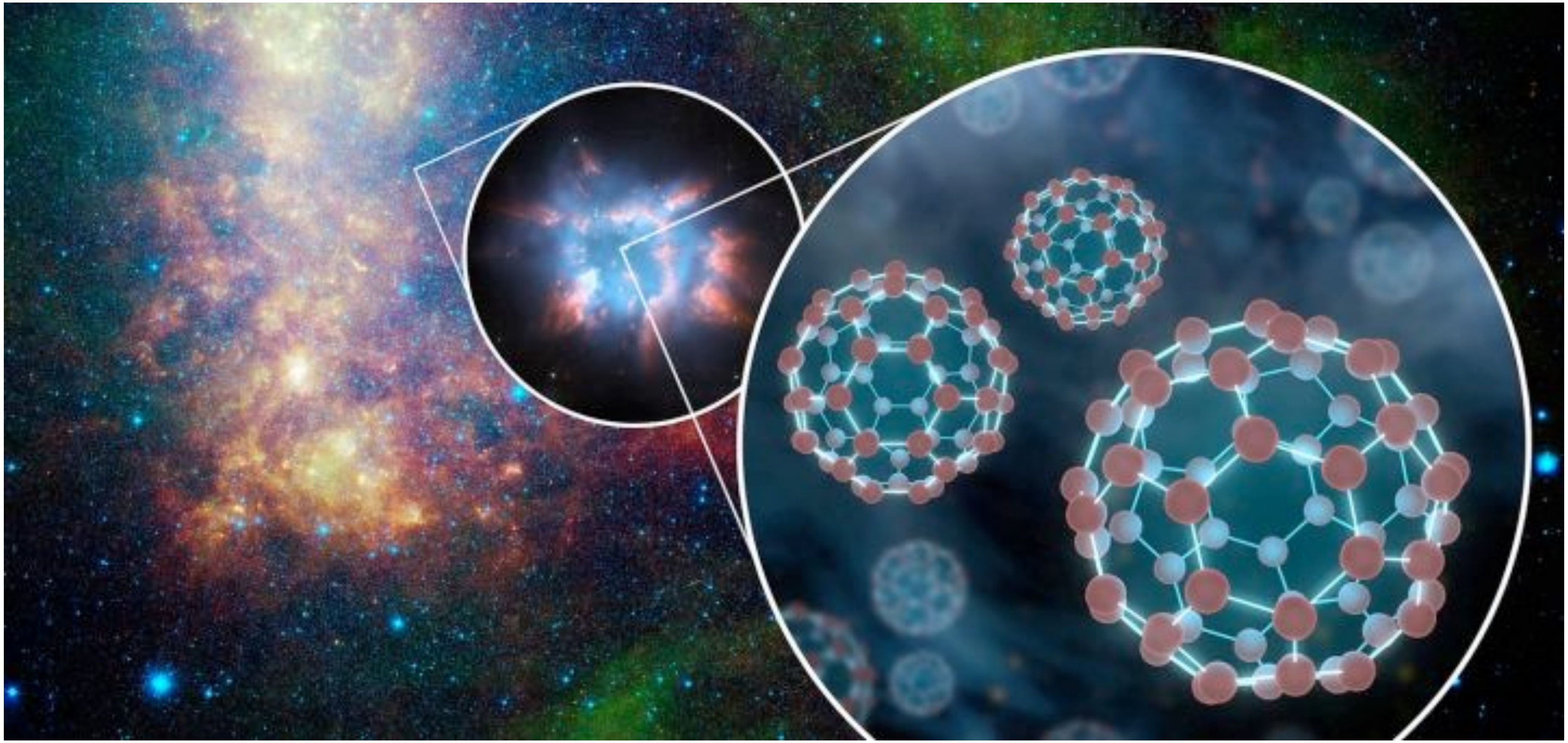
Chemistry of interstellar clouds

Floris van der Tak

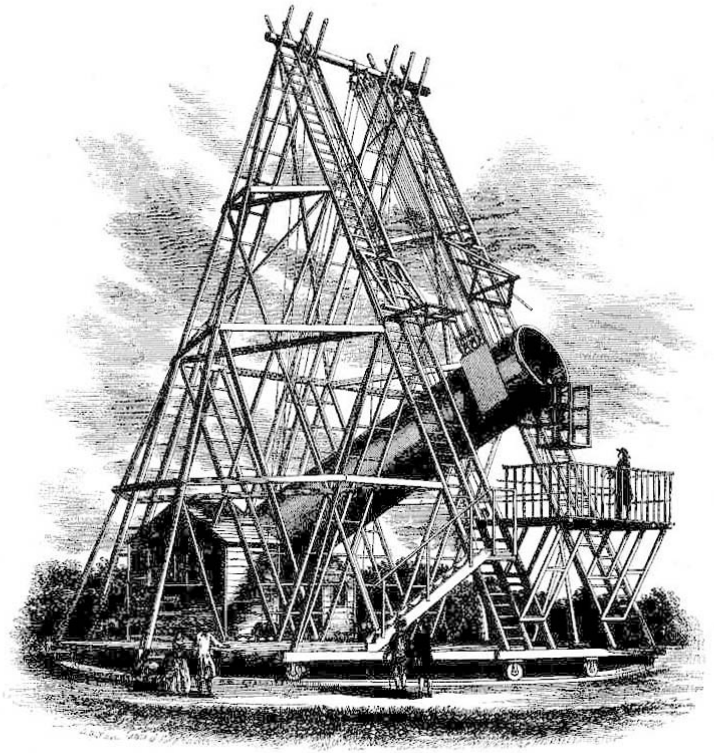


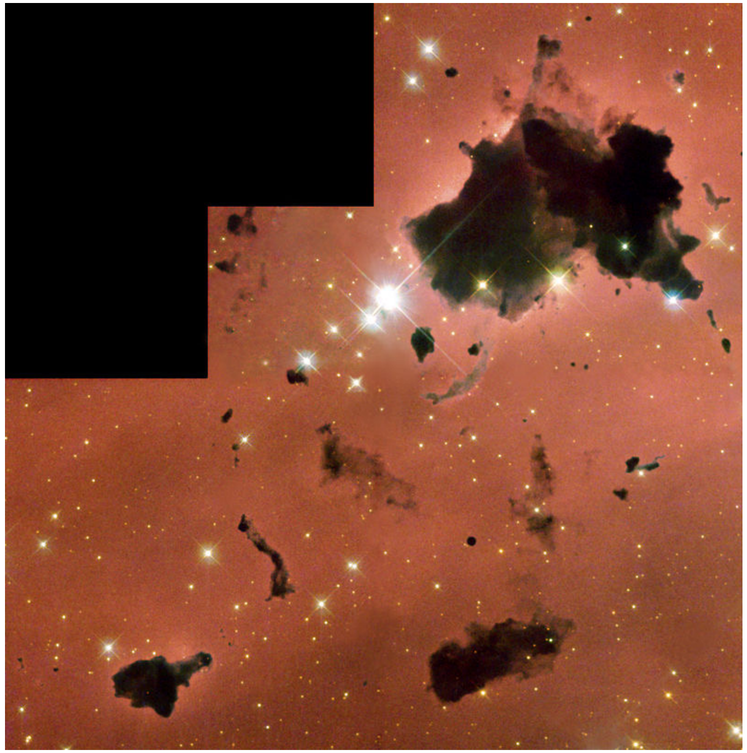
SRON
Netherlands Institute for Space Research

university of groningen

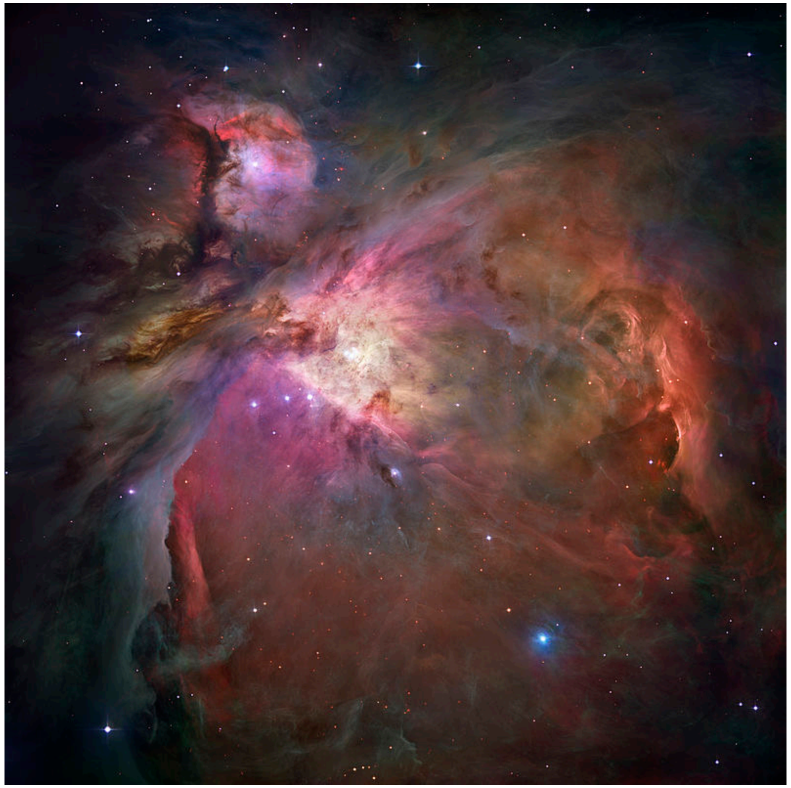
The sky: more than just stars

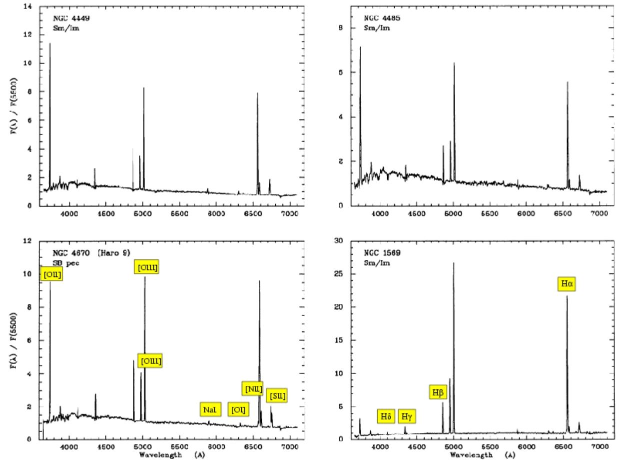
Telescopes: Holes in the sky

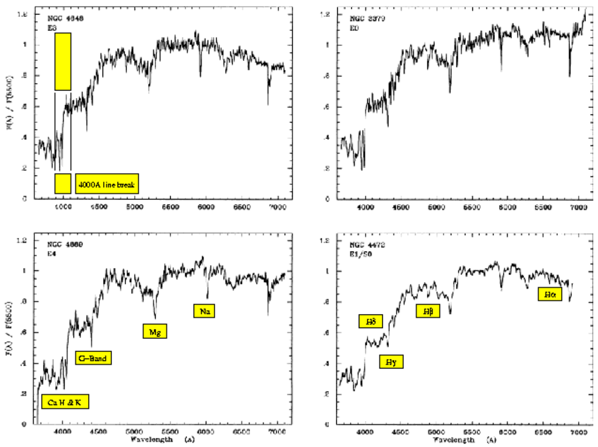


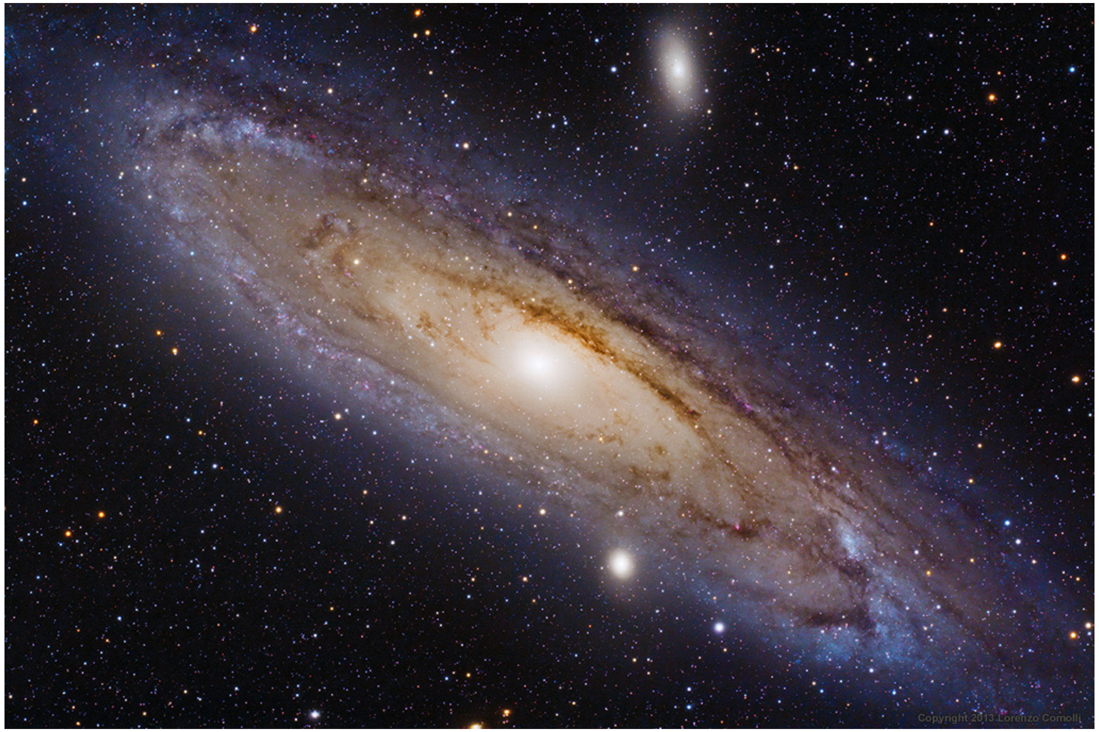


Spectroscopy: Two kinds of nebulae

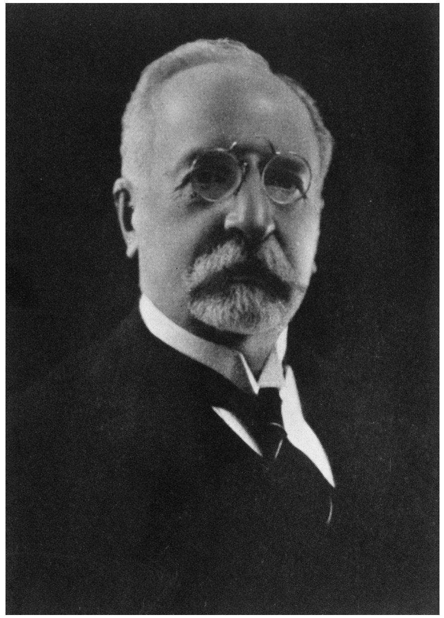








Interstellar gas clouds & molecules



Hartmann 1904: stationary Na absorption

in spectrum of 'spectroscopic binary'

