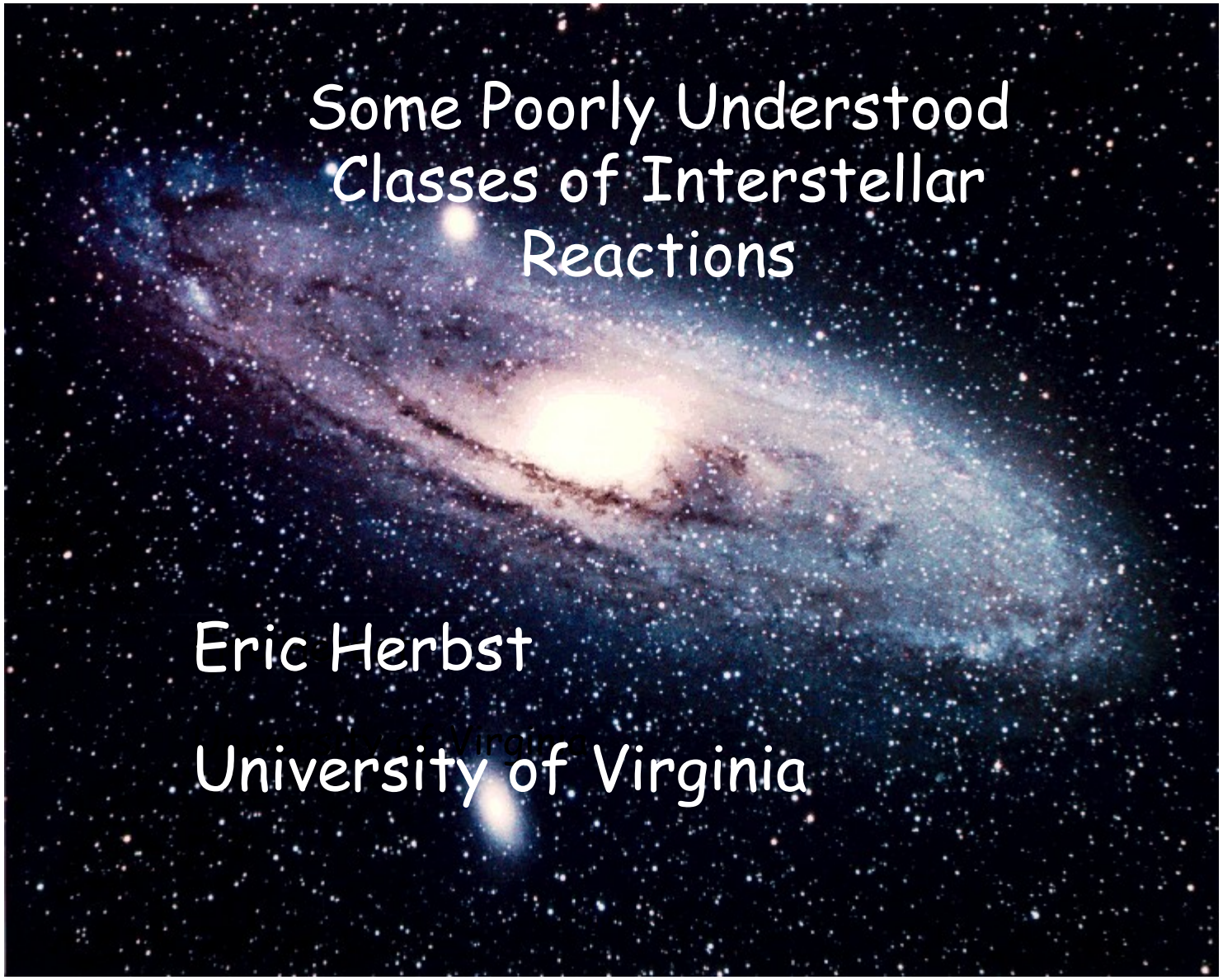
Some Poorly Understood Classes of Interstellar