

Master course: Astrochemistry I:

Lecture 4: Chemistry in quiescent clouds

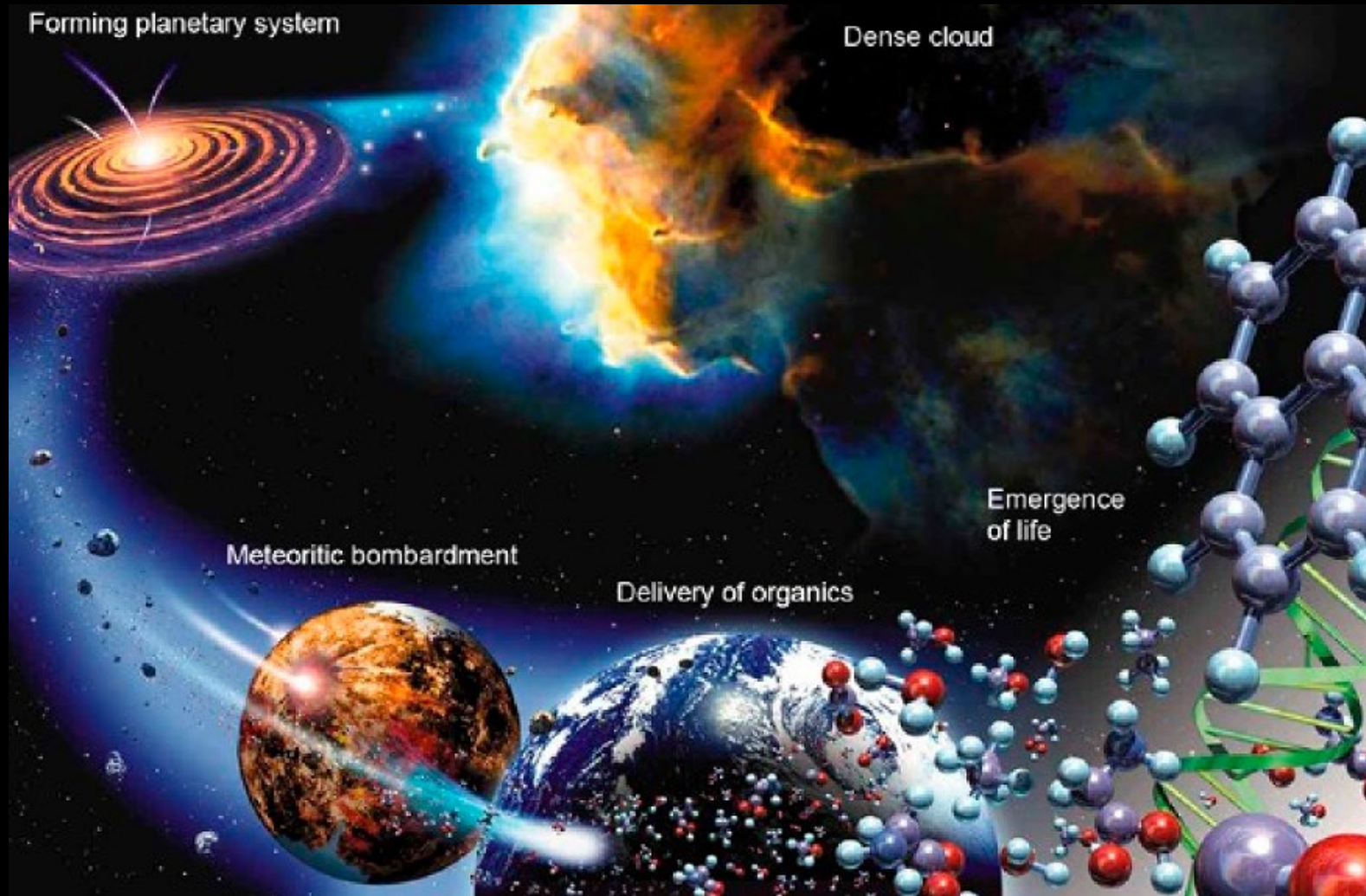
Reading list:

van Dishoeck (1998)
In MA II

Snow & McCall
(2006)

Gerin et al. (2016)
ARA&A

Tielens Chap. 9



Dr. Helgi Rafn Hrodmarsson – UPEC – 2026-2027

Outline

A. Diffuse and translucent clouds

- Introduction
- Physical structure
- Gas-phase chemistry networks
- Steady-state models: $\text{H} \rightarrow \text{H}_2$, $\text{C}^+ \rightarrow \text{CO}$

B. Photon-dominated regions (PDRs)

- Introduction
- Chemical structure

A. Diffuse and translucent clouds

4.1 Introduction

- Diffuse clouds with $A_V \approx 1$ mag are the best testing ground for basic interstellar chemistry because
 - ~~Only~~ **Mostly** ‘simplest’ diatomic molecules found
 - Gas-phase elemental abundances directly measured
 - H and H₂ directly measured
 - UV penetrates => short timescales => chemical equilibrium
 - No embedded / hidden energy sources
- Models first considered by Kramers & ter Haar (1946) and Bates / Spitzer (1951). Subsequent models include ion-molecule network developed by Herbst & Klemperer (1973)

Questions

- To what extent can ion-molecule gas-phase chemistry reproduce observed abundances?
- What is the role of shocks and turbulence?
- What is the role of grains in the formation of molecules other than H₂?
- What is the relation between diffuse and dense clouds?
- => study also *translucent** clouds with $A_V = 1-5$ mag

* Term coined by van Dishoeck & Black (1989)

Observations diffuse clouds

VIS + UV absorption lines

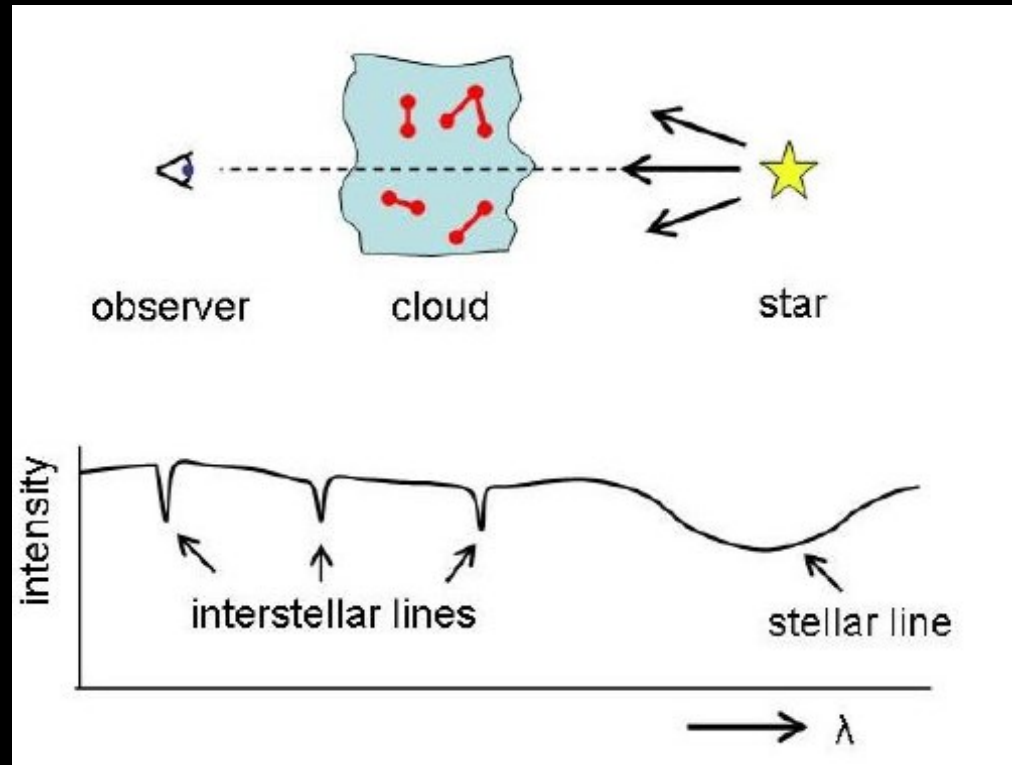
- Many atomic lines => depletion of elements C, O, N, ...
- Chemistry sensitive to C/O ratio
- Few molecular lines detected
 - H_2 , HD
 - CH, CH^+ , C_2 , C_3
 - OH, OH^+ , CO
 - NH, CN, HCl
- Not detected at optical wavelengths:
 - H_2O , H_2O^+ , C_4 , ...
 - MgH, NaH, SH^+

Millimeter/far-IR absorption and emission lines

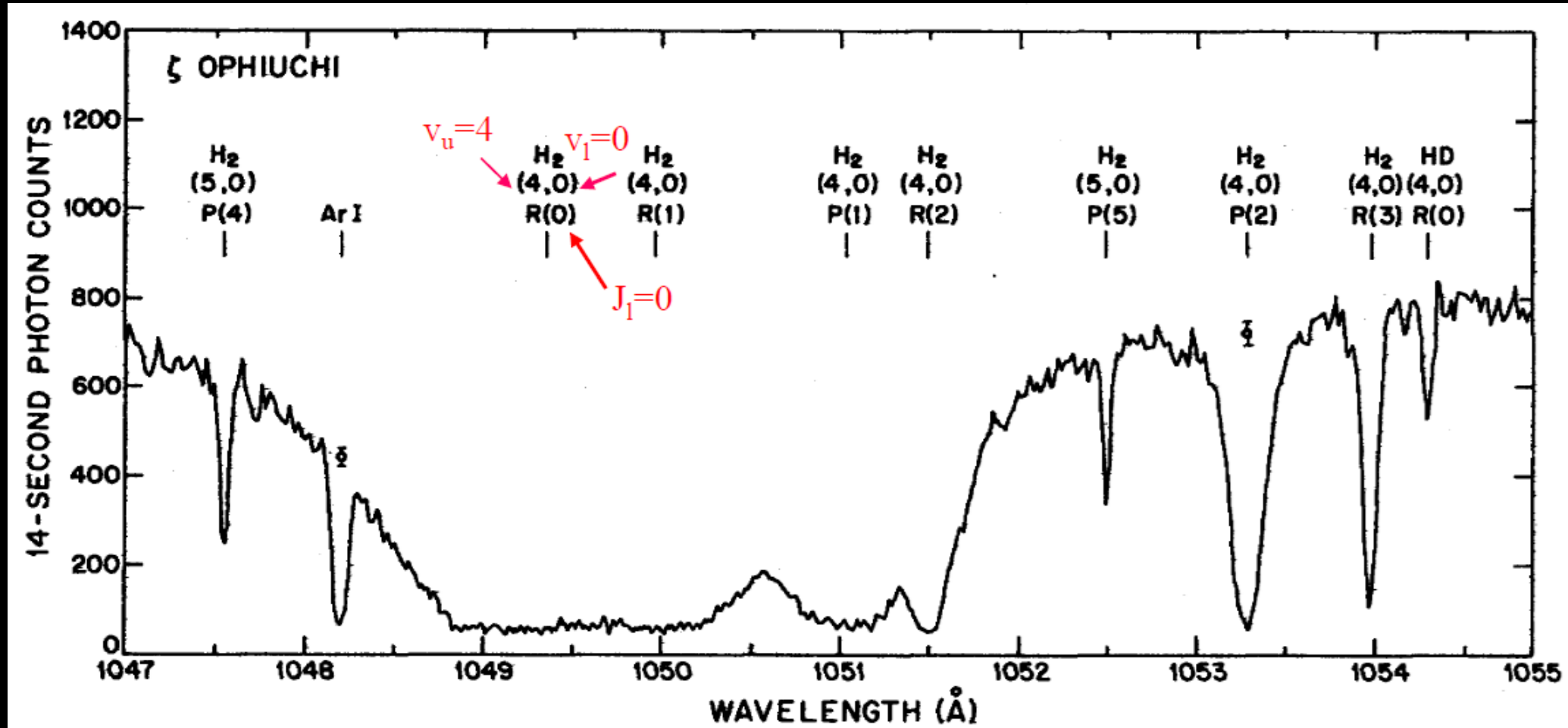
- Weak emission, many absorption lines

Observations of diffuse clouds

- Observed primarily by absorption lines at visible (since 1900's) and UV wavelengths (since 1970's: *Copernicus*, *FUSE*)
- Classical example: line-of-sight toward ζ Oph
- Spectra show sharp interstellar lines super-imposed on broad stellar lines



Interstellar H₂ lines toward ζ Ophiuchi



$\Delta J = J_u - J_l = +1$: R-branch

$\Delta J = J_u - J_l = -1$: P-branch

R(0): $J_u = 1 - J_l = 0$

Federman et al. 1995 Copernicus satellite

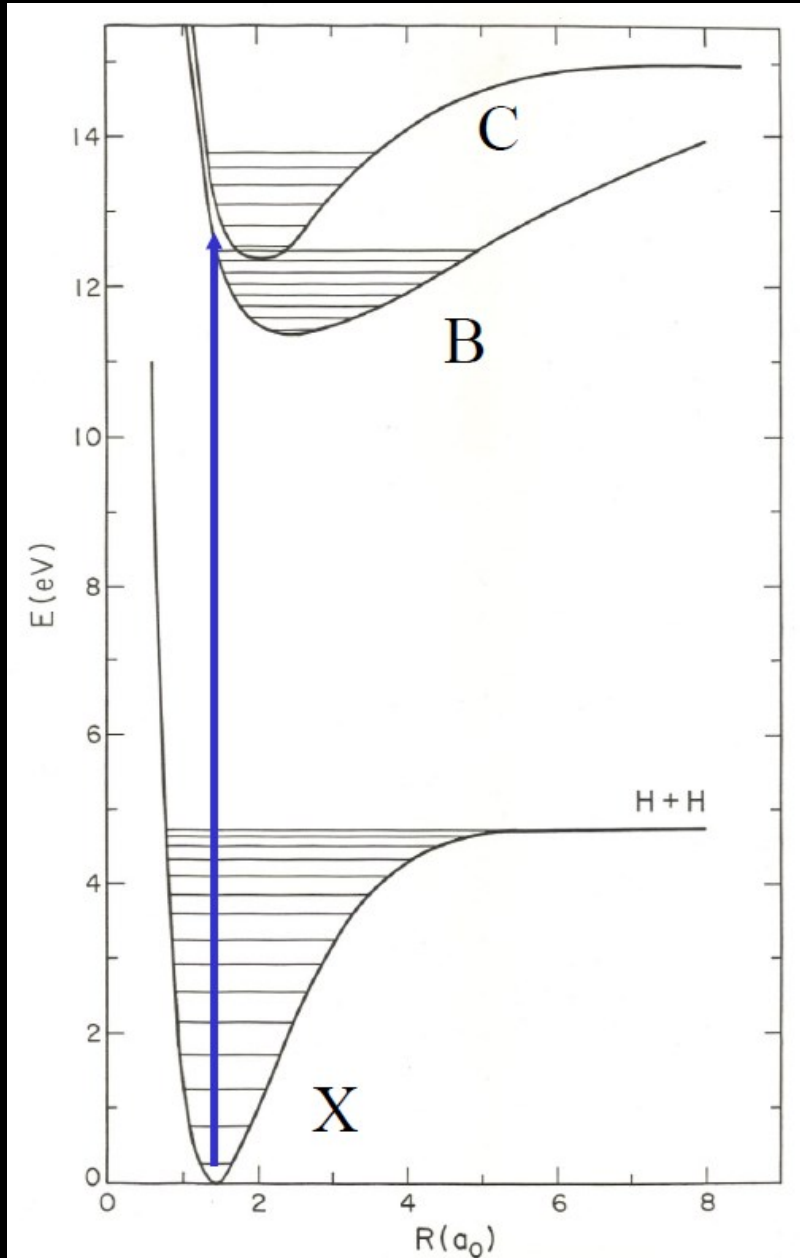
H₂ absorption

B-X: Lyman system

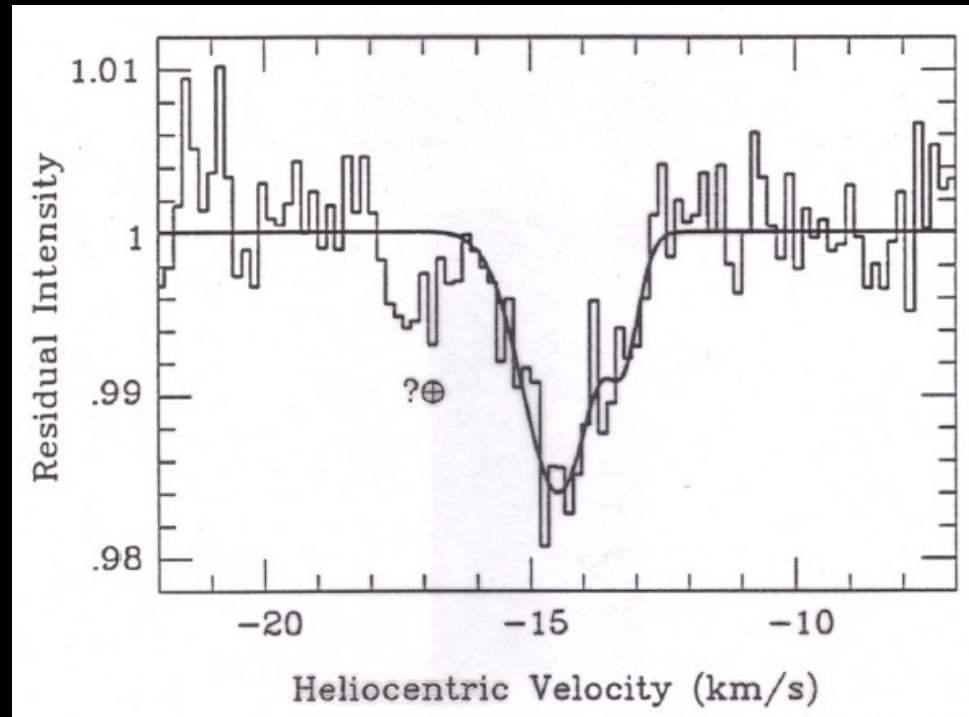
C-X: Werner system

$\Delta J = J_u - J_l = +1$: R-branch

$\Delta J = J_u - J_l = -1$: P-branch



Example: NH toward ζ Ophiuchi



Crawford & Williams 1997

- Ultra high resolution observations $R = 800000$
- Two component fit:
 - $v = -14.5 \text{ km s}^{-1}$, $b = 0.91 \pm 0.15 \Rightarrow T < 750 \text{ K}$
 - $v = -13.2 \text{ km s}^{-1}$, $b = 0.33 \pm 0.13 \Rightarrow T < 100 \text{ K}$
- Upper limits on T from line width exclude $\text{N} + \text{H}_2 \rightarrow \text{NH} + \text{H}$ reaction
Lines are narrow (except CH^+) $\rightarrow$ excludes strong shocks!

