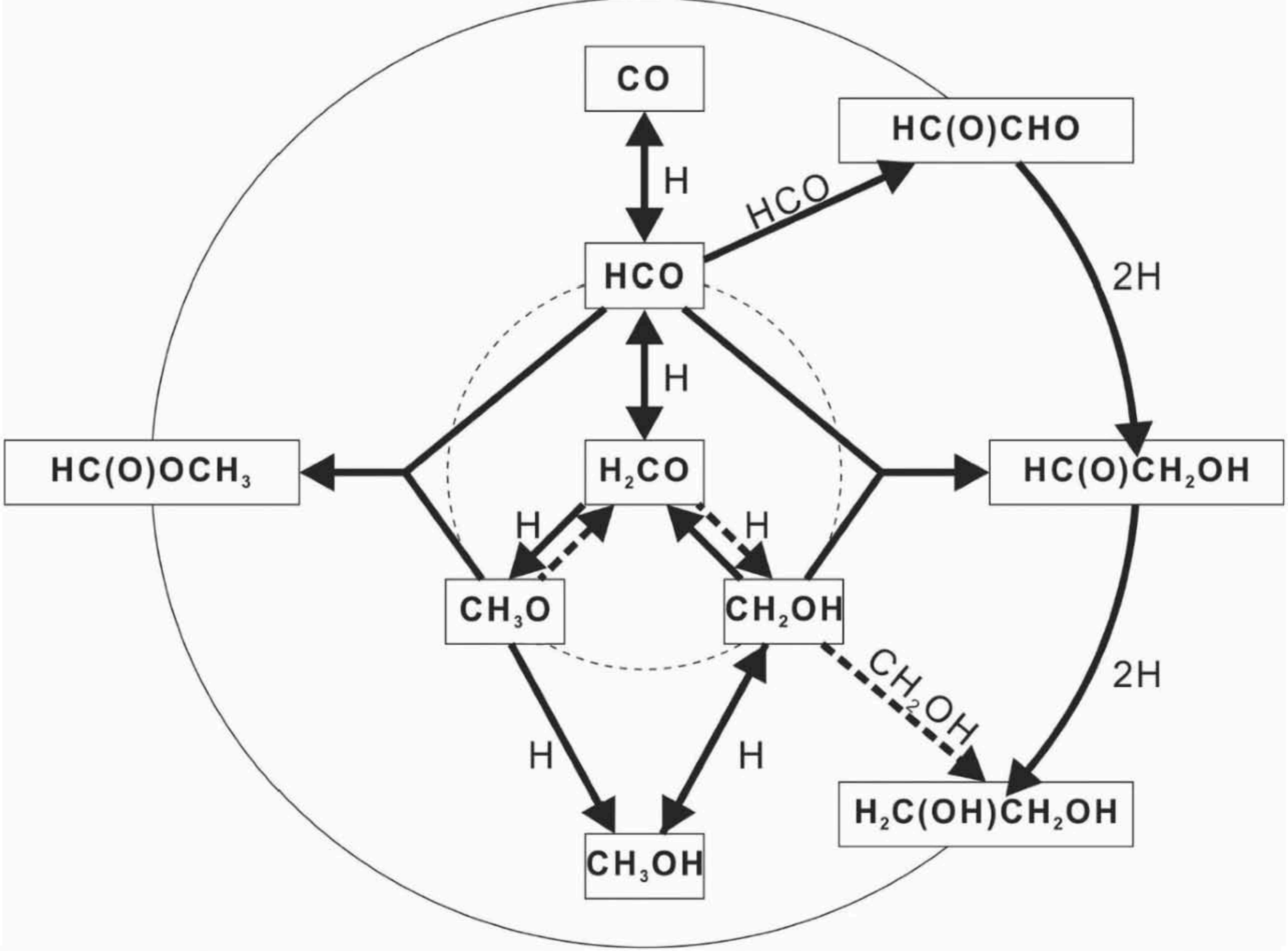


Balucani+ (2015) low temperature neutral-neutral reactions

Some Types of Surface Reactions

- Low temperature (10 K; cold core)
- g-H + g-CO → g-HCO → g-H_2CO → g-H_3CO (CH_2OH)→ g-CH_3OH
- g-H + g-H_2CO → g-HCO + g-H_2

- Higher Temperature (> 20 K; hot core)
- g-CH3 + g-CH3O → g-CH3OCH3



Linnartz group: atom-radical + radical-radical (T≥ 10 K); abstraction reactions?