Eddington 1926: thin ionized ISM, 10^4–10^6 K

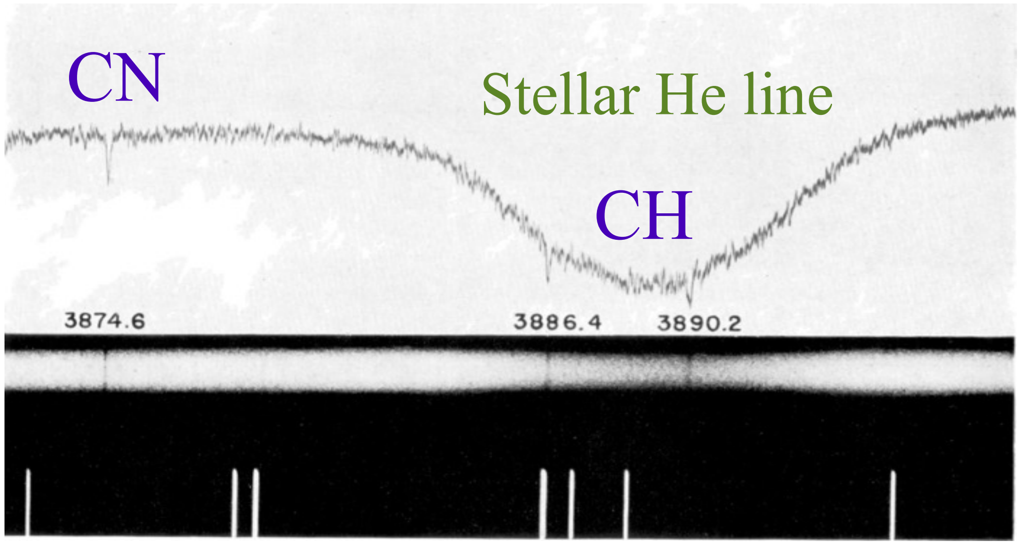
describes *intergalactic* medium

~1940: First gas-phase molecules

CH, CN, CH^+

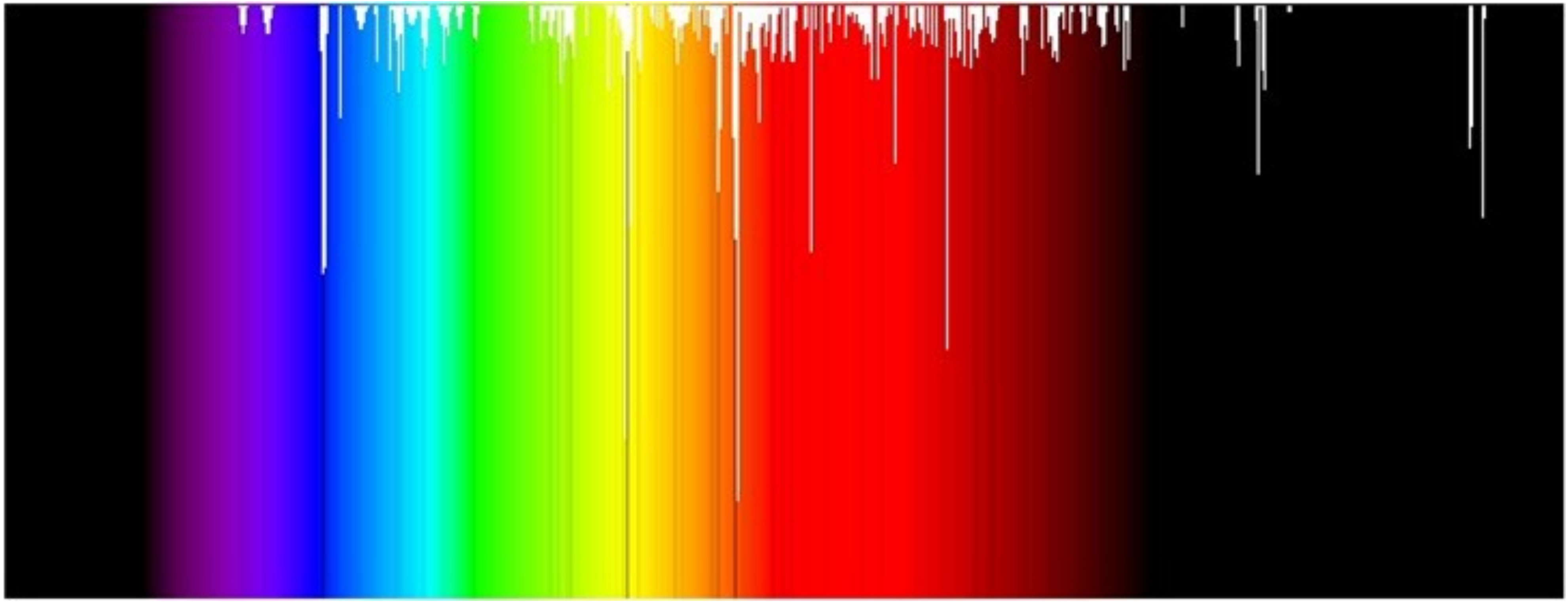
Known from comets since ~1870

Puzzle: low excitation (T_{ex} = 3 K)



Spectrum of ζ Oph (1941)

The ‘diffuse’ interstellar bands: A puzzle for >100 years



Over 300 broad absorption features known from UV to near-IR

also in ‘Magellanic Clouds’ = Milky Way satellites

Remain mostly unidentified since 1922!

Must be exceptionally stable: survive harsh conditions

probably medium-large hydrocarbons (Linnartz +2010, Oka +2013)

Most plausible claim so far: C_{60}^{+} (Campbell / Maier 2015-2018, 5 features)

Beyond optical astronomy

- Radio astronomy (1950s-1960s)

  [H I] 21 cm: weak hyperfine transition

  massive cold interstellar gas clouds

  OH 18 cm: maser *emission*

  collisional pumping = high gas density

  NH_3, H_2O, H_2CO: polyatomics

  significant chemistry

- High energy astrophysics (1970s)

  UV spectra: H_2 as abundant as H

  shielding; importance grain surface chemistry

  X-ray spectra: atomic composition of dust

  elemental depletion in ISM wrt Sun

- Far-IR & submillimeter (1980s)

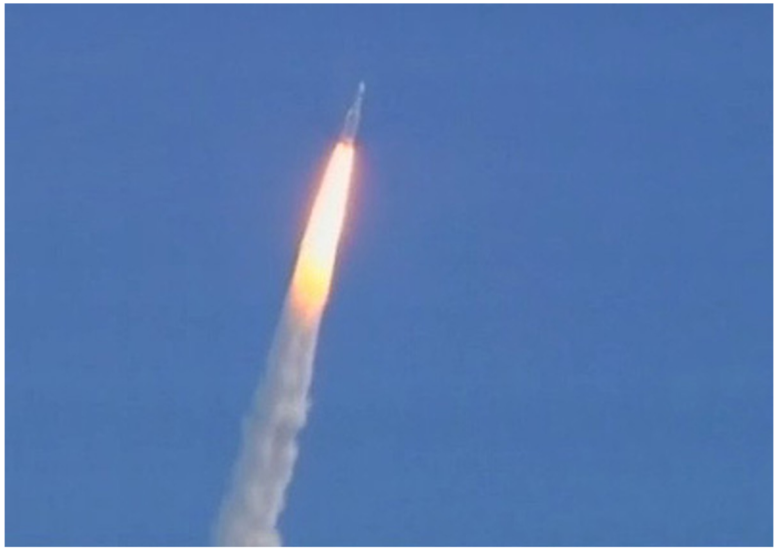
  CO: important to trace cold (=bulk) H_2

  hydride: large level spacing

  (lack of dipole moment is advantage!)

  X-ogen = HCO^+: space < lab

  prevalence ions, radicals, C-chains

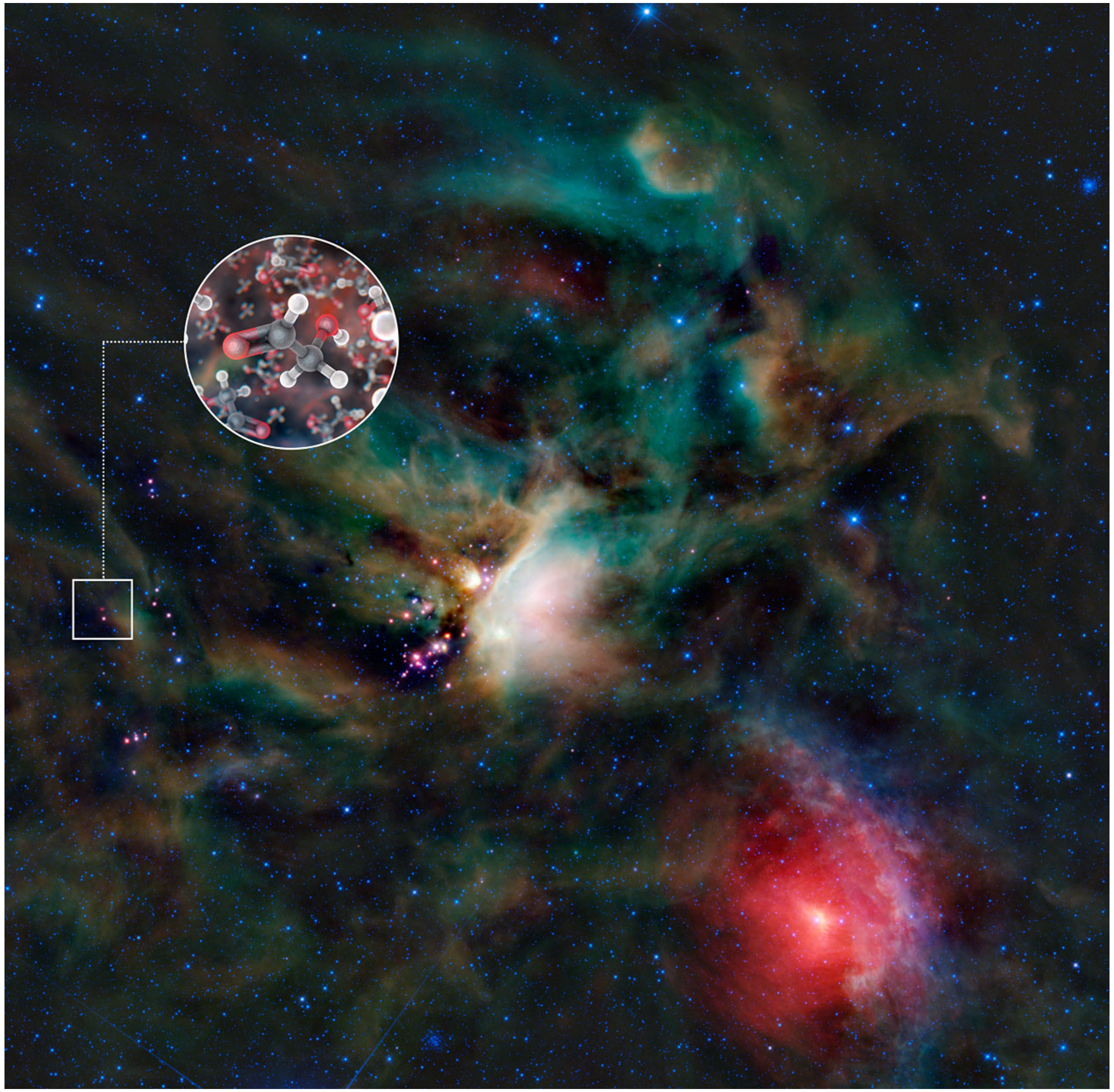


Today's workhorse #1: ALMA

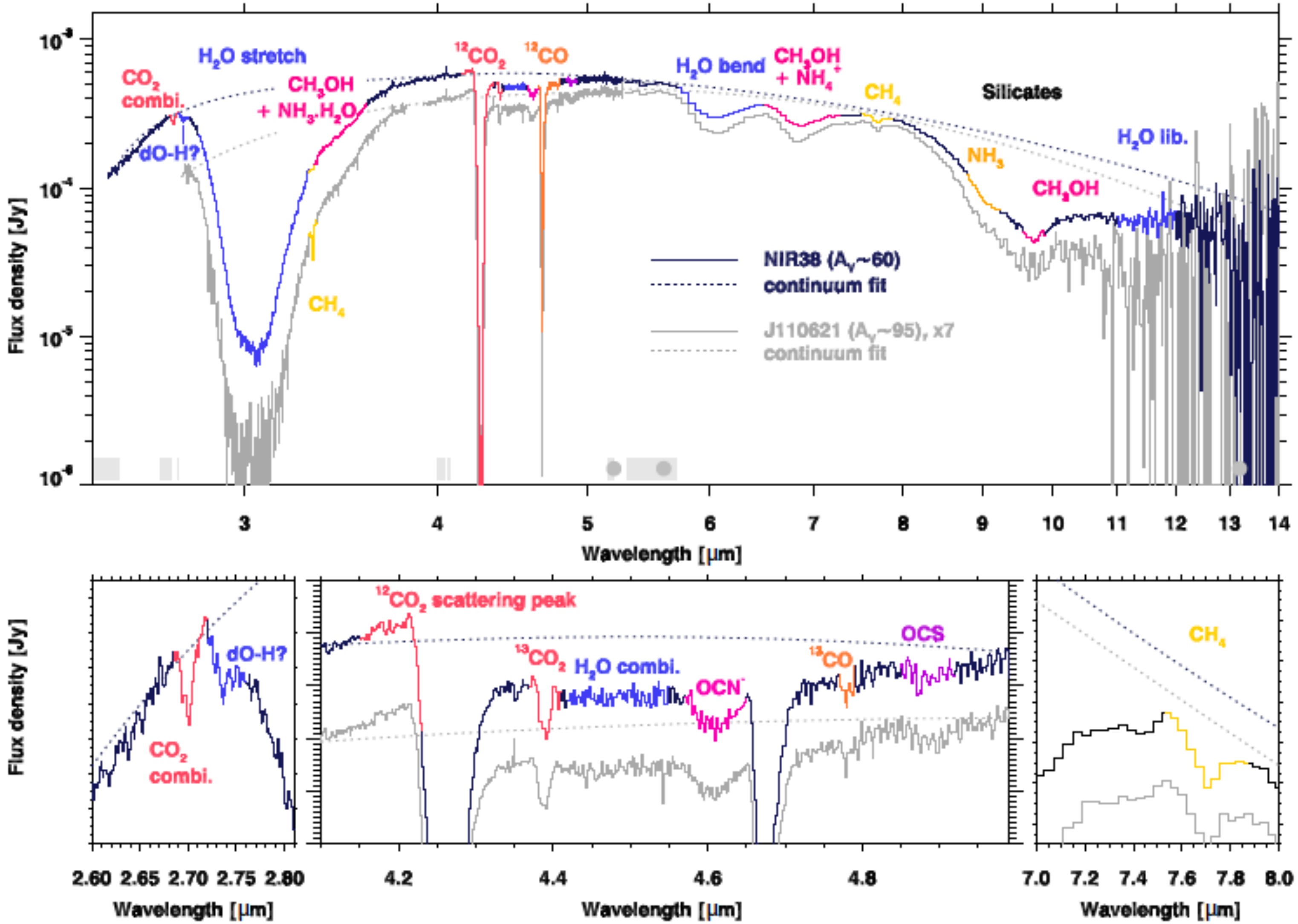
Glycoaldehyde around a young Solar-type star

Building blocks for life
exist in right time at right place
to be included in planets

Formation in 'heated' ice layer?



