

Physics 224

The Interstellar Medium

Lecture #15

a brief note on proposal formatting

You should attempt to use the proposal template for the type of proposal you are submitting.

Your bibliography should include the following information for work thing you cite:

- Wolfire, M., Hollenbach, D., McKee, C. F., Tielens, A. G. G. M., Bakes, E. L. O. 1995, "The neutral atomic phases of the interstellar medium", *The Astrophysical Journal*, vol. 443, pages 152-168.

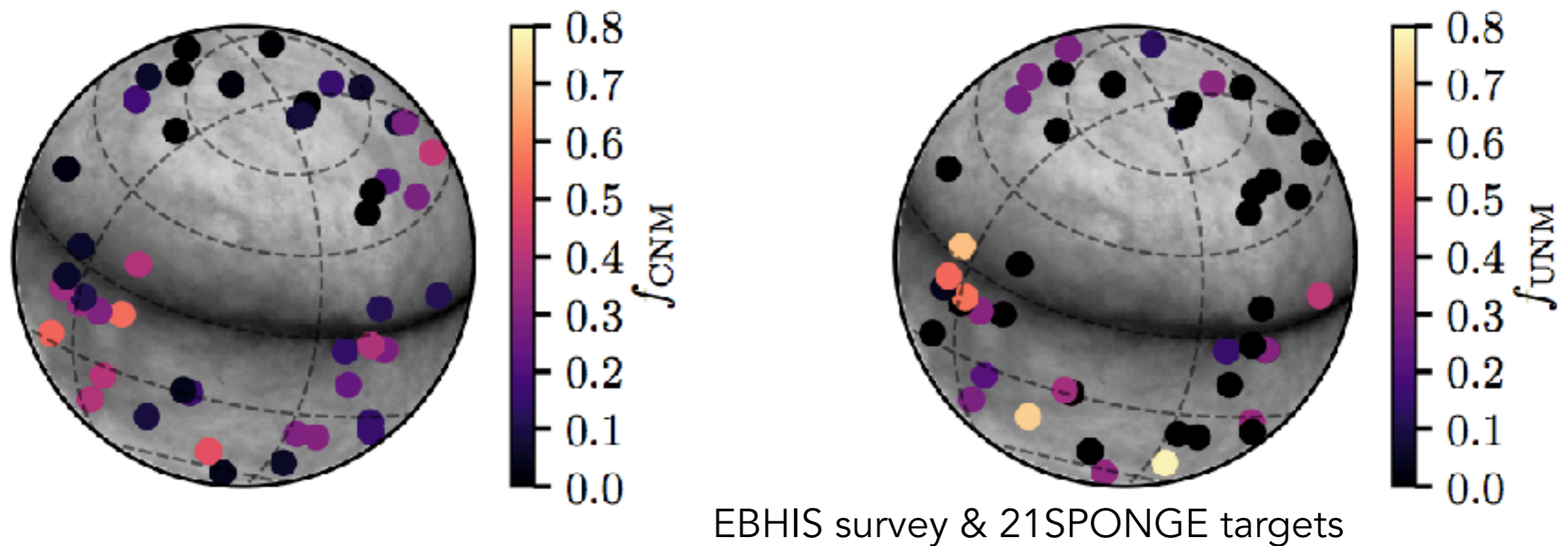
authors, year, title, journal, volume, pages

in latex, I recommend using natbib - good practice!

