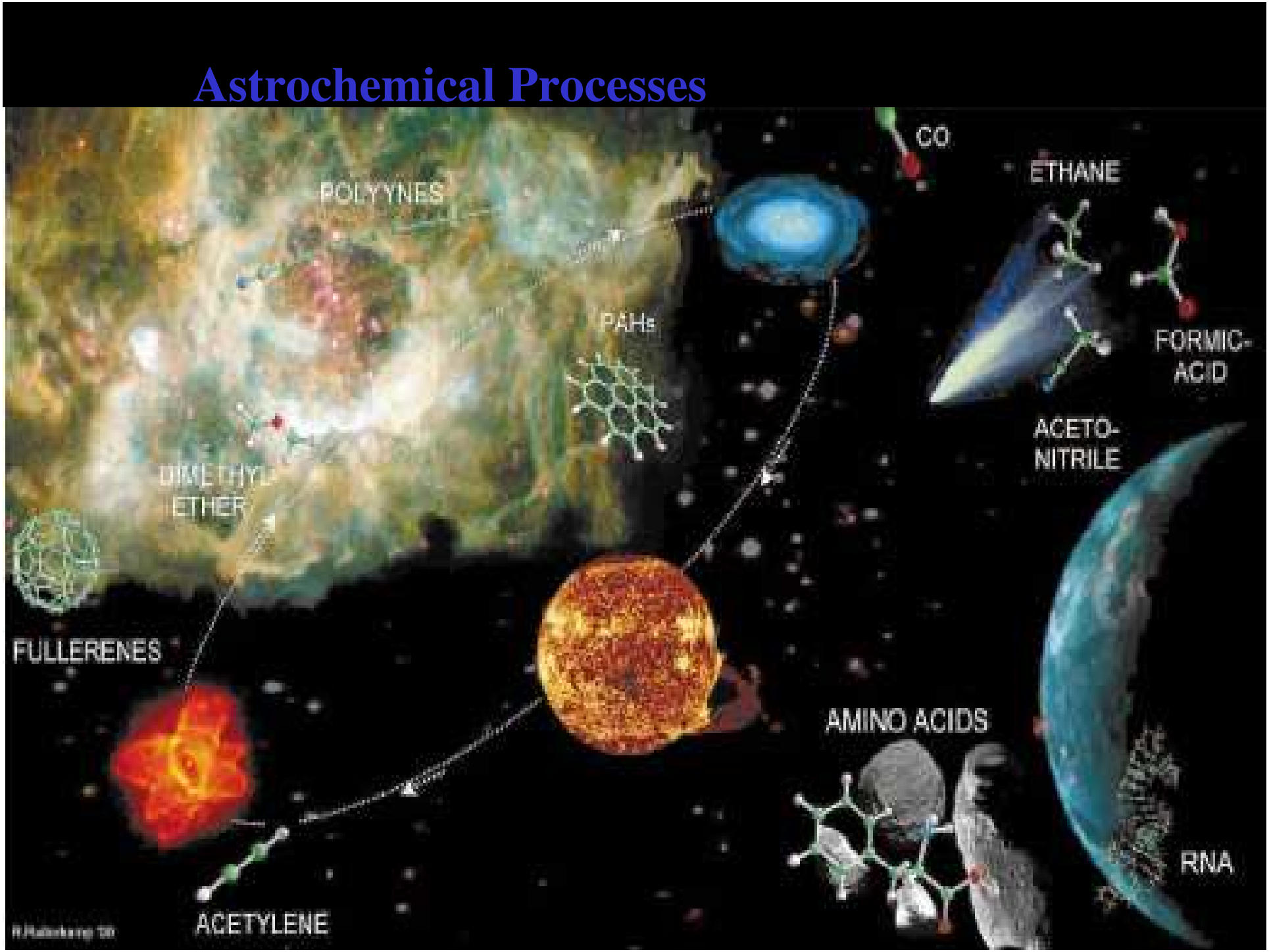
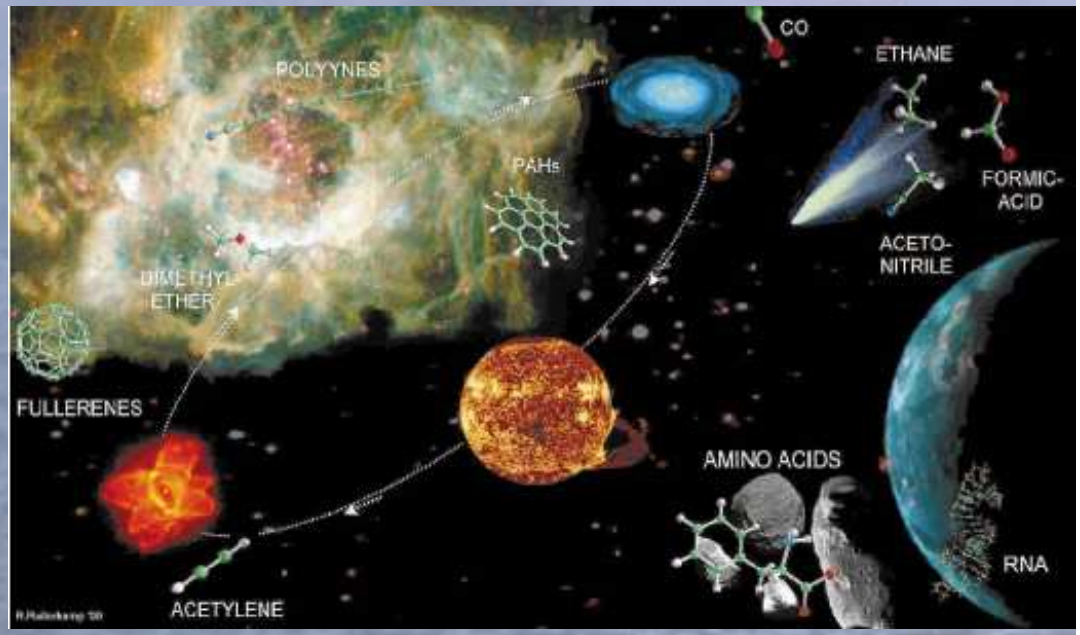
Astrochemical Processes



Outline

1. Gas Phase Chemistry
2. A Case Study in Modelling: outflows from AGB stars
3. Solid State Astrochemistry



Dense interstellar medium

Cosmic rays drive chemistry including gas/solid interactions

- rate ~10^{-17} s^{-1}.
- H_2, CO, N_2, OI, HCO^+.
- cyanopolyynes and carbenes
- dust grains with icy mantles

UV photons drive the chemistry

UV field: 10^8 photons/cm^2/s

- HI, CII, NI, OI
- CH, CN, C_2, HCN, c-C_3H_2
- Soot, AC, HAC, PAHs, carbonaceous networks

Diffuse interstellar medium

CHEMICAL REACTION PROCESSES

Table 4.1. Summary of basic chemical processes for molecules in a molecular cloud operating within the prescribed chemical network

Associative detachment	$A^- + B \rightarrow AB + e^-$
Charge exchange	$AB + C^+ \rightarrow AB^+ + C$
Cosmic ray ionization	$AB \xrightarrow{CR} AB^+ + e^-$
Dielectronic recombination	$e^- + AB^+ \rightarrow AB^{**} \rightarrow AB^* + h\nu$
Dissociation	$e^- + AB \rightarrow A + B^* + e^-$
Dissociative attachment	$e^- + AB \rightarrow A + B^-$
Dissociative ionization	$e^- + AB \rightarrow A + B^+ + 2e^-$
Dissociative photoionization	$h\nu + AB \rightarrow A + B^+ + e^-$
Dissociative recombination	$e^- + AB^+ \rightarrow A + B$
Electronic excitation	$e^- + AB \rightarrow e^- + AB^*$
Ion–molecule reaction	$AB + C^+ \rightarrow D^+ + E$
Neutral–neutral reaction	$AB + C \rightarrow A + BC$
Photodissociation	$h\nu + AB \rightarrow A + B$
Photoionization	$h\nu + AB \rightarrow AB^+ + e^-$
Radiative association	$A + B \rightarrow AB + h\nu$
Rotational and vibrational excitation	$e^- + AB(vj) \rightarrow e^- + AB(v'j')$

** indicates an intermediate resonance state where two electrons are in excited electronic orbitals.

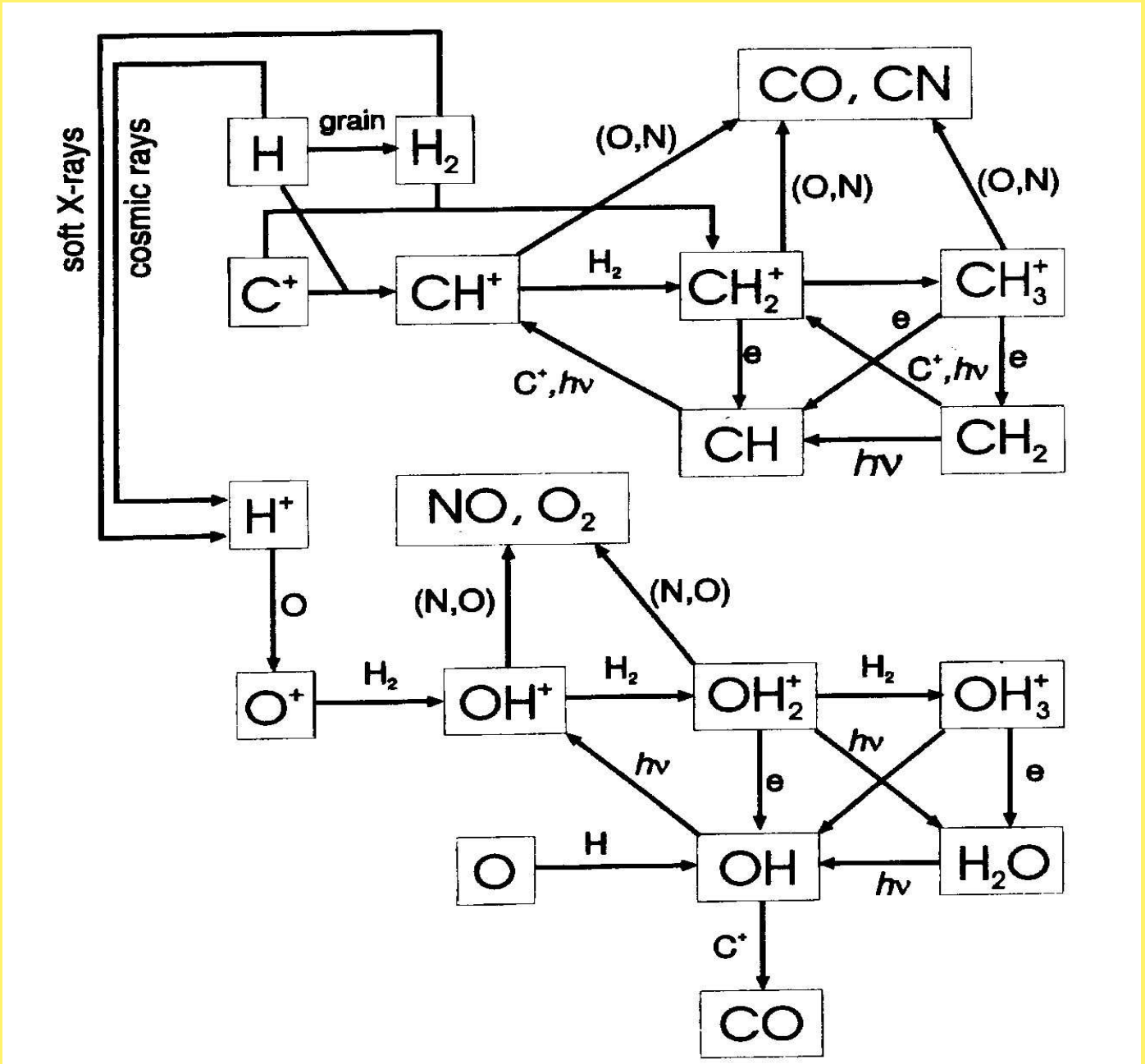
Important Reactions

- H_2 + c.r.p. --> $H_2^+ + e$ $\sim 10^{-17}\ s^{-1}$.
- $H_3^+ + e$ --> $2H + H$ $\sim 10^{-6}\ cm^3 s^{-1}$ at 10K.
- $O + OH$ --> $O_2 + H$ $\sim 10^{-11} T_3^{1/2}\ cm^3 s^{-1}$
- $C + O_2$ --> $CO + H$ $\sim 10^{-11} T_3^{1/2}\ cm^3 s^{-1}$