Today's workhorse #2: JWST



Ice mantles due to condensation of volatile species onto dust grains

visible as broad absorption features in mid-IR

JWST spectra of interstellar clouds: McClure +2023 Nature Astronomy

New molecular detections 2023/2024

FeC	KP 12m	IRC 10216	$(HO)_2CO$	Yebes	IRC 10216
HSO	Yebes	Dense cores	NC_4NH^+	Yebes	IRC 10216
HCNS	IRAM 30m	TMC-1	C_7N^-	Yebes	TMC-1, IRC 10216
NaC_3N	Yebes	IRC 10216	$C_{10}H^-$	GBT	TMC-1, IRC 10216
MgC_3N^+, MgC_5N^+	Yebes	IRC 10216	CH_3CHCO	Yebes	TMC-1
$HMgC_3N$	Yebes	IRC 10216	$HOCH_2C(O)NH_2$	IRAM 30m	G0.693
MgC_4H^+, MgC_6H^+	Yebes	IRC 10216	$H_2C(CH)_3CN$	GBT	TMC-1
$H_2C_3H^+$	Yebes	IRC 10216	$(CH_3)_2C{=}CH_2$	IRAM 30m	G0.693
H_2C_3N	Yebes	IRC 10216	$C_6CH_5C_2H$	Yebes	TMC-1

Some cations

Some anions

Glycine isomer

Census of inter- & circumstellar molecules: www.cdms.de

This lecture

- Motivation & context

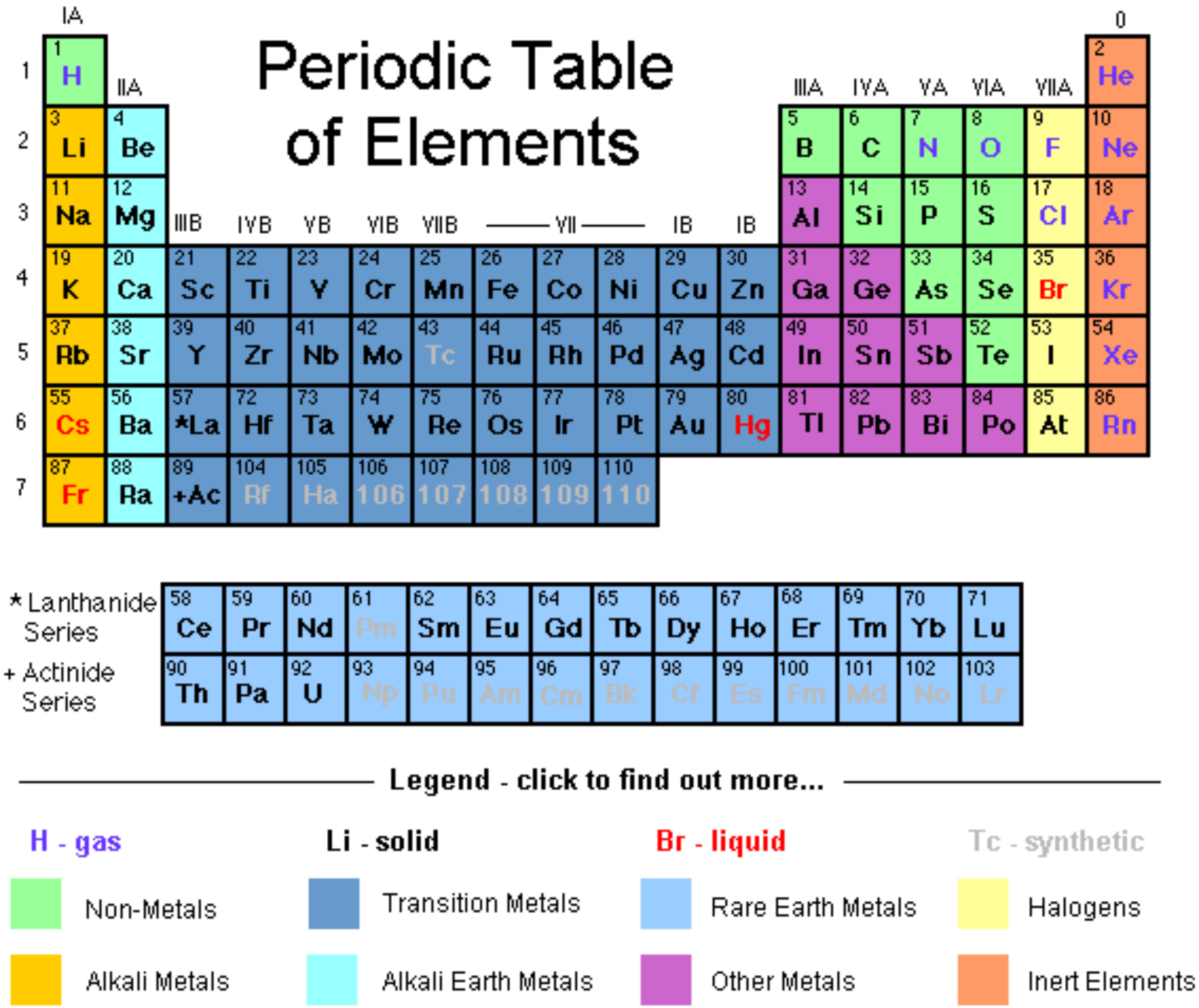
- **Physics of the interstellar medium**

  atoms
  radiation
  dust grains
  cosmic rays
  clouds

- Basic interstellar chemistry

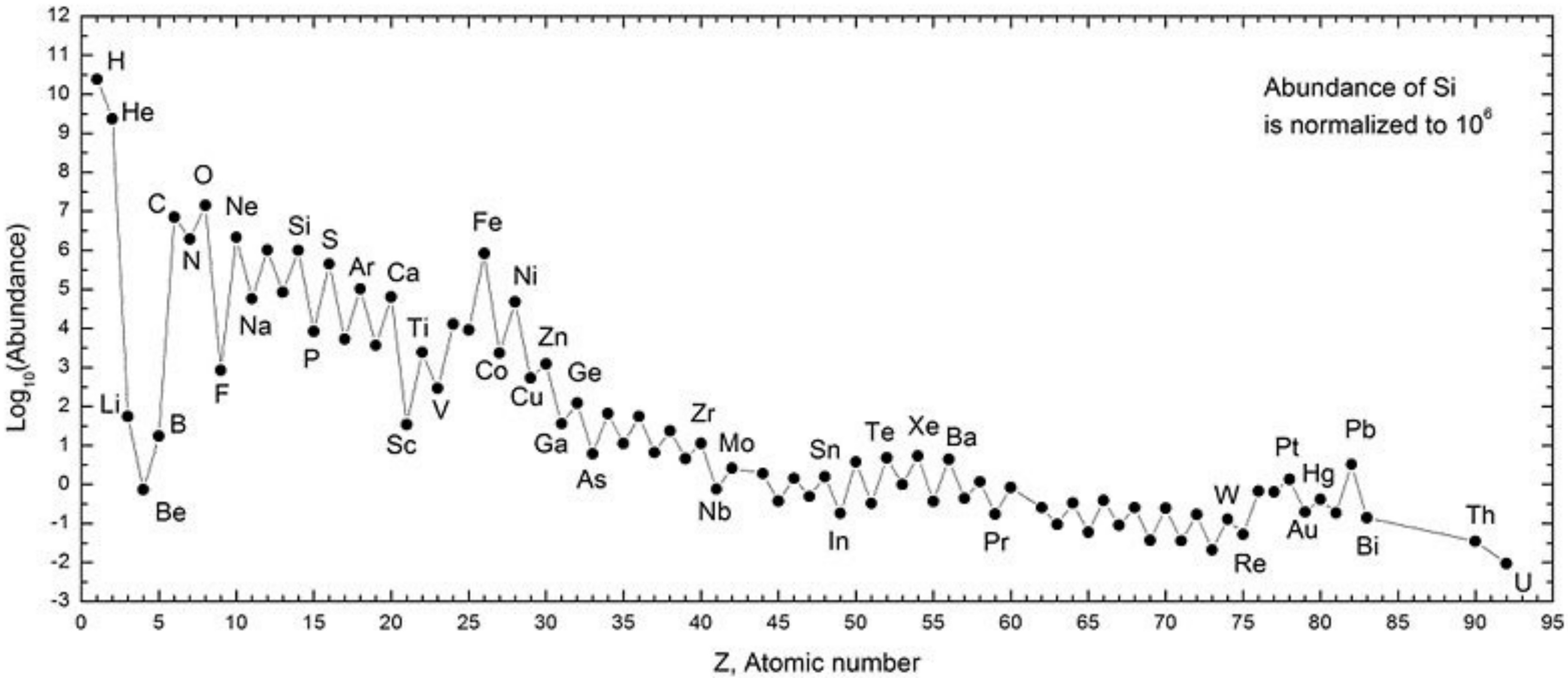
  gas-phase processes
  grain surface processes
  diffuse clouds
  dark / dense clouds

The building blocks of molecules



Useful to understand atomic structure & behaviour, but less representative for ISM

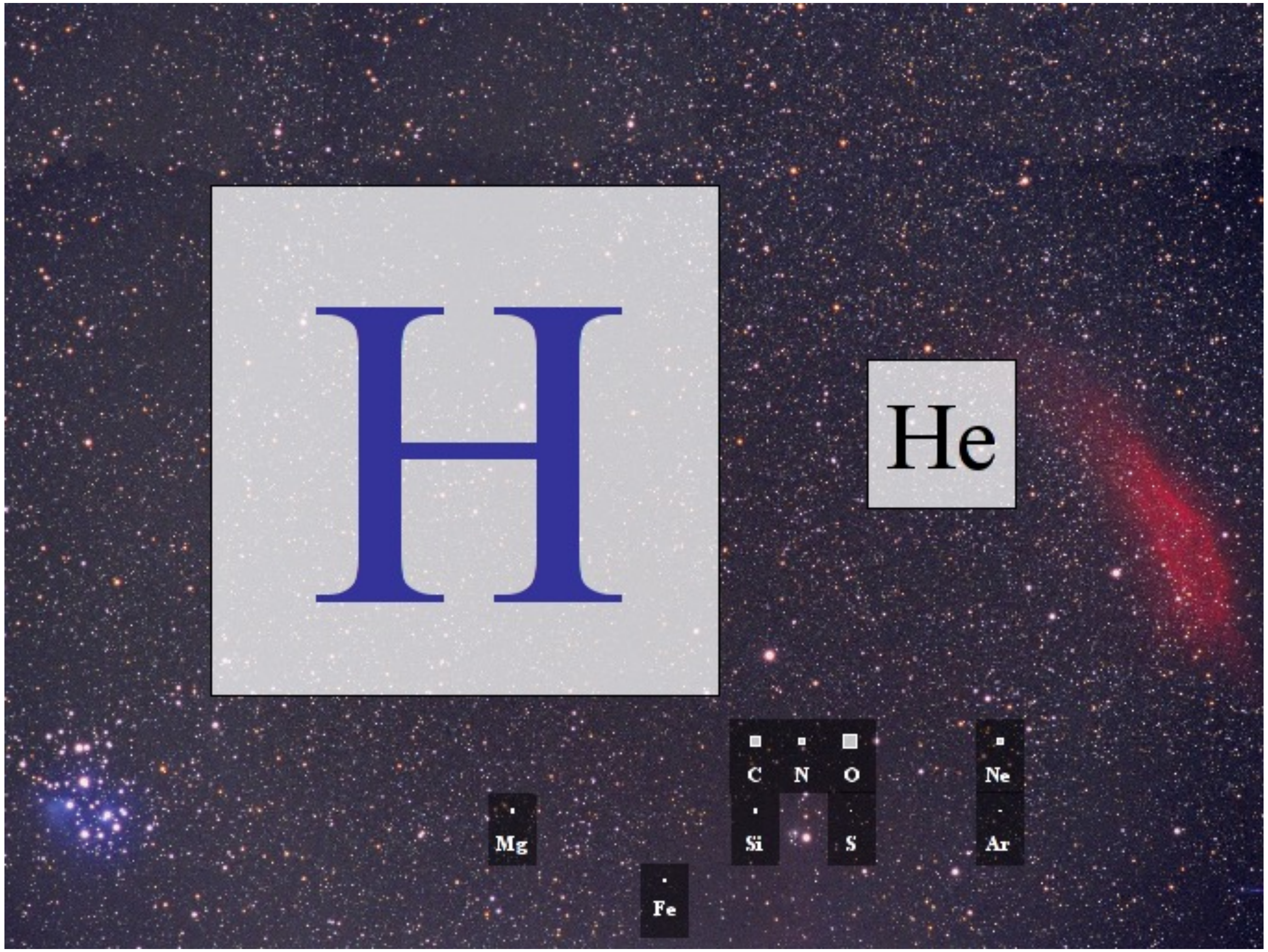
Cosmic abundances reflect young Universe



Combined effect of nuclear and stellar physics:

- primordial H, He production
- Li, Be, B destroyed in stars
- dominance of H/He/C burning: odd-even effect + α capture
- Fe peak: max binding energy
- beyond Fe: peaks around “magic” nuclei (closed neutron shell)

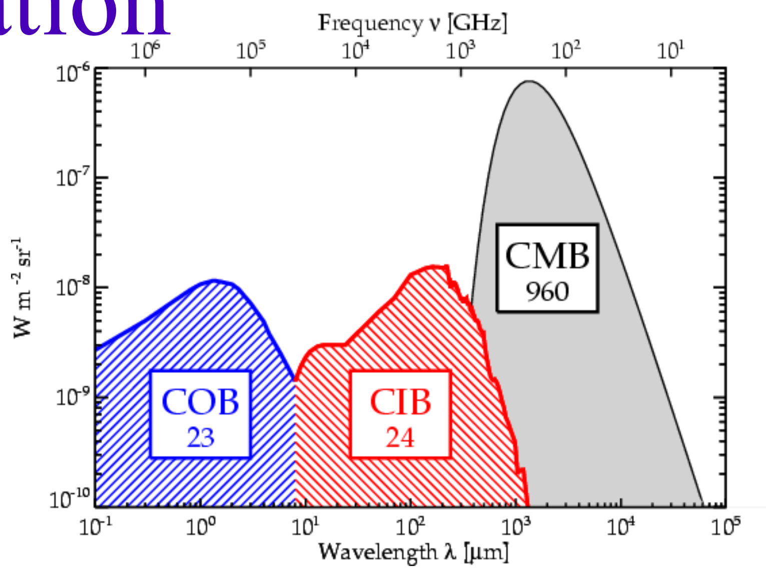
Astronomers' Periodic Table (Ben McCall)