Observed HI Spin Temperature

Best recent constraints for the Milky Way:
28% CNM, 20% unstable, 52% WNM by mass

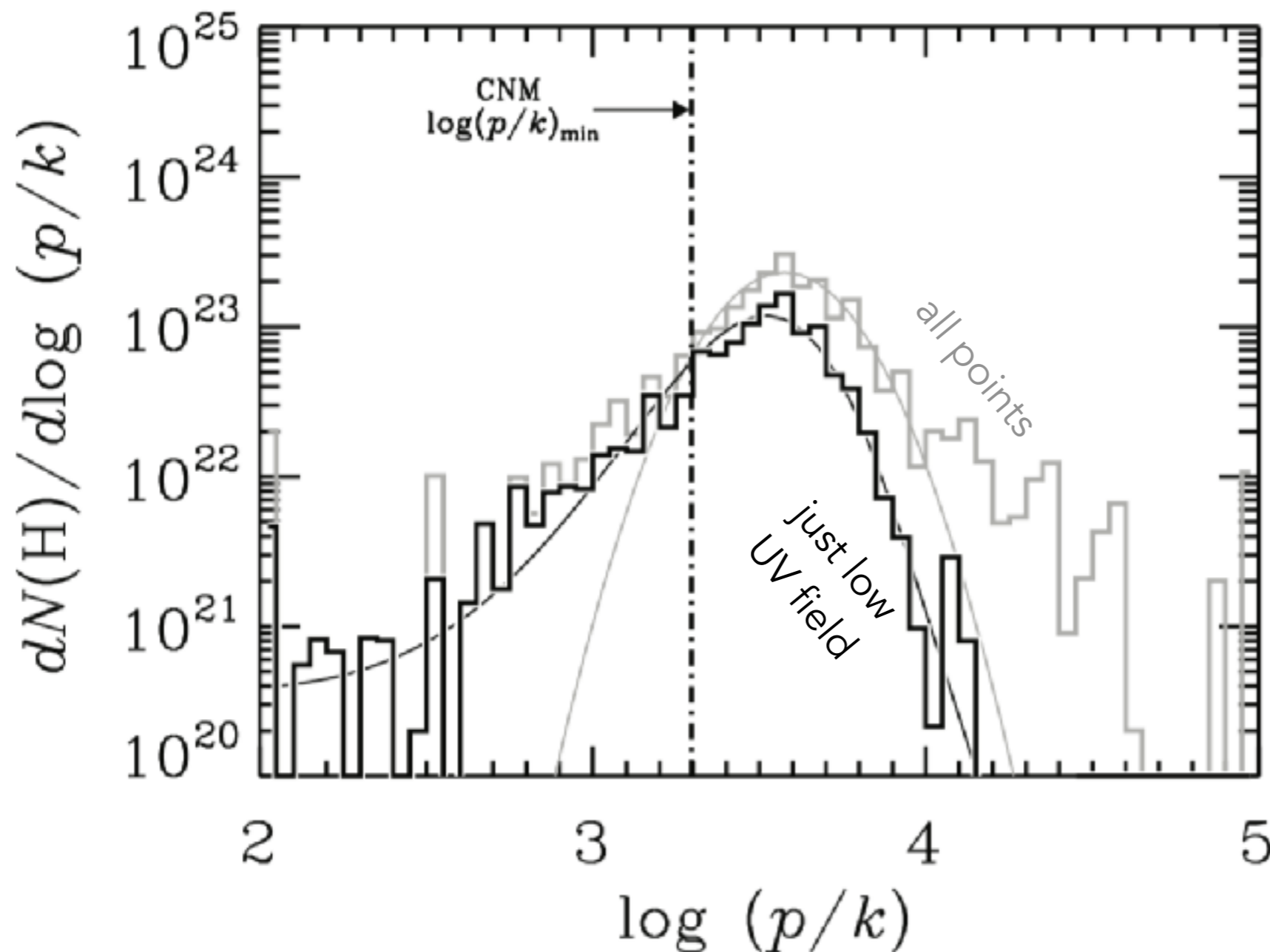
VLA 21SPONGE Survey - Murray et al. 2018



also: WNM is hotter than equilibrium models predict.