Reactions
Eric Herbst
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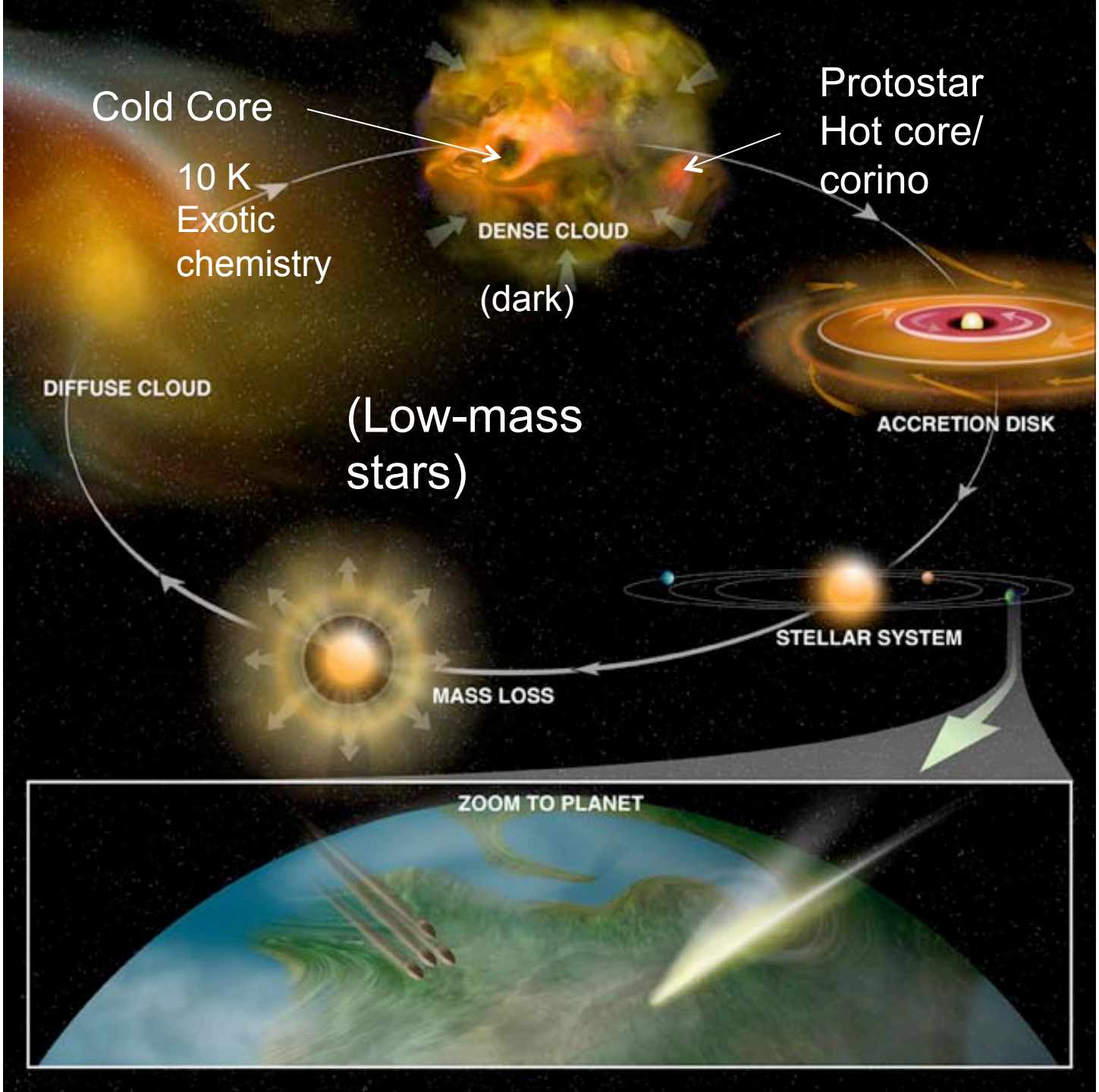
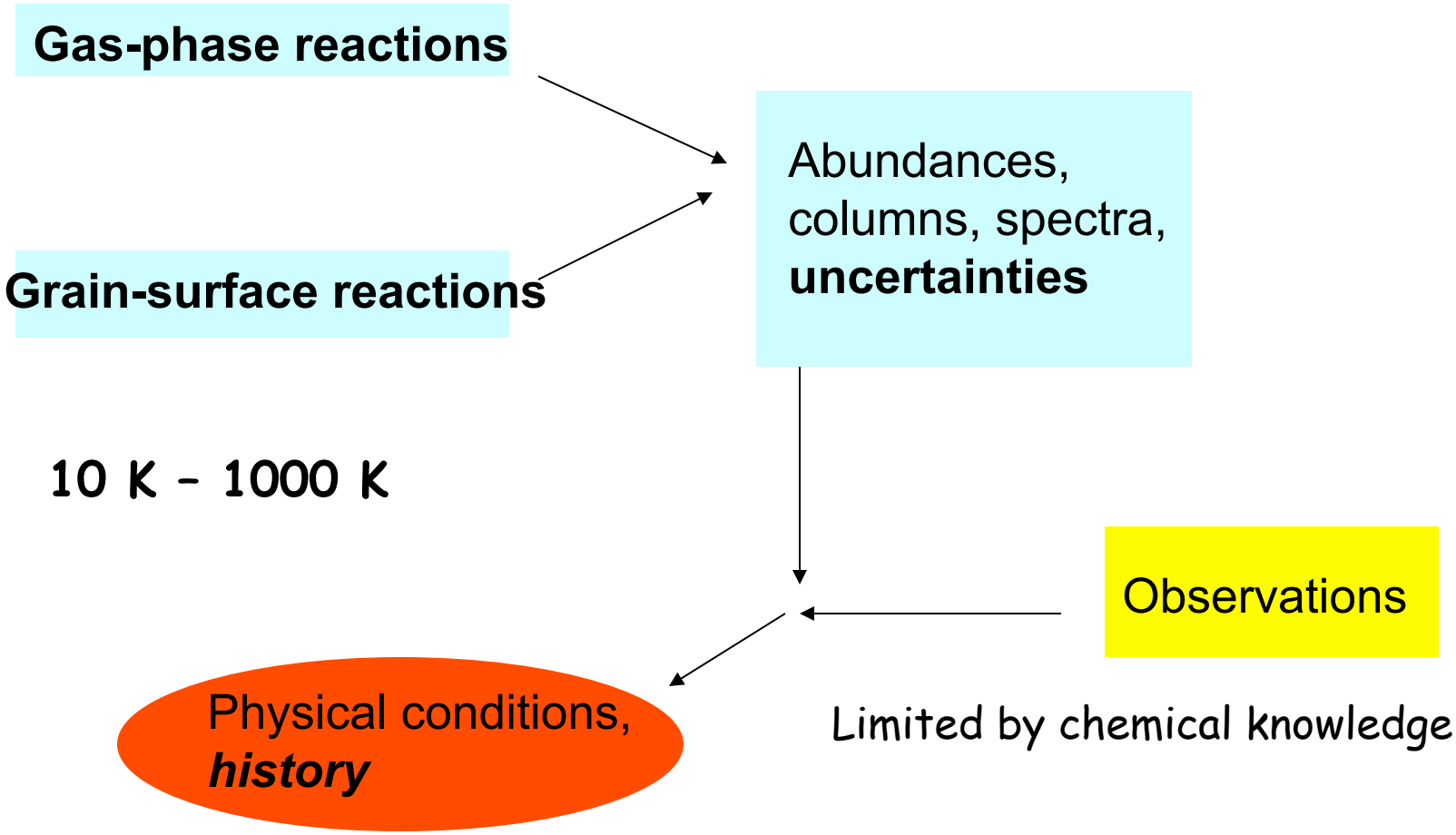