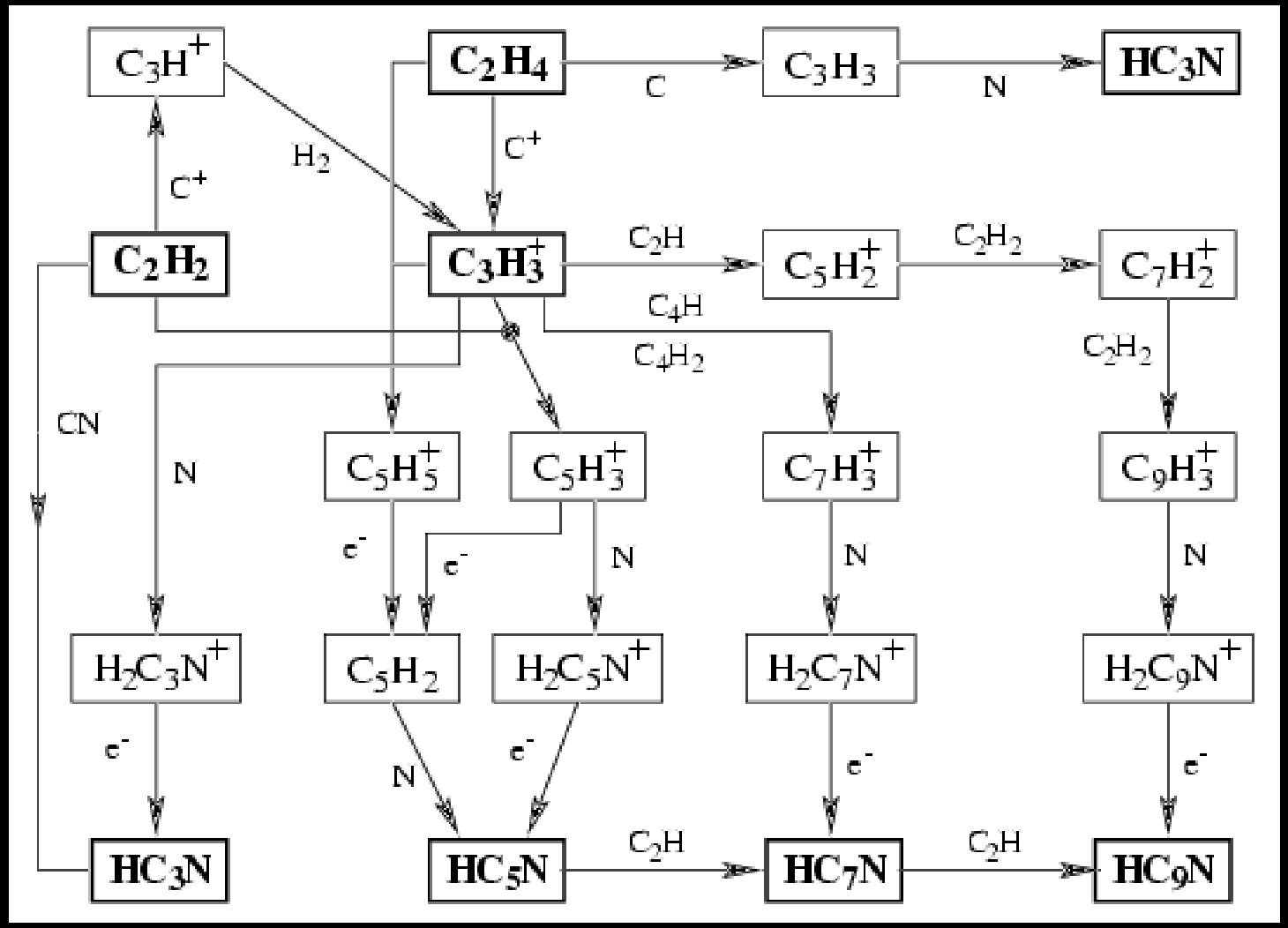
- $CH_3OH_2^+ + CH_3OH$ --> $(CH_3)_2OH^+ + H$ $\sim 10^{-11} cm^3 s^{-1}$
- $CN + C_2H_2$ --> $HC_3N + H$ $\sim 10^{-10}\ cm^3 s^{-1}$

- $C^+ + H_2$ --> $CH^+ + H$ $\sim 10^{-16} T_3^{5/4} e^{-4700/T}\ cm^3 s^{-1}$
- $OH + H_2$ --> $H_2O + H$ $\sim 10^{-11} e^{-2600/T}\ cm^3 s^{-1}$
- $SO + OH$ --> $SO_2 + H$ $\sim 10^{-12} T_3^{1/2}\ cm^3 s^{-1}$

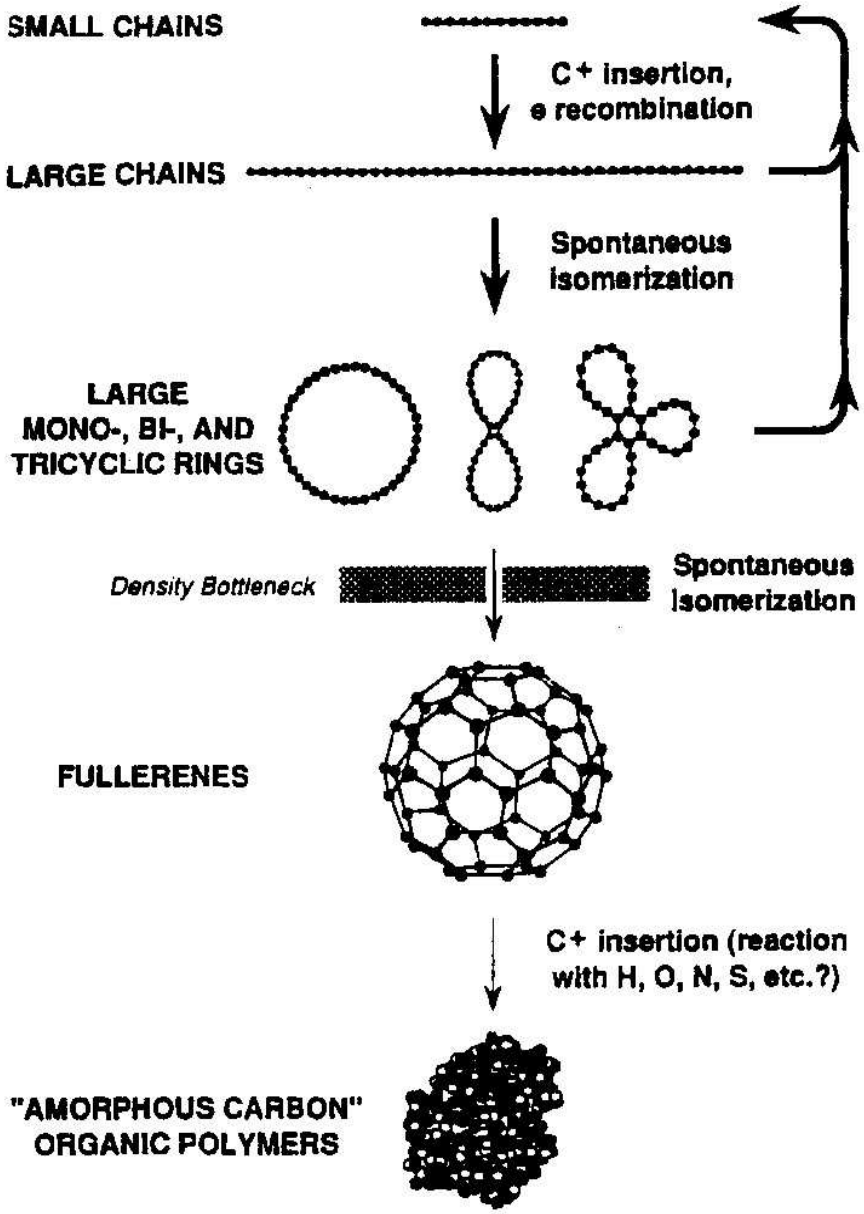
Basic chemistry of UV-radiated diffuse clouds

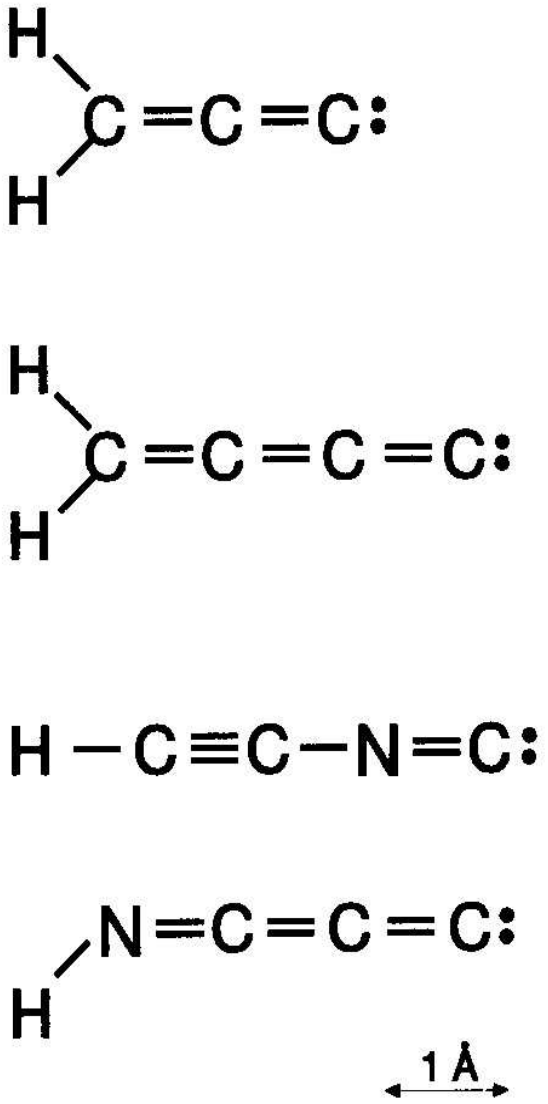


Cyanopolyynes



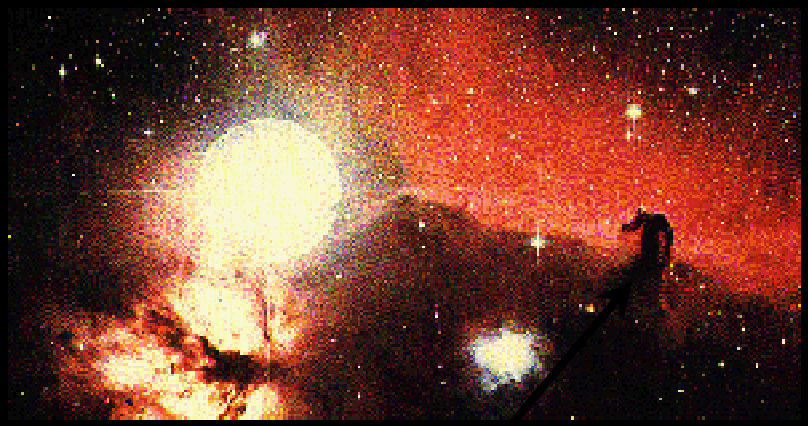
Formation of C-chains and grains C-chains recently detected





Deuterium Fractionation

0.00033



0.001 – 0.2

Isotopic Fractionation

IN 10K GAS: $XH^+ + HD \rightarrow XD^+ + H_2 + E_z$

Roberts, Herbst & Millar (2003)

- $H_3^+ + HD \rightarrow H_2D^+ + H_2$
- $H_2D^+ + HD \rightarrow D_2H^+ + H_2$
- $D_2H^+ + HD \rightarrow D_3^+ + H_2$

Terzieva & Herbst (2000), Charnley & Rodgers (2002)

- $N^{15} + {}^{14}N_2H^+ \rightarrow N^{14} + {}^{15}N_2H^+$

Langer et al. 1984, 1989)