Typical abundances (ζ Oph, ζ Per)

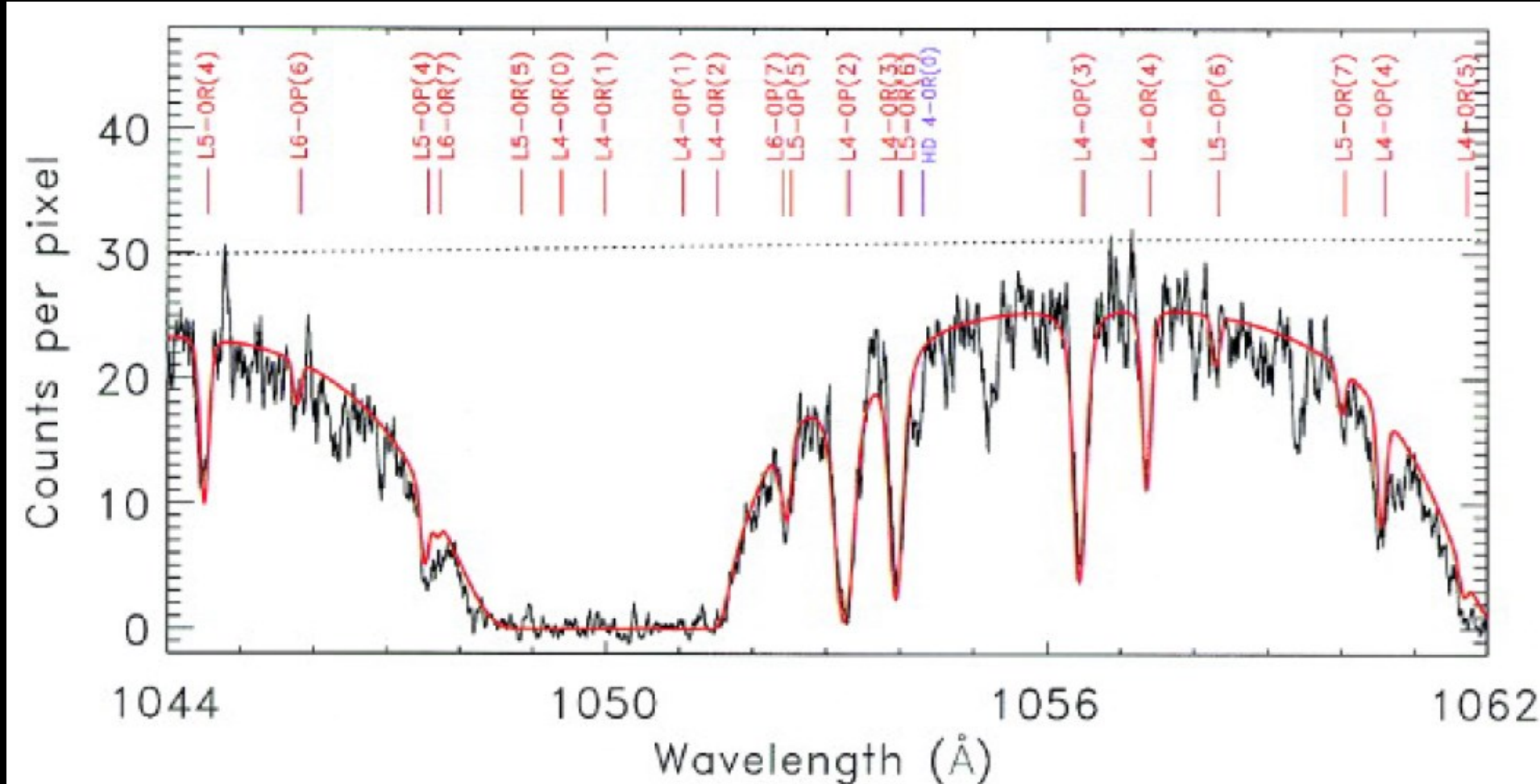
- $\text{CH} \approx 2 \times 10^{13} \text{ cm}^{-2} \Rightarrow x(\text{CH}) = \text{N}(\text{CH})/\text{N}(\text{H}_2) \approx 4 \times 10^{-8}$
- $\text{OH} \approx 4 \times 10^{13} \text{ cm}^{-2} \Rightarrow x(\text{OH}) \approx 8 \times 10^{-8}$
- $\text{NH} \approx 9 \times 10^{11} \text{ cm}^{-2} \Rightarrow x(\text{NH}) \approx 2 \times 10^{-9}$
- $\text{CO} \approx 10^{14} - 10^{15} \text{ cm}^{-2} \Rightarrow x(\text{CO}) \approx 2 \times 10^{-7} - 2 \times 10^{-6}$
- $\text{CH}^+ \approx 10^{12} - 10^{13} \text{ cm}^{-2} \Rightarrow x(\text{CH}^+) \approx 2 \times 10^{-9} - 2 \times 10^{-8}$
- The fact that the observed column densities of CH, OH $\gg$ NH indicates that grain surface chemistry is not dominant for carbon- and oxygen chemistry in diffuse clouds

Translucent clouds

- Can be isolated clouds, edges of dark clouds or GMCs, high-latitude clouds.
- Visible absorption lines of CH^+ , CH , CN , C_2 , ...
- UV absorption lines with FUSE $\Rightarrow$ H_2 , HD , CO
 - Only for some clouds
- Clouds thick enough for mm emission $\Rightarrow$ CO and very weak $[\text{C I}]$, CS , CN , HCO^+ , ... ***‘CO dark gas’***
- mm absorption lines against background quasars $\Rightarrow$ surprisingly large column densities of HCO^+ , HCN , ...
- Infrared absorption $\Rightarrow$ threshold for ice mantle formation at $A_V \geq 3$ mag

UV spectroscopy: FUSE

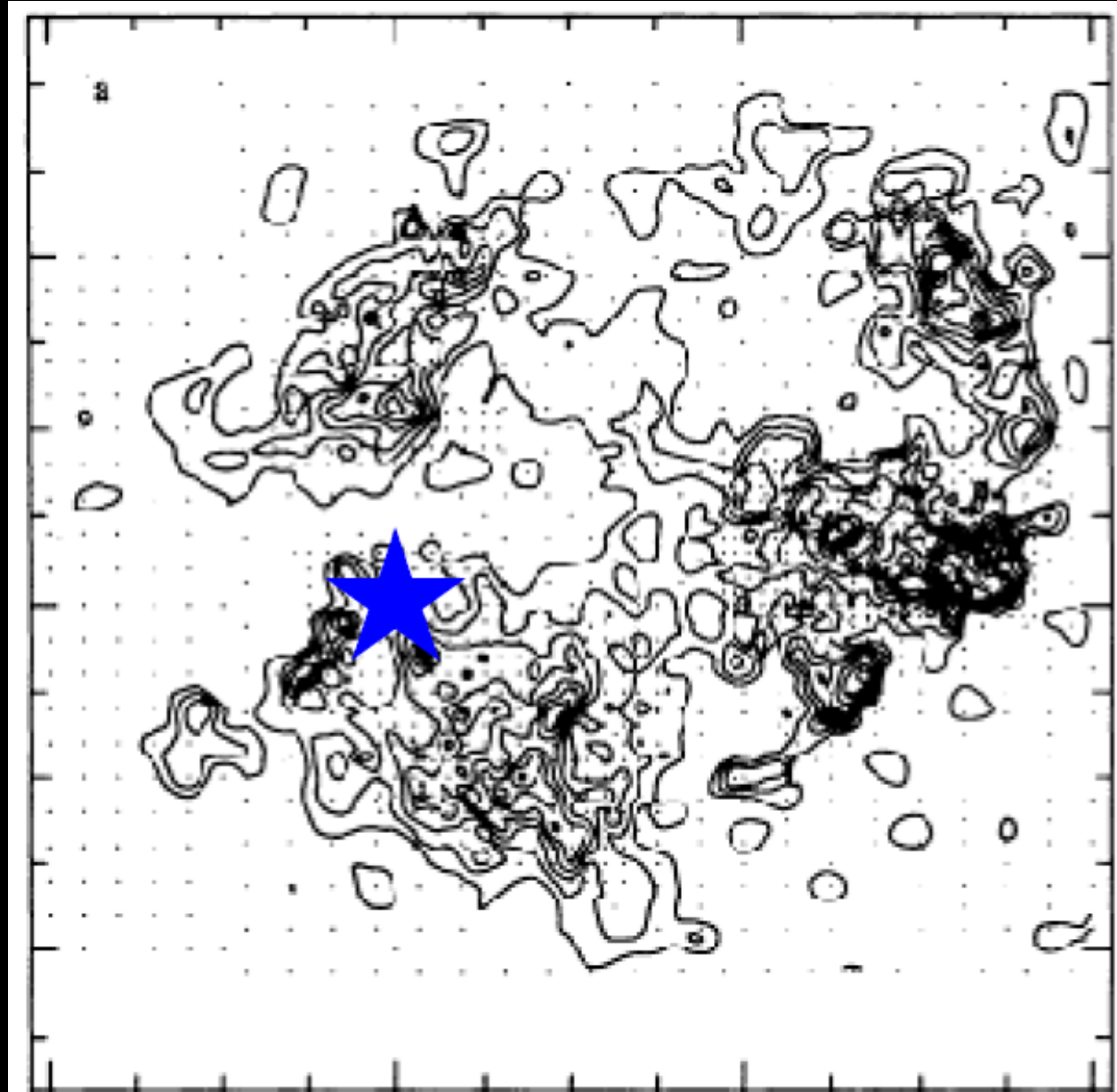
HD 73882



Snow et al. (2000)

FUSE spectrum toward HD 73882 translucent cloud showing H₂ and HD lines

High latitude cloud toward HD 210121



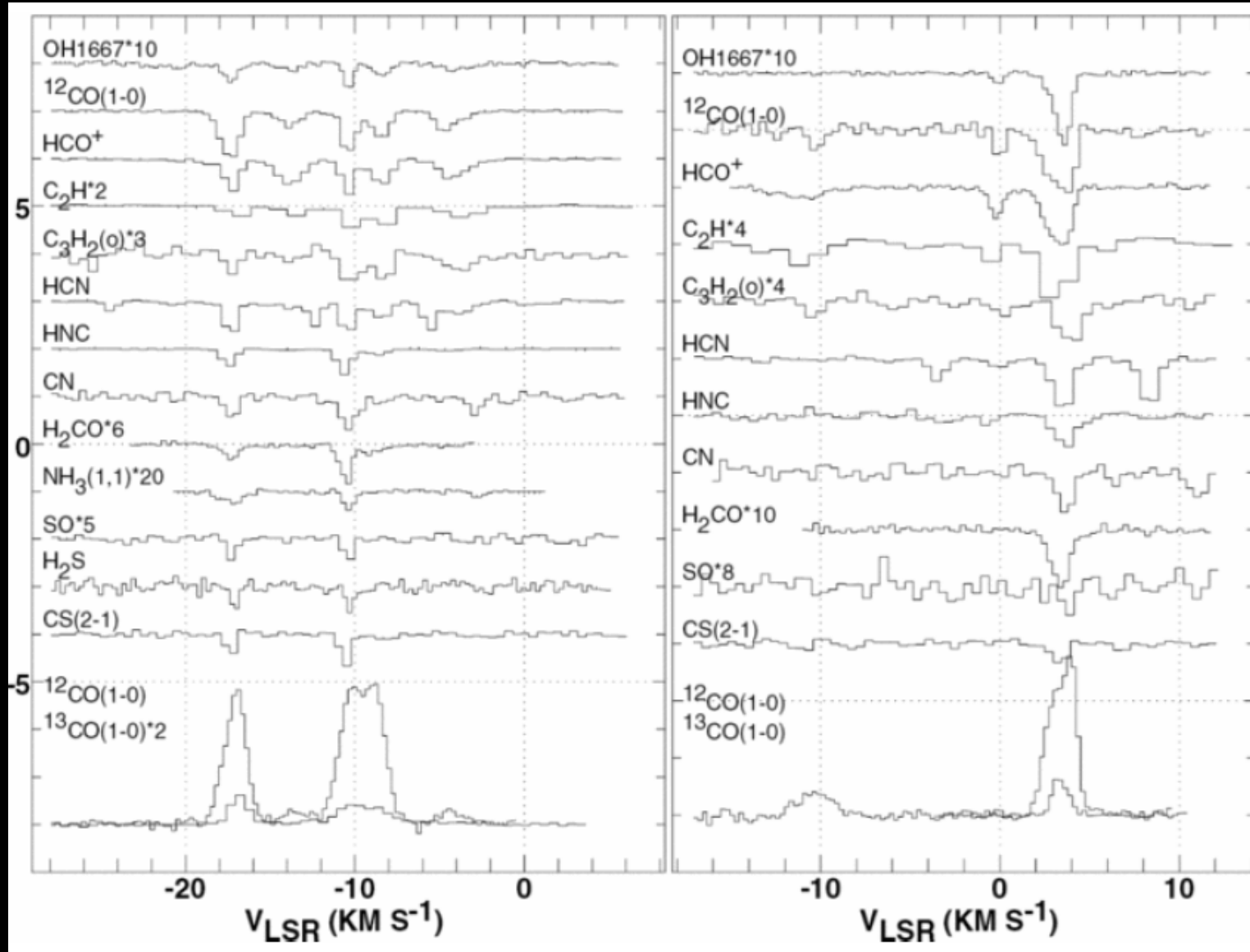
CO $J=1-0$ map

Gredel et al. (1992)

mm absorption lines: quasars

B0355+508

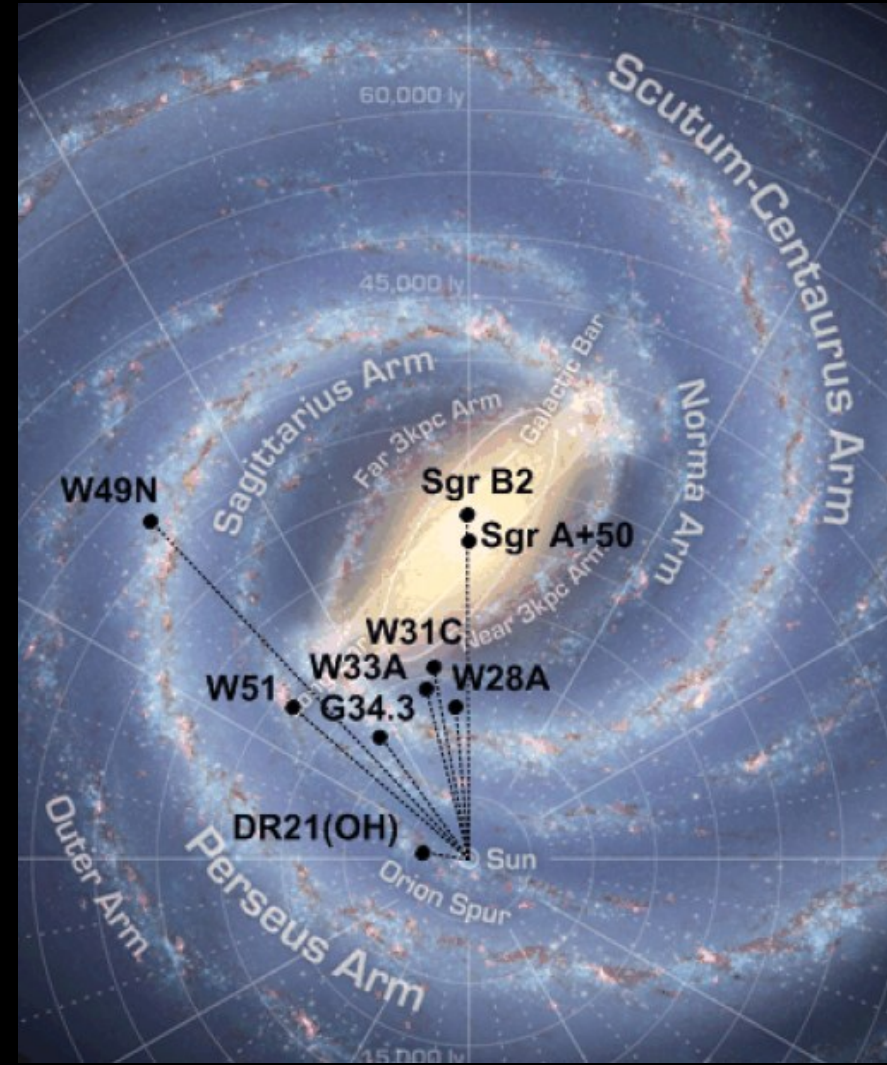
B0212+735



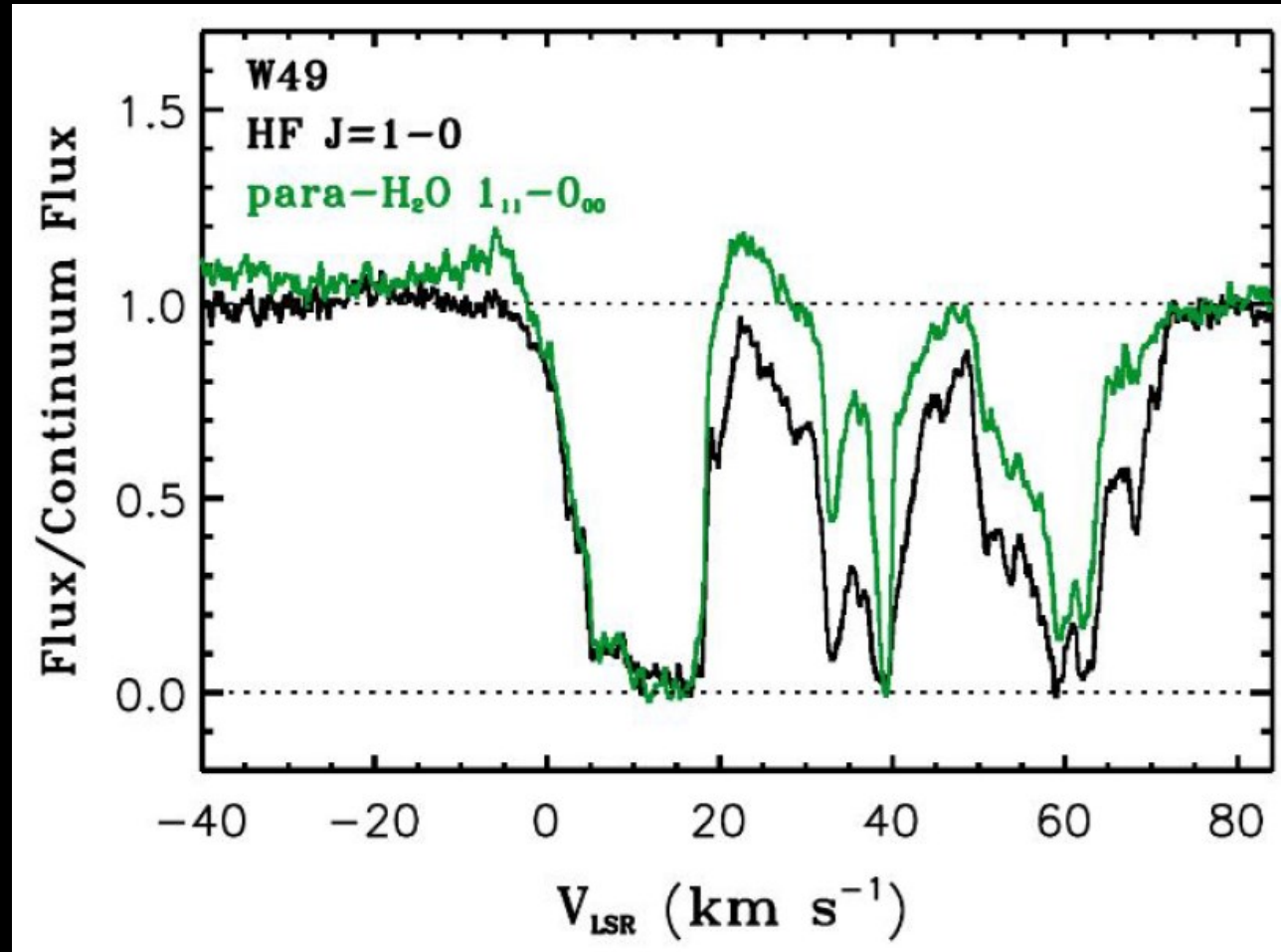
Lucas & Liszt '94-05
Hogerheijde et al. 1995
Liszt 2005, IAU 231

Far-infrared absorption

- Absorption against bright far-IR continuum
- Clouds $A_V \sim \text{few mag}$
- Hydrides have their lowest transitions at higher frequencies (sub-mm/far-IR wavelengths) because of lower mass than CO
- All molecules in ground state $\rightarrow$ simple analysis



Far-IR absorption lines: HF and H₂O



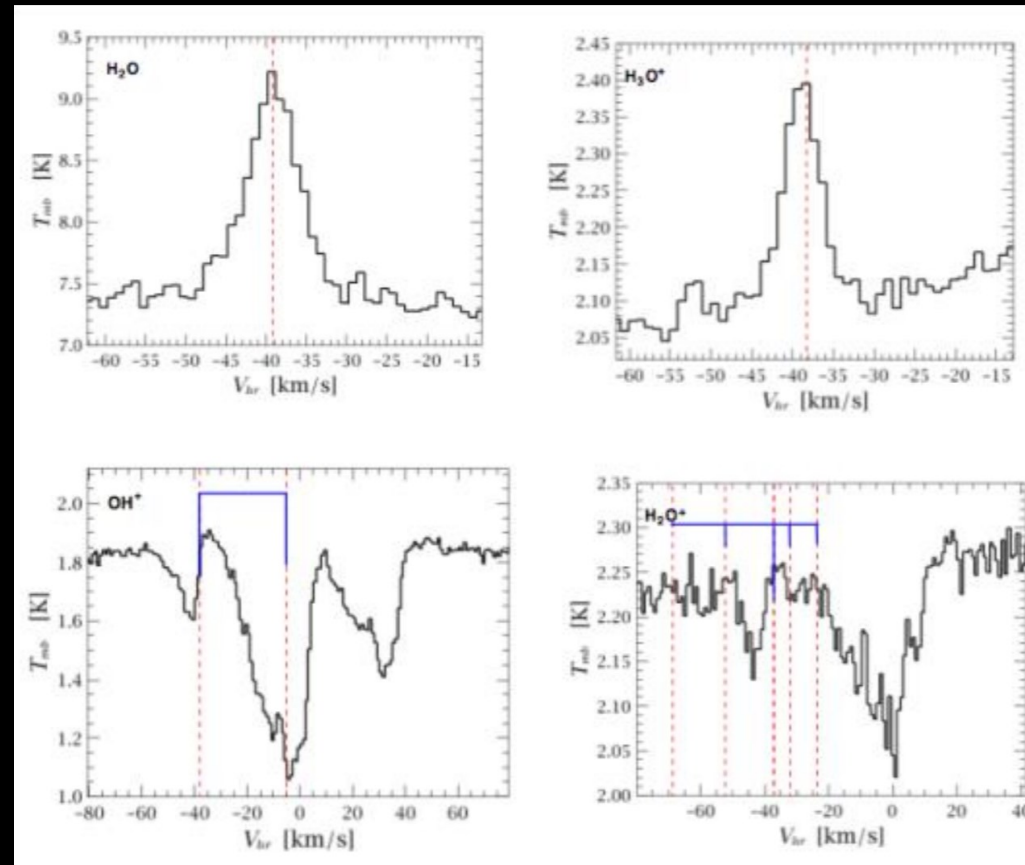
Herschel-HIFI

Gerin et al. 2016

- Diffuse and translucent clouds along the line of sight
- HF as tracer of H₂ column density because of simple chemistry
- Constant H₂O/H₂ abundance of 5×10^{-8}