COSMIC RAY BOMBARDMENT OF GRAINS TO FORM COMS

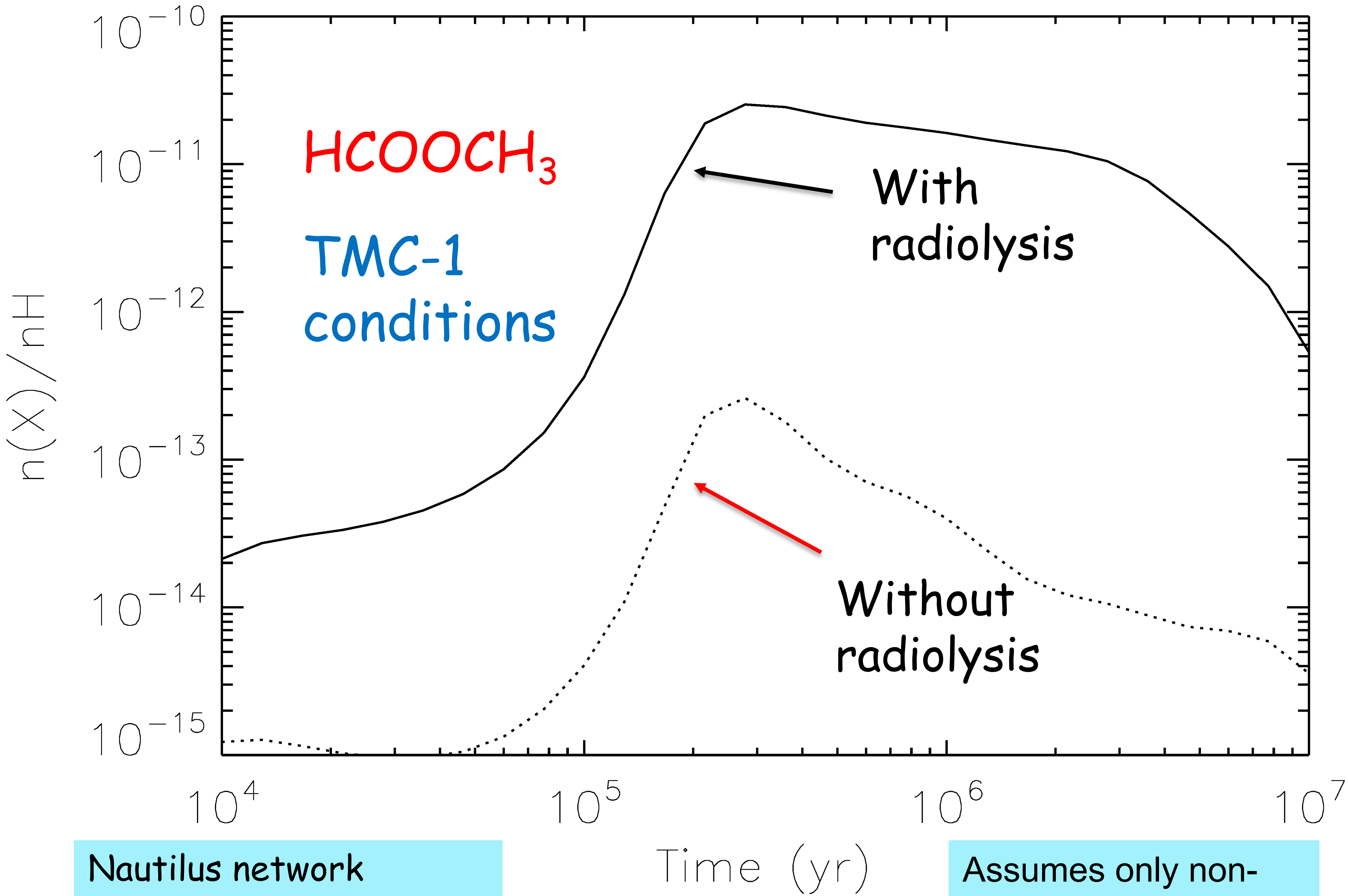
- Bombardment of ices by protons and electrons studied in a number of groups including Kaiser, Hudson, Arumainayagam, Mason and others produces a wealth of organic species on grains. We have developed a theoretical method to produce such species based partially on experimental or quantum chemical evidence if available. (Shingledecker+ 2017,2018a). Two treatments: Monte Carlo & rate equations.

- Problem is to incorporate such processes into large chemical simulations of the ISM. We (Shingledecker+ 2018b) have now succeeded in doing this.

Radiolysis

- Protons → electrons→ molecular ions → energetic neutrals →reactions over barriers (competes with relaxation)→ Products. $H_2O \dashrightarrow OH^* + H$
- $OH^* + CO \rightarrow HOCO$ (largest effect if barriered)

- Three basic pieces of information: product of cosmic ray flux, G (neutral molecules created per 100 eV deposited into system) and stopping power cross sections (S_e) yields first-order formation rate coefficient of energetic neutral.
- Some common energetic neutrals: OH^*, C^*, NH_2^*, CH_3^*. These react with normal species even with barriers.