He ~0.1; C, N, O ~ 10^{-4}; Mg, Fe, Si, S ~10^{-5}

Expect H-dominated chemistry, C+N+O sidekicks, Si+S bystanders

Interstellar radiation



Dole et al 2006

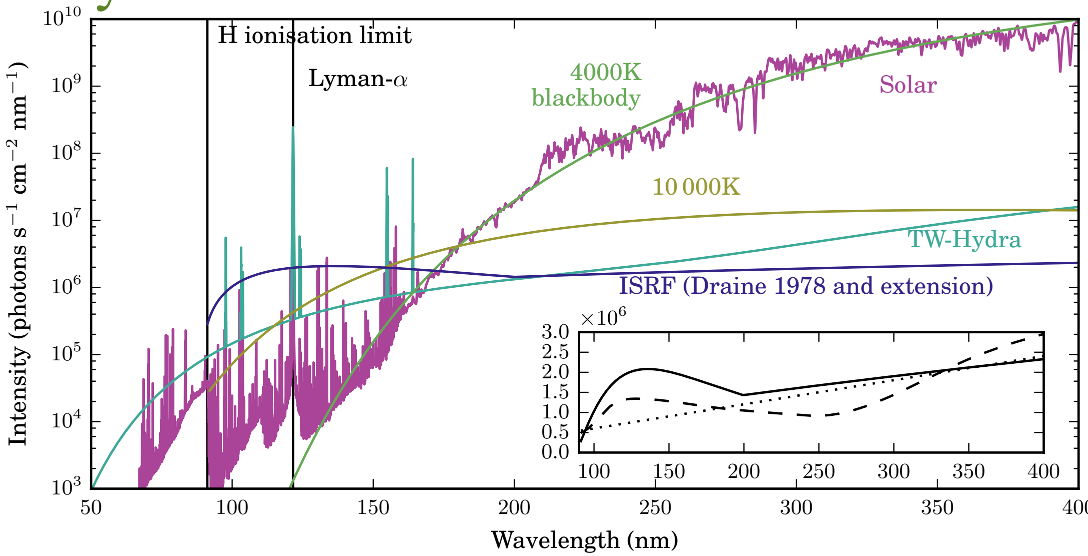
- Components: starlight, dust, and CMB
  μwave dominates by photons (early Universe)
  infrared: rotational / vibrational excitation
  vis/UV: ionization & dissociation

- UV: Habing (1968) & Draine (1978) estimates
  agree within ~2x ($\chi = 1.7\ G_0$)
  i.e. within variation (~3x) within Galactic plane on stellar (~Gyr) timescale

- Dominated by "B-type" stars (~10 M_0)
  hot: spectrum like 20,000 K blackbody
  rare: flux 1.6 10^{-3} erg cm^{-2} s^{-1}

- Deviates from blackbody shape
  cool stars: excess in optical
  atomic hydrogen: 912 Å cutoff

- Consequences for atomic states
  neutral if IP > 13.6 eV (He, O, N)
  otherwise ionized (C, Na, Si)



Heays et al 2017

Interstellar dust

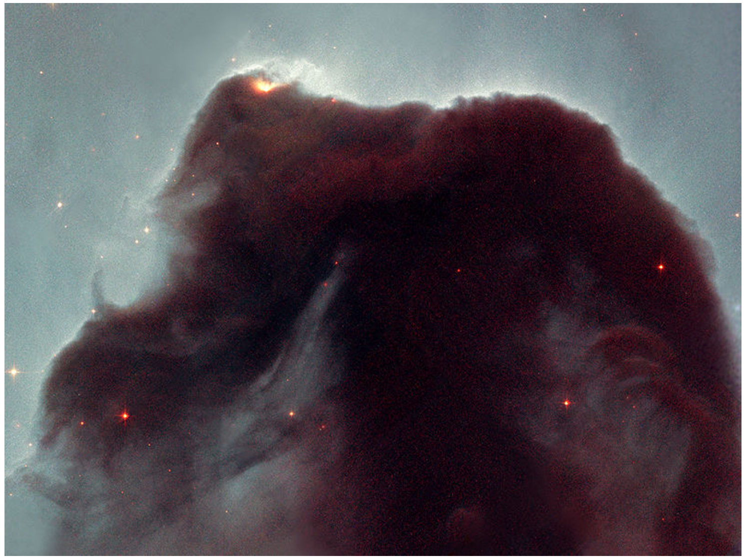
- Optical extinction, polarization, ‘reddening’: size, shape, composition
  infrared emission: temperature, mass, ..

- Solid particles
  silicate (“sand”) + carbonaceous (“soot”)
  in cold dense clouds: ice mantle

- Average size 0.1 μm
  range from 0.01 to 0.5 μm
  larger in protoplanetary disks

- Abundance 1% by mass, 10^{-12} by number
  silicate core contains most Si, Fe, Mg
  carbonaceous part ~60% of C, 30% of O

- Created in outflows from evolved stars
  destroyed in shock waves
  consumed in planet formation
  stellar explosions: both form & destroy



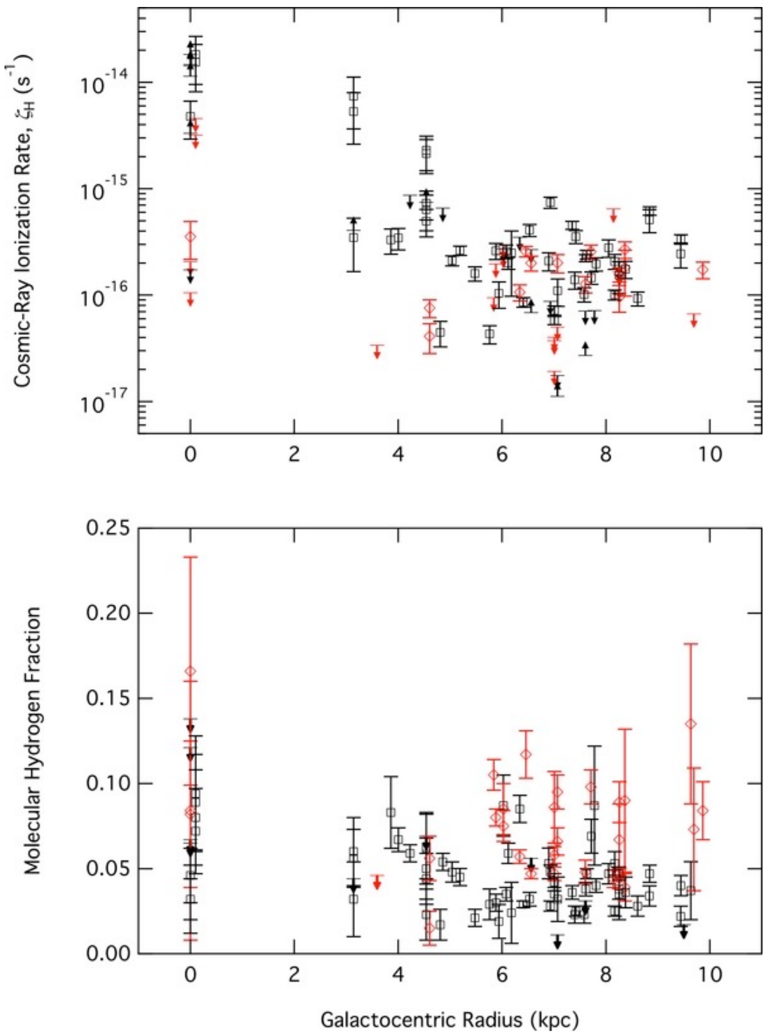
Cosmic rays

- Energetic (MeV – GeV) nuclei traversing the Galaxy
  accelerated in stellar explosions ("supernovae")
  deflected by magnetic fields

- Interact with molecular clouds
  ionization
  induced UV field

- Ionization rate 10^{-17} .. 10^{-16} s^{-1}
  lower in dense clouds
  higher near Galactic Center
  influence chemistry & dynamics

- Induced UV field ~1% of interstellar average
  photodissociation
  heating by photo-electrons
  photodesorption from dust grains



Indriolo et al 2015

Interstellar clouds: The birthplaces of stars & planets

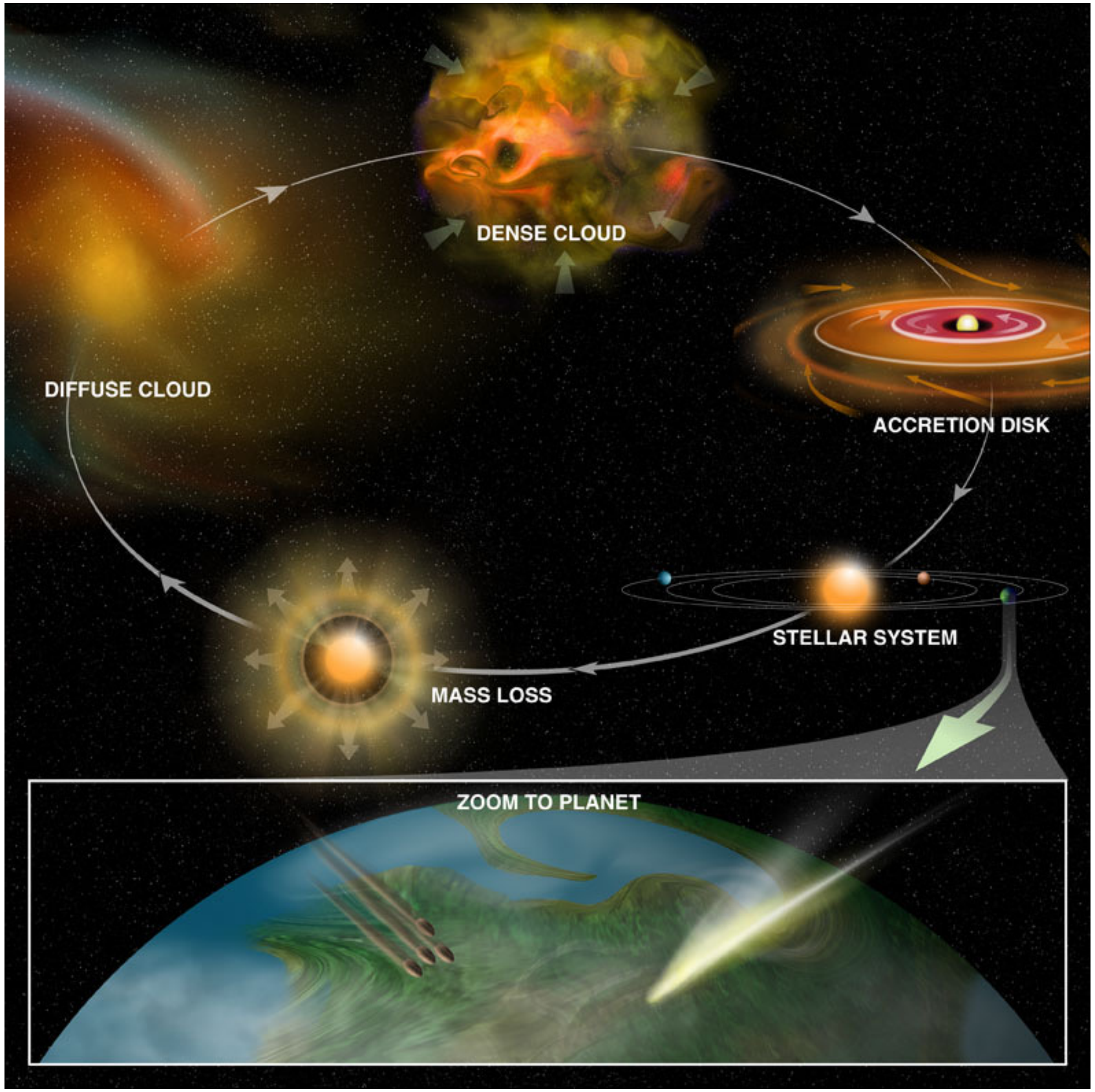
Molecules found so far:

>300 in ISM / CSM
(+20 since 2023)

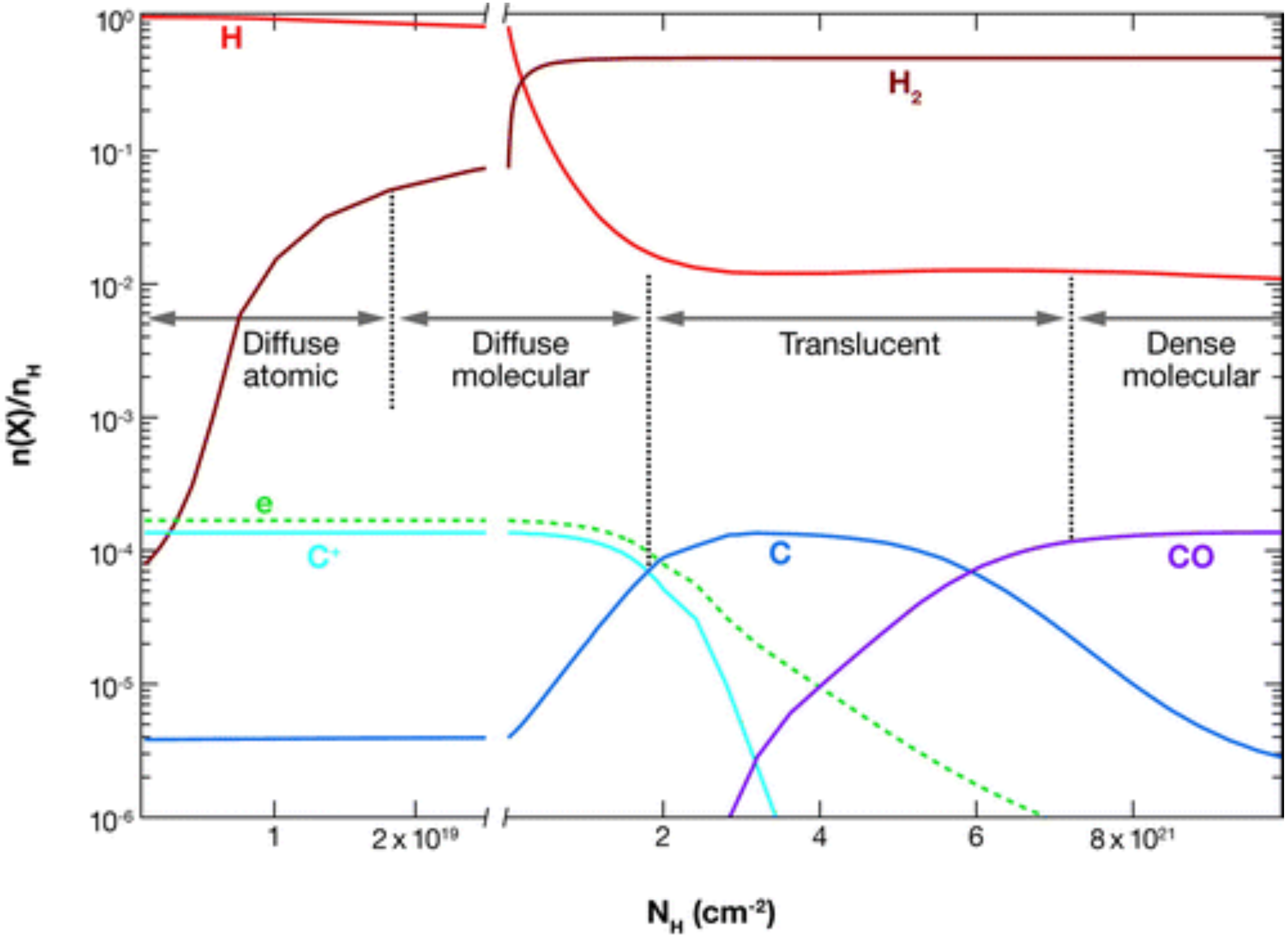
~73 extragalactic

~10 in early Universe

~16 in exoplanet atmospheres



Types of interstellar clouds



Snow TP, McCall BJ. 2006.
Annu. Rev. Astron. Astrophys. 44:367–414

Clouds named after dominant form of hydrogen:
ionized / atomic / molecular
Ionized clouds dominate ISM by volume,
molecular clouds by mass

This lecture

- Motivation & context
- Physics of the interstellar medium
  atoms
  radiation
  dust grains
  cosmic rays
  clouds
- **Basic interstellar chemistry**
  gas-phase processes
  grain surface processes
  diffuse clouds
  dark / dense clouds

Basic interstellar chemistry: Gas phase

- Low temperatures and densities
  chemistry far from thermodynamic equilibrium
  reactions with significant activation barriers inhibited

- Limited by kinetics; only two-body reactions
  3-body interactions enter at $n > 10^{12}$ cm^{-3} (e.g. inner disks)

- Hydrogen dominant element
  reactions with H & H_2 preferred if exoergic

- Time dependence often important
  other parameters: T, n, Z, radiation, ...