Herschel surprise: H_2O^+ widespread

- Points to an ISM phase with high H/H_2 (see exercise on ArH^+)



Benz, Bruderer et al.
2010
Gerin et al. 2010
Ossenkopf et al. 2010
Wyrowski et al. 2010

- Also observed: OH^+ , CH^+ , SH^+ , HCl^+ , H_2Cl^+ , ArH^+ , OH , H_2O , CH , NH , HF , SH , HCl

4.2 Physical structure: diagnostics

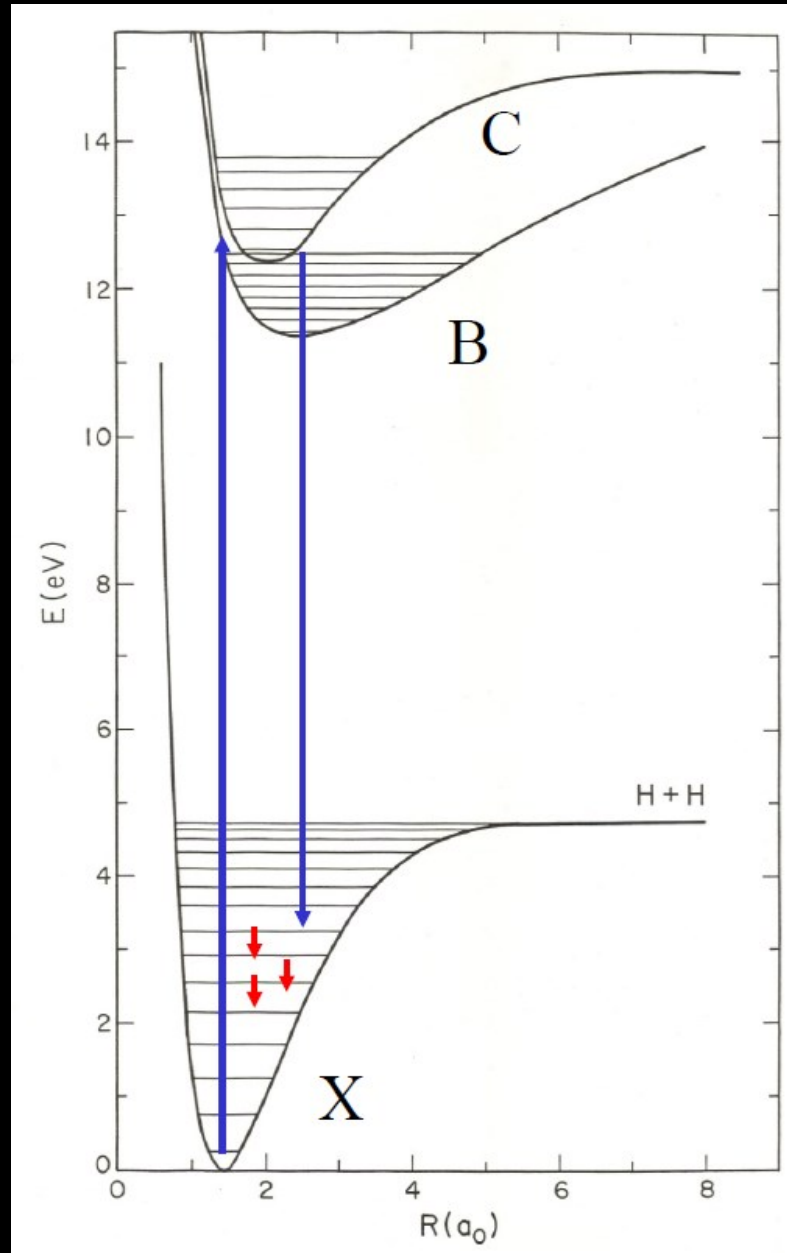
Species	Probes	Diffuse clouds	Translucent clouds
H ₂ low J	T	+	-
H ₂ high J , $v>0$	I_{UV} , formation	+	-
C ₂ low J	T	+	+
C ₂ high J	$I_{\text{R}}/n_{\text{H}}$	+	+
C, C ⁺ , O(J)	n_{H} , T	+	-
CO low	n_{H} , T	+	+
CN J	$n(\text{e})$	+	+
HCO ⁺ , ...	$n(\text{e})$, n_{H}	-	+

a. Rotational excitation of H₂

- H₂ lines out of $J = 0-7$ detected with Copernicus + FUSE
- Population distribution non-thermal
 - Low J : excitation dominated by collisions
 - $\Rightarrow$ *sensitive to T and n_H*
 - Abundance H⁺ large enough that ortho/para exchange rapid and $J=1/J=0$ gives T_{kin}
 - High J : energy levels lie very high (> 1000 K) $\Rightarrow$ not populated by collisions at $T = 40-80$ K $\Rightarrow$ populated by optical pumping process through B $\rightarrow$ X and C $\rightarrow$ X systems
 - $\Rightarrow$ *proportional to interstellar radiation field I_{UV}*
 - Formation process may play a small role as well
- I_{UV} is scaling factor w.r.t. general interstellar radiation field (ISRF) in 6 – 13.6 eV range (also called G_0)

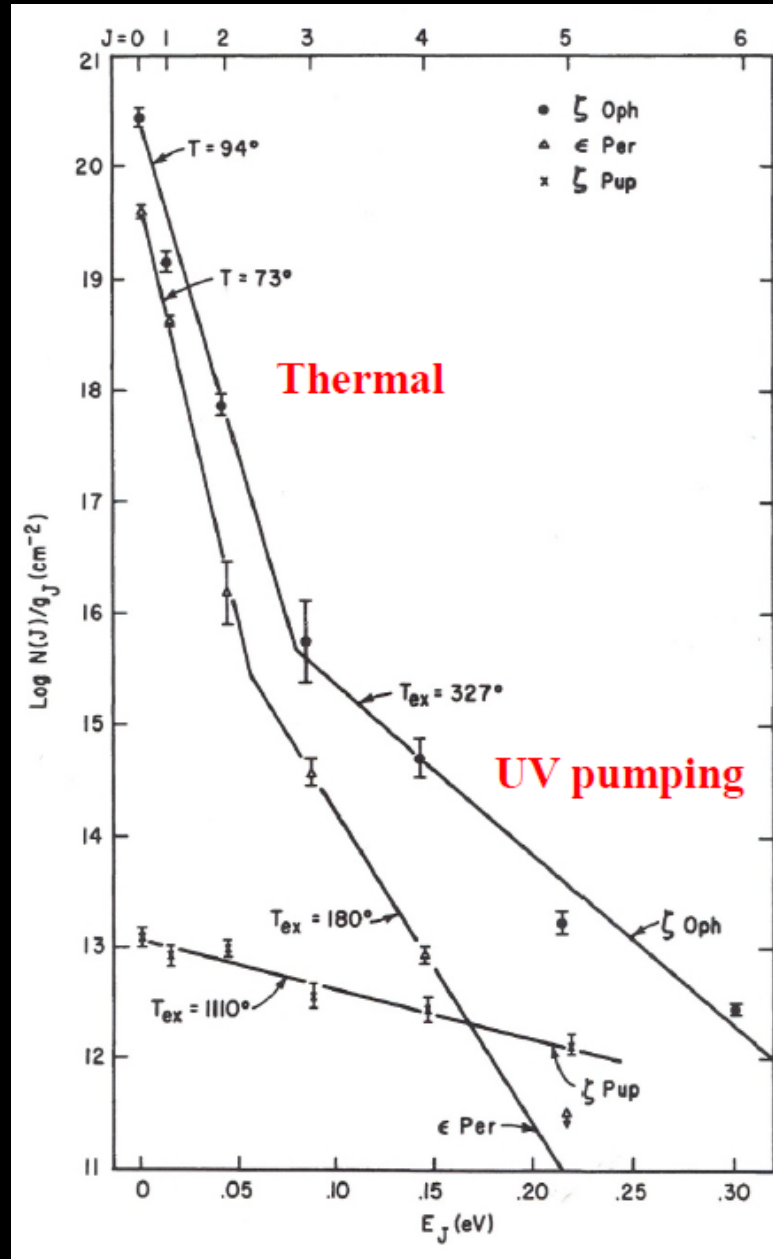
H₂ excitation

B-X: Lyman system
C-X: Werner system



Observed H₂ rotational excitation

$\ln N_J/g_J$

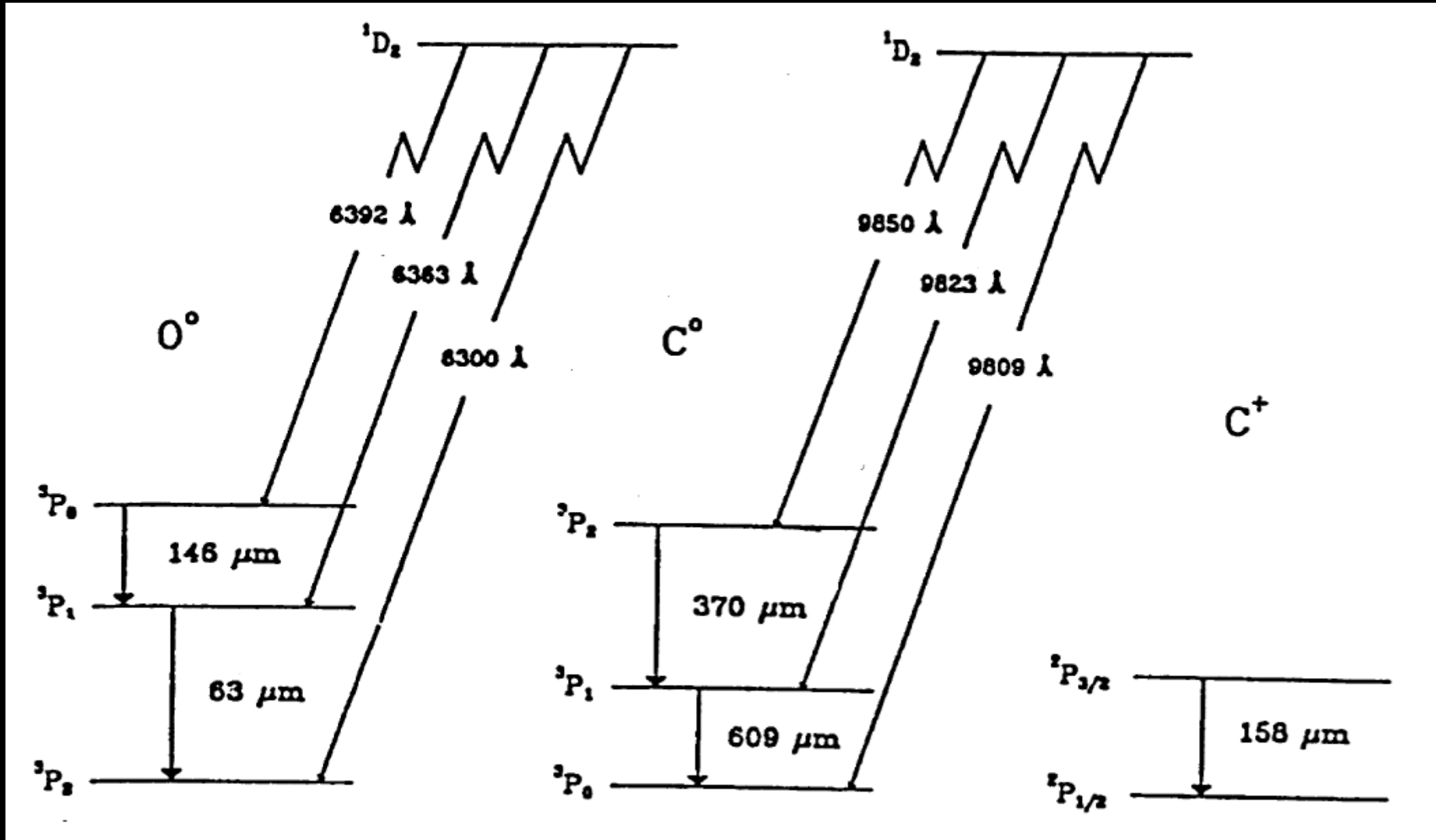


Diffuse clouds

b. Other diagnostics

- C_2 : similar to H_2 , but pumping by radiation around $1\ \mu\text{m}$ => **sensitive to I_R , T , and n_H**
- CO rotational excitation
 - Small dipole moment => lowest levels can be populated by collisions even at low densities => **sensitive to T and n_H**
- C, C^+ , O fine-structure excitation
 - Fine-structure populations determined by collisions => **sensitive to T and n_H**

O I, C I, and C II fine structure lines



Results physical parameters

- Diffuse clouds

Edge

Center

- n_{H} : 100 → 500 cm⁻³ gradient?
- T : 100-200 → 25-40 K
- I_{UV} : 1-2 x ISRF → decrease depending on λ

- Translucent clouds

- C₂: $T \approx 15\text{-}40$ K; $n_{\text{H}} \approx 500\text{-}5000$ cm⁻³
- CO: if $T \geq 15$ K $\Rightarrow n_{\text{H}} \approx 1000$ cm⁻³
- CN: $n(e) \approx 0.02\text{-}0.1$ cm⁻³ $\Rightarrow n_{\text{H}} \approx 500\text{-}5000$ cm⁻³
- No constraints on I_{UV} for translucent clouds
- CO maps reveal inhomogeneous / ‘clumpy’ structure

*Bottom line: diffuse cloud densities a few hundred cm⁻³,
translucent cloud densities a few thousand cm⁻³*

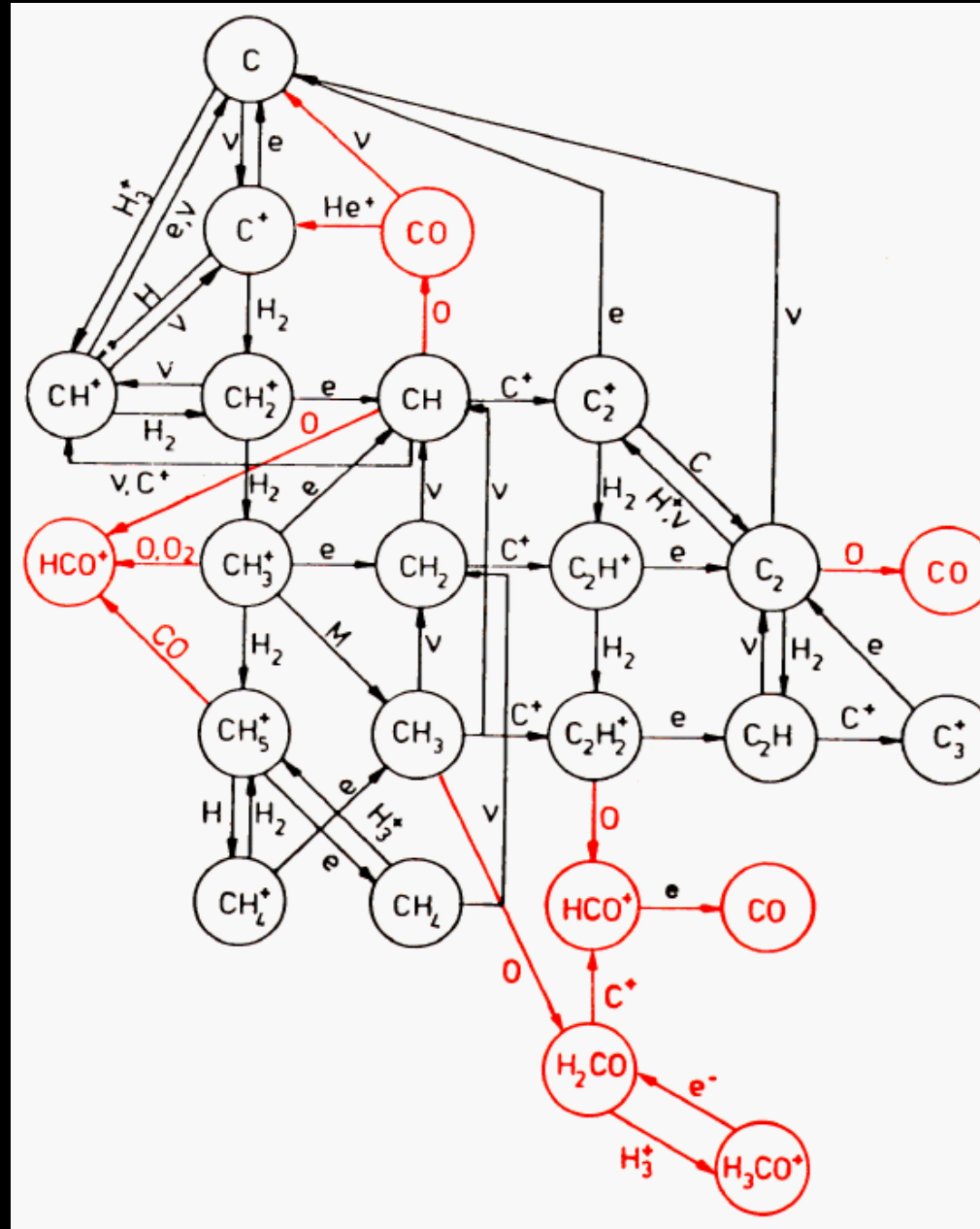
4.3 Chemistry networks

- Formation of bonds $k \text{ (cm}^3 \text{ s}^{-1}\text{)}$
 - Radiative association: $\sim 10^{-17} - 10^{-14}$
 - Grain surface: $\sim 10^{-17}$
- Destruction of bonds
 - Photodissociation: $\sim 10^{-10} - 10^{-8}$
 - Dissociative recombination: $\sim 10^{-7} - 10^{-6}$
- Rearrangement of bonds
 - Ion-molecule reactions: $\sim 10^{-9} - 10^{-8}$
 - Neutral-neutral reactions: $\sim 10^{-10} - 10^{-9}$
- Hydrogen is dominant element => if species can react with H or H₂, it will be the dominant route

Carbon chemistry

- Need to have ions and molecules to start ion-molecule chemistry
- I.E. of C < 13.6 eV => Carbon mostly C⁺
- $\text{C}^+ + \text{H}_2 \rightarrow \text{CH}_2^+ + h\nu$ possible at low T (initiating reaction)
- Once CH₂⁺ formed, rapid ion-molecule reactions lead to CH, C₂, ...
- $\text{C}^+ + \text{H}_2 \not\rightarrow \text{CH}^+ + \text{H}$ endothermic by 0.4 eV