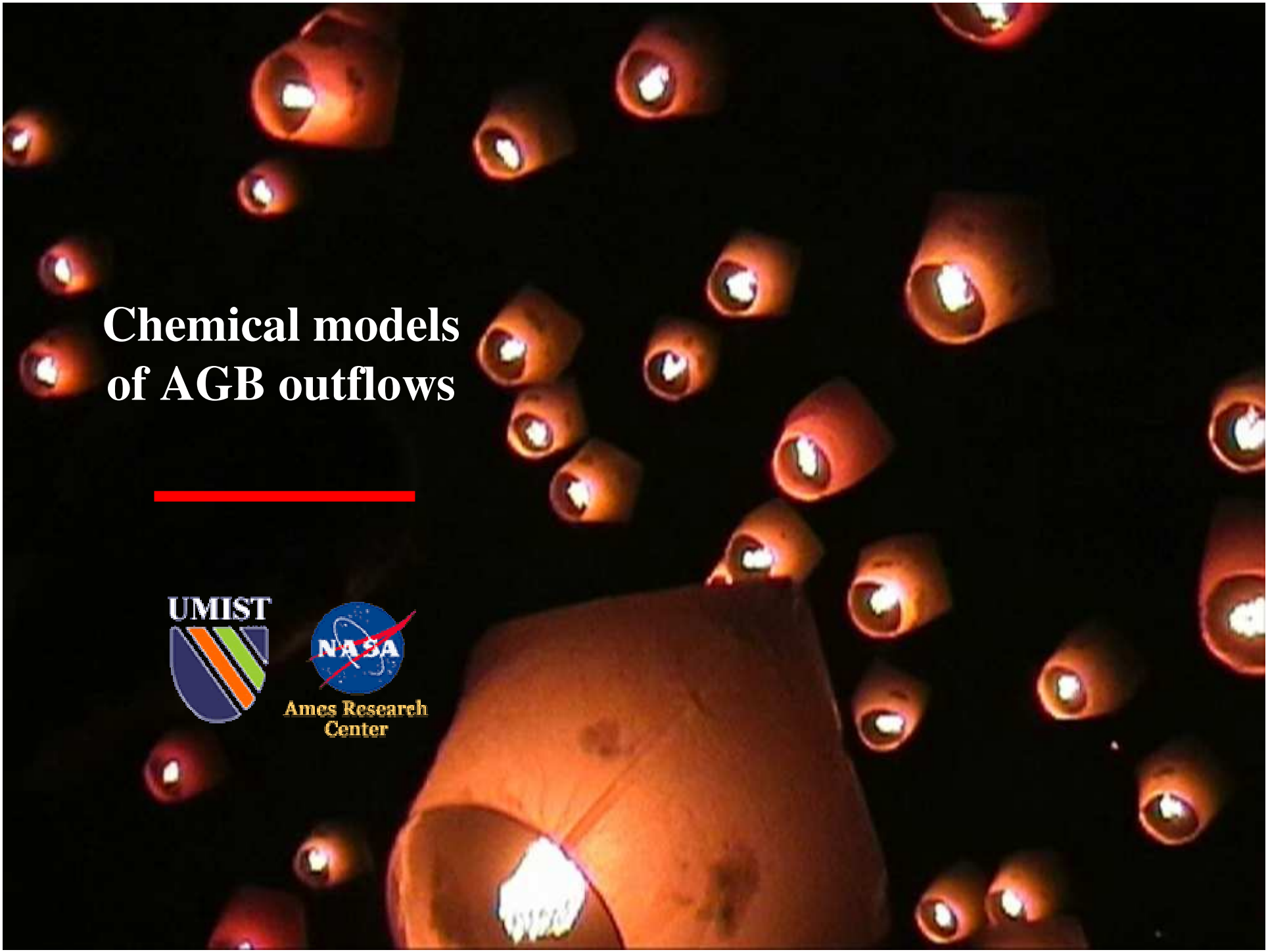
- $^{13}C^+ + {}^{12}CO \rightarrow {}^{12}C^+ + {}^{13}CO$

Chemical Modelling

- **chemical network: 1000s reactions, 100s species**
- **UMIST database for astrochemistry: www.rate99.co.uk**
  www.rate99.co.uk
- **physical parameters: temperature, density, cosmic ray ionisation rate, visual extinction etc.**
- **ODE system to solve for number densities $n_i = X_i/V$**

$$dn_i/dt = P_i - L_i n_i \quad ; i = 1,N$$

- **Alternatively: Monte Carlo simulation of chemical master equation for the joint PDF : $P(\{X_i\};t)$, and obtain $\langle X_i(t) \rangle$ from statistics (Gillespie 1976; Charnley 1998)**