- Modern models: 1000s of reactions
  of just 9 different types

The 3x3 types of chemical reactions

Formation of bonds		
radiative association	$X + Y^+ \rightarrow XY^+ + h\nu$	Diffuse clouds
associative detachment	$X + Y^- \rightarrow XY + e$	Diffuse clouds
grain surface	$X + Y{:}g \rightarrow XY + g$	Dense clouds

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grain surface	$X + Y{:}g \rightarrow XY + g$	Dense clouds
Destruction of bonds		
photodissociation	$XY + h\nu \rightarrow X + Y$	Stellar vicinities
dissociative recombination	$XY^+ + e \rightarrow X + Y$	Diffuse clouds
collisional dissociation	$XY + M \rightarrow X + Y + M$	Shocks

The 3x3 types of chemical reactions

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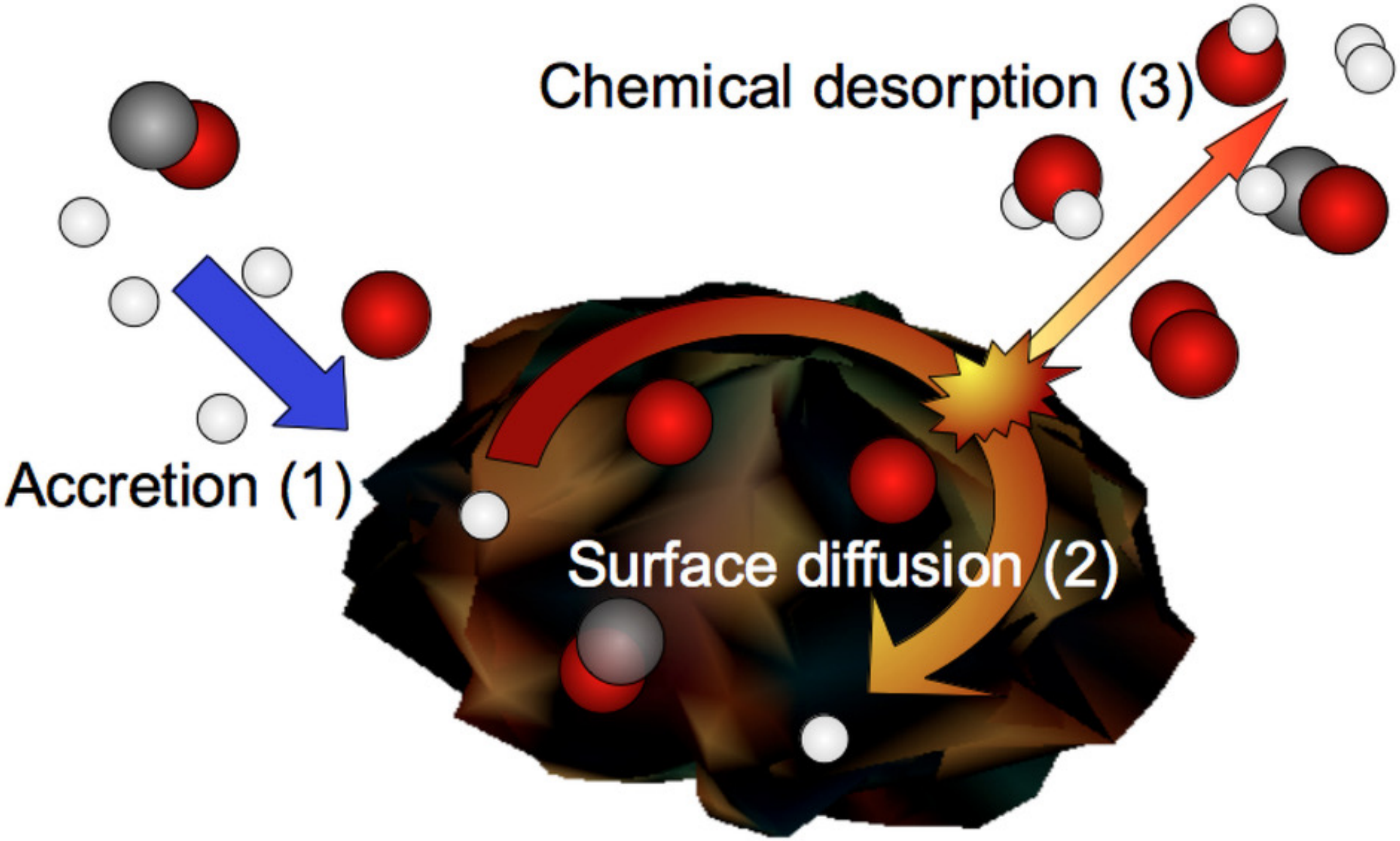
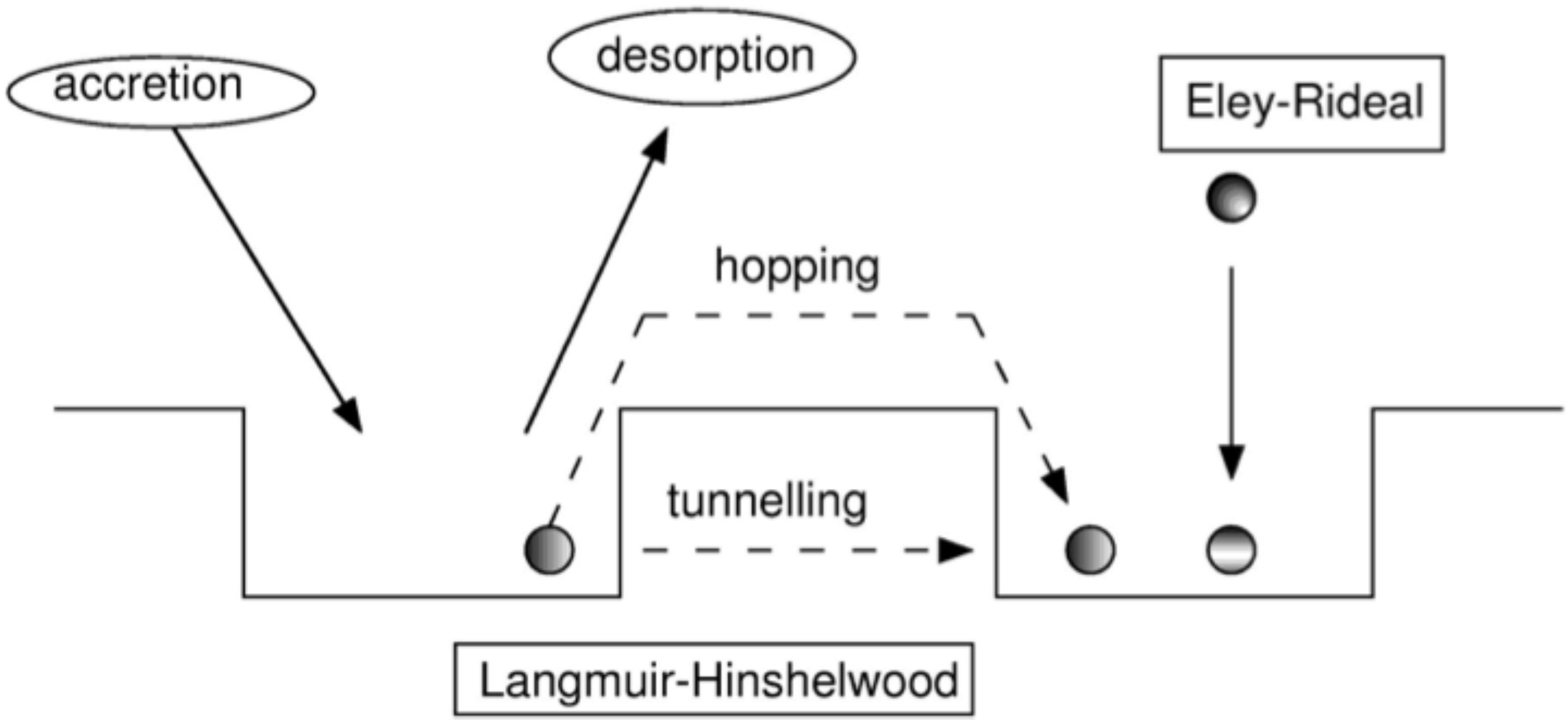
Rearrangement of bonds		
ion-molecule reaction	$X^+ + YZ \rightarrow XY^+ + Z$	Cold dense clouds
charge transfer reaction	$X^+ + YZ \rightarrow X + YZ^+$	Diffuse clouds
neutral-neutral reaction	$X + YZ \rightarrow XY + Z$	Warm dense clouds

Basic processes: Grain surface chemistry



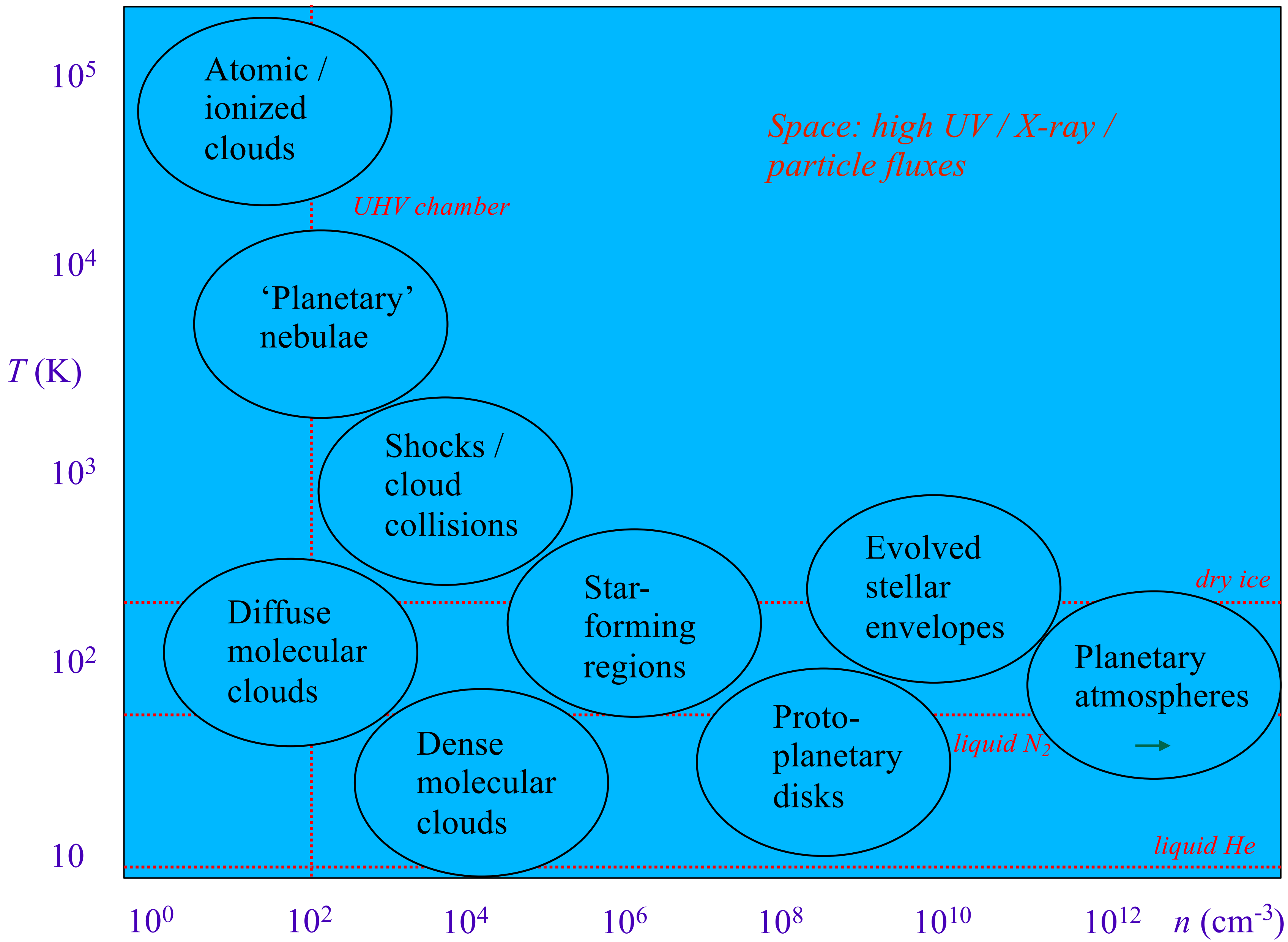
evidence: interstellar H_2, H_2O, CH_3OH; CO_2 ice, ...