Carbon chemistry and its coupling with oxygen



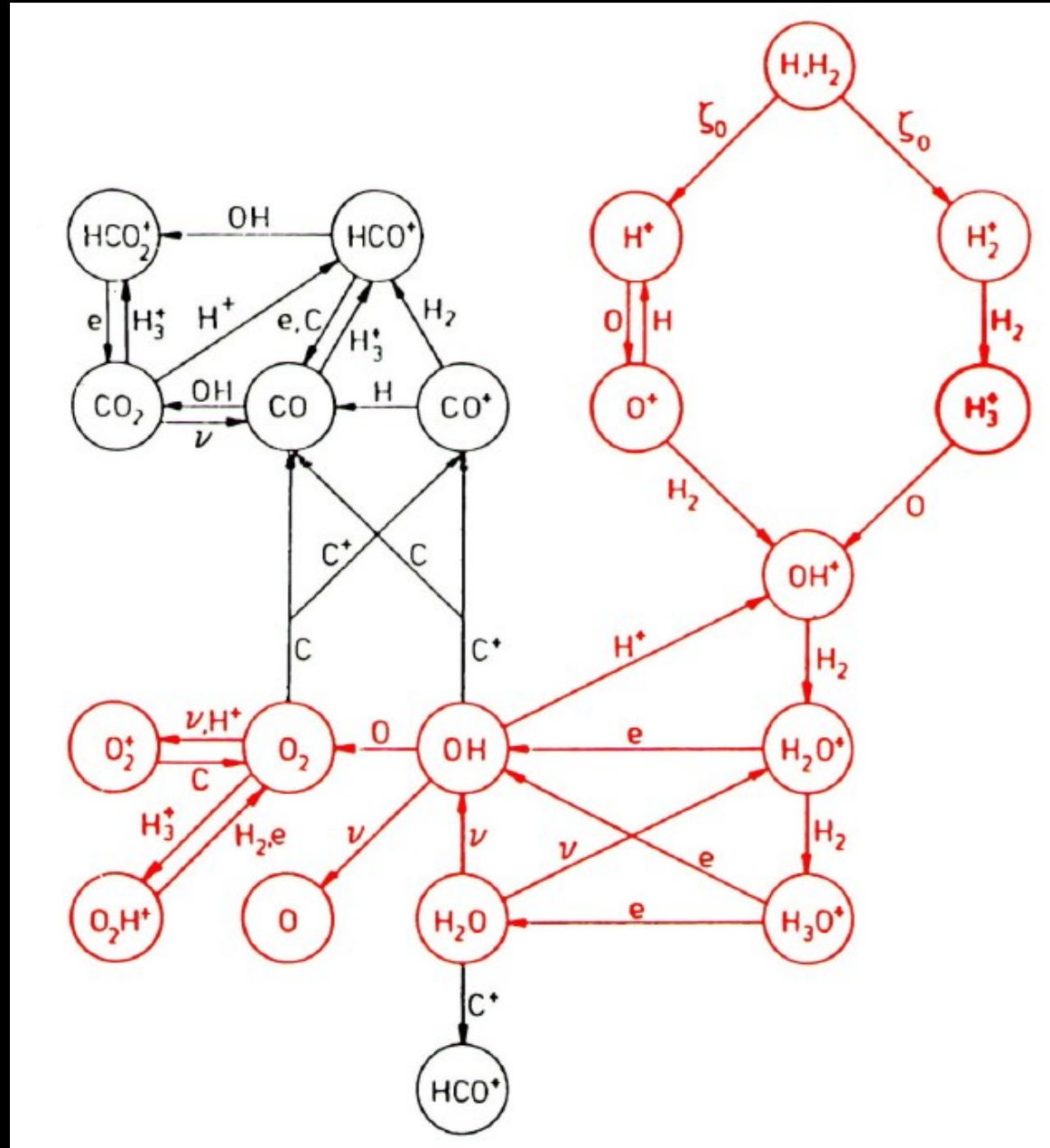
Vertical
Down: H_2
Up: photon ν

Horizontal
Ion: e
Neutral: C^+

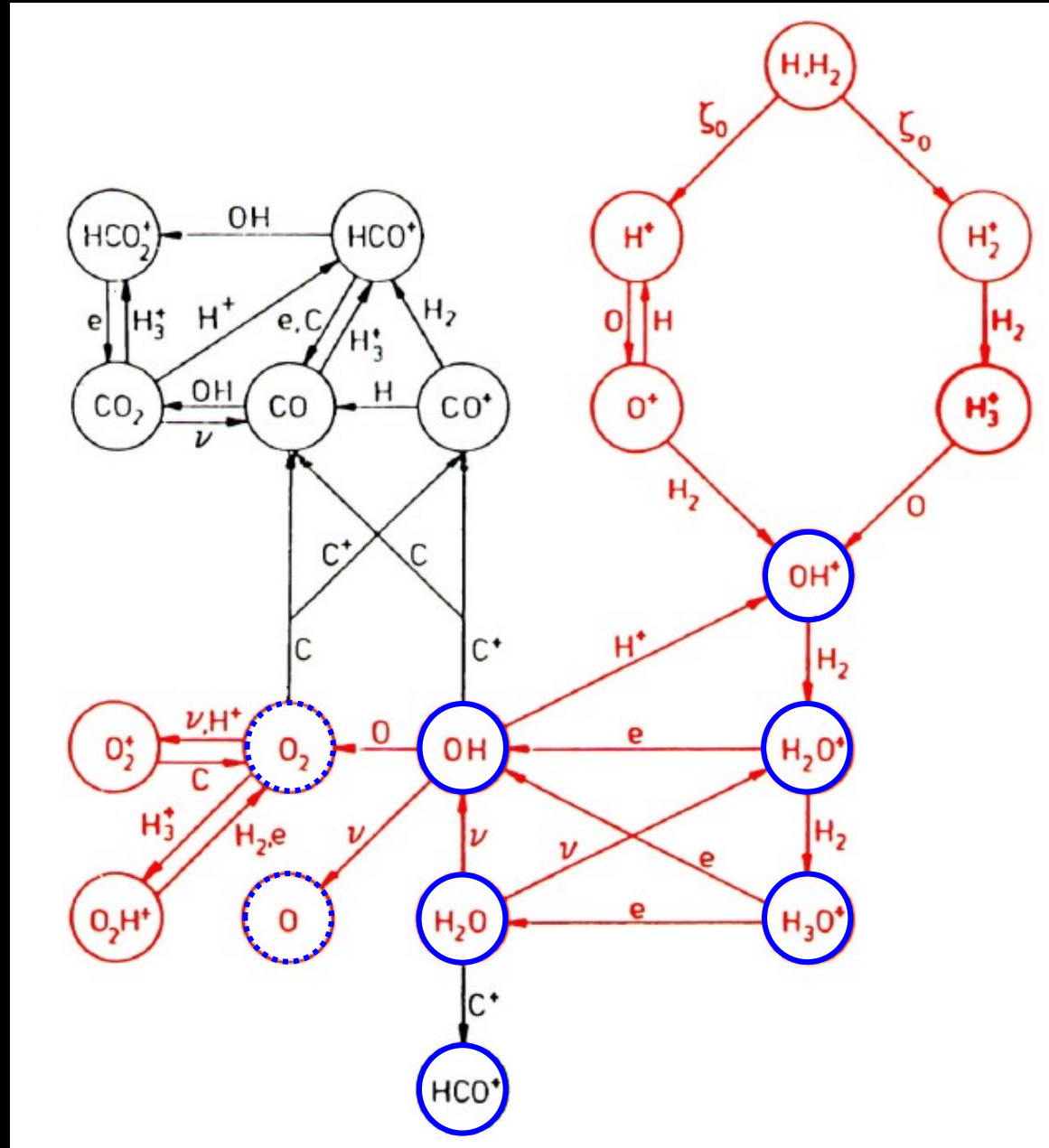
Oxygen chemistry

- I.E. of O > 13.6 eV $\Rightarrow$ Oxygen mostly neutral O
- Ionization provided by cosmic rays
 - H_2 or $\text{H} + \text{C.R.} \rightarrow \text{H}_2^+$ or $\text{H}^+ + \text{C.R.} + \text{e}^-$
 - $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ (very fast)
- H^+ or H_3^+ can react with oxygen
 - $\text{H}^+ + \text{O} \leftrightarrow \text{H} + \text{O}^+ \quad \Delta E = 227 \text{ K}; \text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+ + \text{H}_2$
 - $\text{H}_3^+ + \text{O} \rightarrow \text{OH}^+ + \text{H}_2$
- Once OH^+ formed, rapid ion-molecule reactions lead to OH, H_2O and CO
- Note that OH abundance is proportional to cosmic ray ionization rate $\zeta_{\text{CR}} \Rightarrow$ can use observed OH abundance to determine ζ_{CR}

Oxygen chemistry and its coupling with carbon



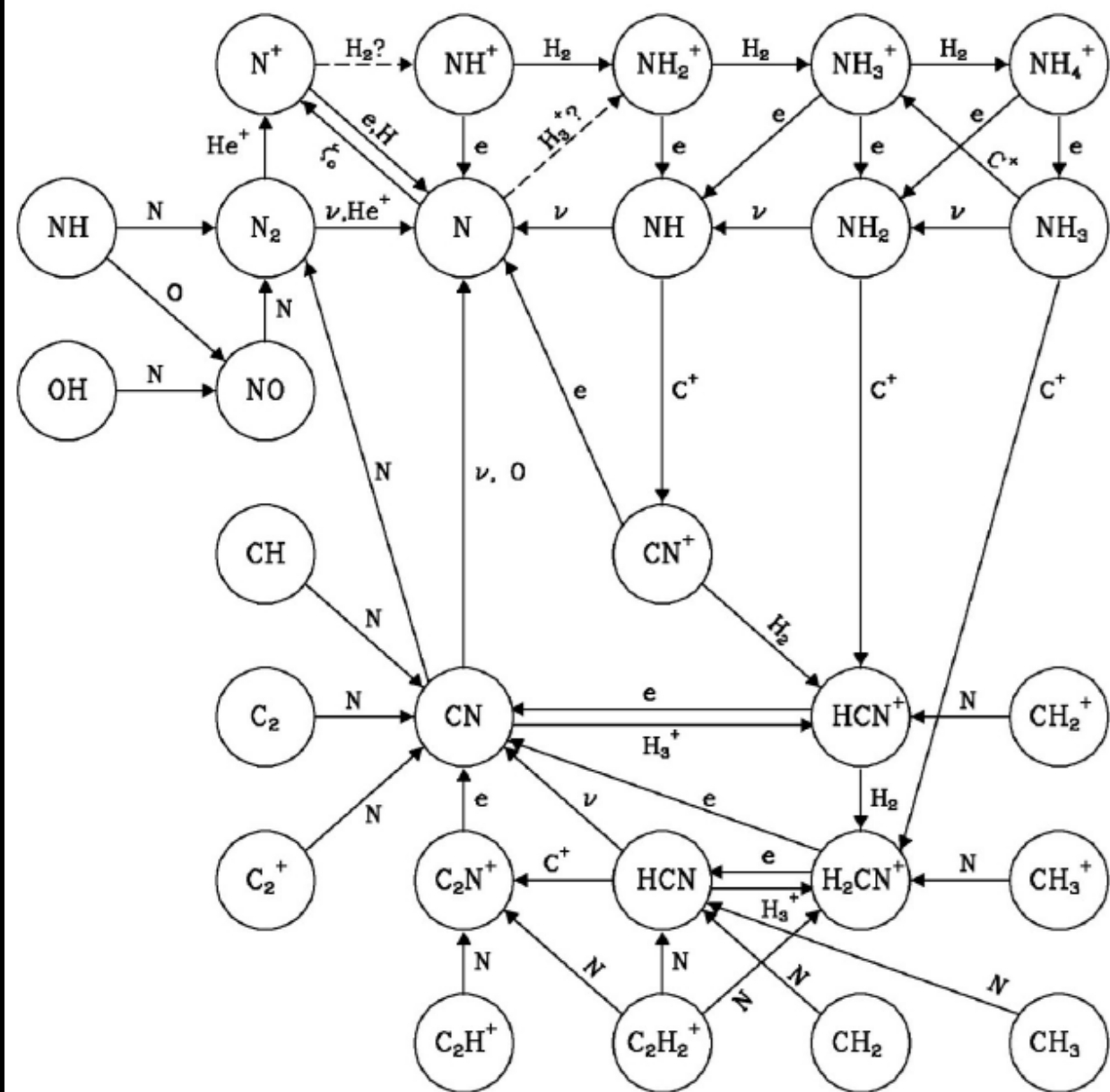
All key species in oxygen chemistry detected!



Nitrogen chemistry

- I.E. of N > 13.6 eV $\Rightarrow$ Nitrogen mostly neutral N
- Nitrogen chemistry initiated by
 - $\text{N} + \text{H}_3^+ \rightarrow \text{NH}_2^+ + \text{H} ?$ Energy barrier?
 - $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H} ?$ Small barrier ~ 100 K
- Link with carbon chemistry
 - $\text{CH}, \text{C}_2 + \text{N} \rightarrow \text{CN} + \text{H}, \text{C}$
 - $\text{CH}_3^+ + \text{N} \rightarrow \text{H}_2\text{CN}^+ + \text{H}$
 - $\text{H}_2\text{CN}^+ + \text{e}^- \rightarrow \text{HCN or HNC} + \text{H}$

Nitrogen chemistry



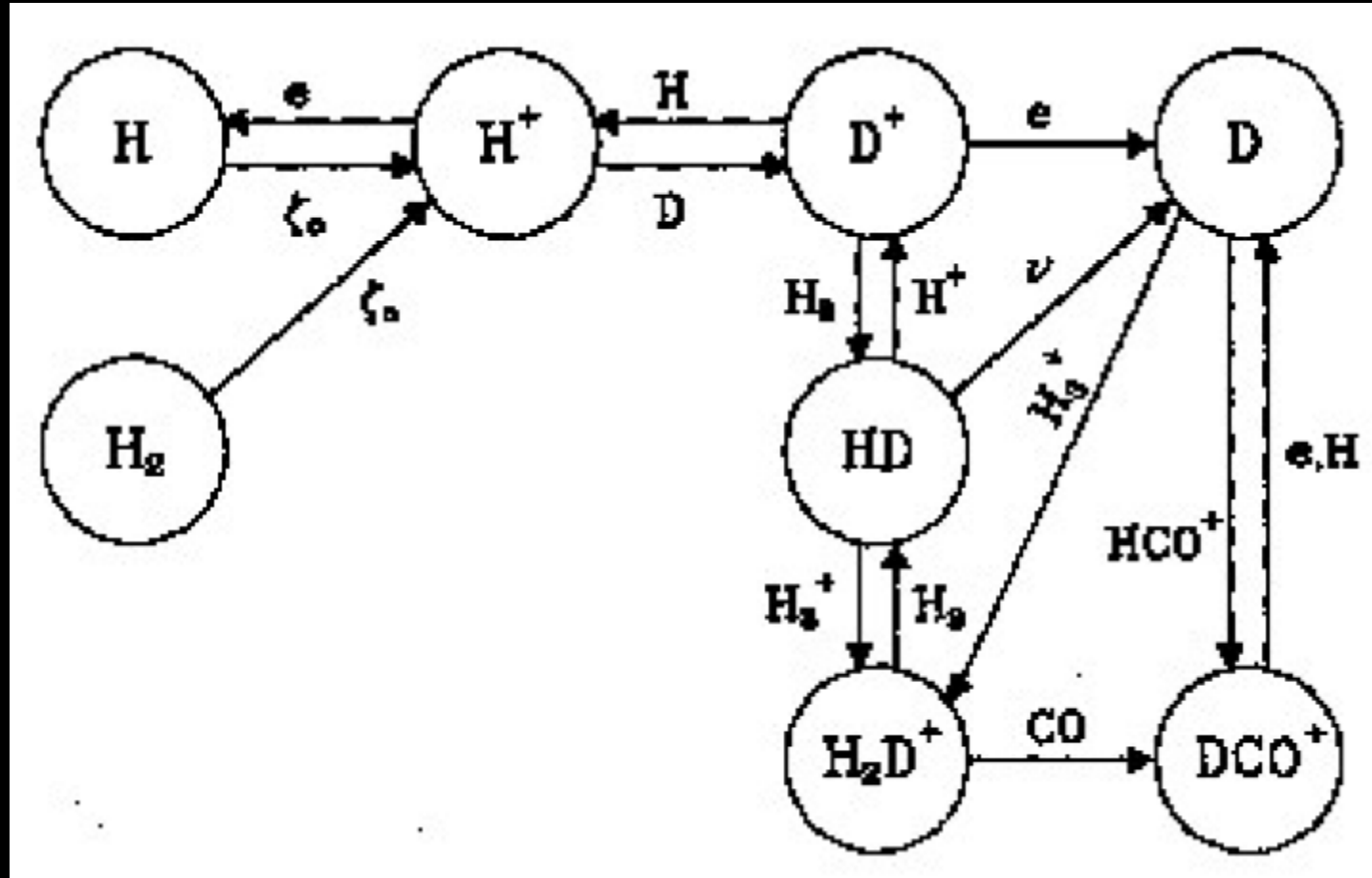
Deuterium chemistry

- HD formed mostly by rapid gas-phase reactions (not on grains), in contrast with H₂
 - $\text{H}^+ + \text{D} \leftrightarrow \text{H} + \text{D}^+$
 - $\text{D}^+ + \text{H}_2 \rightarrow \text{HD} + \text{H}^+$
- HD more rapidly destroyed by photodissociation than H₂, because column densities too small for self-shielding

=> Both formation and destruction up 10⁵–10⁶ times faster;

Result: overall HD/H₂ ~ 10⁻⁶–10⁻⁵ vs [D]/[H] = 1.5 x 10⁻⁵

Deuterium chemistry



4.4 Steady-state models

- Because photorates change with depth into cloud, models of diffuse clouds need to be depth-dependent.
- Most reaction are fast (except H_2 formation) $\Rightarrow$ steady-state usually a good assumption: $dn_i/dt = 0$

density

$$n_i(z) = \frac{\text{formation rate}}{\text{destruction rate}} \quad \text{cm}^{-3}$$

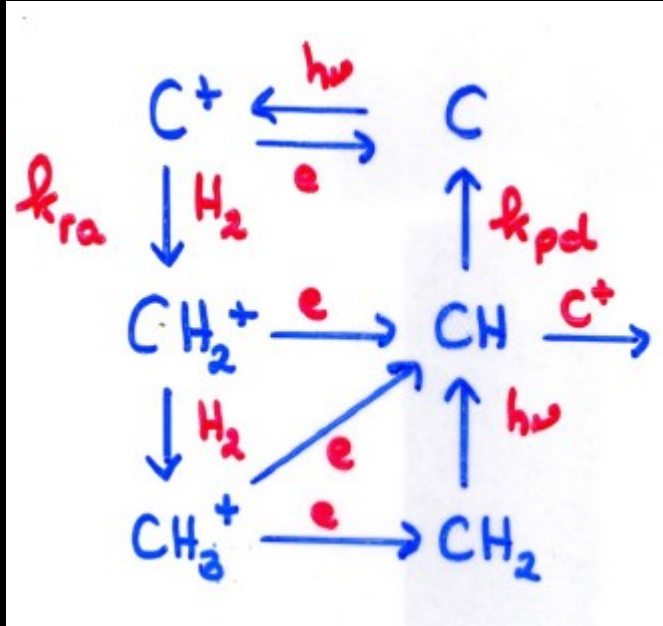
Column density

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

Parameters

- Geometry: plane parallel
- Elemental abundances: C, O, N, S, Fe, Mg,
 - Often constrained by observations
- Density structure: $n_{\text{H}}(z)$
 - Constrained by observations
- Temperature structure: $T(z)$
 - Constrained by observations or by solving thermal balance
- Incident radiation field: I_{UV} x standard field, plus grain absorption + scattering parameters
 - Constrained by observations
 - $I_{\text{UV}} = I_0 10^{-0.4A_{\text{V}}}$ (definition of A_{V})
 - $I_{\text{UV}}(\lambda) = I_0 \exp(-\tau_{\text{d}}(\lambda)) \quad \tau_{\text{d}}(\lambda) = n_{\text{d}} C_{\text{ext}}(\lambda) L$
- Cosmic ray ionization rate: $\zeta \text{ (s}^{-1}\text{)}$

Example: CH



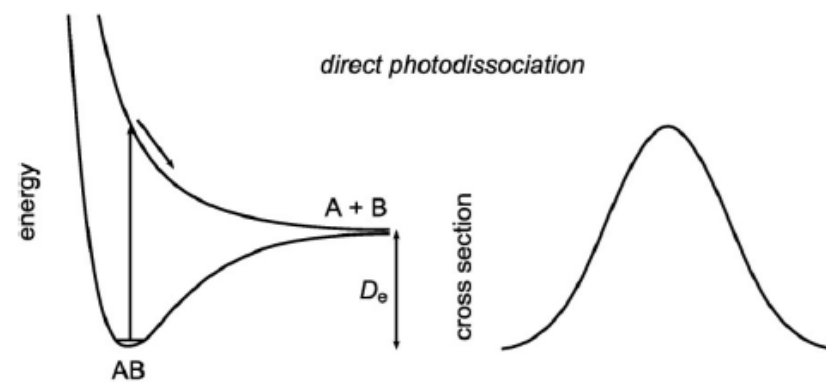
$$n(CH) \propto \frac{n(C^+)n(H_2)k_{ra}}{k_{pd}}$$

- All rates well known (within factor 2) $\Rightarrow$ possible to fit observed CH column densities
 - Cannot claim that all CH is formed by this scheme; up to 50% could result from other processes
- Test: can a consistent model be made that reproduces all observational data with same set of physical conditions and molecular parameters?