Thermal Pressure from [C I]

Jenkins & Tripp 2001, 2011

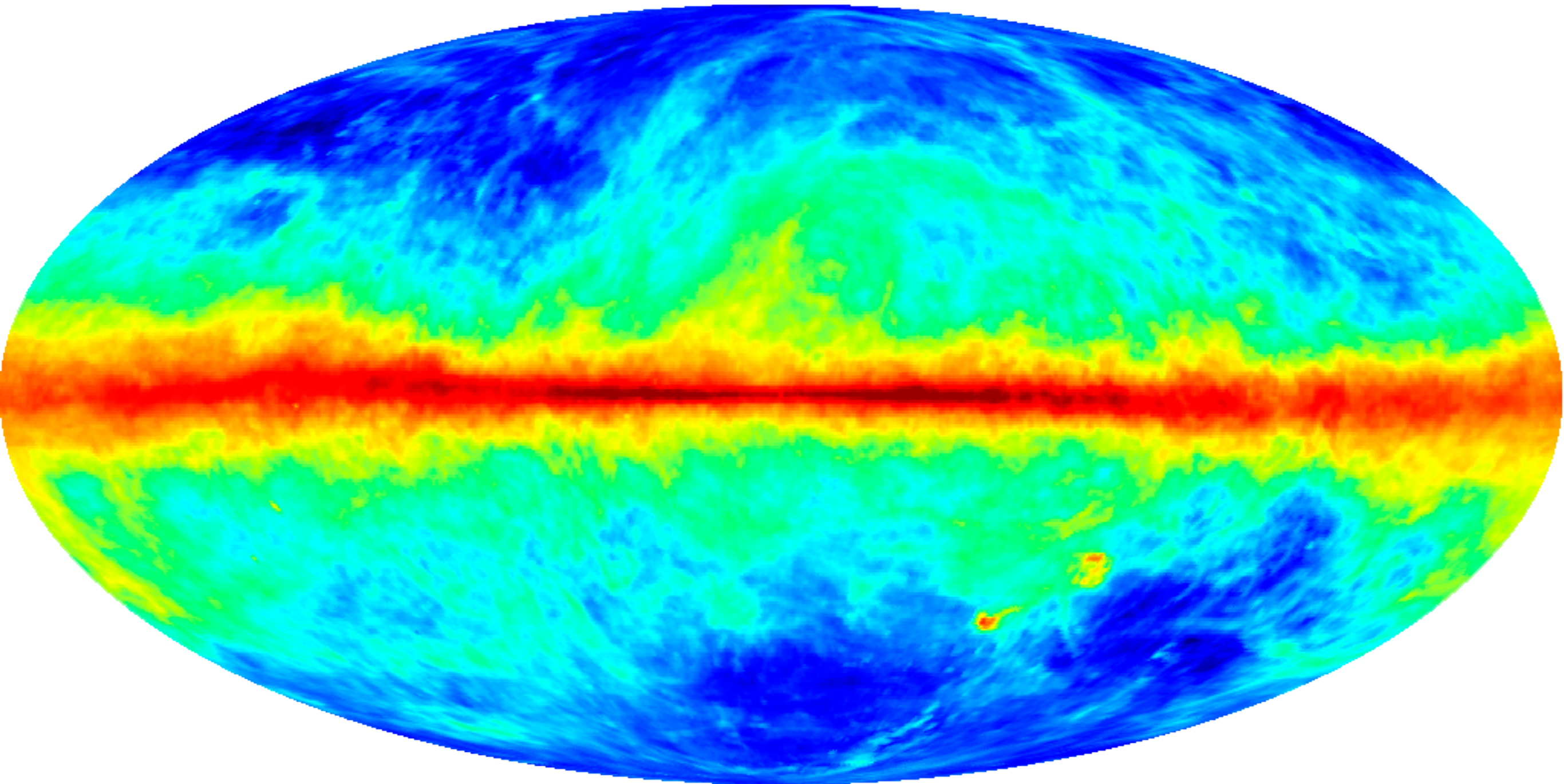


Most gas is at pressures that agree with the FGH picture, but there are tails of low & high pressure that are probably related to turbulence.

Is the FGH model a good
representation of the ISM?