Mechanisms of grain surface chemistry



LH route: sticking / diffusion / reaction / desorption
ER route: direct reaction + desorption
Grain surface can be silicate, carbonaceous, or ice
Reaction rates hard to measure (unlike gas phase)
Modern models include radical reactions within heated ice layer

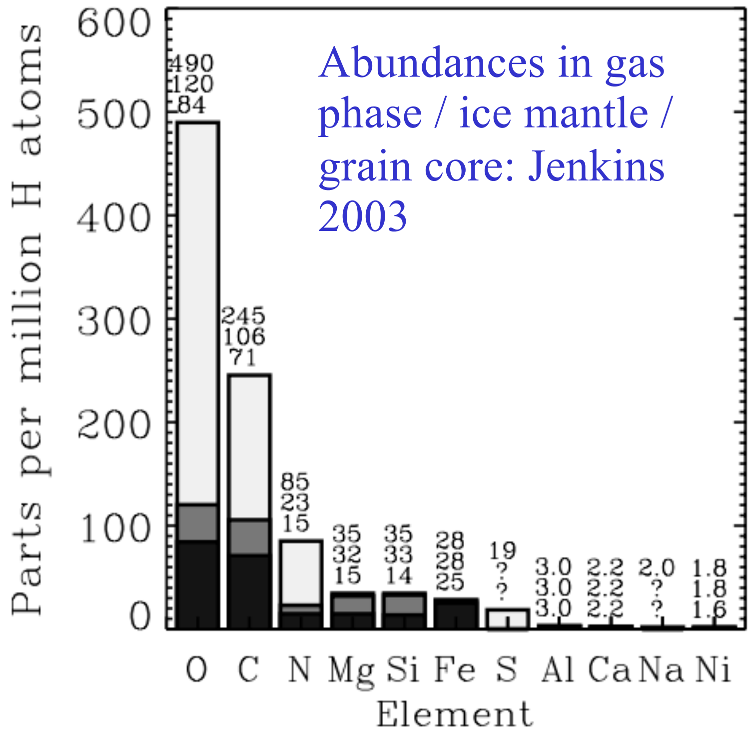
Interstellar space: Wide range of conditions



Observations of diffuse clouds

Conditions: $T = 100$ K, $n = 10^2 - 10^3$ cm^{-3}

atomic lines: depletion of C, N, O, ...
chemistry sensitive to C/O ratio



- Strong VIS/UV absorption lines
  - H_2, HD (ground / FUSE / HST)
  - CH, CH^+, C_2, C_3
  - OH, OH^+, CO
  - NH, CN, HCl
- Weak mm-wave emission lines
  - CO, HCO^+, CN, CS

... and absorption: CO, HCO^+, HCN, ... (Lucas & Liszt 1995–2014)

- Herschel & SOFIA: added hydrides (Gerin et al 2016)
  - H_2O, H_2O^+, H_3O^+, NH_2, NH_3, SH, SH^+, ArH^+, ...
- ALMA: added organics up to N=7
  - H_2CO, CH_3CN, c-C_3H_2, HC_3N

Chemical networks for diffuse clouds

Carbon chemistry starts from RA of C^+ with H_2 into CH_2^+ + hν

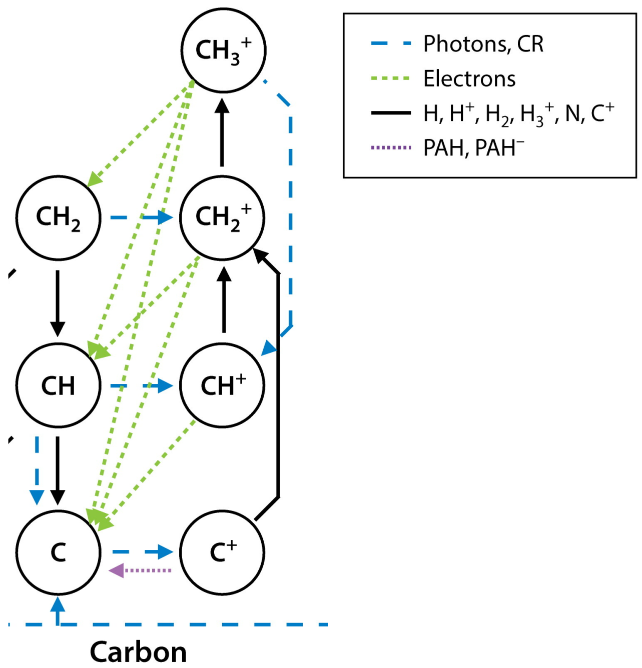
ion-molecule reactions: small (ionized) hydrides

Oxygen chemistry needs CR ionization of H_2 & charge transfer to O

mainly OH & H_2O; CO acts as sink

Nitrogen like oxygen; both connected to carbon via C^+ reaction

note absence direct N-O connection



Gerin M, et al. 2016.

Annu. Rev. Astron. Astrophys. 54:181–225

Example: CH

- Formation mostly by RA of C^+ and H_2
  destruction mostly by photodissociation

$$n(\mathrm{CH}) \propto \frac{n(\mathrm{C}^+)n(\mathrm{H}_2)k_{\mathrm{RA}}}{k_{\mathrm{pd}}}$$

- Rates known within factor of 2
  possible to fit observed column densities

- Most but not all CH forms by this scheme
  up to 50% forms by other processes

- Goal: model that reproduces *all* species
  with same set of conditions / parameters

Depth-dependent models

UV field is attenuated

photodissociation rate decreases with depth

realistic models must be depth-dependent

Most reactions are fast (except H_2 formation)

steady state = good assumption

$$\frac{dn_i(z)}{dt} = F_i - n_i D_i$$

=> density

$$n_i(z) = \frac{F_i}{D_i}\,\mathrm{cm}^{-3}$$

column density

$$N_i = \int n_i(z)dz\,\mathrm{cm}^{-2}$$

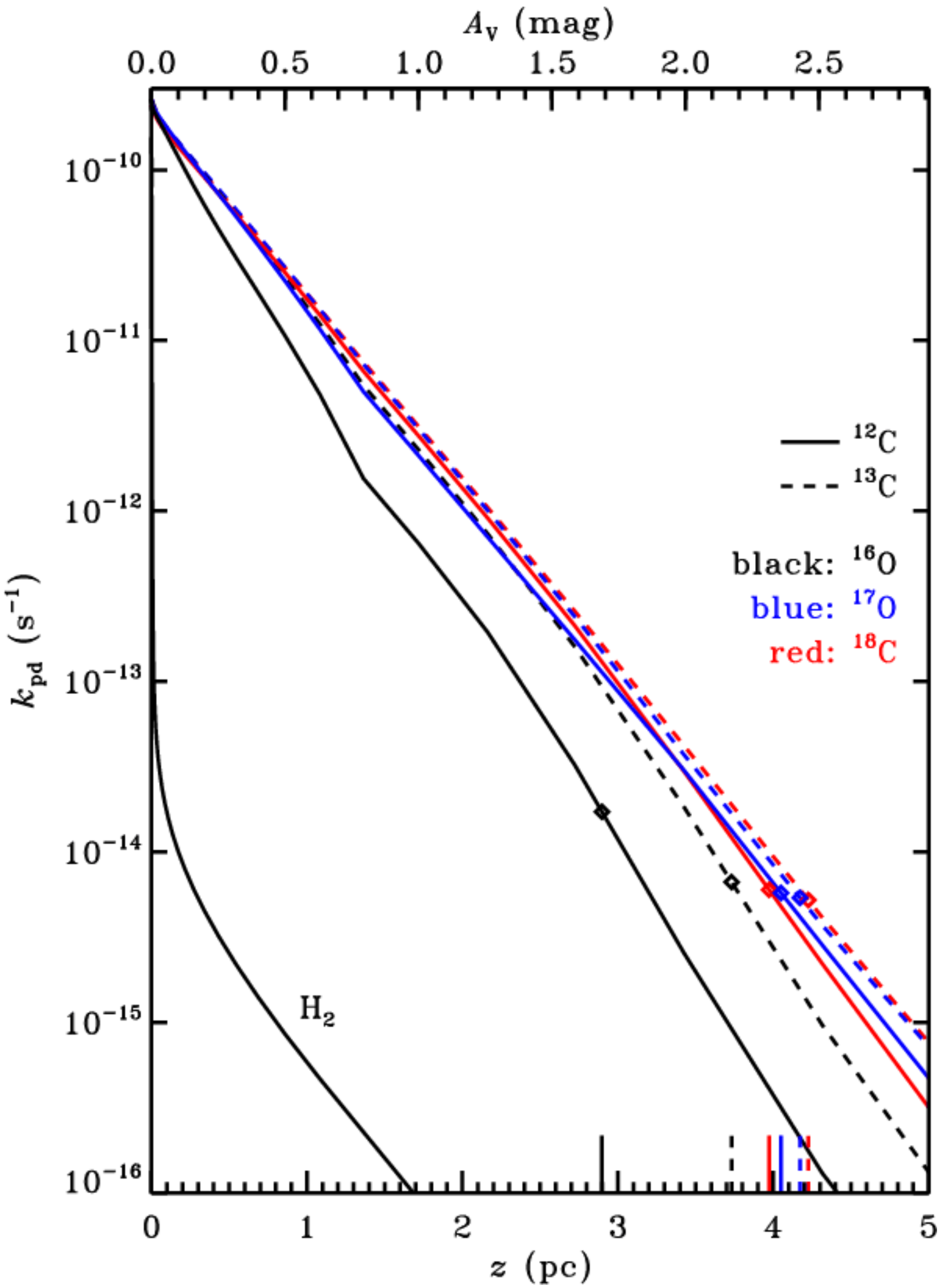
Q: Why do F_i & D_i have different dimensions?

Rate of CO photodissociation

Line by line calculation
+ CO-H_2 shielding
+ dust attenuation

Model parameters:
$n_H = 300$ cm^{-3}
$T_{kin} = 50$ K
χ = 1

Visser et al 2009



CO formation and destruction

Most abundant molecule after H_2

easily observed at radio frequencies

good tracer of cold (=most) H_2

Very stable molecule:

only dissociated by 912 – 1118 Å photons

$D_e = 11.09$ eV

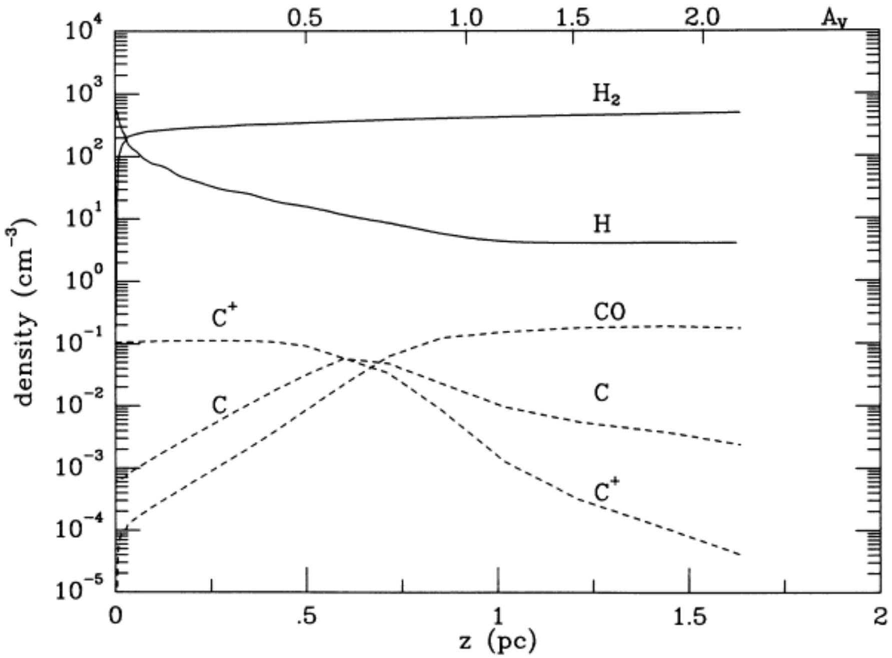
triple bond

Carbon chemistry:

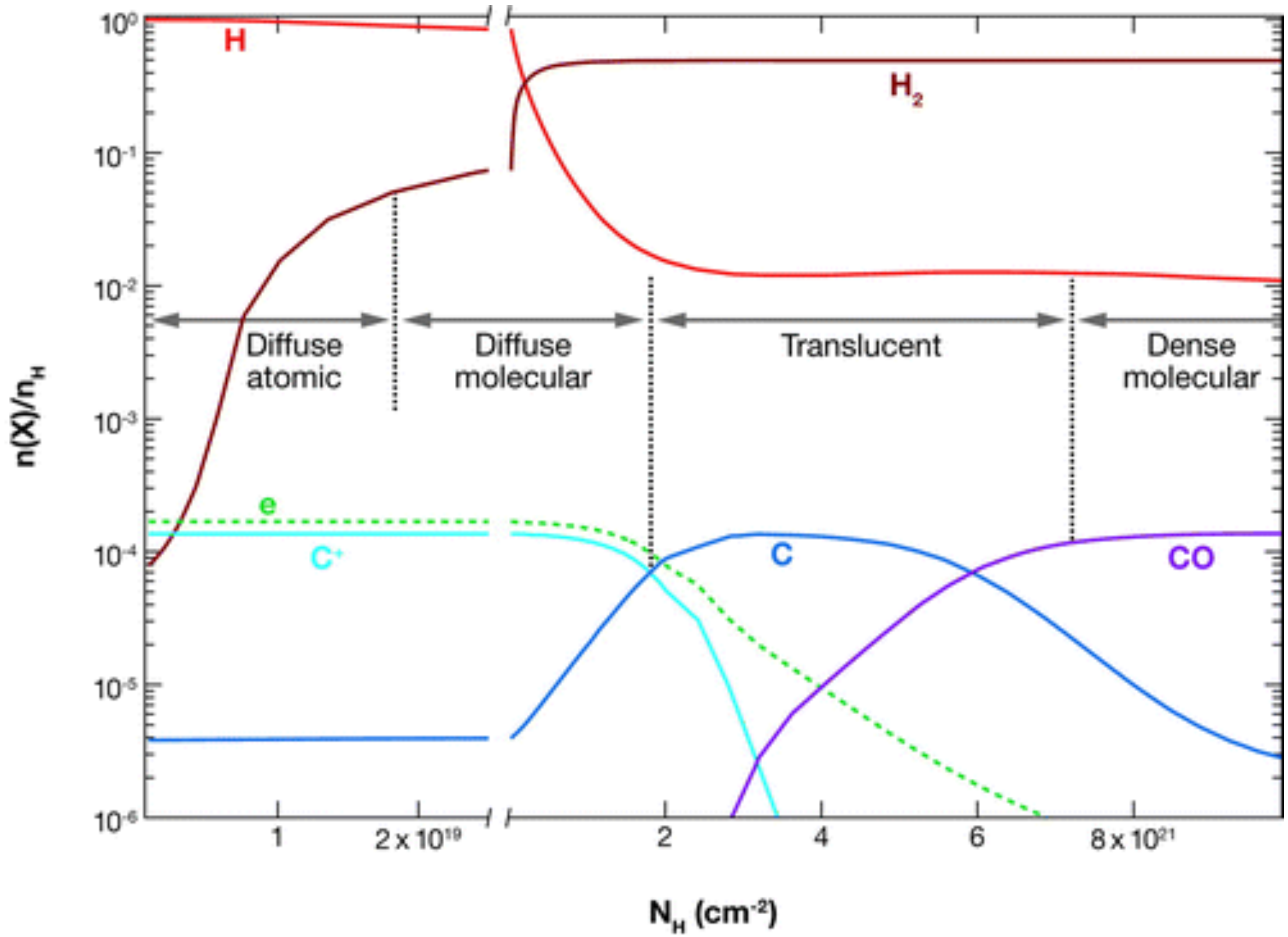
at cloud edge: mostly C^+

interior: mostly CO

interface layer: C



Types of interstellar clouds



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Diffuse cloud chemistry fairly well understood:
mainly small radicals & ions
Main outlier CH^+:
role of turbulent gas motions?

From diffuse to dense clouds

Photoprocesses less important
  just CR-induced UV field

Gas-grain interaction more important
  strong depletion of volatile elements

Long chemical timescales
  dependence on initial conditions

Dark clouds: mm-wave observations

Conditions: $T = 10$ K, $n = 10^4 - 10^5$ cm^{-3}

strong mm-wave low-J line emission

Prototype: TMC-1

found since 1980s: radicals, C-chains

since 2000s: anions, saturated chains

Abundance variations between cores

NH_3 cores: more evolved?