Comprehensive models

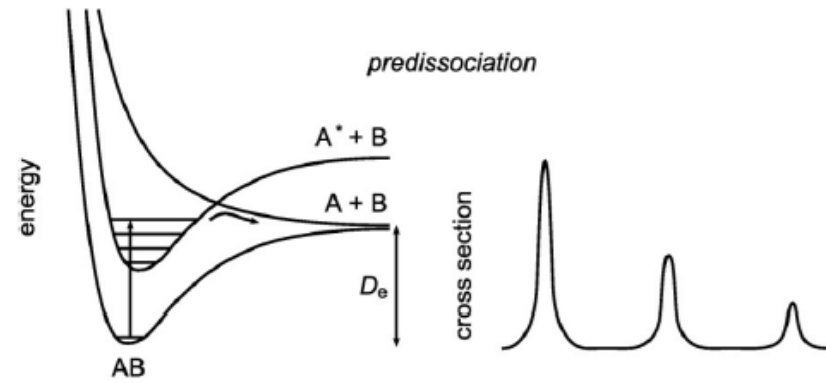
- Comprehensive models attempted by several groups, e.g., Black & Dalgarno (1977), van Dishoeck & Black (1986), Meudon group (Roueff et al.), UMIST (Millar et al.), ...
- Chemistry governed by $\text{H} \rightarrow \text{H}_2$ and $\text{C}^+ \rightarrow \text{C} \rightarrow \text{CO}$ transitions
- Because of self-shielding, these transitions are sharp as functions of depth into cloud

Recall photodissociation Lecture 1



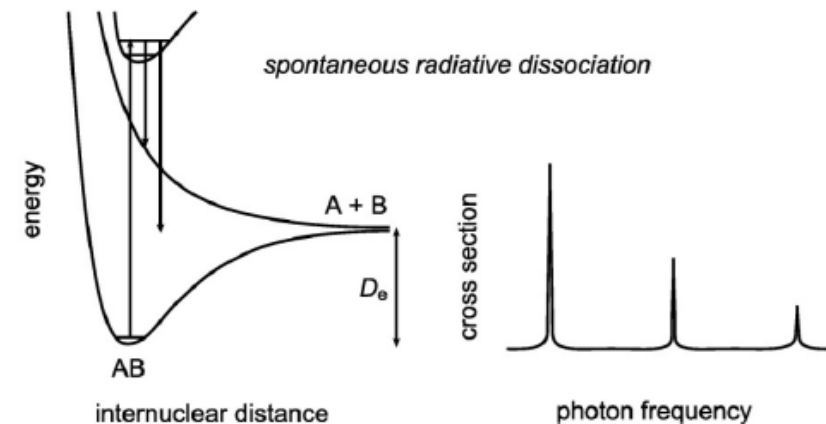
Direct p.d.

Ex: H_2^+ , OH, H_2O



Predissociation

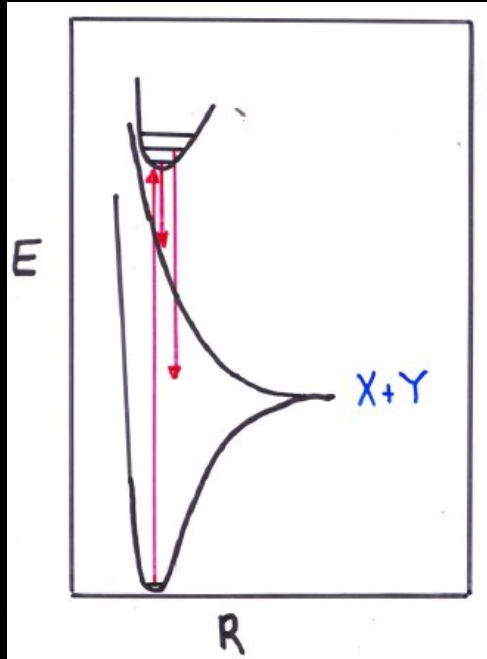
Ex: CO



**Spontaneous
radiative
dissociation**

Ex: H_2

Photodissociation: self-shielding

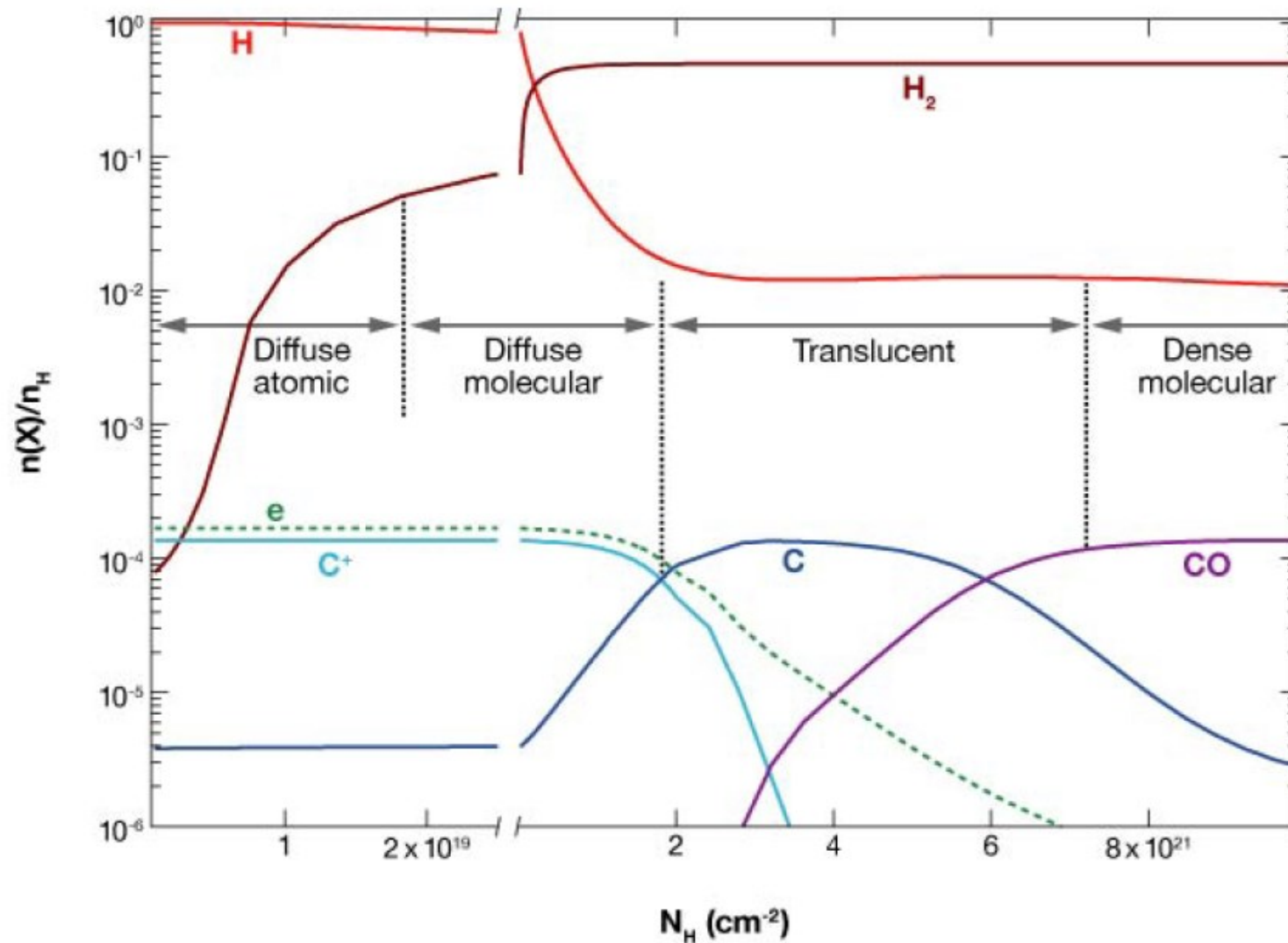


Spontaneous radiation dissociation

Ex: H₂

- Photodissociation of both H₂ and CO occurs by line absorption => lines can become optically thick => *self-shielding* inside clouds
 - Molecules lying at the edge of the cloud absorb all available photons at that wavelength, so that molecules lying deeper in the cloud are protected: *sharp* transition!

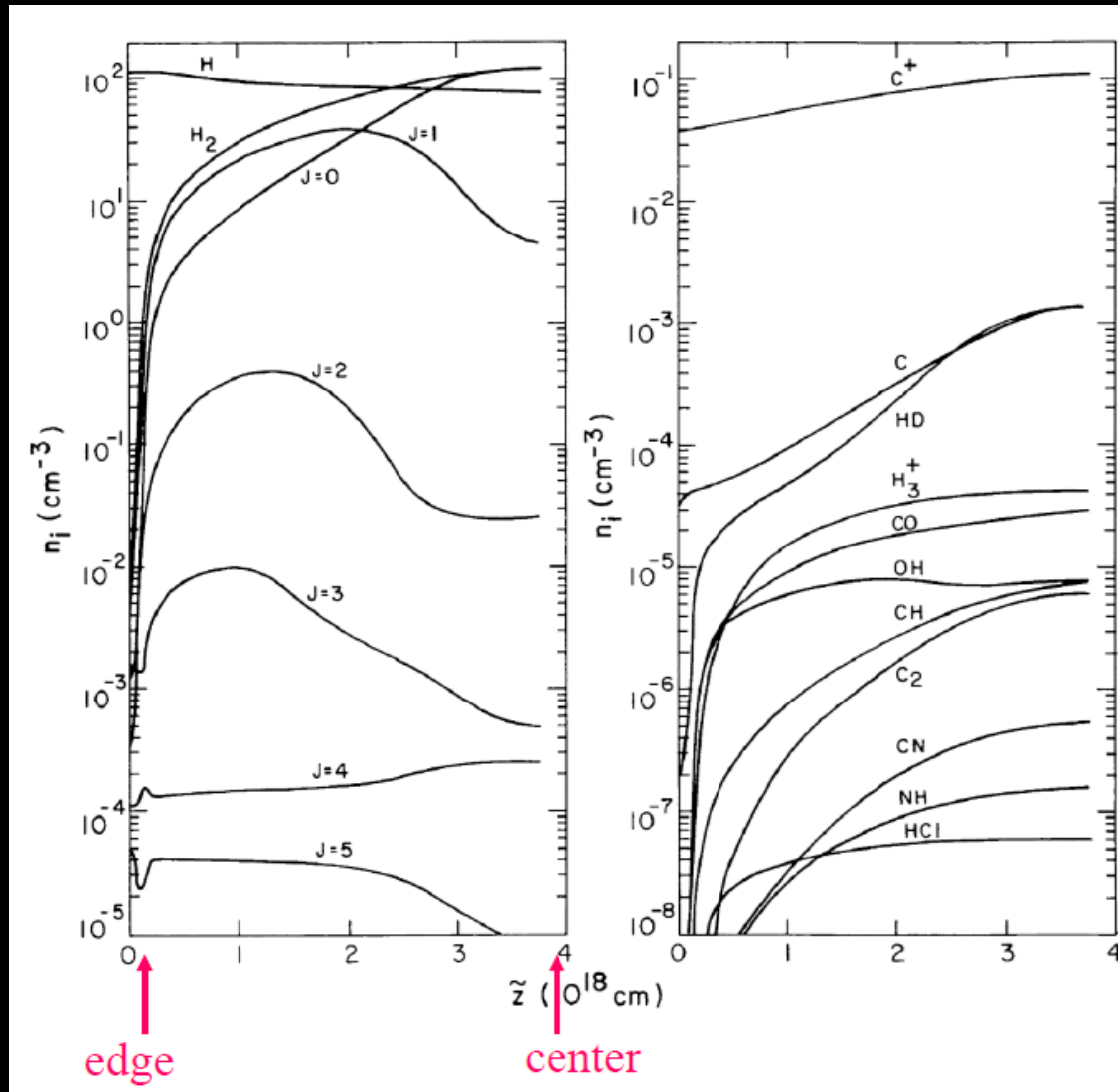
Types of molecular clouds



Snow TP, McCall BJ. 2006.

Annu. Rev. Astron. Astrophys. 44:367–414

Depth dependence of major species ζ Per cloud



Note: overall
density increases
slightly with depth

van Dishoeck &
Black (1986)

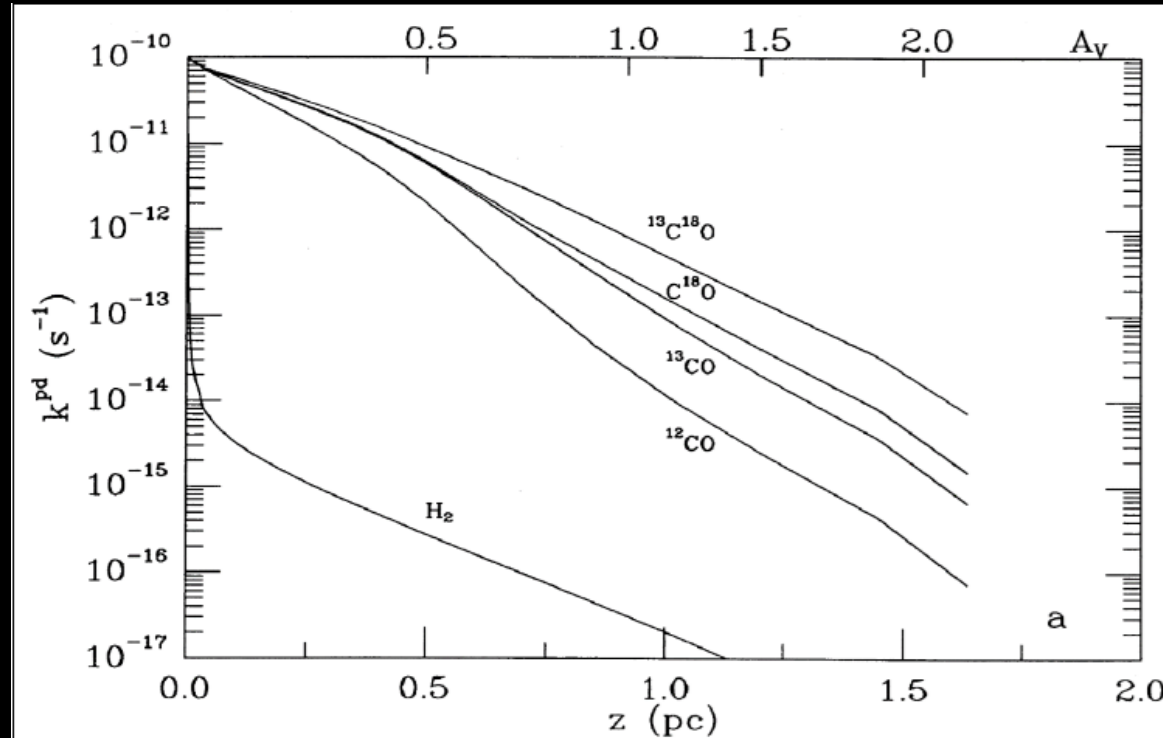
CO formation and destruction

- CO is most abundant molecule after H_2 and is easily observed through (sub-)mm lines
 - Good tracer of H_2
- At edge of cloud, most carbon is C^+
- Transition: $\text{C}^+ \rightarrow \text{C} \rightarrow \text{CO}$ with increasing depth
- CO is very stable ($D_e = 11.09 \text{ eV} \leftrightarrow 1118 \text{ \AA}$)
- $\Rightarrow$ can only be dissociated at $912 \text{ \AA} < \lambda < 1118 \text{ \AA}$

CO photodissociation

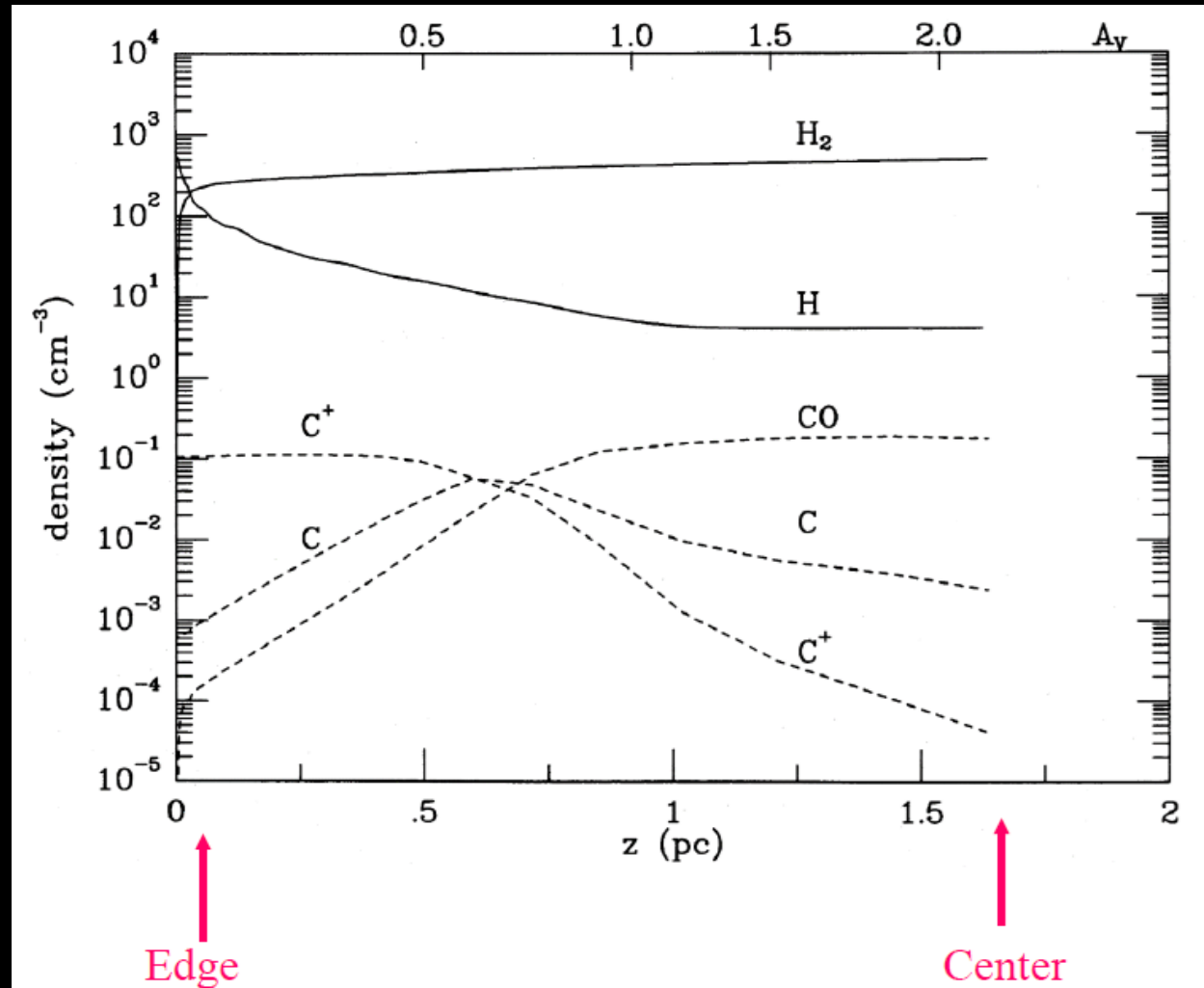
- Like H_2 , CO has no direct dissociation channels $\Rightarrow$ dissociation through line absorption (pre-dissociation) $\Rightarrow$
 - Self-shielding, but at greater depth than H_2 because of lower abundance
 - Mutual shielding of CO by H_2
 - Mutual shielding of ^{13}CO by ^{12}CO
 - Attenuation by dust
 - $\Rightarrow$ complicated UV radiative transfer!
- Note that H_2 and CO photodissociation and C photoionization all occur in the same λ range (912 – 1100 Å)
 - Important to know shape of UV radiation field at short λ
- At $A_V \approx 1\text{-}2$ mag, CO / H_2 increases from 10^{-7} to 10^{-4}

Self-shielding of CO and H₂ Photodissociation rates



- Decrease of CO p.d. rate with depth is less steep than that of H₂ because of larger competition with dust for UV photons
- CO self-shielding starts at $N(\text{CO}) \approx 10^{15} \text{ cm}^{-2}$

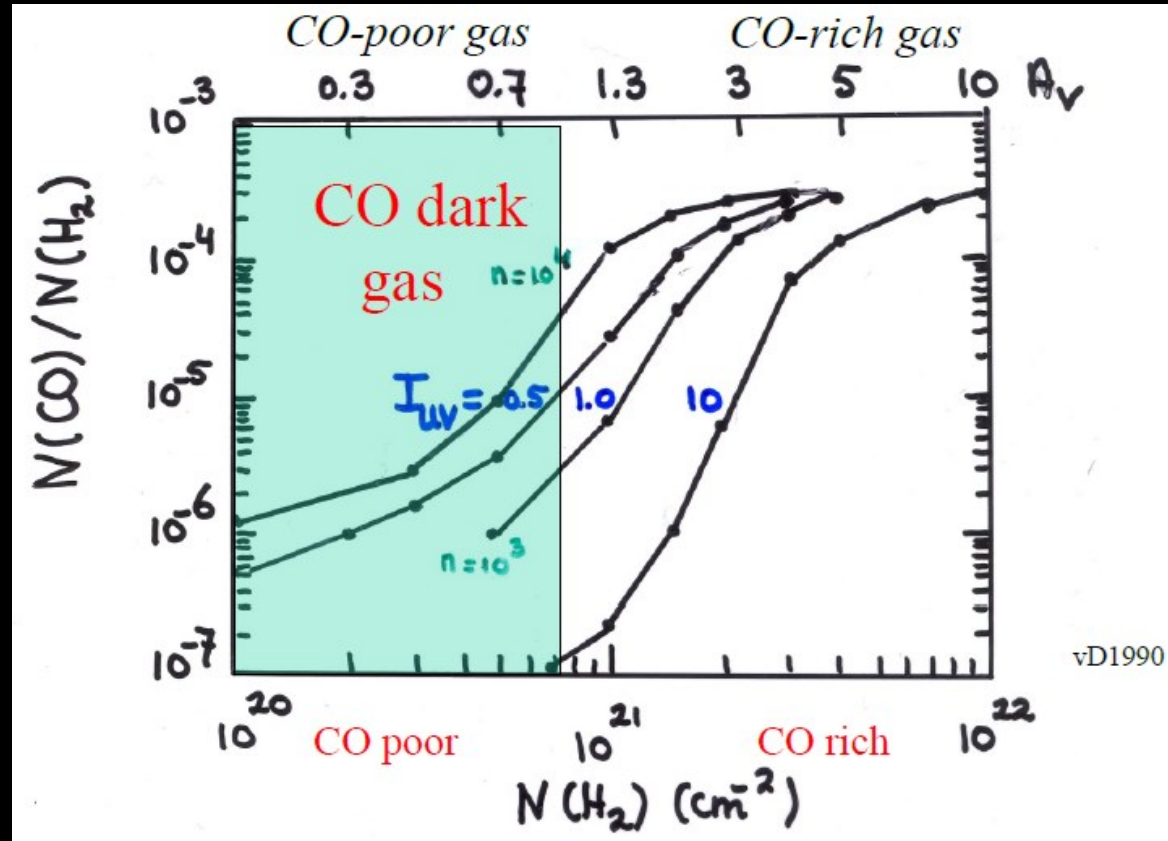
Densities of major species in translucent cloud