Chemical models
of AGB outflows
UMIST
NASA
Ames Research
Center

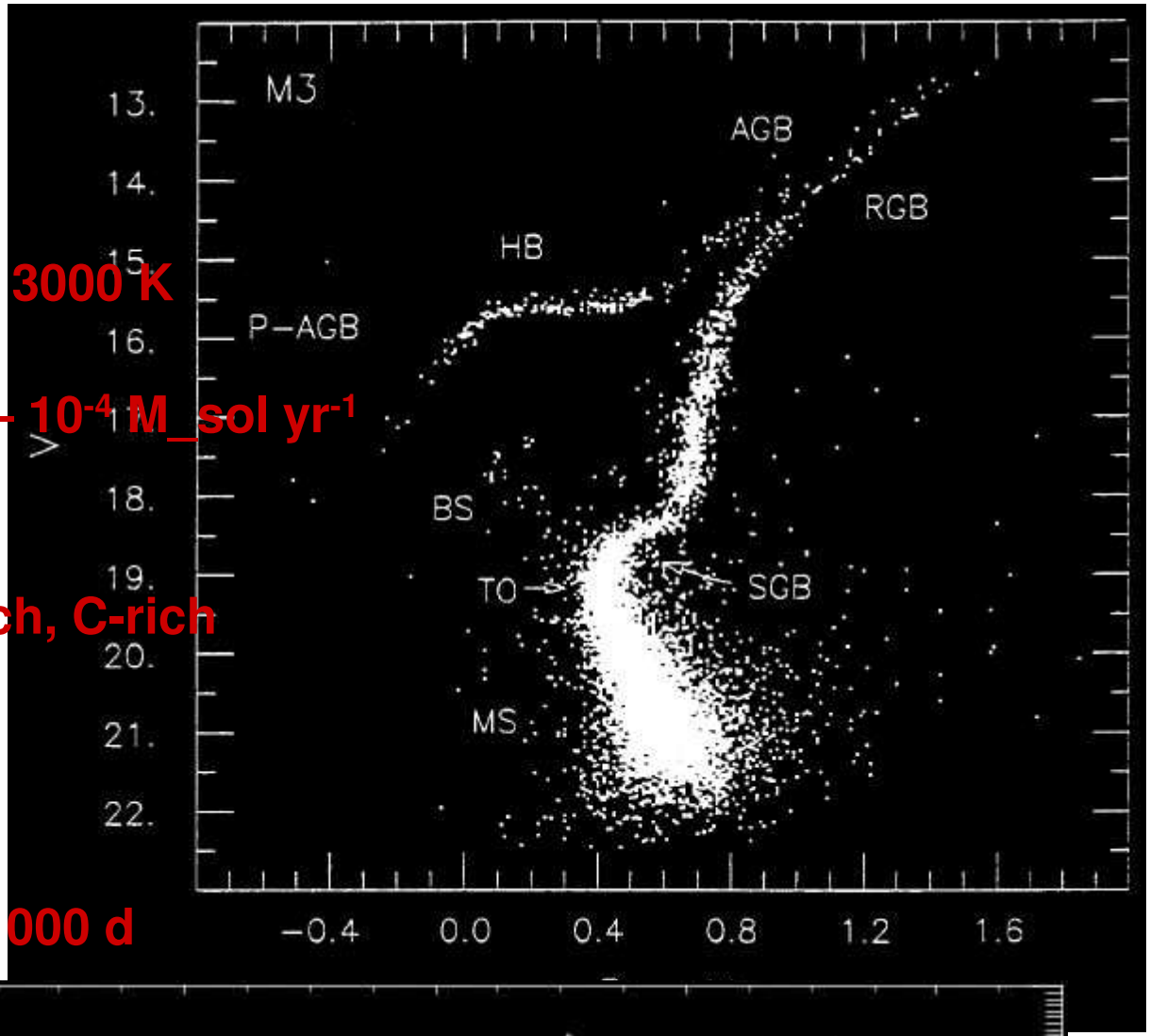
AGB stars

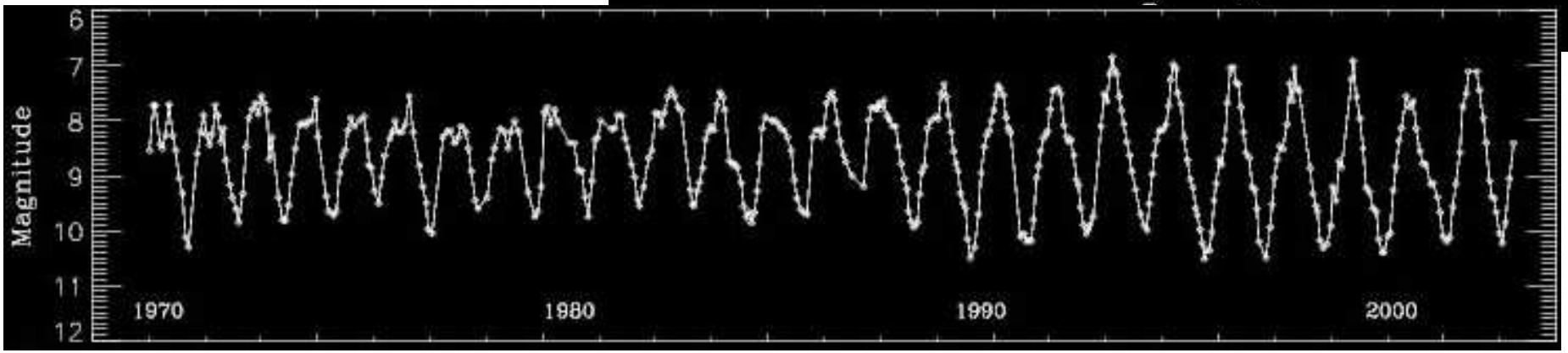
old, cold stars; T = 2000 - 3000 K

undergo mass loss; 10^{-7} – 10^{-4} M_sol yr^{-1}

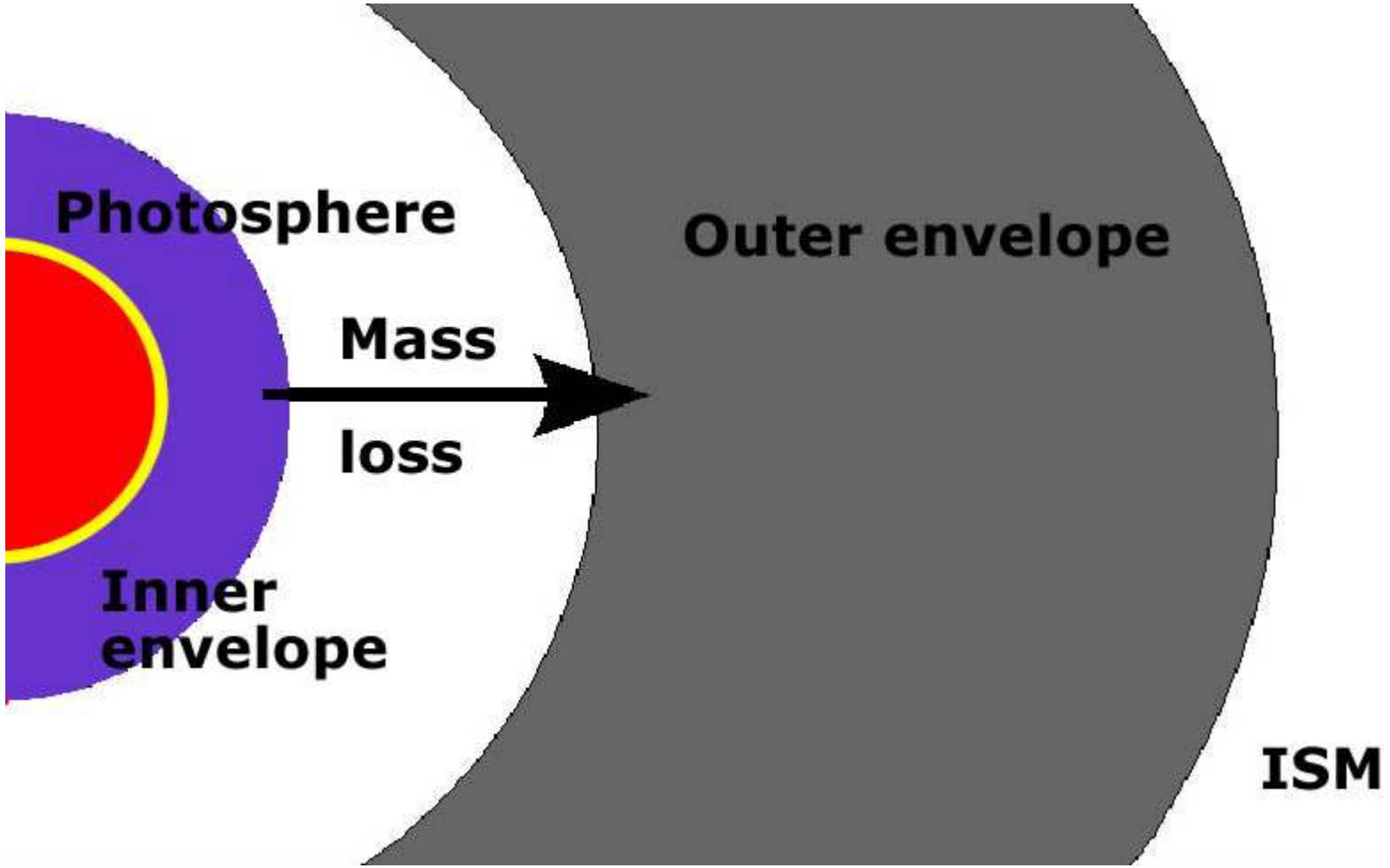
classified chemically O-rich, C-rich

Mira variables; P = 100 – 1000 d

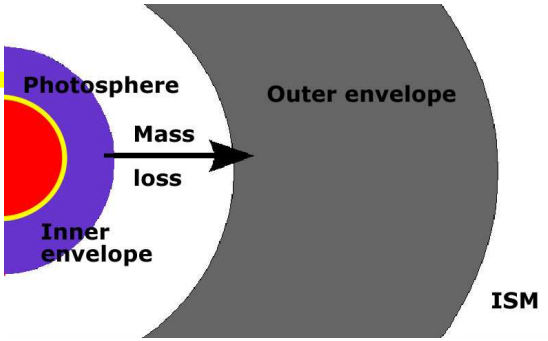




AGB CIRCUMSTELLAR ENVELOPE



Photospheric Chemistry



chemical equilibrium

$$G = \sum_i f_i x_i$$

$$f_i = \left(\frac{G}{RT}\right)_i + \ln P + \ln\left(\frac{x_i}{\bar{x}}\right)$$

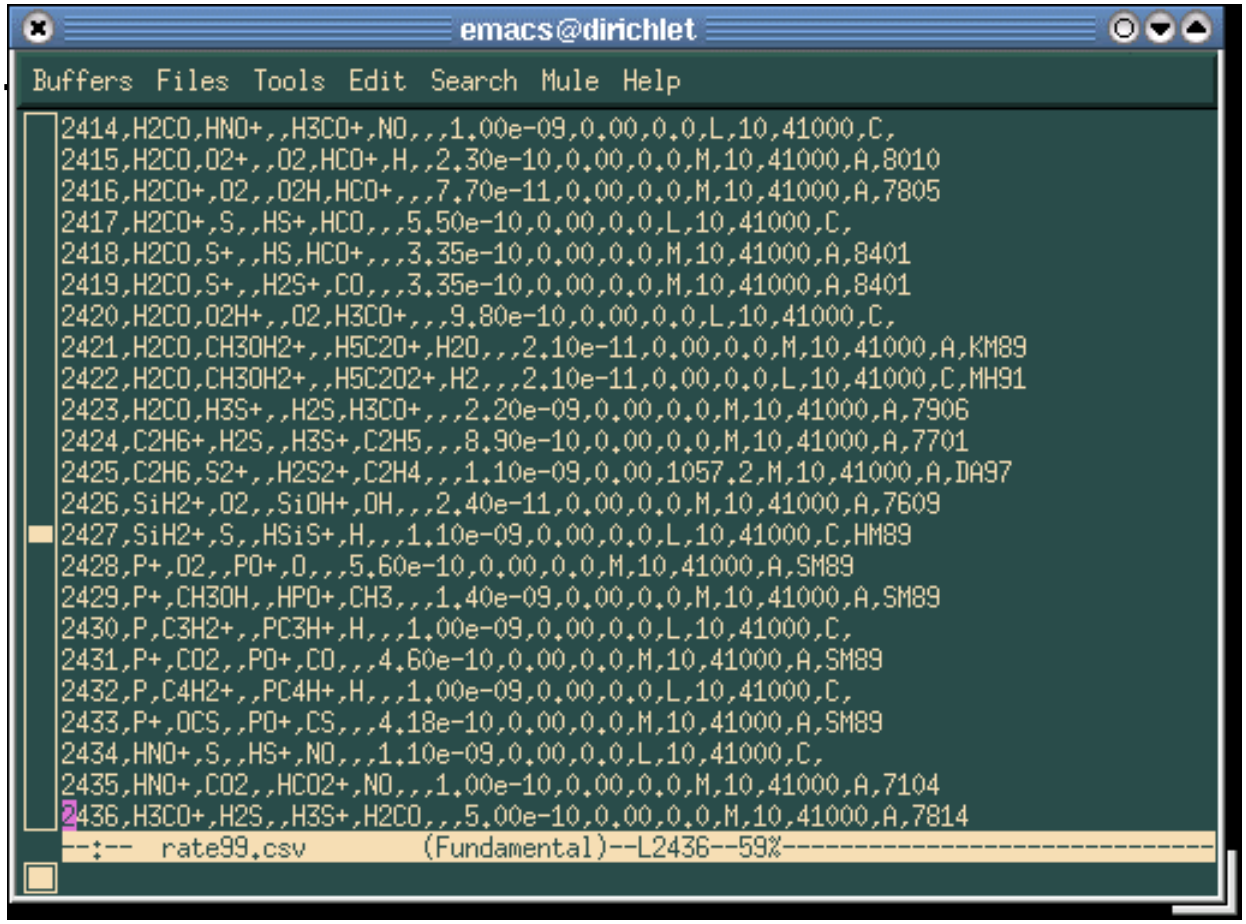
at equilibrium, G is a minimum

find x_i that minimize G

inputs: total pressure, elemental abundances, C/O ratio, temperature

Astrochemical kinetic models

chemical network:



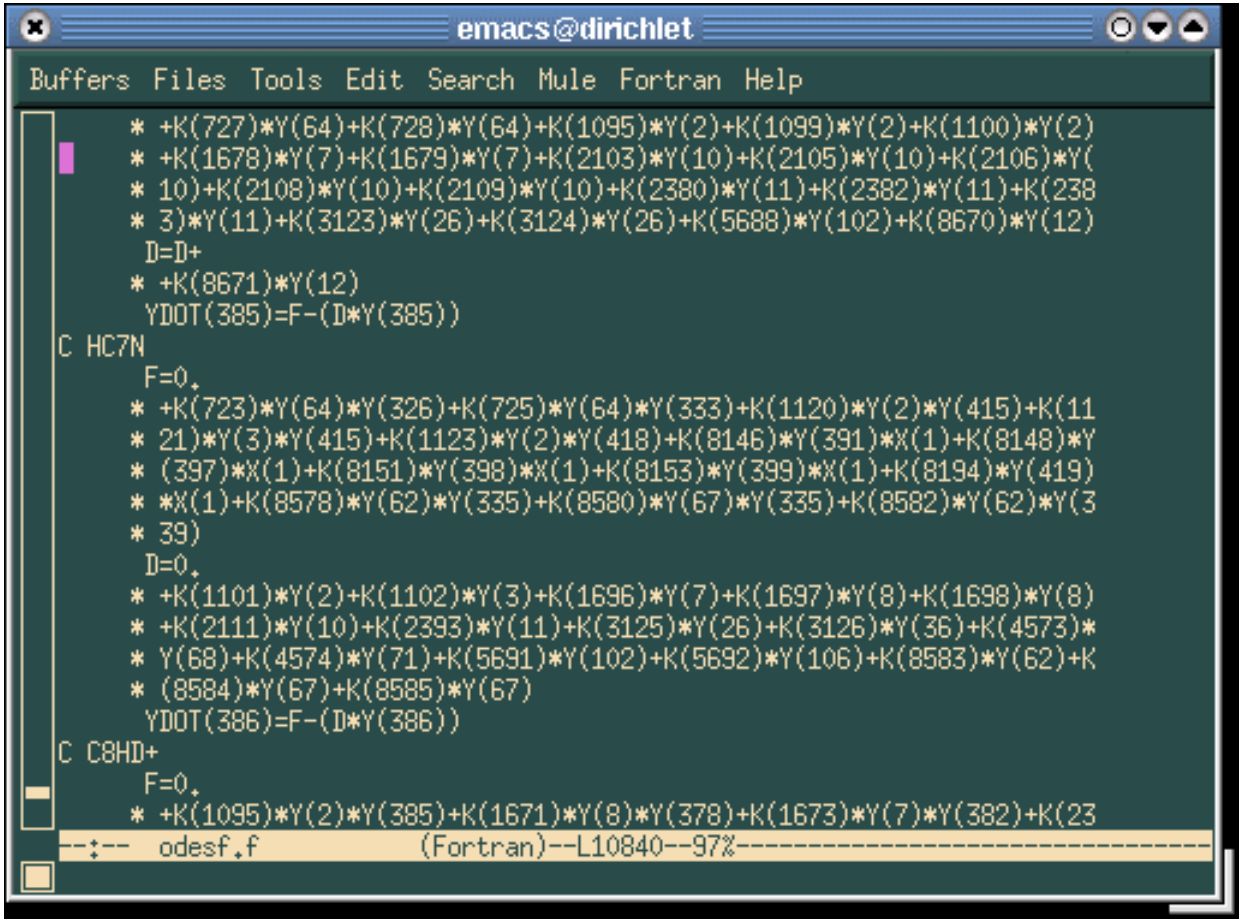
rate of change of abundance of X =

formation rate of X

- destruction rate of X

Astrochemical kinetic models

… chemical ODE system to solve plus equations for n(r), T(r) & G(r).