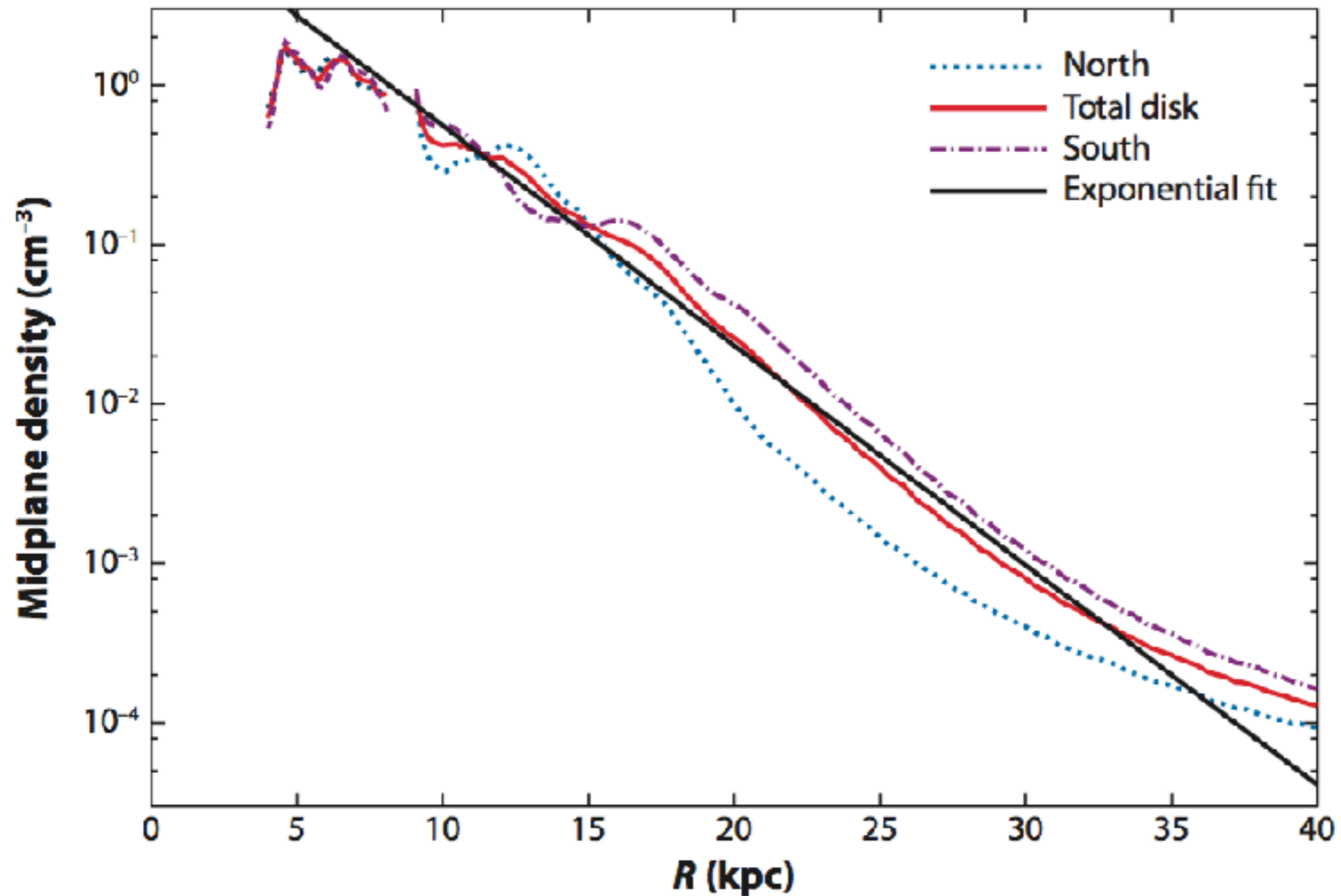
Maybe.