$T = 15 \text{ K}$
 $n_{\text{H}} = 1500 \text{ cm}^{-3}$
 $I_{\text{UV}} = 1$

- Only column densities are observed $\Rightarrow$ integrate over z

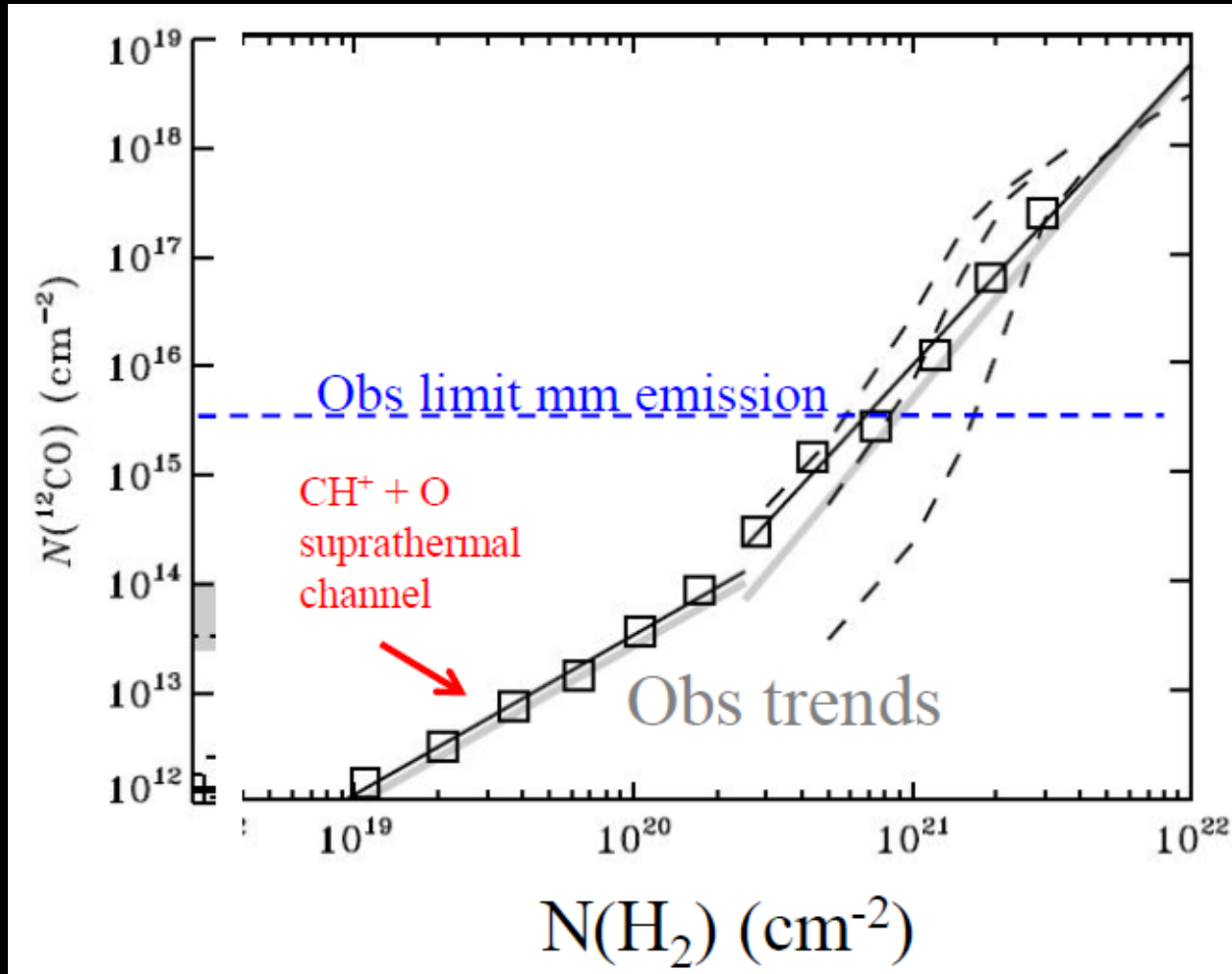
Column densities with N_H or A_V



→ Increase in CO/H₂ at $A_V = 1-2$ mag from 10^{-7} to 10^{-4}

- Exact location and sharpness transition depend on
 - I_{UV} , n_H , elemental abundances
 - Presence of PAHs, chemistry details (S), ζ , grain details, geometry,...

CO vs H₂ column density



Visser et al. 2009
Sheffer et al. 2008

- At low A_V , formation of CH⁺ through superthermal chemistry of C⁺ + H₂ needs to be invoked to fit observations of CO in diffuse clouds.

Model successes

- Column densities of CH, C₂, C₃, CN, OH, HCl OK within a factor of 2
- Constraints on ζ and [D]/[H]
 - $\zeta = (7 \pm 3) \times 10^{-17} \text{ s}^{-1}$ (but see below H₃⁺, OH⁺)
 - $[\text{D}]/[\text{H}] \approx (1-2) \times 10^{-15}$

Model failures

- CH^+ too low by a factor of 100
- NH too low by a factor of 20
- Polyatomic molecules HCO^+ , HCN , CH_3 , ... too low by a factor of 100

Possible remedies

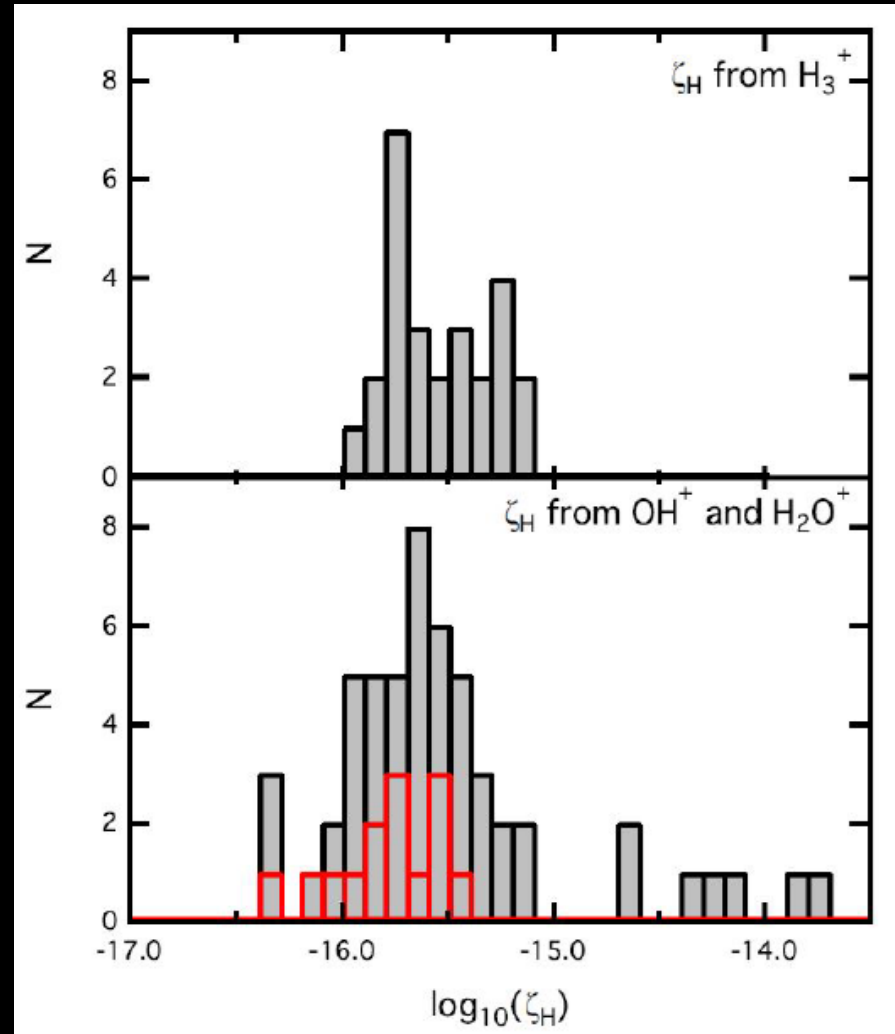
- Weak shocks or turbulence
 - CH^+ : see Lecture 5
 - HCO^+ , HCN , CO , CH_3 enhanced if CH^+ enhanced
- Surface chemistry
 - NH , CH_3 ?
- Cloud structure: clumpy, high H/H_2 , ...
 - CO
 - OH^+ , H_2O^+ , ArH^+

H_3^+ as a tracer of ζ

- Large column densities of $\sim 10^{14} \text{ cm}^{-2}$ found in several diffuse clouds (Galactic center, ζ Per, others)
 - $n(\text{H}_3^+) = (\zeta/k_{\text{DR}})n(\text{H}_2)/n(e)$
 - $N(\text{H}_3^+) = n(\text{H}_3^+)L$ L = path length
 - $n(e)/n(\text{H}_2) \approx N(e)/N(\text{H}_2) \approx N(\text{C}^+)/N(\text{H}_2) \approx 3.8 \times 10^{-4}$ **observed ζ Per**
 - $k_{\text{DR}} = 2.6 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ **from exp**
 - $N_{\text{H}} = 1.6 \times 10^{21} \text{ cm}^{-2}$, $\overset{\text{obs}}{\uparrow} \langle n_{\text{H}} \rangle = 250 \text{ cm}^{-3} \overset{\text{obs}}{\uparrow} \Rightarrow L = 2.1 \text{ pc}$
- **$\zeta = 1 \times 10^{-15} \text{ s}^{-1}$** , factor of 10-20 larger than ‘canonical value’
- Survey gives range of 10^{-16} – 10^{-15} s^{-1} for number of sources

McCall et al. 2003
Le Petit et al. 2004
Indriolo et al. 2007

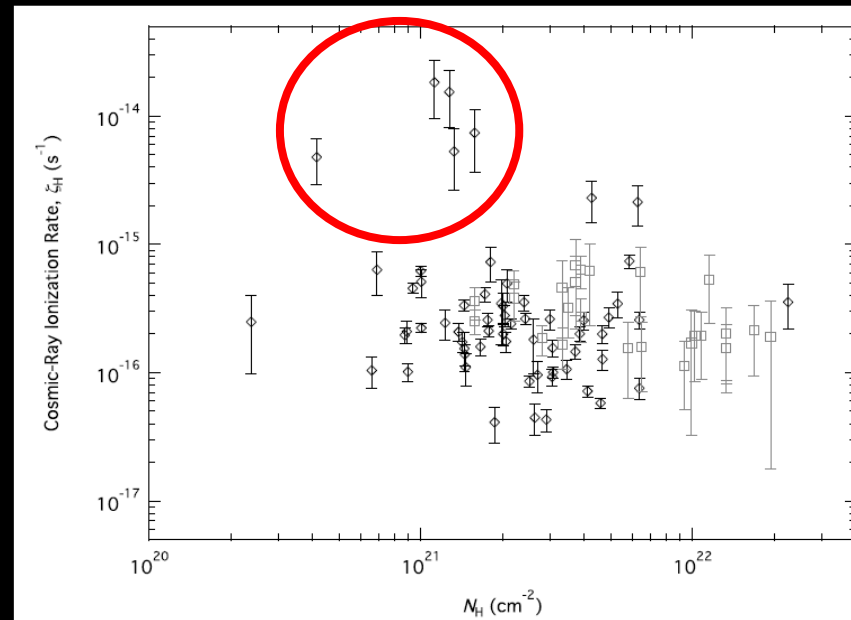
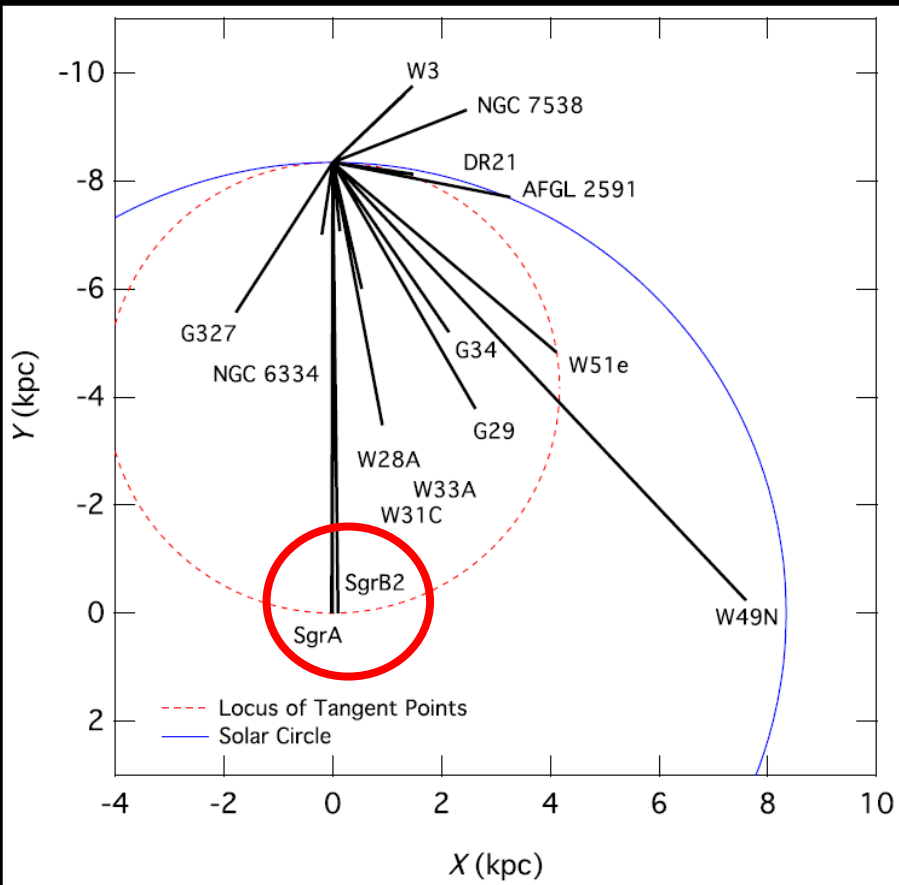
Cosmic ray ionization rate



Indriolo et al. 2015
Neufeld et al. 2017

- Use both H_3^+ and OH^+ , H_2O^+ as probes

Cosmic ray ionization rate



ξ_{CR} 1-2 orders of magnitude
larger toward the Galactic center
compared to the Galactic disk.

Indriolo et al. 2015
Neufeld et al. 2017

Photon dominated regions (PDRs)

- Diffuse and translucent clouds are examples of PDRs, i.e., clouds in which UV photons control the physical and chemical state of the cloud
- Traditionally, PDRs are dense molecular clouds located close to an OB star, in which the UV radiation field is enhanced by a factor of 10^5 w.r.t. average interstellar radiation field (ISRF)
 - Example: Orion Bar
- PDRs show very strong atomic fine-structure lines
 - E.g. [C II] 158 μm , [C I] 610 μm , [O I] 63 μm
- And submillimeter lines of molecules
 - E.g. CO 7-6, HCO⁺ 4-3
- And strong H₂ mid- and near-IR lines