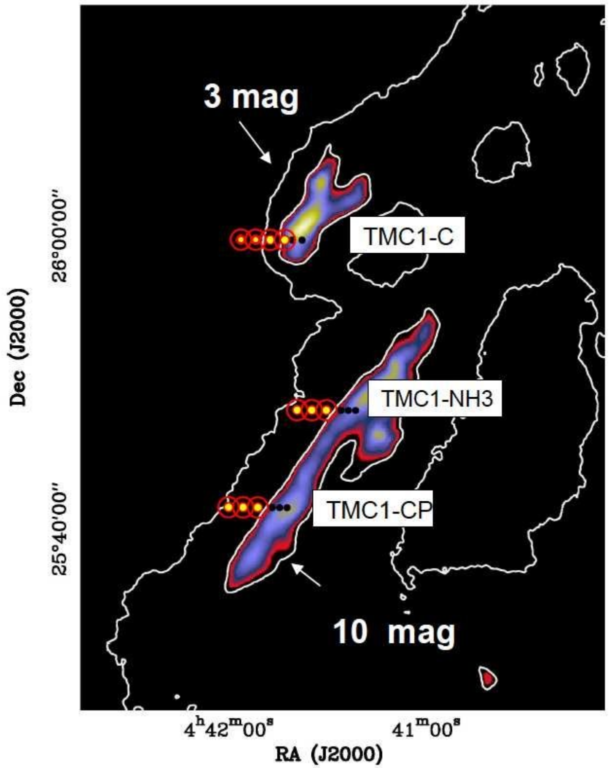
HC_xN cores: younger?

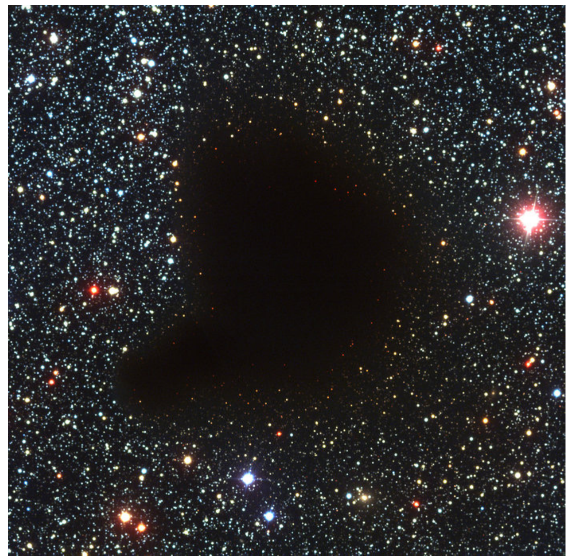
Recent focus: pre-stellar cores

prototypes: B68, L1544

centrally condensed, about to collapse

Review: Bergin & Tafalla 2007



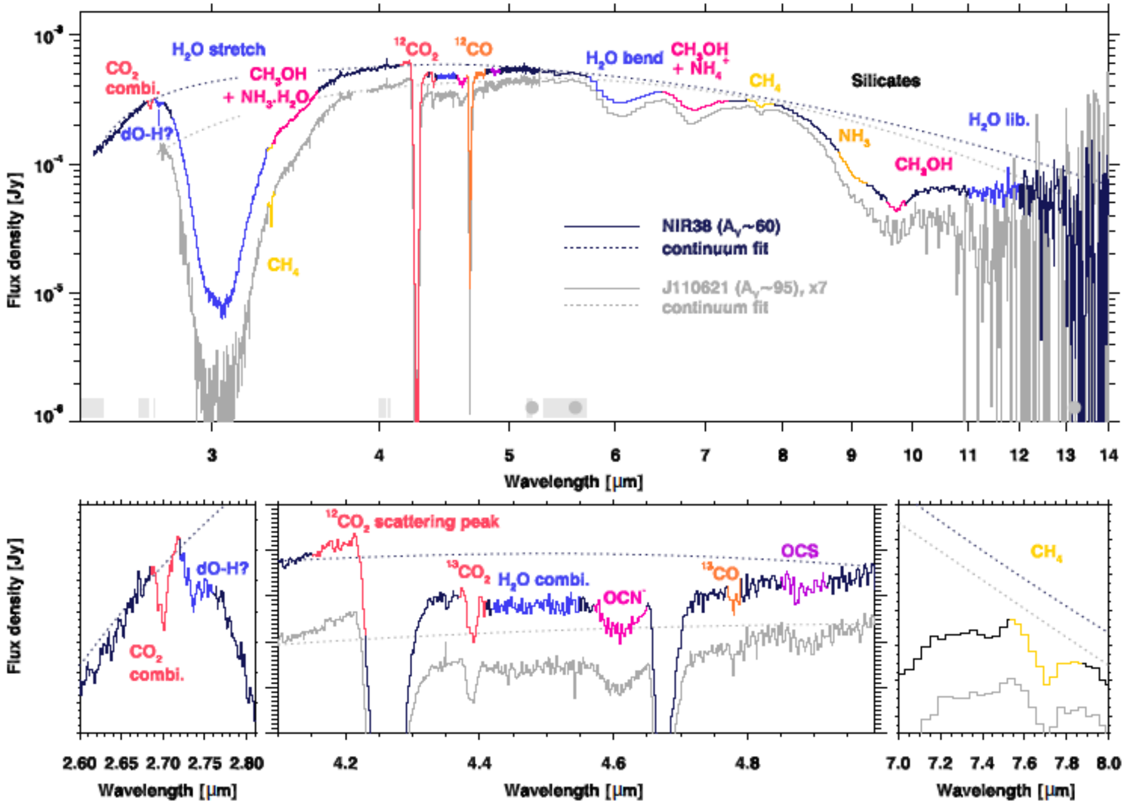


Mid-IR observations: Solid state

Probe clouds prior to star formation
    unaffected by heating and processing

See same features as toward protostars
    starlight does not change composition

Abundances similar to comets: Sign of inheritance
    Assignment NH_4^+ disputed, no good alternative



Ice species	Abundance
H_2O	1
CO	0.27 – 0.32
CO_2	0.19 – 0.35
CH_3OH	0.02 – 0.05
NH_3	0.05 – 0.10

IceAge program JWST: McClure +2023

Gas-phase models: Time dependence

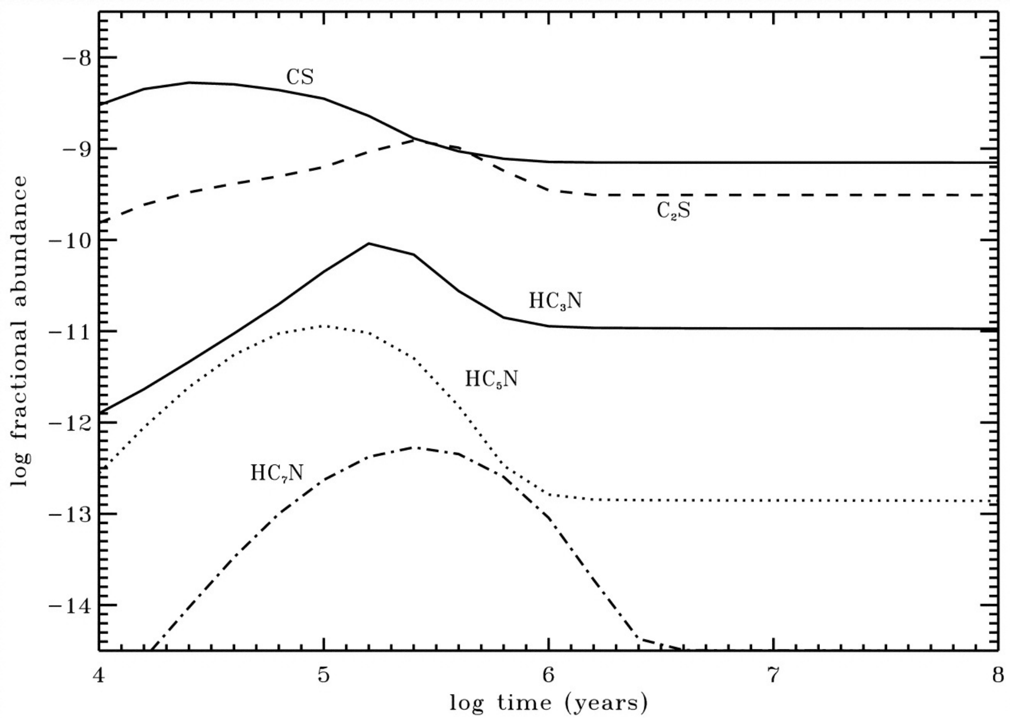
Most species need $10^5 - 10^6$ yr to reach equilibrium
- solve chemical network as function of time
- keep T & n constant (2×10^4 cm^{-3}, 10 K)

Initial conditions:
- usually H_2 molecular; C in C^+; He, N, O atomic
- represents diffuse clouds

Main result:
- conversion of $C^+ \rightarrow C \rightarrow CO$ in 10^6 yr

Consequence:
- early-time / steady-state species
- C-chains need C for formation

Markwick et al 2000

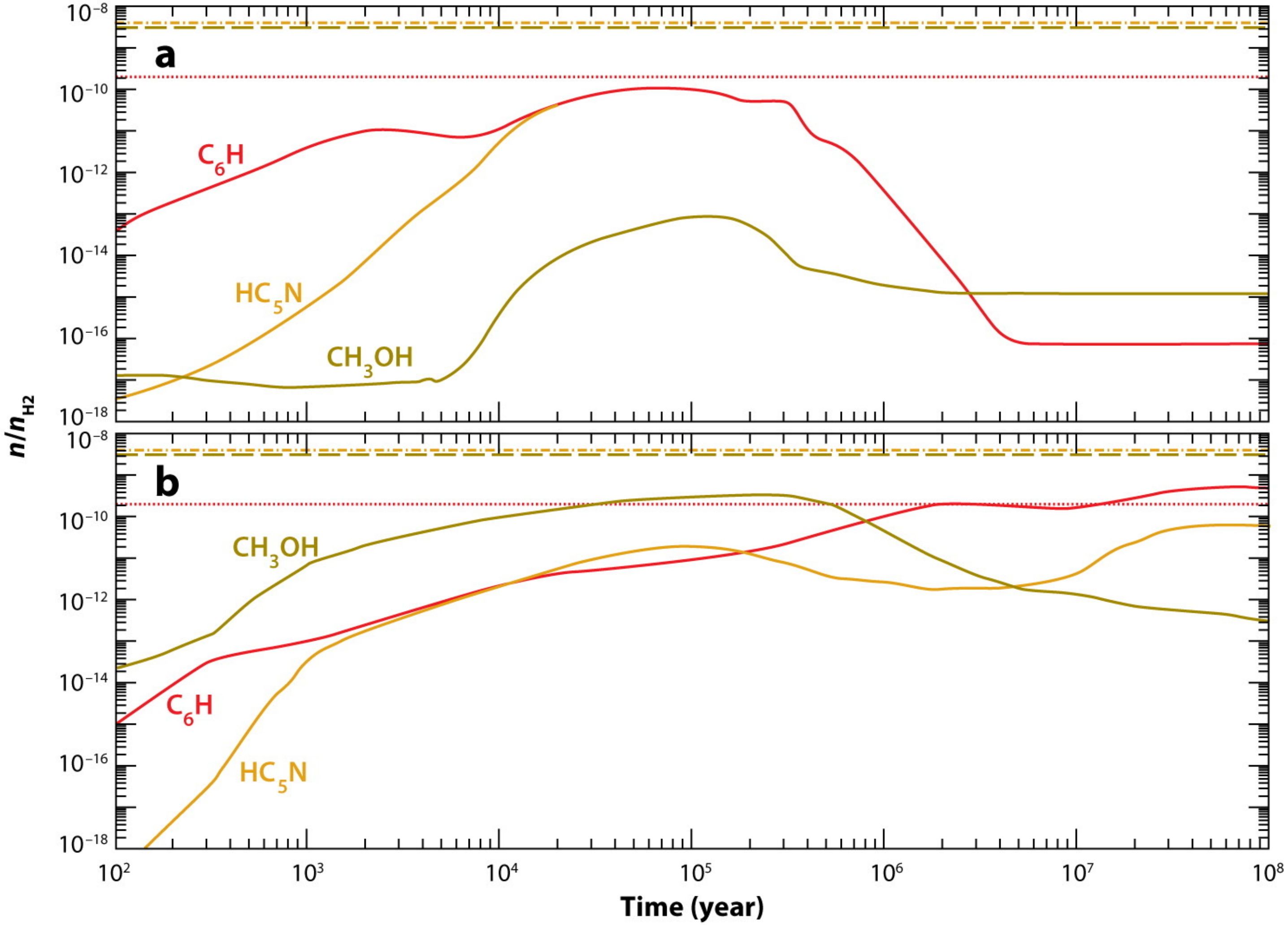


Methanol in cold clouds

Models with and without grain surface chemistry:

need grains to make observed amount of methanol

Herbst & van Dishoeck 2009



Gas-grain chemistry

Gas depletion timescale: $2 \times 10^{9}\, y_S^{-1}\, n_H^{-1}$ yr

with y_S = sticking coefficient ~1 at 10 K

at $n_H > 10^4$ cm^{-3}, gas-grain collisions change the chemistry

A few atoms / molecules collide with grain each day

H, He, C, O, CO, N / N_2

All species but He stick to surface with $y_S \approx 1$

(Sulfur & nitrogen reservoirs in dense clouds unknown)

Light species migrate over surface

tunneling: only H & H_2

thermal hopping: H, C, N, O

maybe: CH, NH, OH, NH_2, CH_2, CH_3

Reactions occur if barrier low enough ... See next lecture

Interaction between gas phase & grain surface

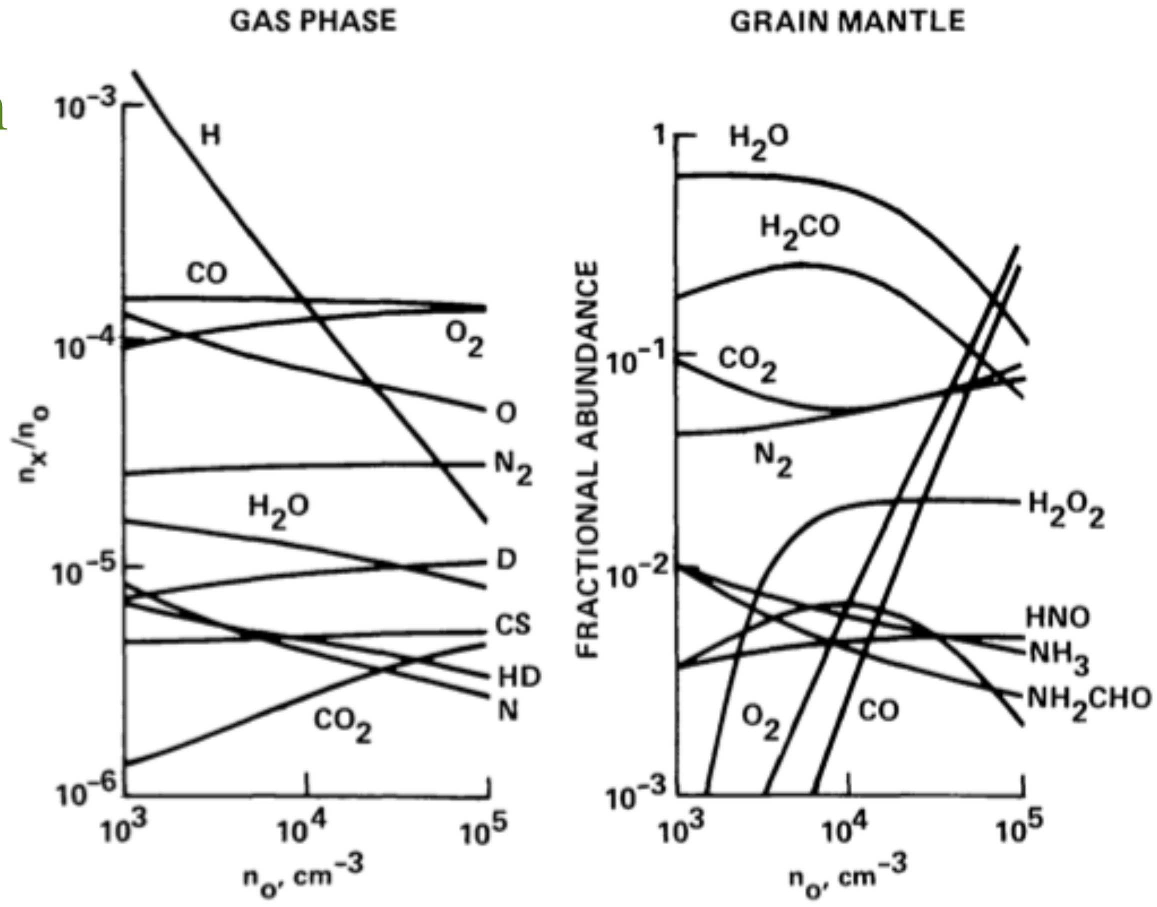
Low gas-phase density

larger H abundance (from cosmic-ray ionization): mainly *hydrogenation* H_2O, CH_4, NH_3, ...