Nautilus network

Assumes only non-thermal desorption

Other Grain Processes/Revisions

- 1. Eley-Rideal surface reactions
- 2. Three-body surface reactions
- 3. van der Waals formation
- 4. Lowered diffusion barriers
- 5. Enhanced reactive desorption
- 6. Thermal co-desorption
- 7. Abstraction

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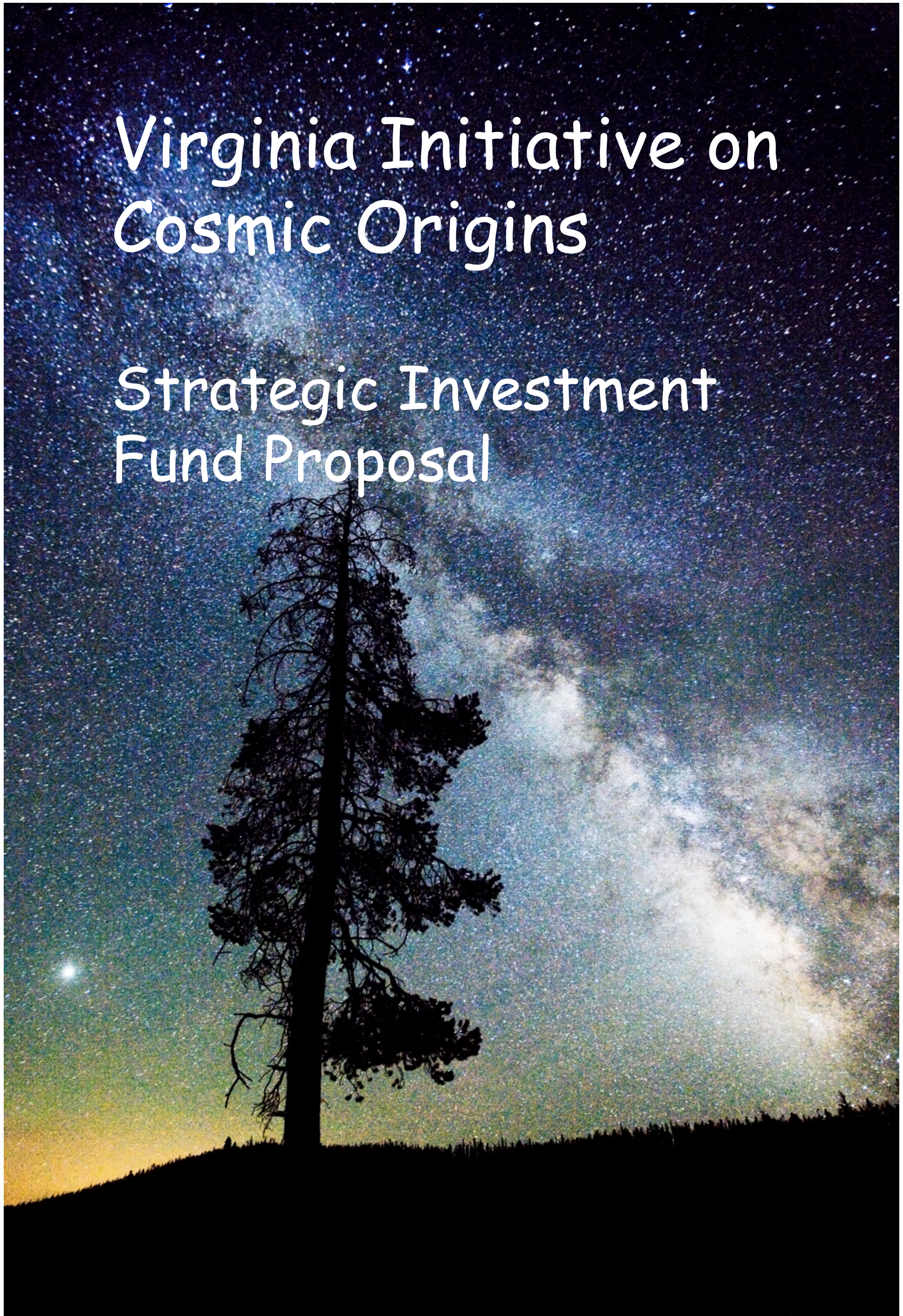

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Journal Scope

- We publish articles, letters, and reviews that cover:
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  - Earth surface
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  - Ocean
  - Space (astrochemistry)
  - Analytical methods