Fortran software to write chemical routines and ODE stiff solver

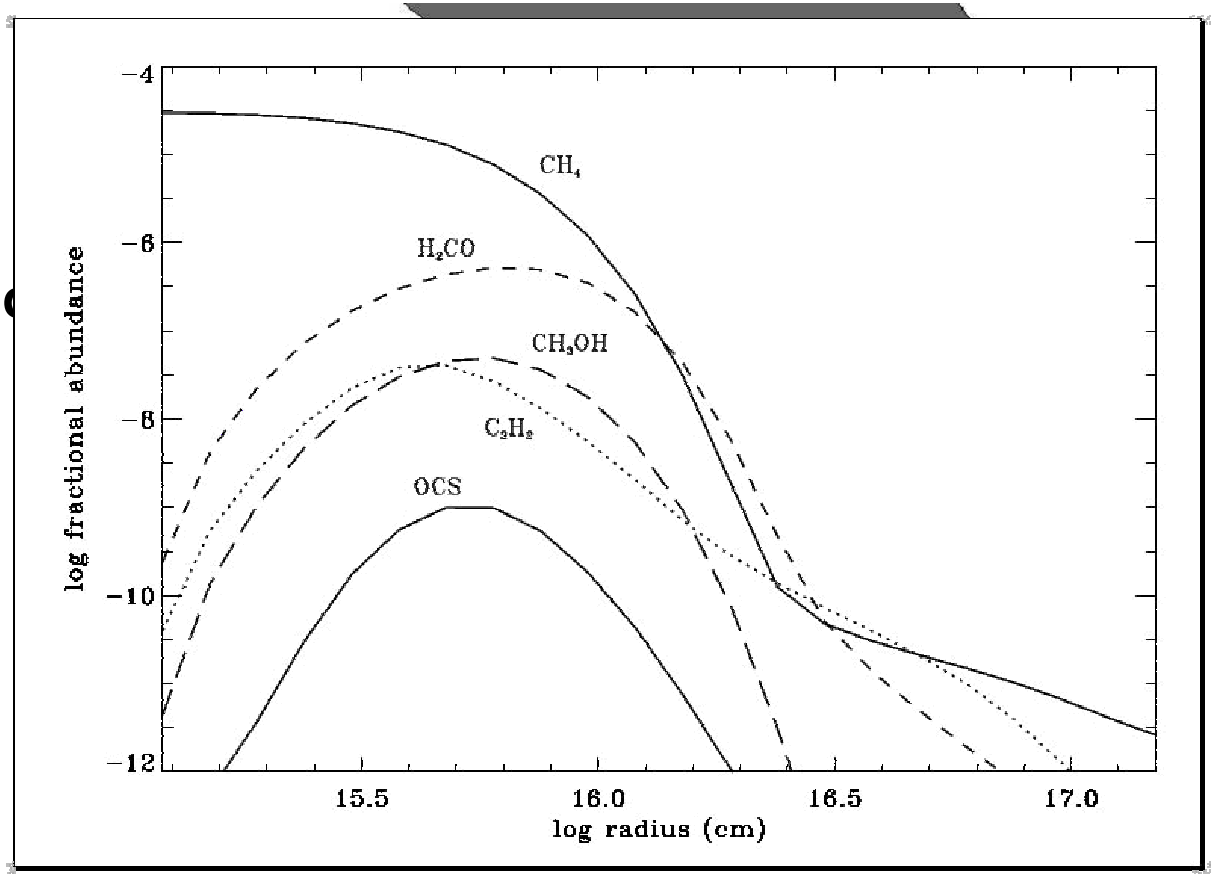
Outer envelope photochemistry

1D radial model

assume constant mass loss rate and geometric dilutio

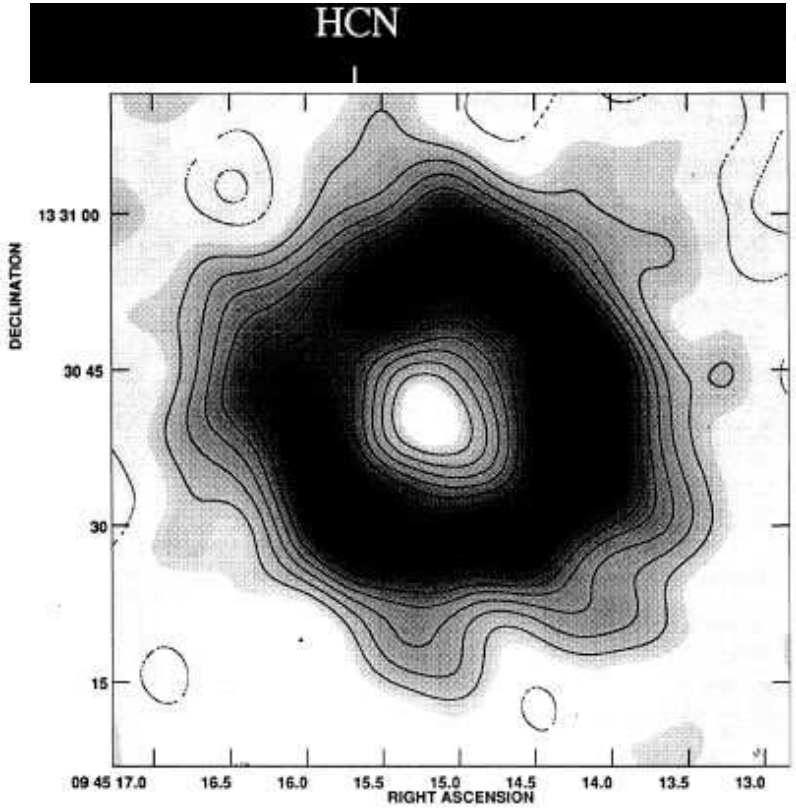
time dependent chemistry, t=r/v

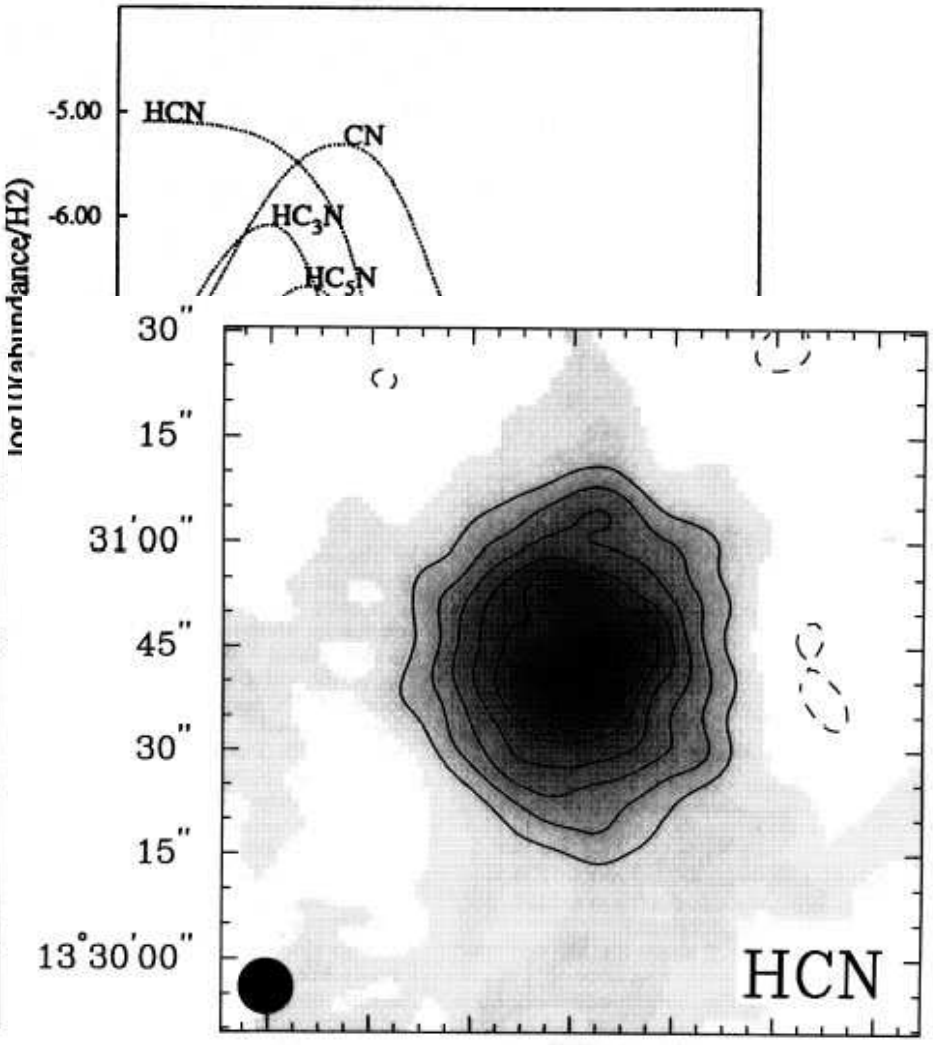
choice of parent species depend on type of CSE