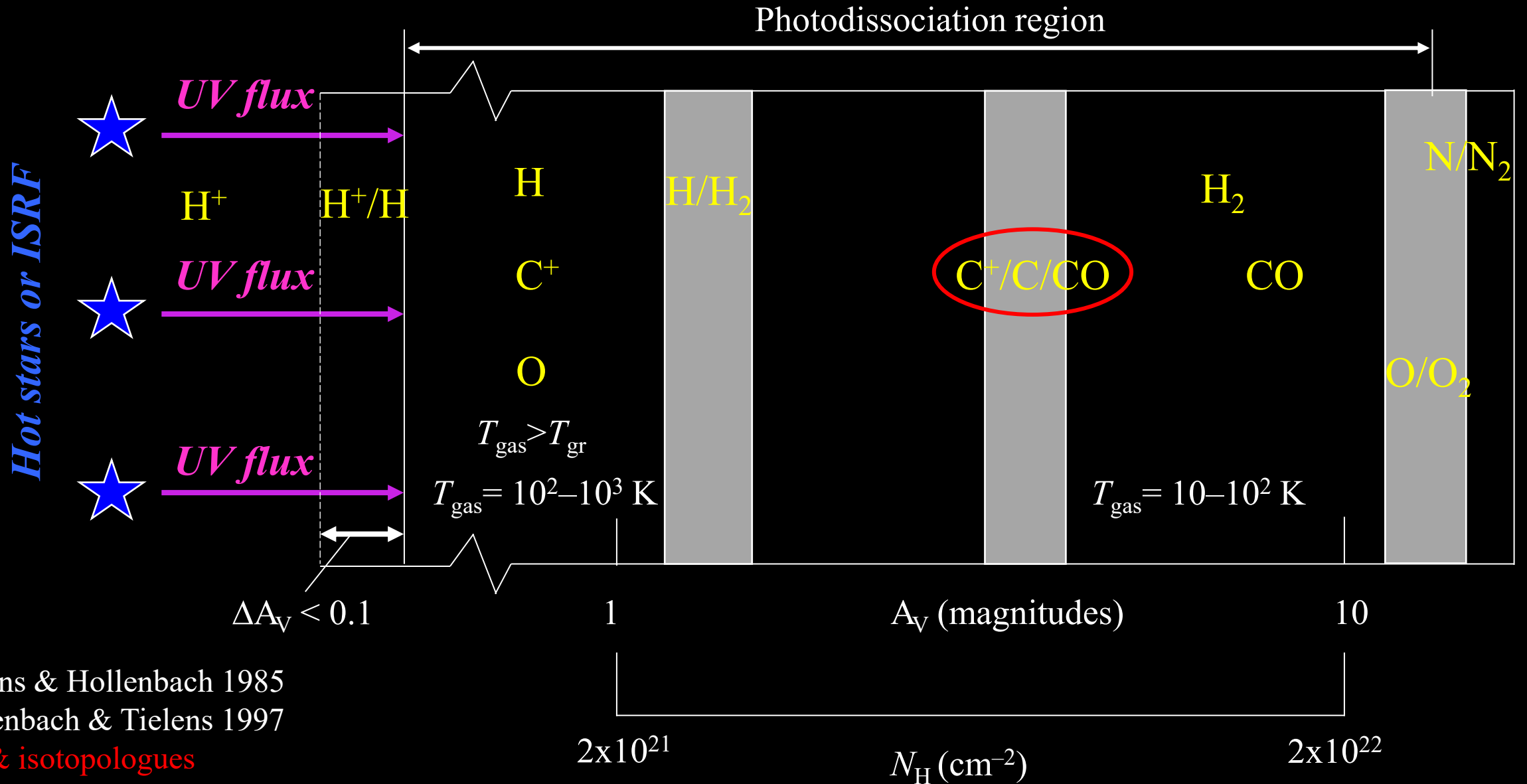
Tielens chapter 9

Tielens & Hollenbach 1997

Horsehead nebula as PDR



PDR structure



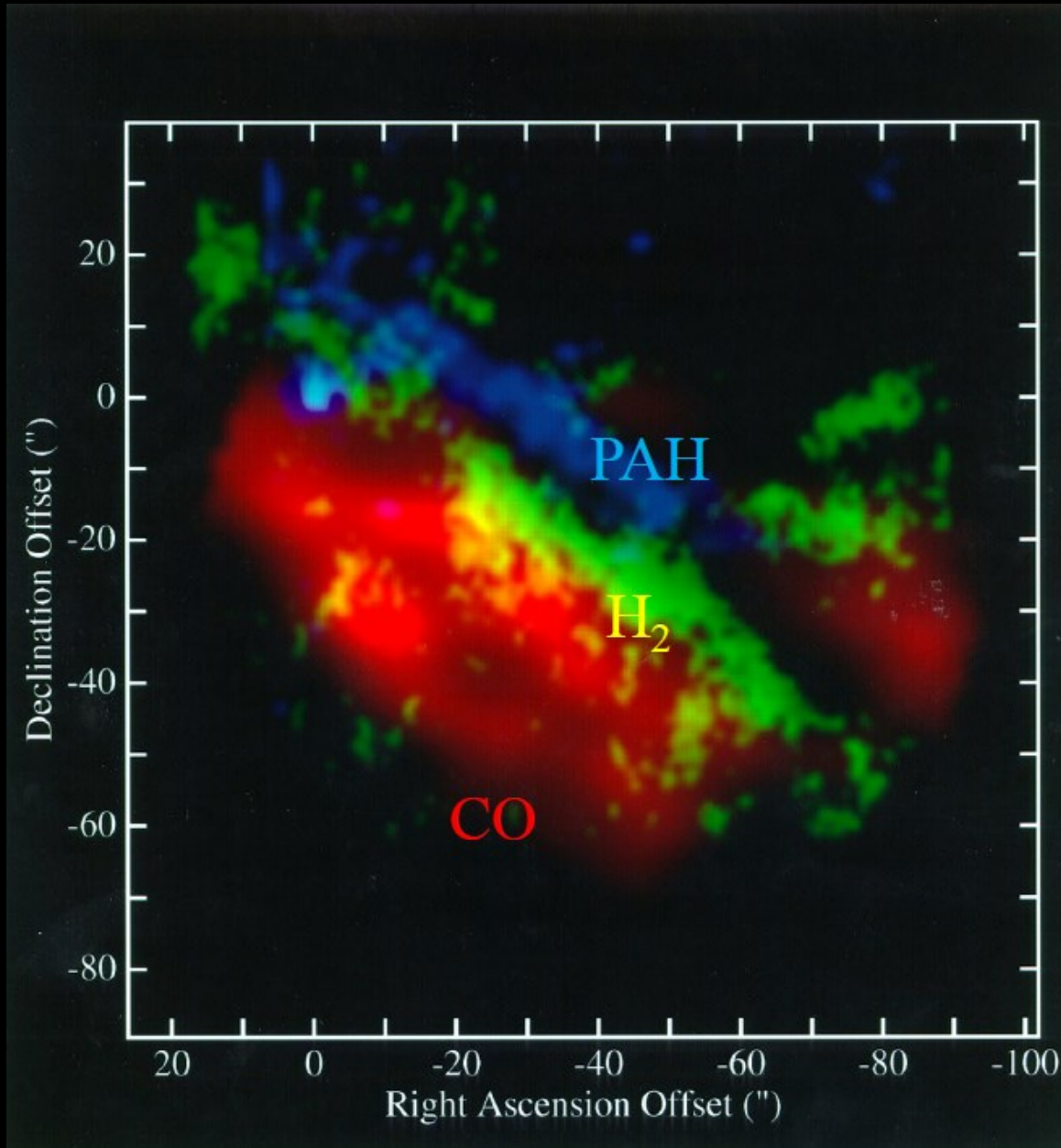
Tielens & Hollenbach 1985

Hollenbach & Tielens 1997

CO & isotopologues

Visser et al. 2009

Orion bar PDR



Yellow: H₂ $v = 1-0$

Blue: PAH

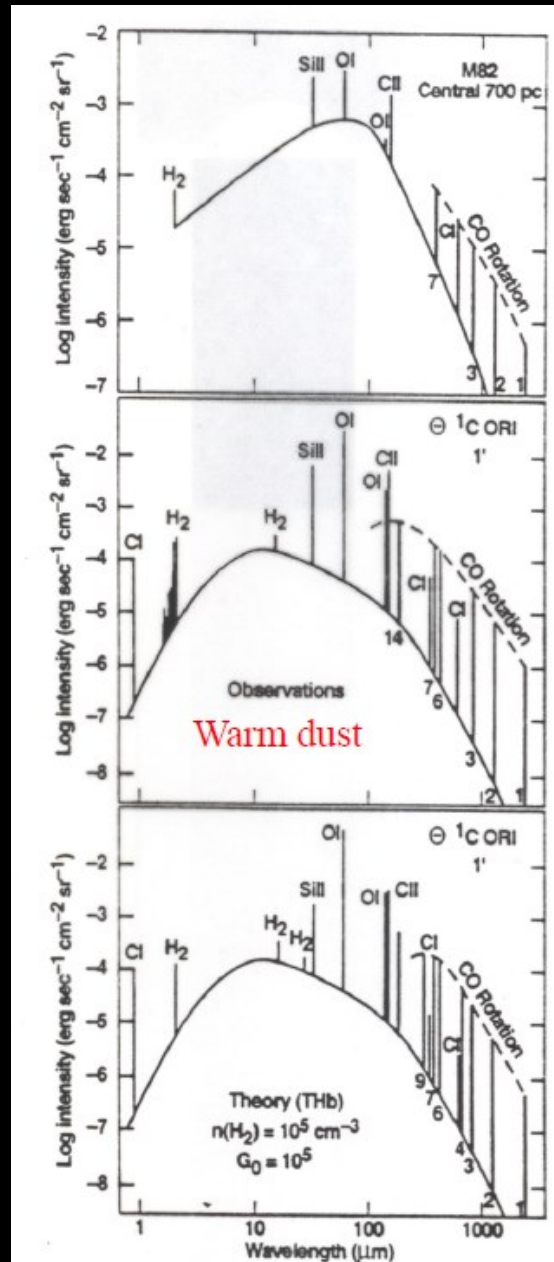
Red: CO

(0,0) = Θ^2 A Ori

Note layered structure!

Tielens et al. 1993

Global PDR emission



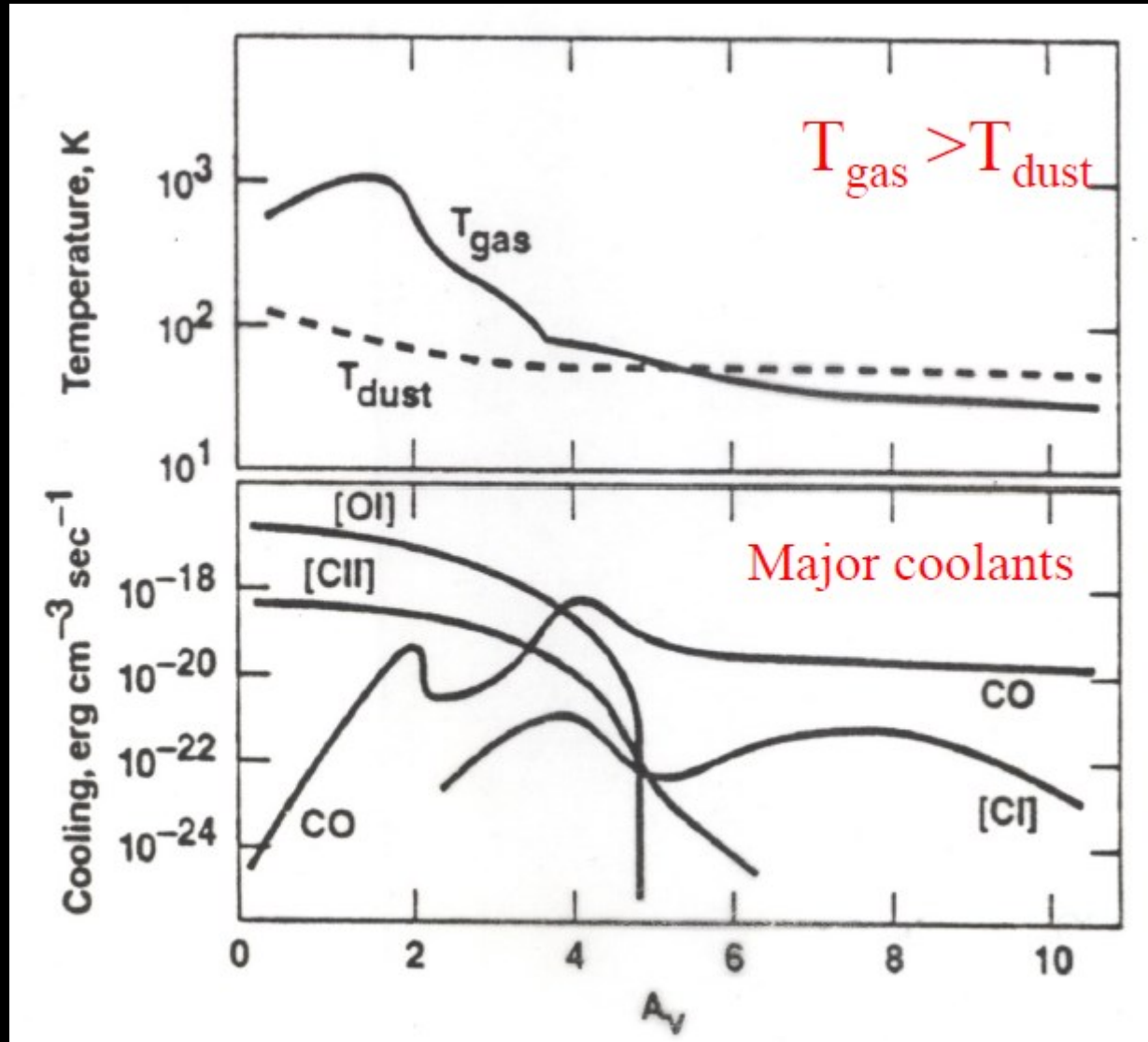
M82 galaxy

Orion

Dense PDR model

Genzel et al. 1989

Orion PDR physical structure



$$n_{\text{H}} = 10^5 \text{ cm}^{-3}$$

$$I_{\text{UV}} = 10^5$$

4.5 PDR chemistry

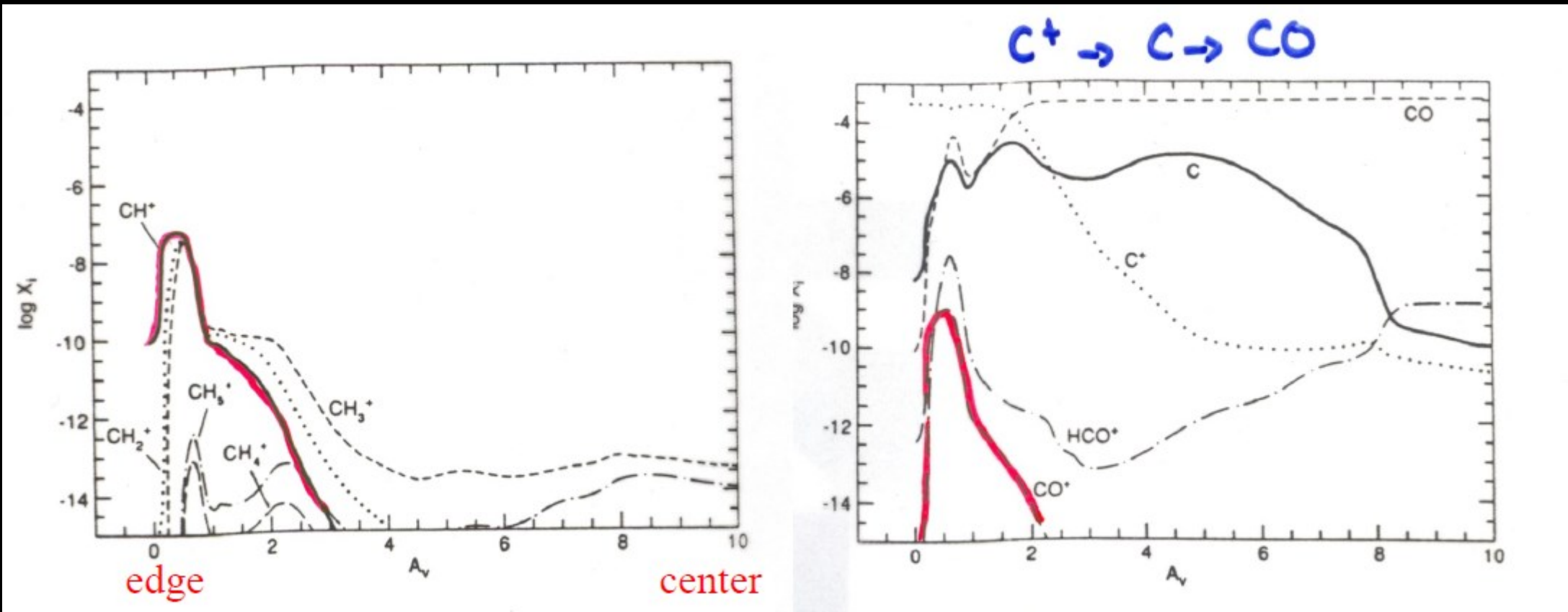
- General PDRs physics $\rightarrow$ Astrochem 2
 - Heating: photoelectric effect on grains
 - Cooling: [C II], [O I], CO
- Consider here chemistry
 - Orion Bar: $n_{\text{H}} = 10^6 \text{ cm}^{-3}$, $I_{\text{UV}} = 10^5$
- Main chemical characteristics linked to transition atomic $\rightarrow$ molecular form
 - $\text{H} \rightarrow \text{H}_2$
 - $\text{C}^+ \rightarrow \text{C} \rightarrow \text{CO}$
 - $\text{O} \rightarrow \text{O}_2$

Note: these conditions are also representative of surface layers of protoplanetary disks.

Orion

- **H $\rightarrow$ H₂ transition layer:** $A_V < 0.5$ mag
 - Because of high I_{UV} , $T > 1000$ K $\Rightarrow$ endoergic reactions
 - $O + H_2 \rightarrow OH + H$
 - $C^+ + H_2 \rightarrow CH^+ + H$
 - $N + H_2 \rightarrow NH + H$
 - $S + H_2 \rightarrow SH + H$
- Large abundance of OH leads to other species
- Note that CO^+ prominent in PDRs.

Orion PDR

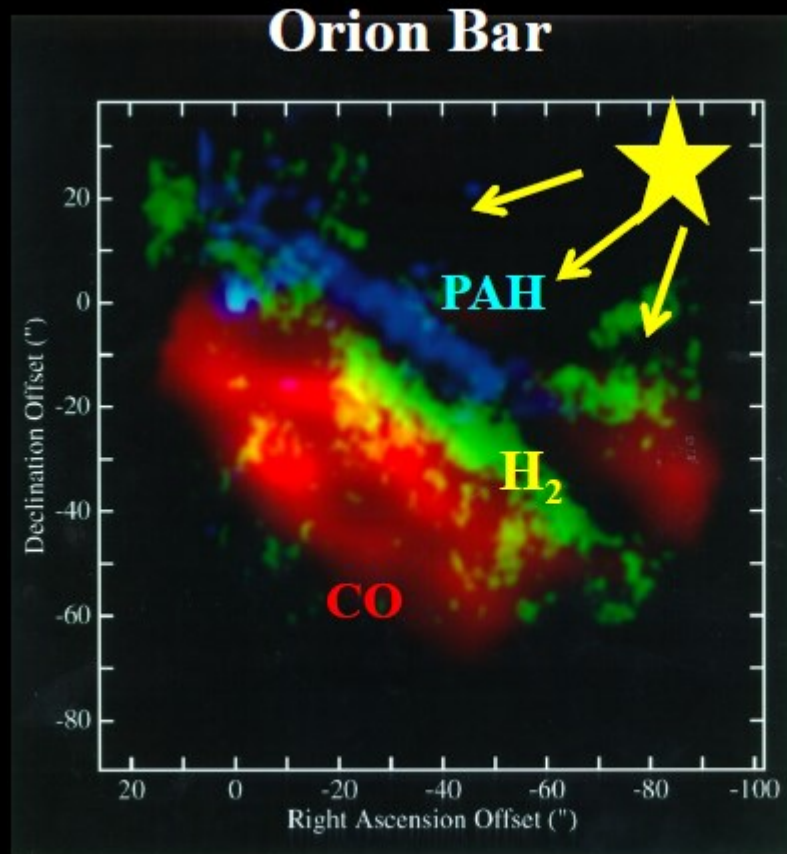


PDR tracers: CH^+ , CO^+

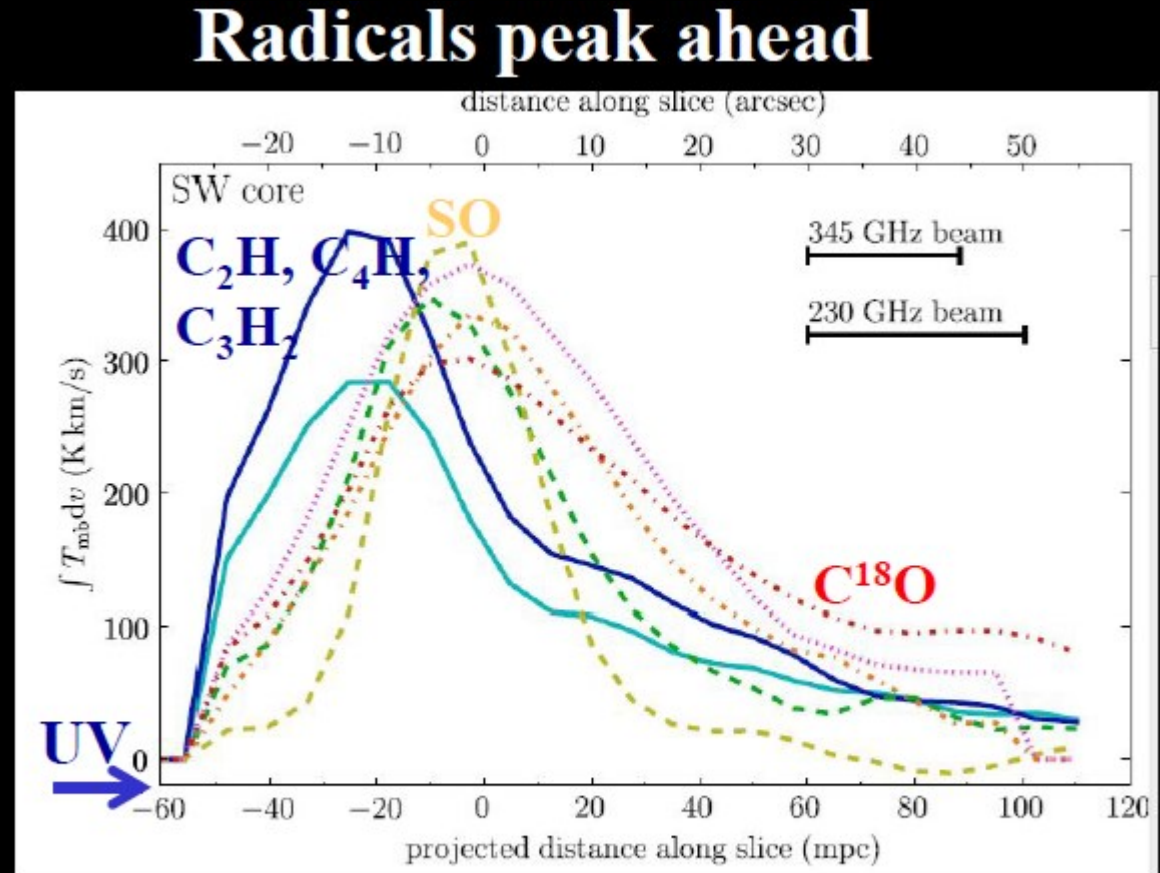
Orion PDR chemistry

- **C⁺, S⁺ zones:** $A_V = 0.7\text{-}1.7$ mag; $1.7\text{-}3.7$ mag
 - $T \sim \text{few hundred K} \Rightarrow$ form CH⁺ through C⁺ + H₂^{*} reaction
 - Ion-molecule reactions lead to CH, C₂H, CN, ...
 - $\text{C}^+ + \text{S} \rightarrow \text{C} + \text{S}^+$ maintains S⁺
- **Si⁺, S zones:** $A_V = 3.7\text{-}7$ mag
 - Charge transfer with Si⁺ maintains S⁺ and S
 - Reactions with O important; CS and SO formed
- **Dark cloud chemistry**