Cold Core
10 K
Exotic
chemistry
DENSE CLOUD
(dark)
Protostar
Hot core/
corino
DIFFUSE CLOUD
(Low-mass
stars)
ACCRETION DISK
STELLAR SYSTEM
MASS LOSS
ZOOM TO PLANET

Chemical Models: Need for KIDA, UDFA,…



Some Problematic Reaction Classes

- 1. Barriered radical-neutral reactions (low T)

$$OH + CH_3OH \rightarrow CH_3O + H_2O$$

- 2. Radiative association (low to moderate T)

$$CH_3 + CH_3O \rightarrow CH_3OCH_3 + h\nu$$

3. Radiative attachment (low to moderate T)

$$e + C_6H \rightarrow C_6H^- + h\nu$$

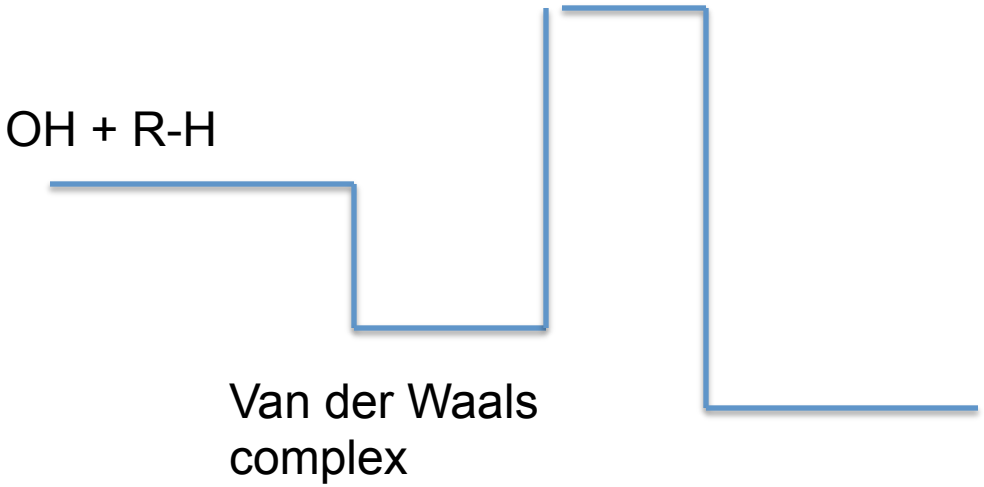
4. Nuclear spin selection rules leading to OPR's

$$HCl^+ + o/p - H_2 \rightarrow o/p - H_2Cl^+ + H$$

5. Radical-radical reactions on dust grains powered by radiation or energetic particles (30 K – 100 K)

$$g - CH_3 + g - CN \rightarrow g - CH_3CN$$

Barriered Radical-Neutral Reactions

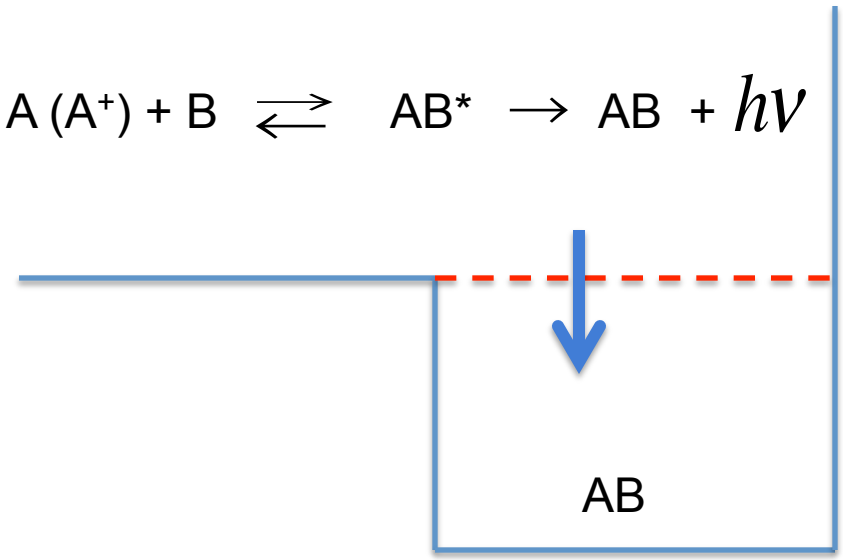


Third body assistance?