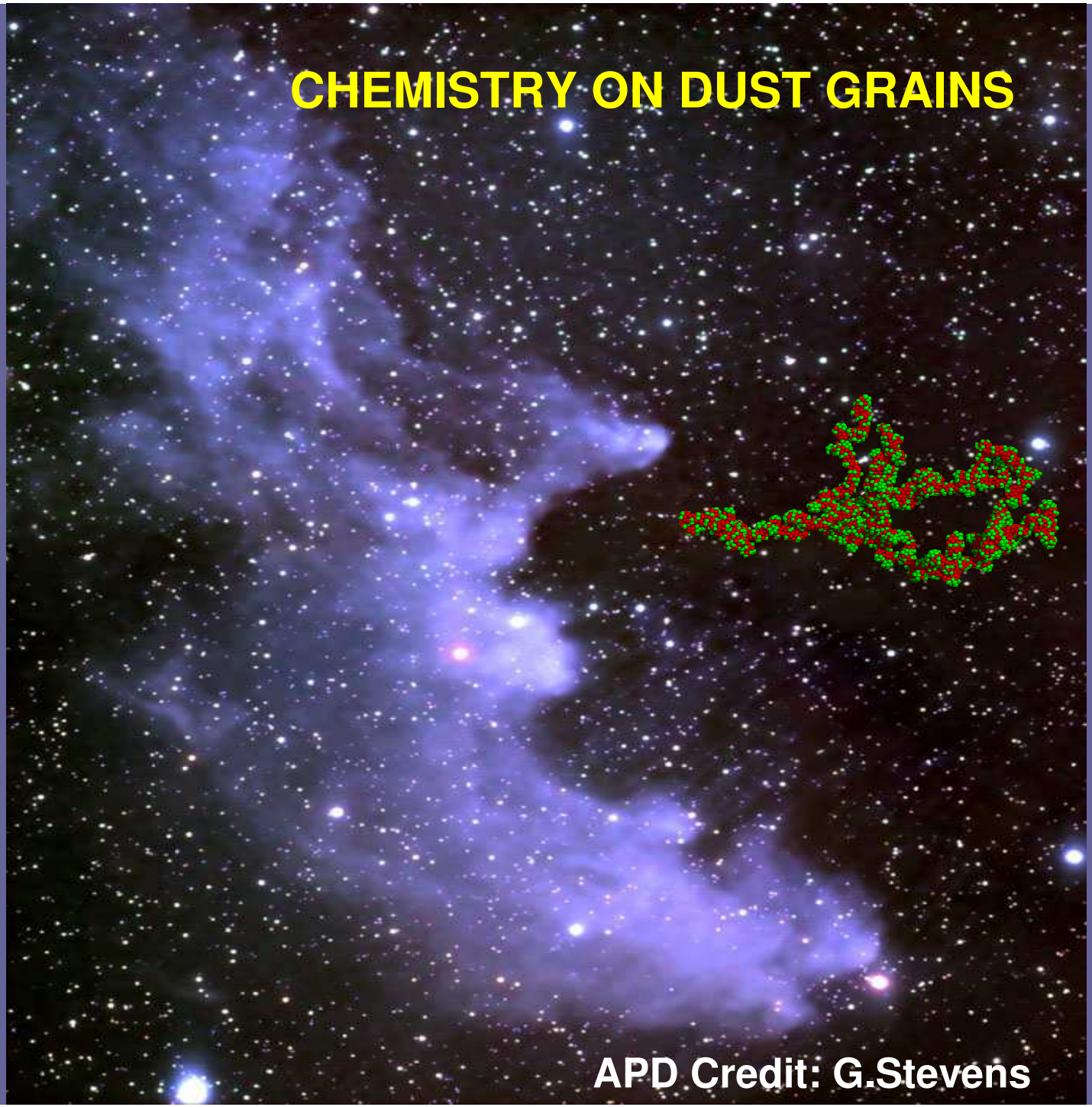


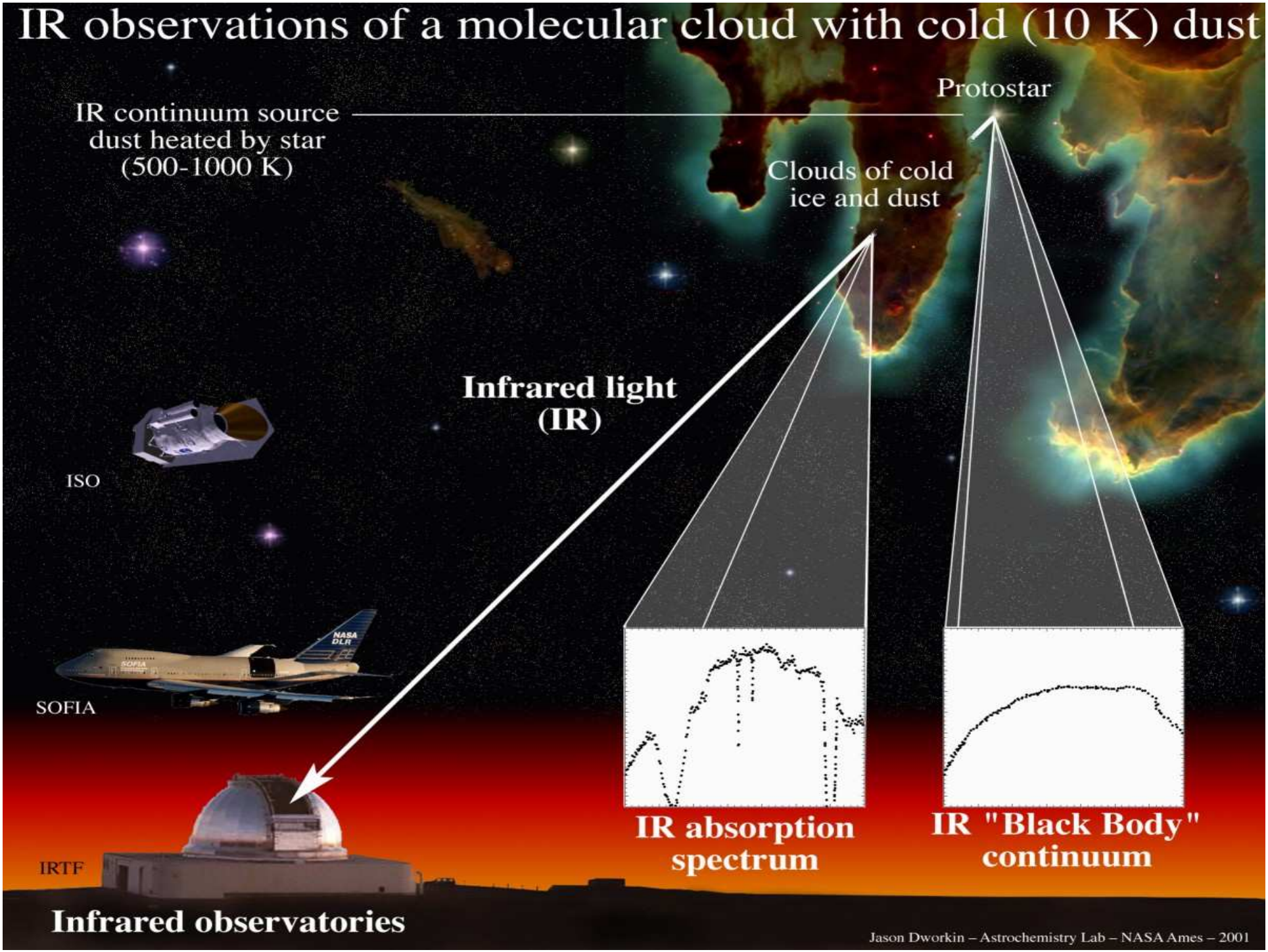
Application to IRC+10216

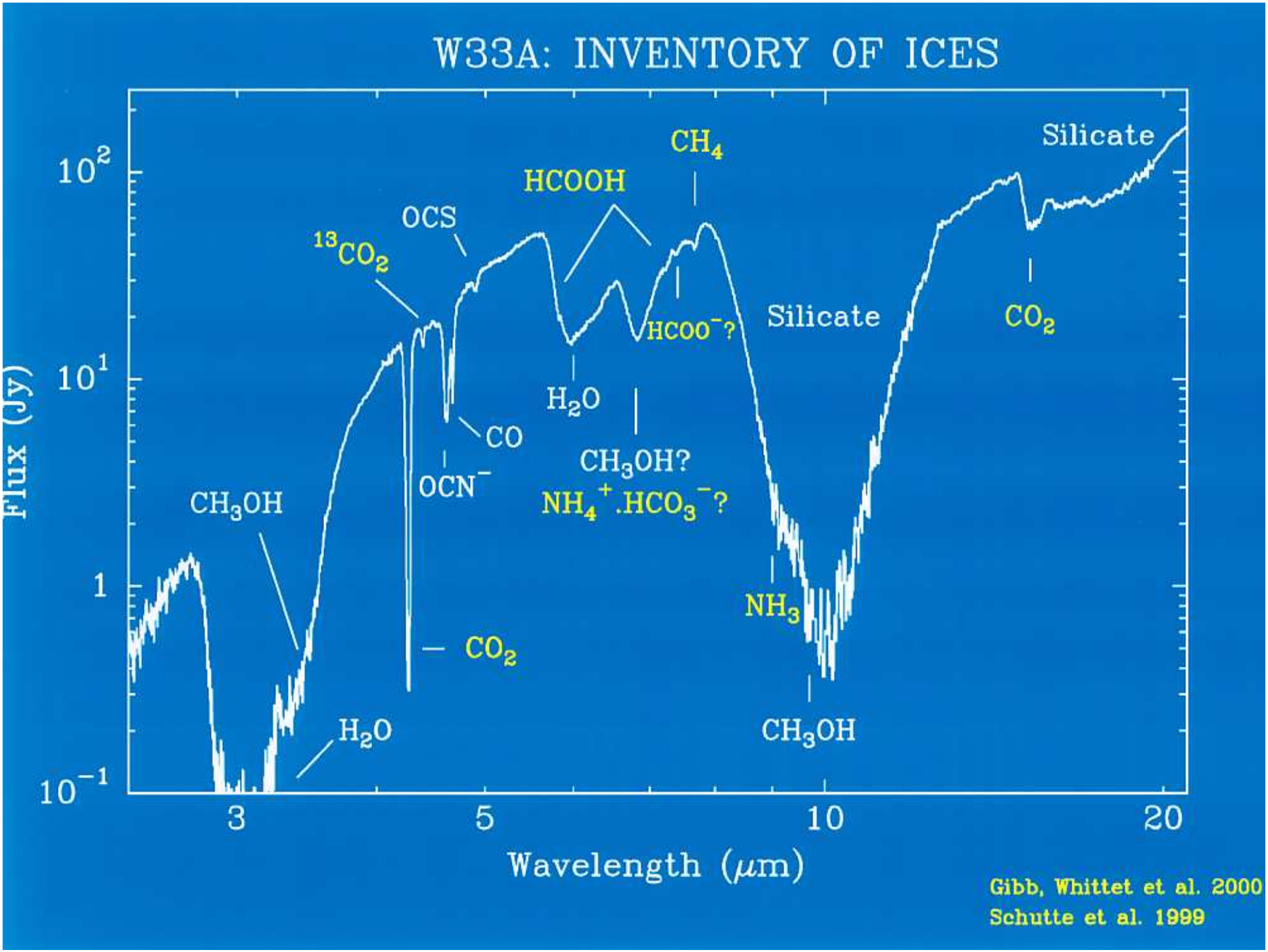
parent species: He, CO, CH_4, C_2H_2, HCN, N_2, NH_3, SiS






CHEMISTRY ON DUST GRAINS
APD Credit: G.Stevens


IR observations of a molecular cloud with cold (10 K) dust
Protostar
IR continuum source
dust heated by star
(500-1000 K)
Clouds of cold
ice and dust
Infrared light
(IR)
ISO
SOFIA
IRTF
IR absorption
spectrum
IR "Black Body"
continuum
Infrared observatories
Jason Dworkin – Astrochemistry Lab – NASA Ames – 2001


W33A: INVENTORY OF ICES
Flux (Jy)
10^2
10^1
1
10^{-1}
3
5
10
20
Wavelength (μm)
CH_3OH
H_2O
$^{13}CO_2$
OCS
OCN^-
CO
CO_2
HCOOH
H_2O
CH_3OH?
$NH_4^+.HCO_3^-$?
CH_4
$HCOO^-$?
Silicate
NH_3
CH_3OH
Silicate
CO_2
Gibb, Whittet et al. 2000
Schutte et al. 1999

CATALYSIS ON GRAIN SURFACES

Accretion of atoms on interstellar grains slow: 1 atom/day
At low T the sticking coefficients are close to unity.

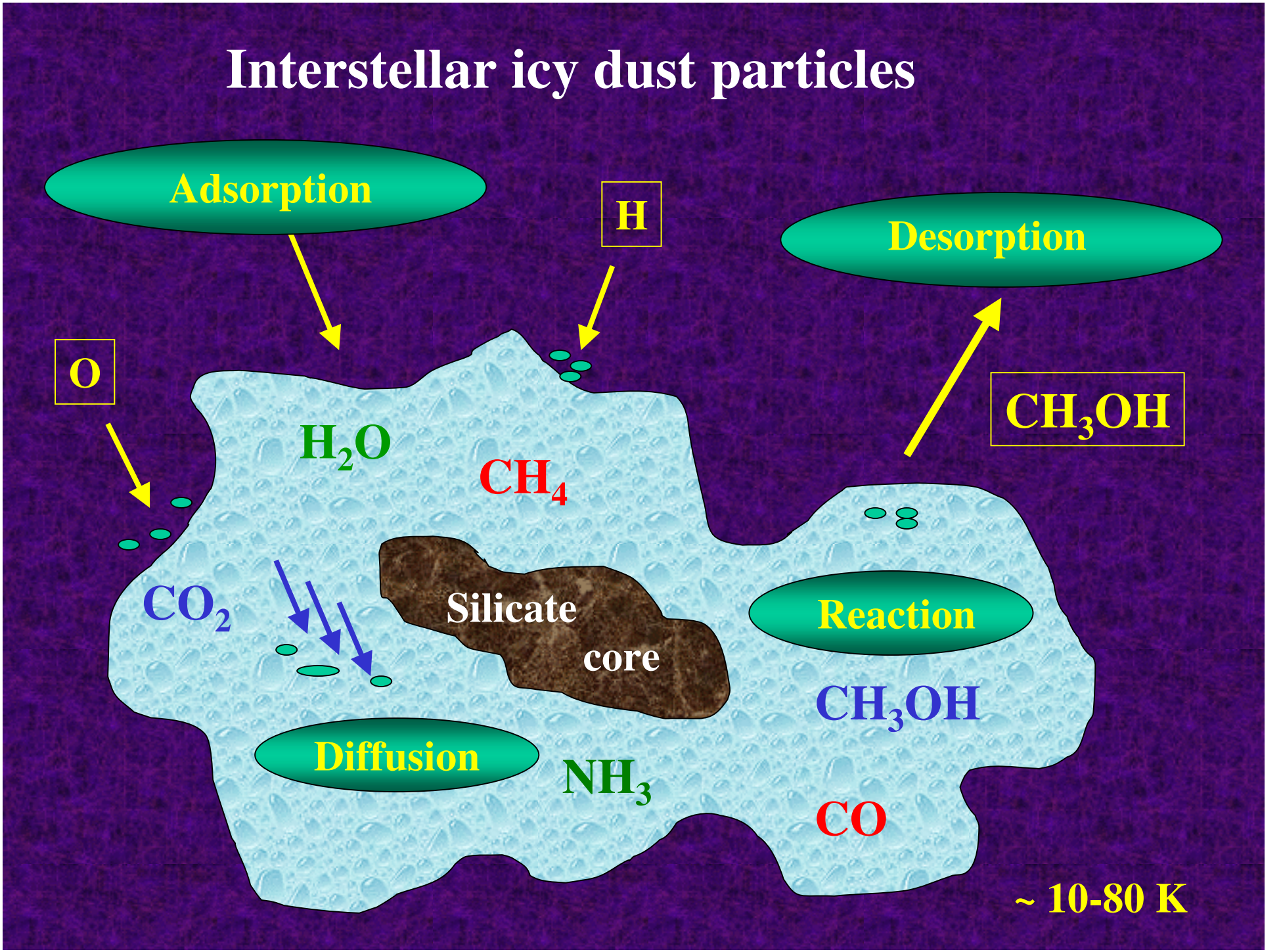
Accreted atoms such as H, C, N, O are very mobile:

migration time scales range from 10^{-12} to 10^{-3} s
quantum tunnelling or thermal hopping

H_2O, NH_3, CH_4 can be formed by exothermic H addition reactions without activation energy barriers.