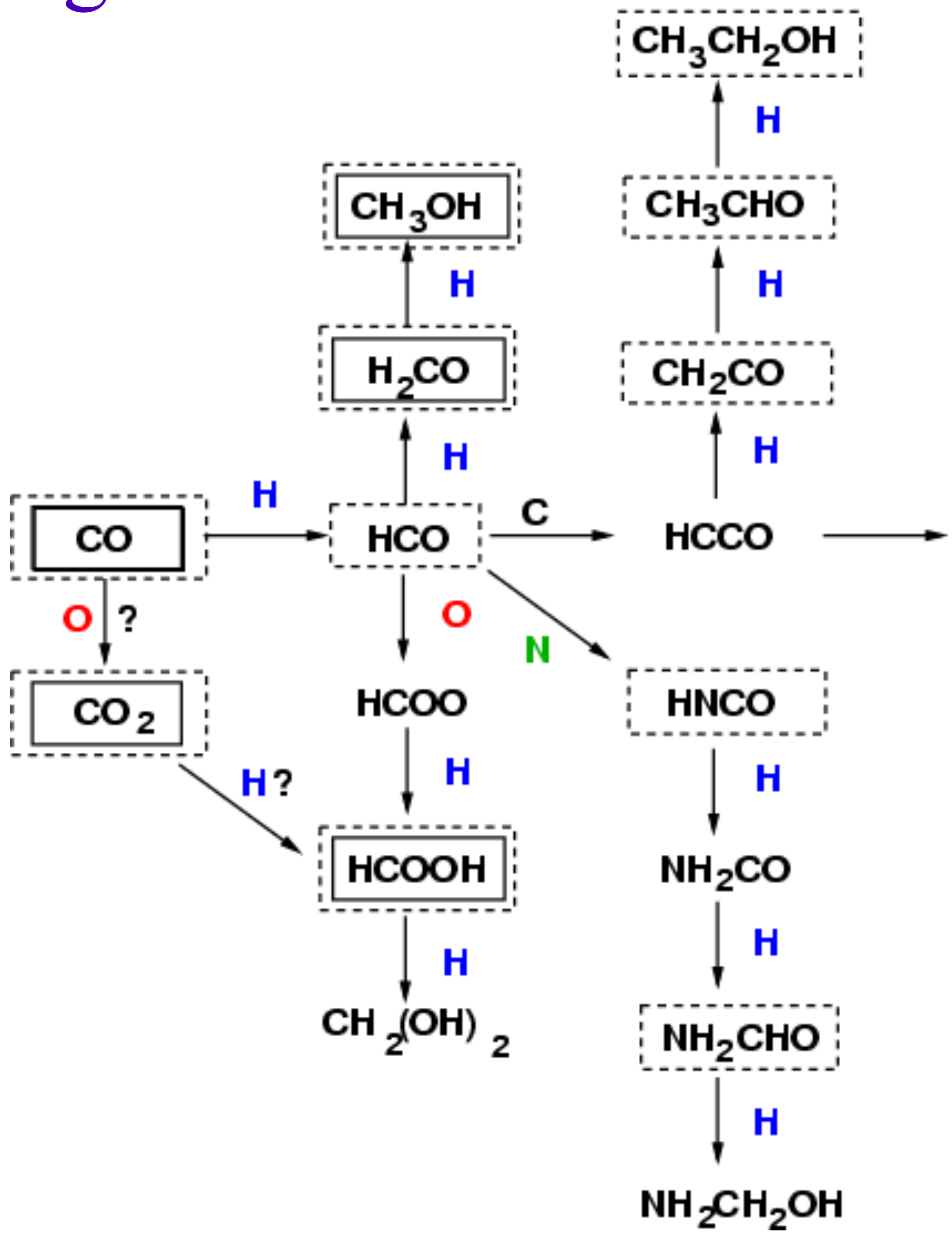
High gas-phase density

larger O abundance: mainly *oxidation* CO_2, O_2, ...

Accretion-limited regime: Tielens 1989



Formation of larger molecules



Dashed: detected in gas
Solid: detected in ice

Bisschop et al 2007

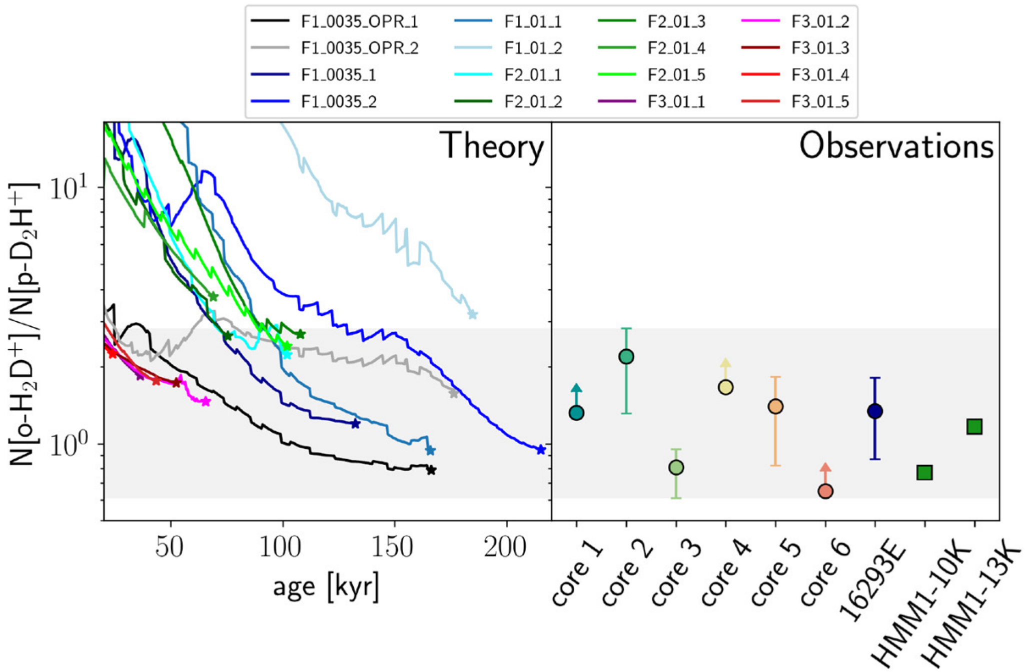
The chemical ages of pre-stellar cores

APEX observations of ortho-H_2D^+ & para-D_2H^+

6 pre-stellar cores
in Ophiuchus cloud

Core are chemically young:

ages ~ free-fall time
<< ambipolar diffusion



Brünken et al 2014; Bovino et al 2021

Origin of strong deuteration

$$H_3^+ + HD \rightleftharpoons H_2D^+ + H_2$$

$$H_2D^+ + X \rightleftharpoons XD^+ + H_2$$

- Forward reaction exothermic by 230 K
  more rapid at low *T*
- Reason: zero point vibration of H_2D^+ lower than H_3^+
  enhanced by nuclear spin statistics (Herbst 1982; Hugo et al 2007)
- Proton affinity of H_2 low
  deuteration passed on to other species (CO, N_2, ...)
- Freeze-out of CO enhances deuteration
  main destroyer of H_2D^+ gone

Chemical structure of dense cores

- Starless cores: abundant carbon chains

  indicates young age

  atomic C available

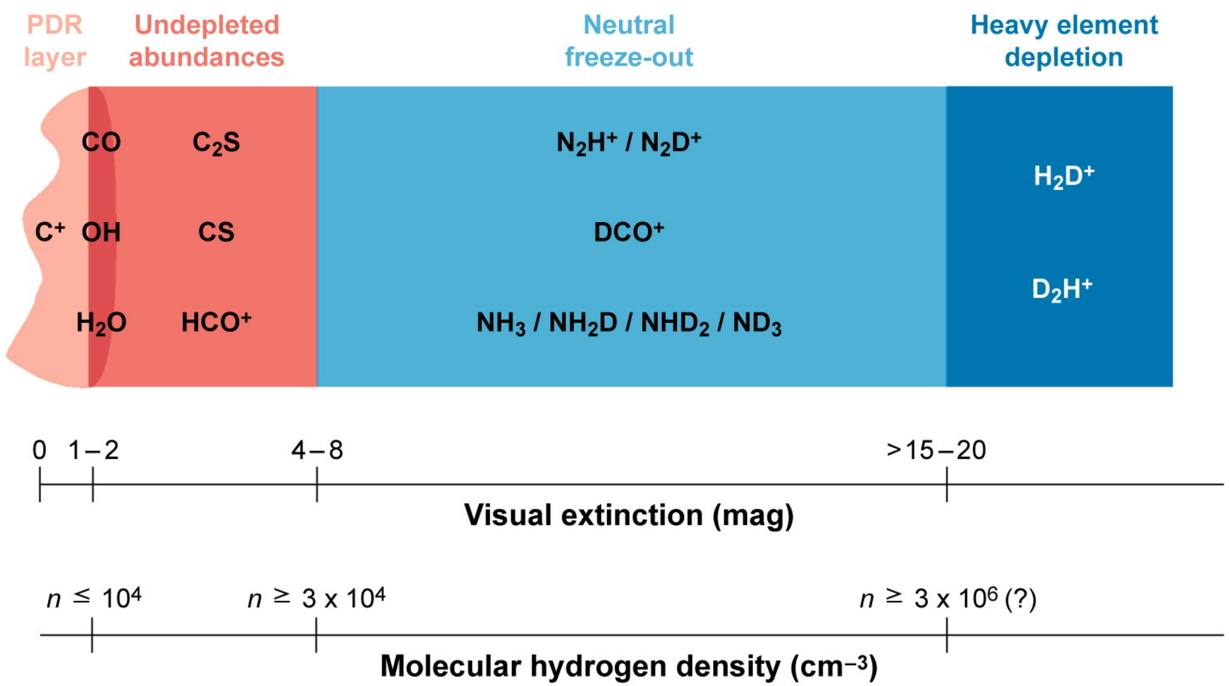
- Pre-stellar cores: centrally condensed

  CO freeze-out in center

  N- and D-species enhanced

Grain chemistry essential

Major gas-phase tracers in starless cores



Bergin EA, Tafalla M. 2007.
Annu. Rev. Astron. Astrophys. 45:339–96

Summary

- Chemistry in space is quite unlike on Earth ...
  - Low densities: Limited by kinetics
  - Low temperatures: Ionization acts as starter
  - Light elements: mainly H with CNO
- ...and varies between environments
  - Diffuse clouds: Photodissociation (radicals, ions); chemistry depth-dependent
  - Dark clouds: Grain surface processes (organics, ices); chemistry time-dependent

Exercise: Talking to strangers

Astronomers: explain to a chemist

–what magnitudes per square arcsecond are
–how dust extinction reddens starlight
–what the stellar and galaxy main sequences are
–how distances to stars and galaxies are measured
–what you mean by ‘metals’, ‘water’, ‘oxygen’, and ‘complex’ molecules

Chemists: explain to an astronomer

–what the Arrhenius law is
–how Lewis structures work
–how group theory helps to understand molecular symmetry
–what π and σ bonds are, and sp^2/sp^3 hybrids
–what you mean by ‘metals’, ‘water’, ‘oxygen’, and ‘complex’ molecules

In memoriam Harold Linnartz 1965–2023

- Career in astrochemistry

  PhD 1994 Nijmegen / Göttingen
  postdoc Bonn & Basel
  researcher VU Amsterdam
  Head of Leiden laboratory

- Research interests

  DIBs, e.g. EDIBLES survey
  organic molecules
  surface reactions

- Expertise

  gas-phase / PAH / solid-state
  optical & IR spectra

- Active member of DAN since inception

Interstellar cloud chemistry in context

- Insight into star & planet formation
  Inga Kamp, Maryvonne Gerin
- Molecular structure & interaction
  Jacques Le Bourlot, Gerrit Groenenboom
- Basic chemistry at exotic conditions
  Thanja Lamberts, Alessandra Candian, Valentine Wakelam
- Link with laboratory technology
  Sandra Brünken, Sergio Ioppolo

Enjoy your week!

	Monday 26 August	Tuesday 27 August	Wednesday 28 August	Thursday 29 August	Friday 30 August
9:00		Star & planet formation *Inga Kamp*	Observational techniques *Maryvonne Gerin*	Reaction networks *Valentine Wakelam*	Gas phase laboratory *Sandra Brünken*
10:00					
10:30		Coffee	Coffee	Coffee	Coffee
11:00		Mesoscopic astrochemistry *Alessandra Candian*	Laboratory spectroscopy *Sandra Brünken / Sergio Ioppolo*	Molecular collisions *Jacques Le Bourlot*	Observational future *Maryvonne Gerin*
11:45					Laboratory future *Sergio Ioppolo*
12:00	Registration				
12:30	Sandwich lunch	Buffet lunch	Buffet lunch	Buffet lunch	Computational future *Gerrit Groenenboom*
13:15					Goodbye & sandwich lunch
13:30	Welcome & logistics				
14:00	Interstellar clouds *Floris van der Tak*	Molecular structure *Thanja Lamberts*	Gas phase processes *Valentine Wakelam*	Laboratory surface physics *Sergio Ioppolo*	
14:30					
15:00					
15:30	Tea break	Tea break	Tea break	Tea break	
16:00	Grain surface processes *Thanja Lamberts*	Spectroscopy & radiative transfer *Jacques Le Bourlot*	Exercise session	Social event	
16:30					
17:00					
17:30	Poster pitches I	Poster pitches II	Poster pitches III		
18:00					
18:30	Buffet dinner	Buffet dinner	Buffet dinner	Barbecue	