Layered PDR structure



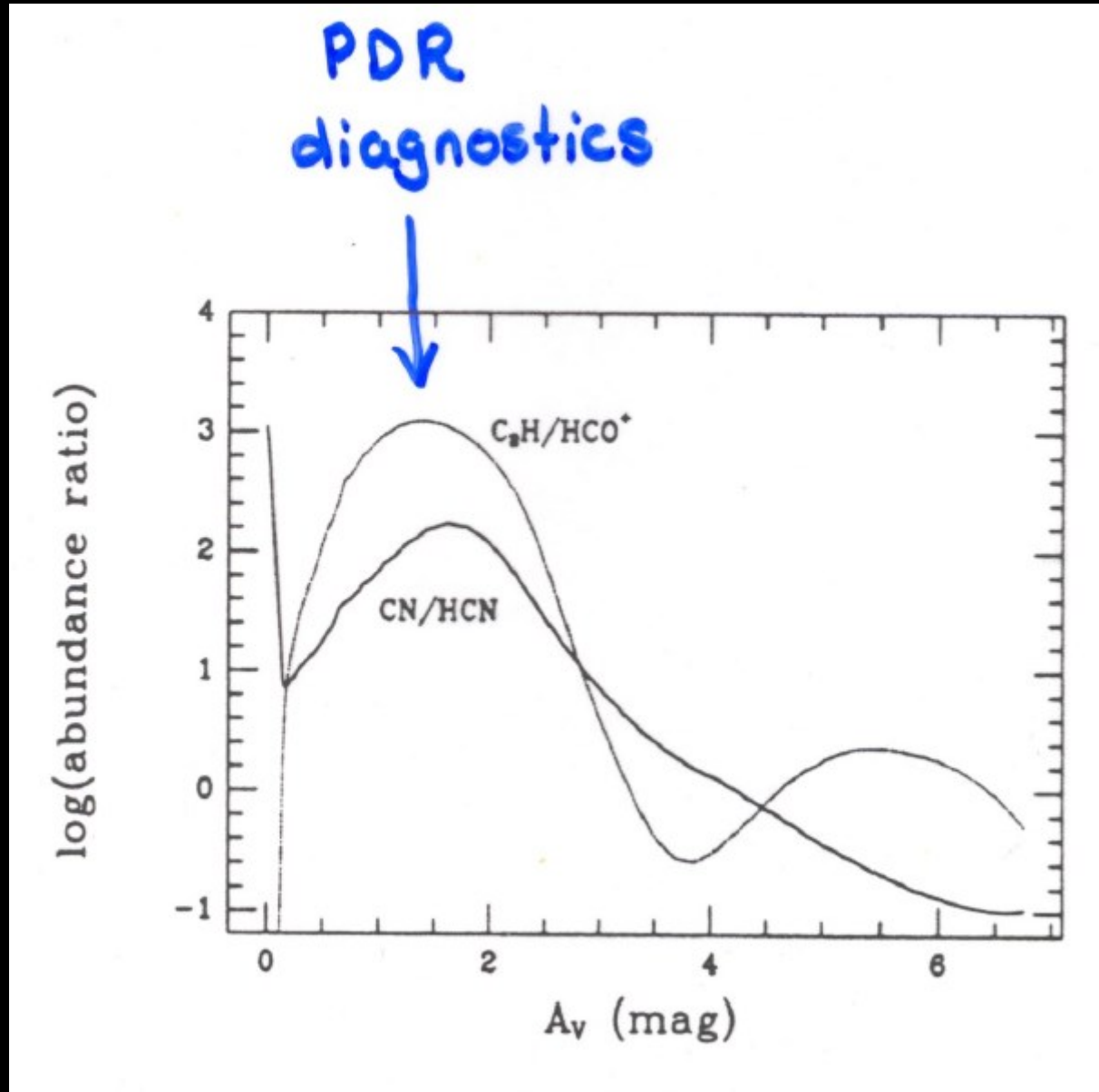
Tielens et al. 1993



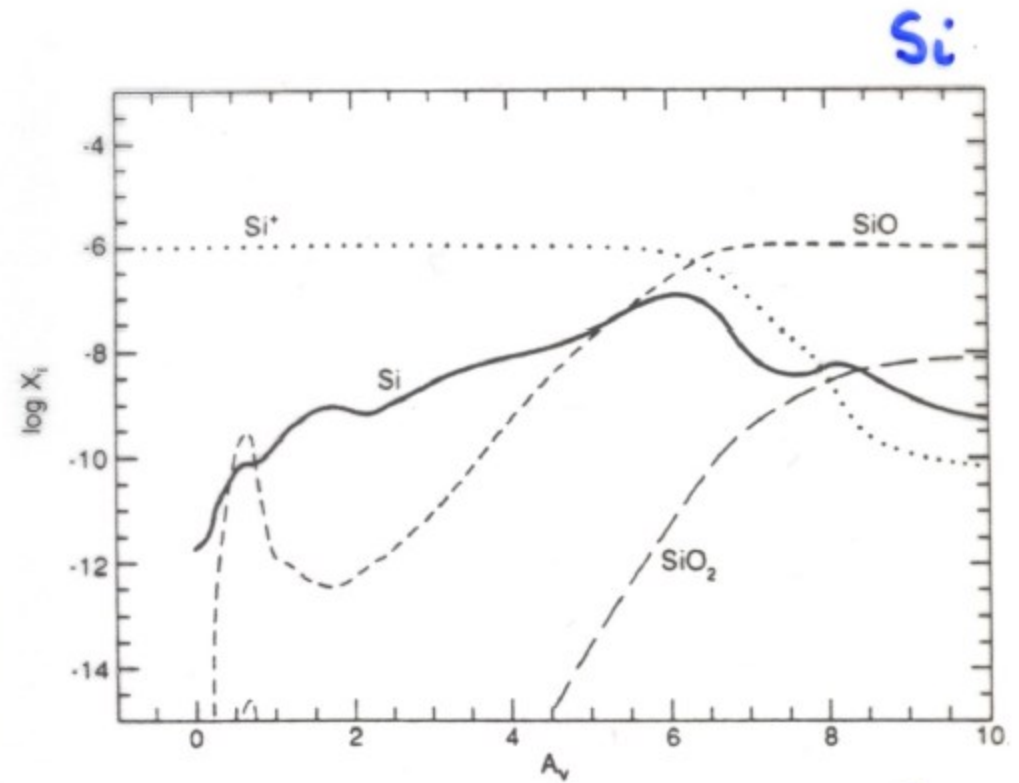
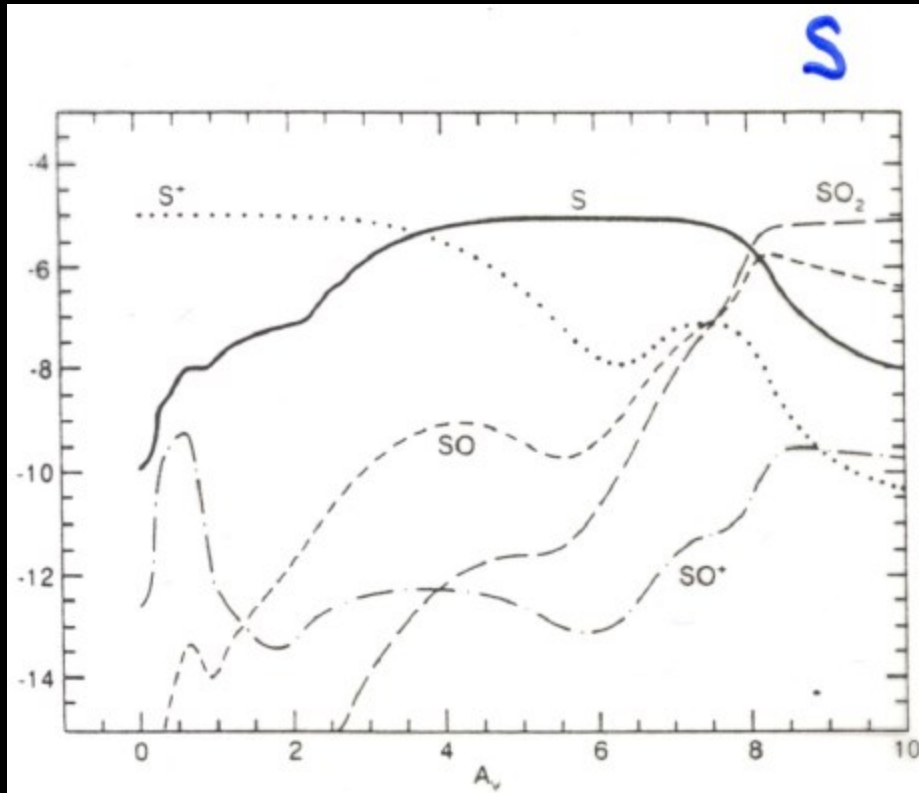
Hogerheijde et al. 1995, van der Wiel et al. 2009

- Radicals C_2H , CN peak at $\text{C}^+ \rightarrow \text{C}$ transition
- Stable HCN , CO peak deeper into cloud

PDR diagnostics: CN/HCN



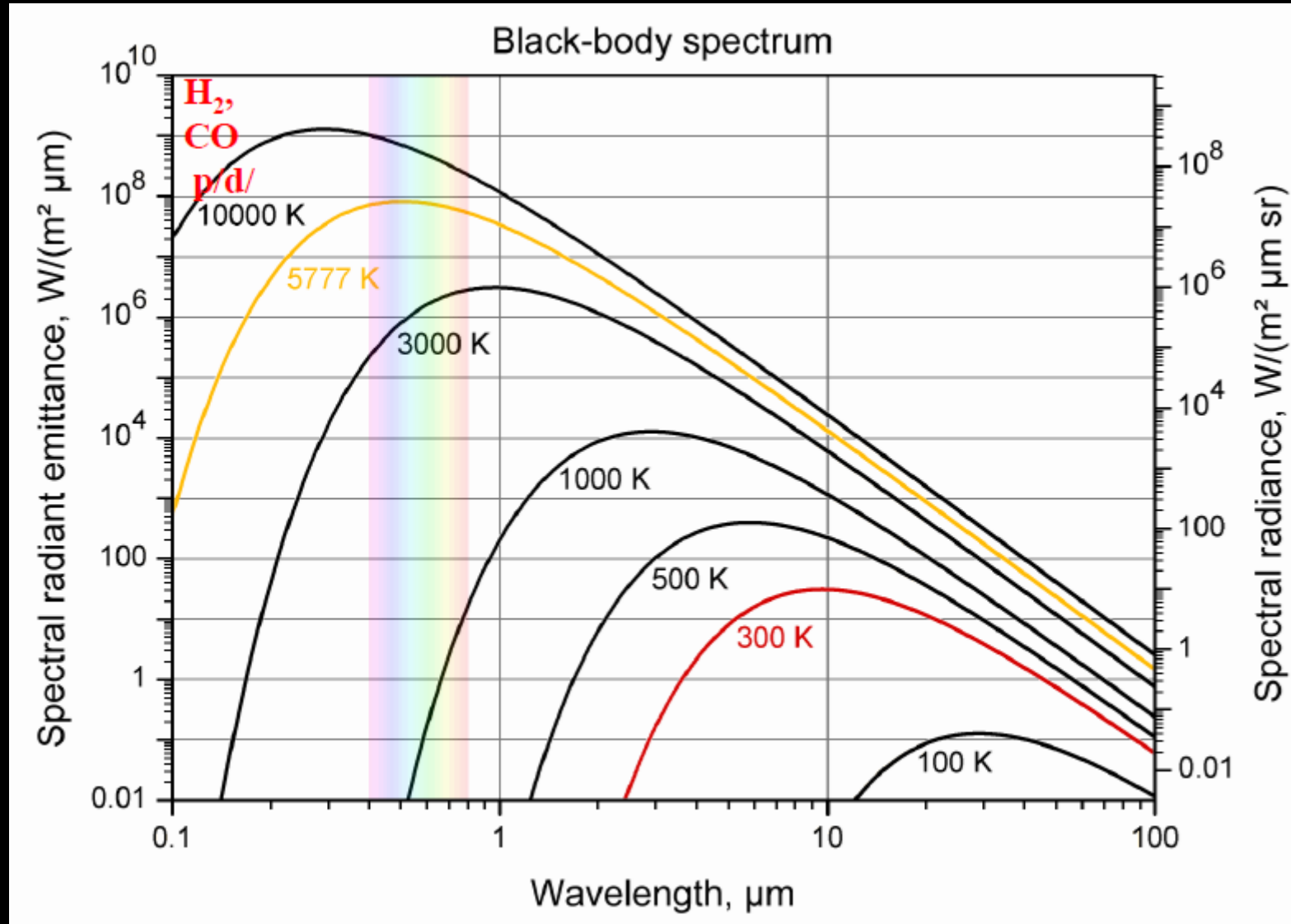
Orion chemistry



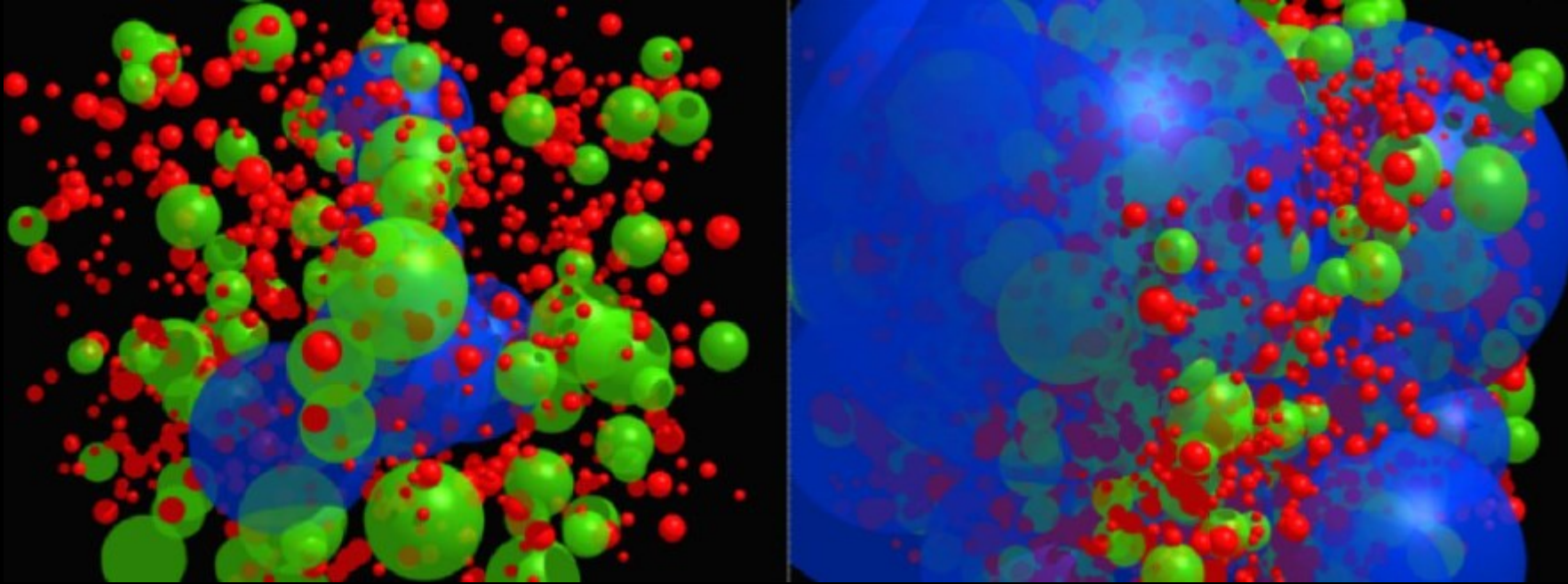
Beyond the standard model

- Cool PDRs
 - Clouds exposed to A, F, ... Stars with $T_{\text{eff}} = 6000\text{-}10000$ K => fewer photons between 11 and 13.6 eV to dissociate H_2 and CO
- Metal poor PDRs
 - Regions with C, O, ... depleted by factors > 4 . Large gas/dust ratios (ex: LMC, SMC)
- Inhomogeneous, clumpy PDRs
 - Regions with large density contrasts and small filling factors clumps
- Time-dependent PDRs
 - Regions with evolving radiation field (e.g., planetary nebulae) or flowing gas (e.g., expanding H II region)
- XDRs
 - Regions exposed to X-rays, which ionize H, He, and multiply ionized atoms (e.g., S^{2+}). Penetrate farther into cloud than UV

Cool radiation fields



Clumpy molecular clouds



Stutzki et al. 1998, Stutzki 2009

- **Do molecular clouds indeed have such a structure?**
- **Adds additional parameters to models**

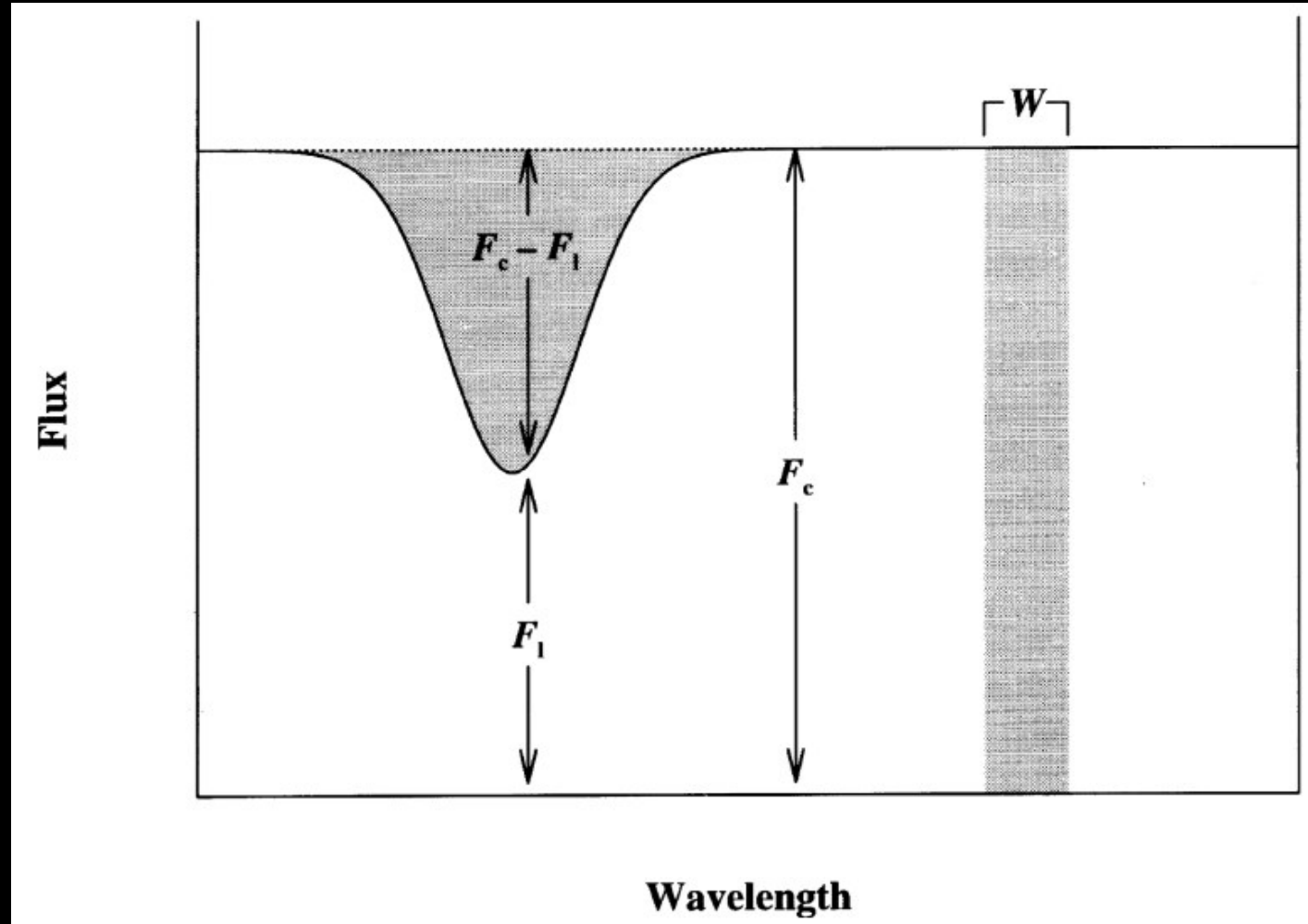
Summary Lecture 4

- Diffuse and translucent clouds are unique laboratories for testing gas-phase chemistry
- Data and insight from mm+FIR absorptions
 - Herschel, ALMA
- Several successes, but also some problems
 - Sometimes physics rather than chemistry not understood (e.g., turbulence)!
- Structure of diffuse and translucent clouds as well as dense PDRs controlled by $\text{H} \rightarrow \text{H}_2$, and $\text{C}^+ \rightarrow \text{C} \rightarrow \text{CO}$ transitions

Appendix: equivalent width of spectral lines

- In practice, resolution at optical wavelengths often insufficient to resolve line $\Rightarrow$ measure only line strength or equivalent width
- Definition of equivalent width of line:
- $$W_\nu = \int_{-\infty}^{+\infty} (1 - e^{-\tau_\nu}) d\nu = \int_{-\infty}^{+\infty} \left[\frac{I_\nu(0) - I_\nu}{I_\nu(0)} \right] d\nu \text{ [Hz]}$$
- W_ν is the width of a rectangular profile from 0 to $I_\nu(0)$ that has the same area as actual line
- W_ν measures line strength, but units are Hz
- In wavelength units: $W_\lambda = \frac{d\lambda}{d\nu} W_\nu = \frac{\lambda^2}{c} W_\nu \text{ [cm]}$

Schematic drawing of equivalent width of line



Column density: $N \propto W/f$ if line optically thin with f = oscillator strength