Many neutral molecules, such as CO possess activation barriers.

$$CO \xrightarrow{H} HCO \xrightarrow{H} H_2CO \xrightarrow{H} CH_3O \xrightarrow{H} CH_3OH$$


Interstellar icy dust particles
Adsorption
H
Desorption
O
CH_3OH
H_2O
CH_4
CO_2
Silicate
core
Reaction
CH_3OH
Diffusion
NH_3
CO
~ 10-80 K

SURFACE CHEMISTRY MODELS

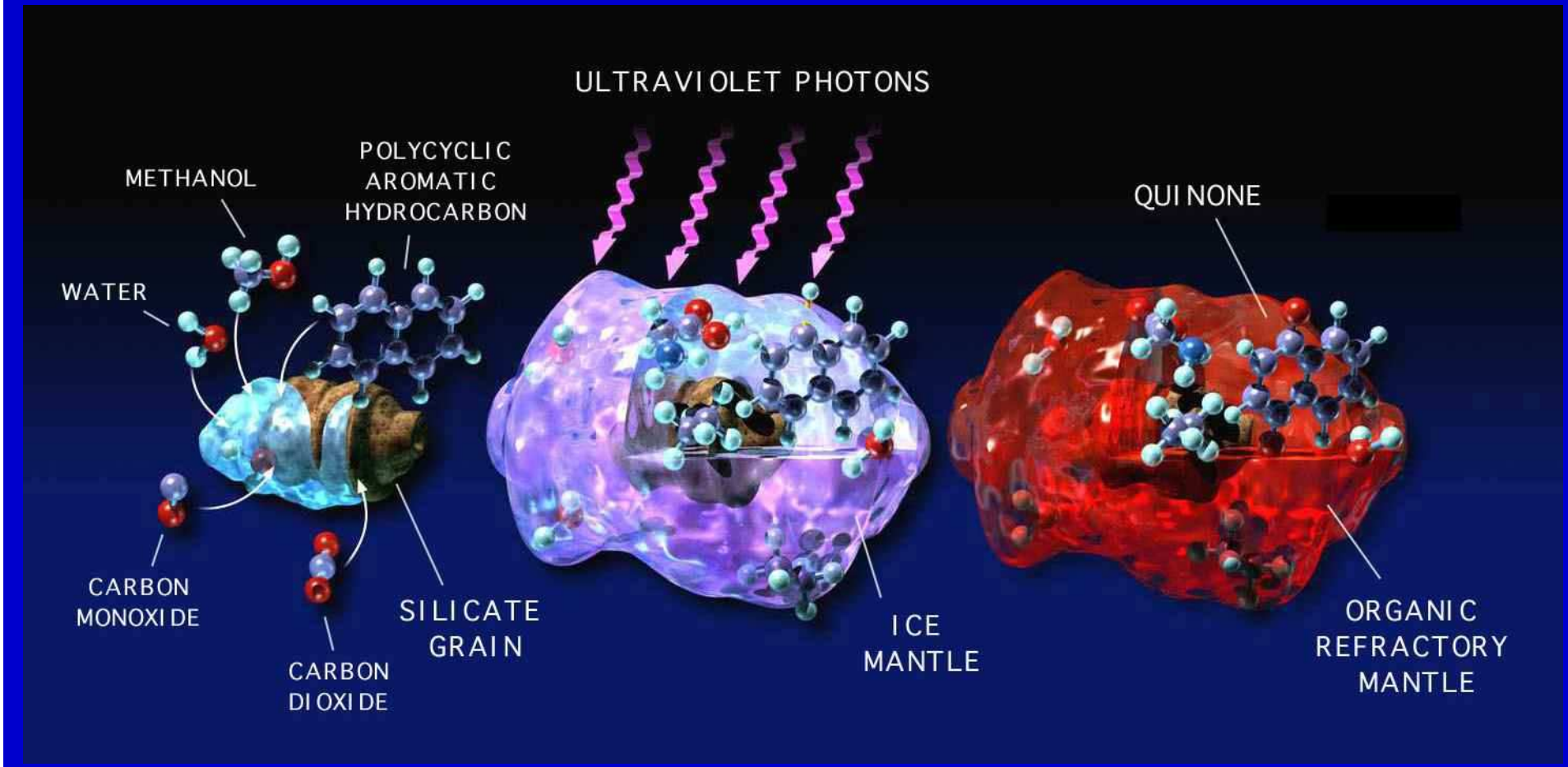
Conceptual problem:

1) Deterministic ODE treatment with $n_i(t)$ as variable is fundamentally flawed (Pickles & Williams 1977).
2) Must use X_i explicitly and a stochastic Monte Carlo simulation of the master equation (Charnley 2001; Biham et al. 2001).

Solid State Astrochemistry Experiments

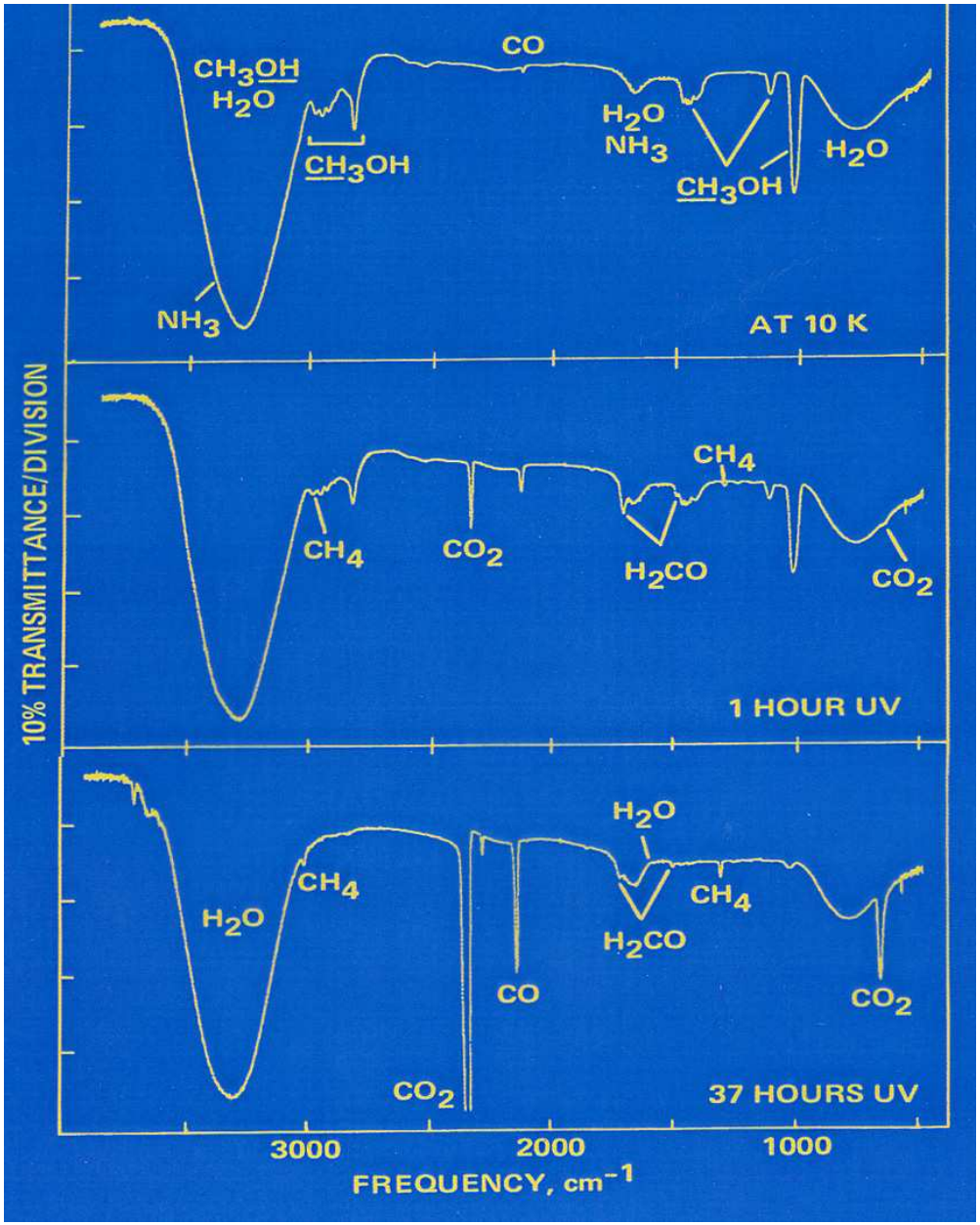
- **COLD ATOM ADDITION REACTIONS ON SURFACES (Hiraoka, Kouchi, Schutte, Vidali)**
- **PHOTOLYSIS OF BULK ICE MIXTURES (Allamandola, Bernstein)**
- **RADIOLYSIS OF BULK ICE MIXTURES (Moore & Hudson, Strazulla))**

Interstellar Dust: ice mantle evolution



Bernstein, Sandford, Allamandola , Sci. Am. 7,1999, p26

Photochemical Evolution of $H_2O : CH_3OH : CO : NH_3$
100 : 50 : 1 : 1

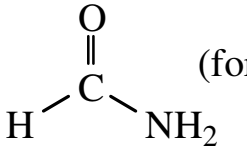


Courtesy Doug Hudgins

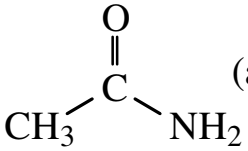
Photoproducts from Realistic Interstellar Ice Laboratory Simulations

Species evident at 200 K

CH_3CH_2-OH (ethanol)

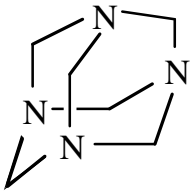


(formamide)



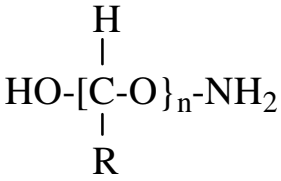
(acetamide)

Species remaining at 300 K



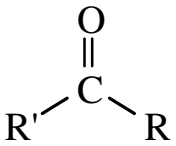
$(CH_2)_6N_4$

(HMT)

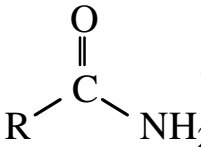


(POMs)

CH_3CH_2-OH (ethanol)



(ketones)



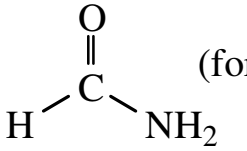
(amides)

Courtesy Max Bernstein

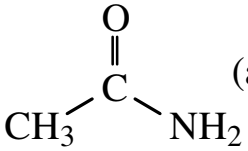
Photoproducts from Realistic Interstellar Ice Laboratory Simulations

Species evident at 200 K

CH_3CH_2-OH (ethanol)

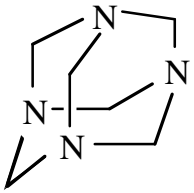


(formamide)



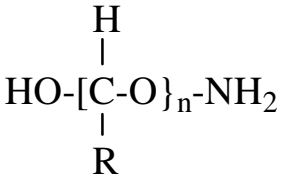
(acetamide)

Species remaining at 300 K



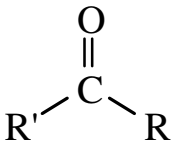
$(CH_2)_6N_4$

(HMT)

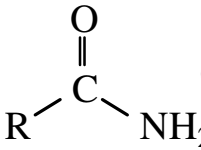


(POMs)

CH_3CH_2-OH (ethanol)



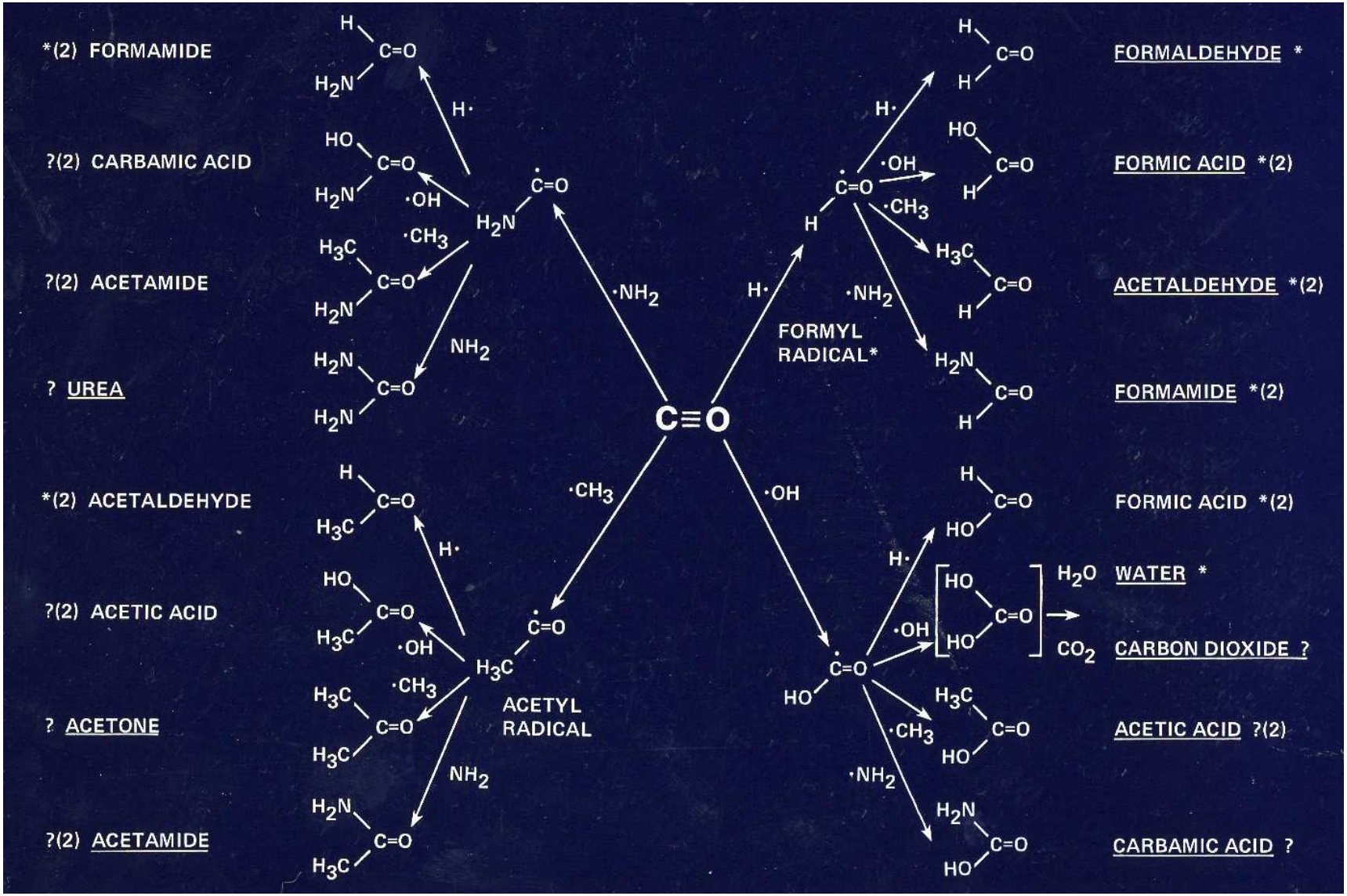
(ketones)