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.

Radiative Association



Few experiments, some with ion traps

Statistical theories

Large rate coefficient requires one or more of the following: large number of atoms, deep well, no barriers on entrance channel.

Rate coefficient can reach collisional limit, especially at low T..

What about competitive channels: series or parallel?

Negative Ions in Clouds

- Herbst (1981) considered the possible abundance of anions in cold regions of the ISM based on radiative attachment mechanism:

- $A + e \rightarrow A^- + h\nu$
- and estimated their maximum abundance to be 1% of the neutral counterparts for species with large electron affinities and at least 4-5 atoms (namely, radicals). Based on phase space theory.

Attachment Rate Constants for C_nH^-

No. of C atoms	k_{att} (cm^3 s^{-1})(10 K)
2	1 10(-14)
4	6 10(-8)
6	3 10(-7)
8	3 10(-7)

STILL QUITE CONTROVERSIAL!

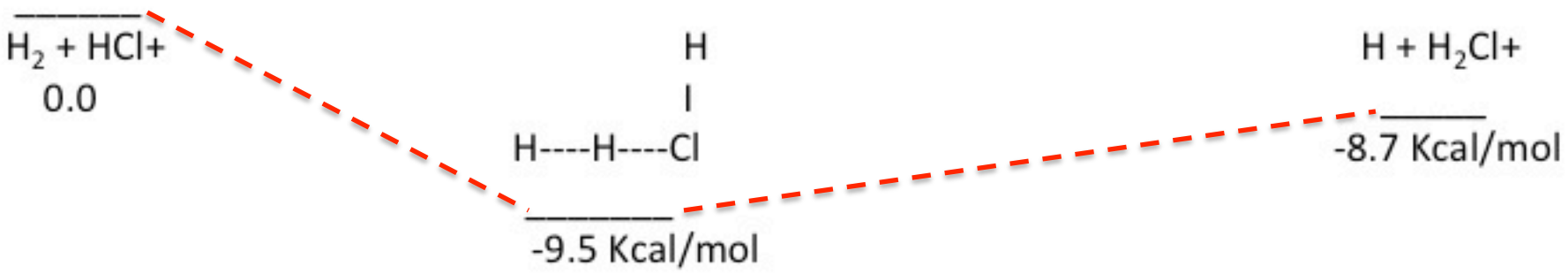
Nuclear Spin Selection Rules & o/p Ratios

1. O/P ratios of interstellar molecules are often measurable, but difficult to understand (e.g. NH_2; H_2O; H_2O^+).
2. We must include reactions in which the O/P ratios of the products are determined by spin selection rules (Oka, Quack):

$$HCl^+ + \text{o,p-}H_2 \longrightarrow \text{o,p-}H_2Cl^+ + H$$

3. Gas-phase spin selection rules depend upon complex scrambling or simple hopping, as well as exothermicity

4. Destruction must compete with thermalization via proton exchange (e.g. H^+-H_2; H-H_2O^+).



Hopping appears to be favored over scrambling for this reaction.

Talbi & Herbst

Surface Radical-Radical Reactions

- g-CH3O + g-HCO → g-HCOOCH3
- g-CH3 + g-CH3O → g-CH3OCH3
- Yates has studied some individual radical "recombination" reactions. Theory by Woon and others.
- Oberg et al. have studied ice photochemistry (many reactions)
- Competitive mechanisms.
- Radicals formed by "activation."

The Future of KIDA: "Surface" Processes

- Diffusive surface reactions on bare grain and ice as well as reactions in bulk
- Eley-Rideal reactions
- Unusual mechanisms
- Photodissociation
- Chemisorption vs. Physisorption
- Adsorption
- Non-thermal desorption (photodesorption, reactive desorption, etc.)
- Thermal desorption

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