(amides)

Courtesy Max Bernstein

Combination of CO with the radicals •H, •OH, •CH_3 and •NH_2 yields a rich chemistry

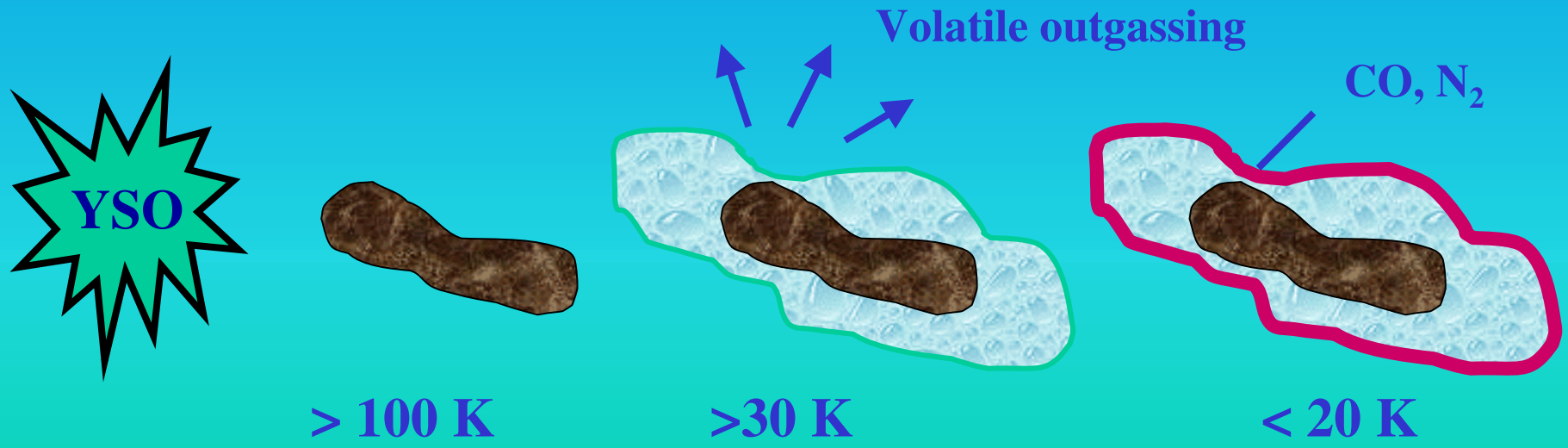


Evolution of dust grains in star-forming regions

Thermal effects → **segregation, crystallization**

Cosmic ray induced UV radiation ~ 10^3 photons/cm^2/s

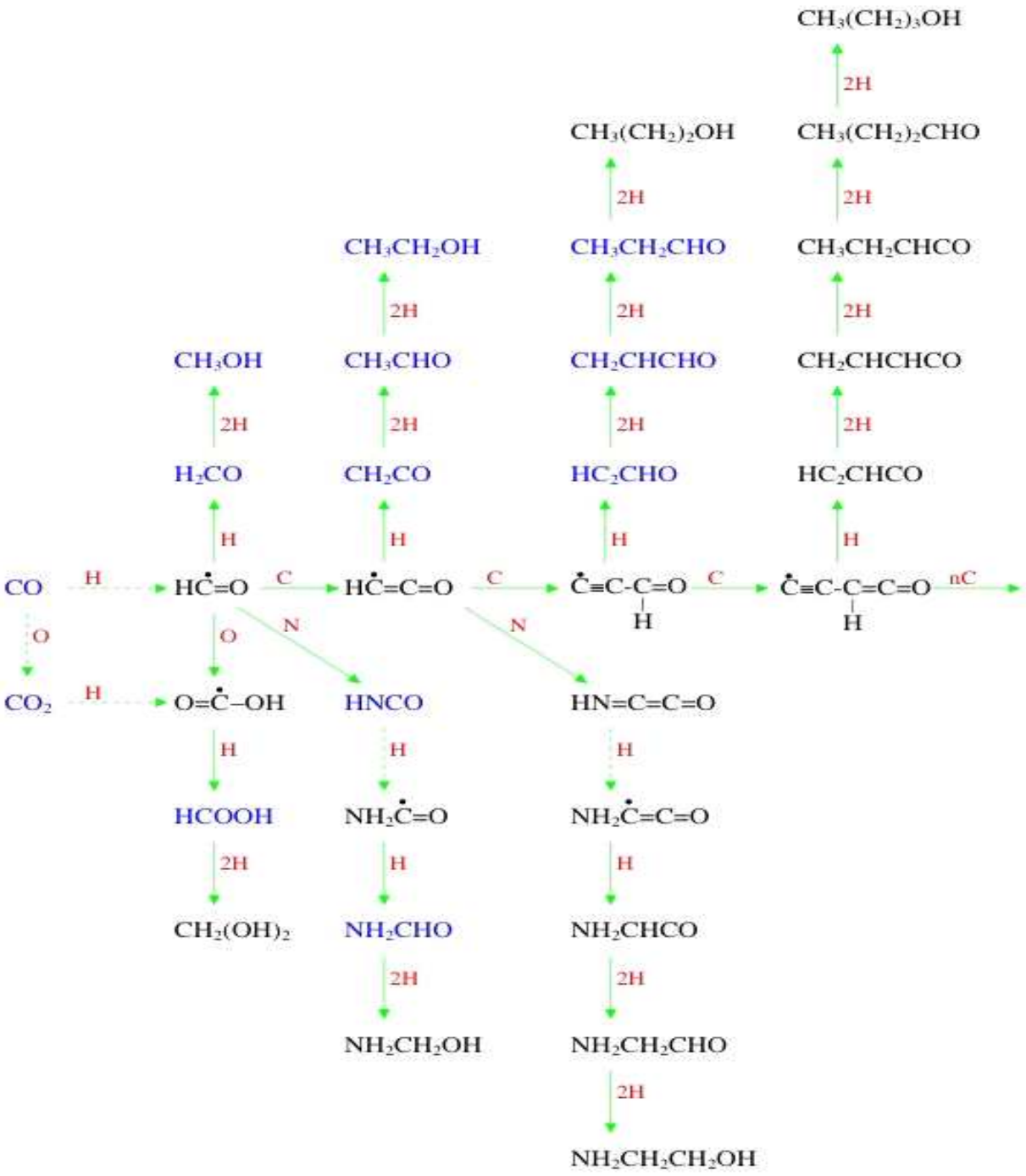
Mantle evaporation of CO_2, H_2O and trace organic species



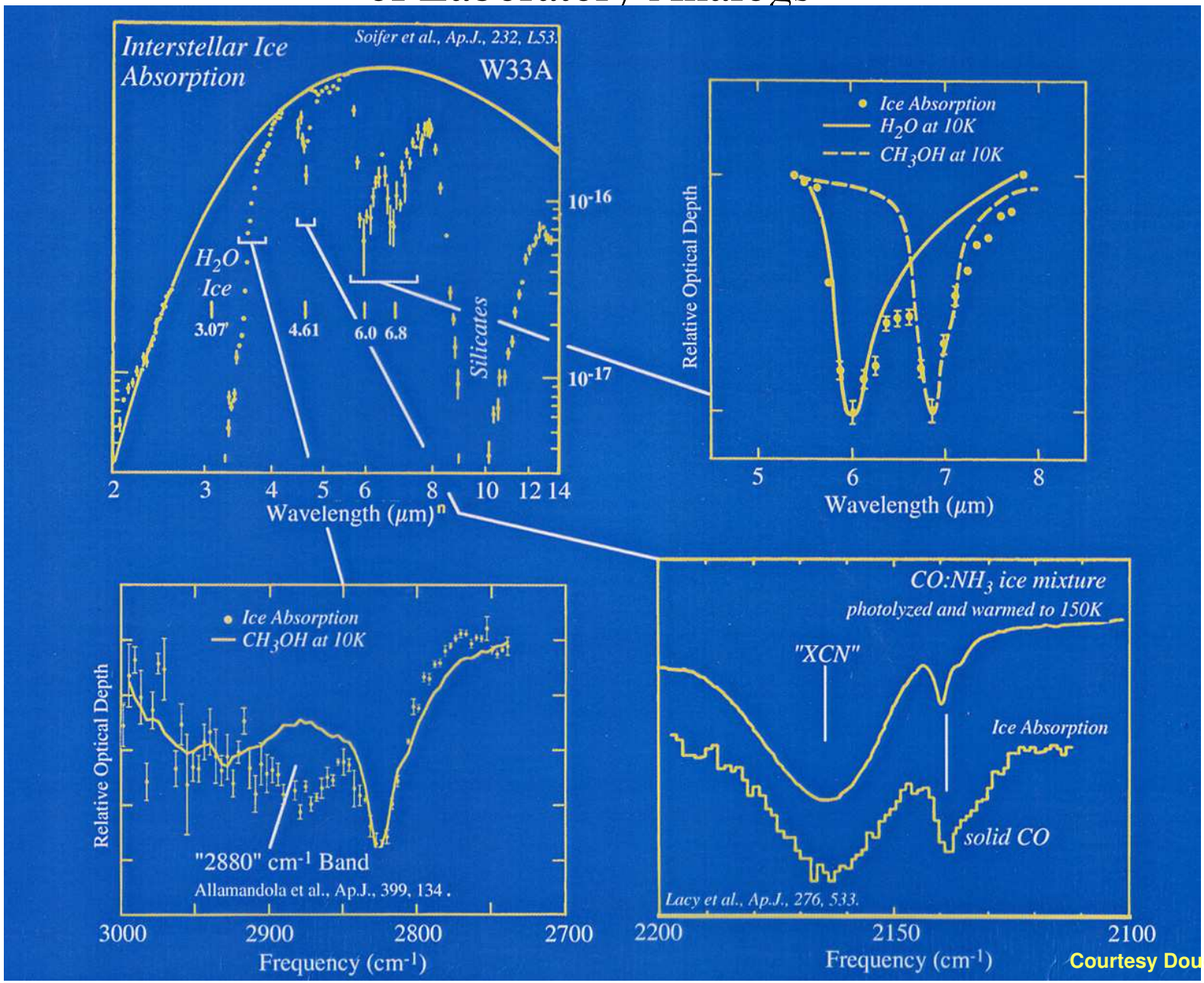
Summary

1. Main chemical pathways in gas known for simple species
2. Deterministic modelling OK for gas but surface reactions need stochastic treatment
3. Solid state lab. experiments at an advanced stage but difficult to distinguish between specific processes in the ISM
4. More obsvns. needed!

Tomorrow:


CH3(CH2)3OH
2H
CH3(CH2)2OH
CH3(CH2)2CHO
2H
2H
CH3CH2OH
CH3CH2CHO
CH3CH2CHCO
2H
2H
2H
CH3OH
CH3CHO
CH2CHCHO
CH2CHCHCO
2H
2H
2H
H2CO
CH2CO
HC2CHO
HC2CHCO
H
H
H
H
CO
H
HC=O
C
HC=C=O
C
C≡C-C=O
H
C
C≡C-C=C=O
H
nC
O
O
N
N
CO2
H
O=C–OH
HNCO
HN=C=C=O
H
H
H
HCOOH
NH2C=O
NH2C=C=O
2H
H
H
CH2(OH)2
NH2CHO
NH2CHCO
2H
2H
NH2CH2OH
NH2CH2CHO
2H
NH2CH2CH2OH

Interstellar Ice Infrared Absorption Features Compared with the Spectra of Laboratory Analogs



Courtesy Doug Hudgins

Basic chemistry in dense clouds