All-Sky Map of N(HI) from the
Leiden-Argentine-Bonn Survey (Kalberla et al. 2005)



Distribution of HI in the MW

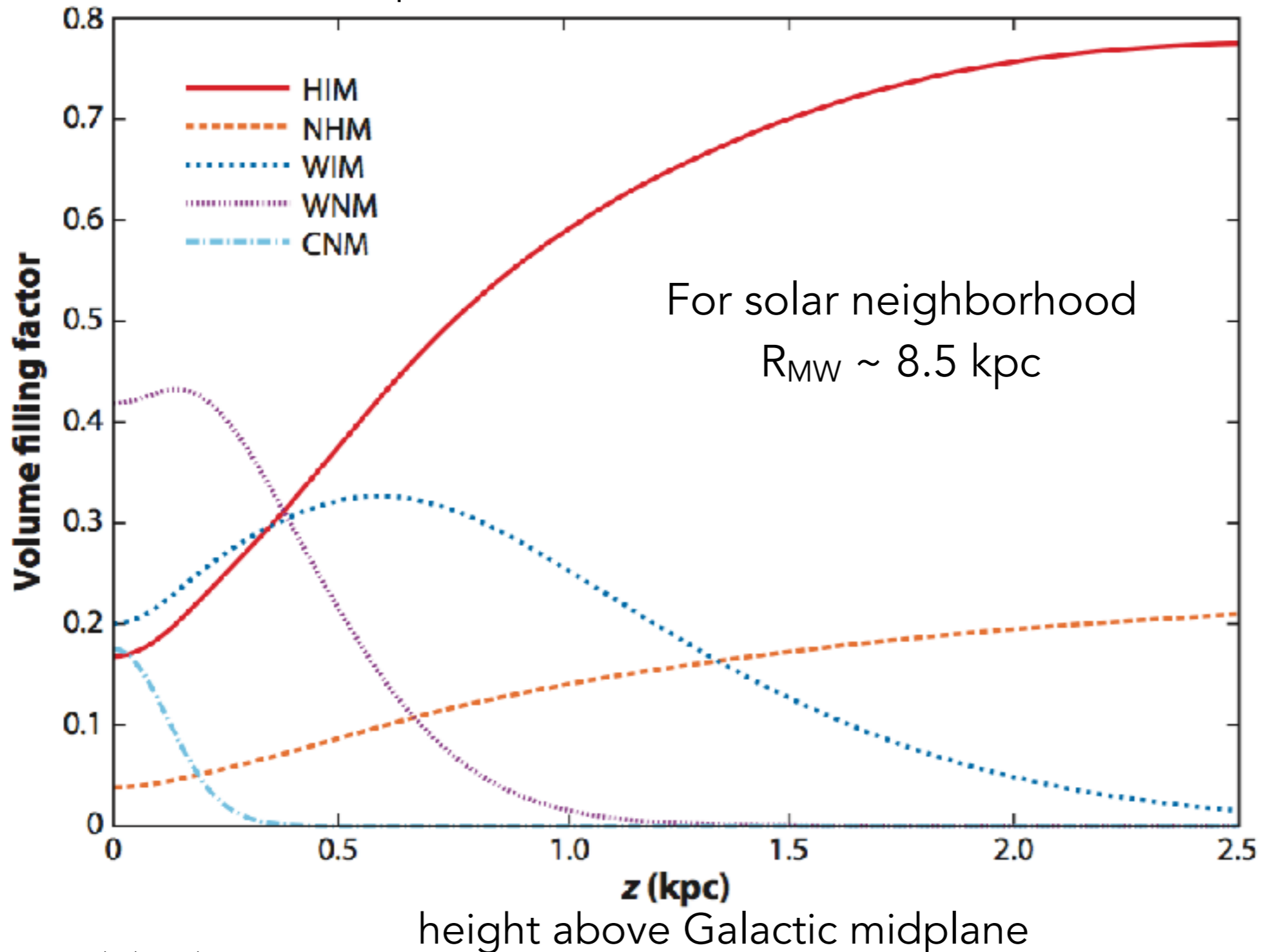
Kalberla & Kerp 2009, ARA&A



distance from Galactic center

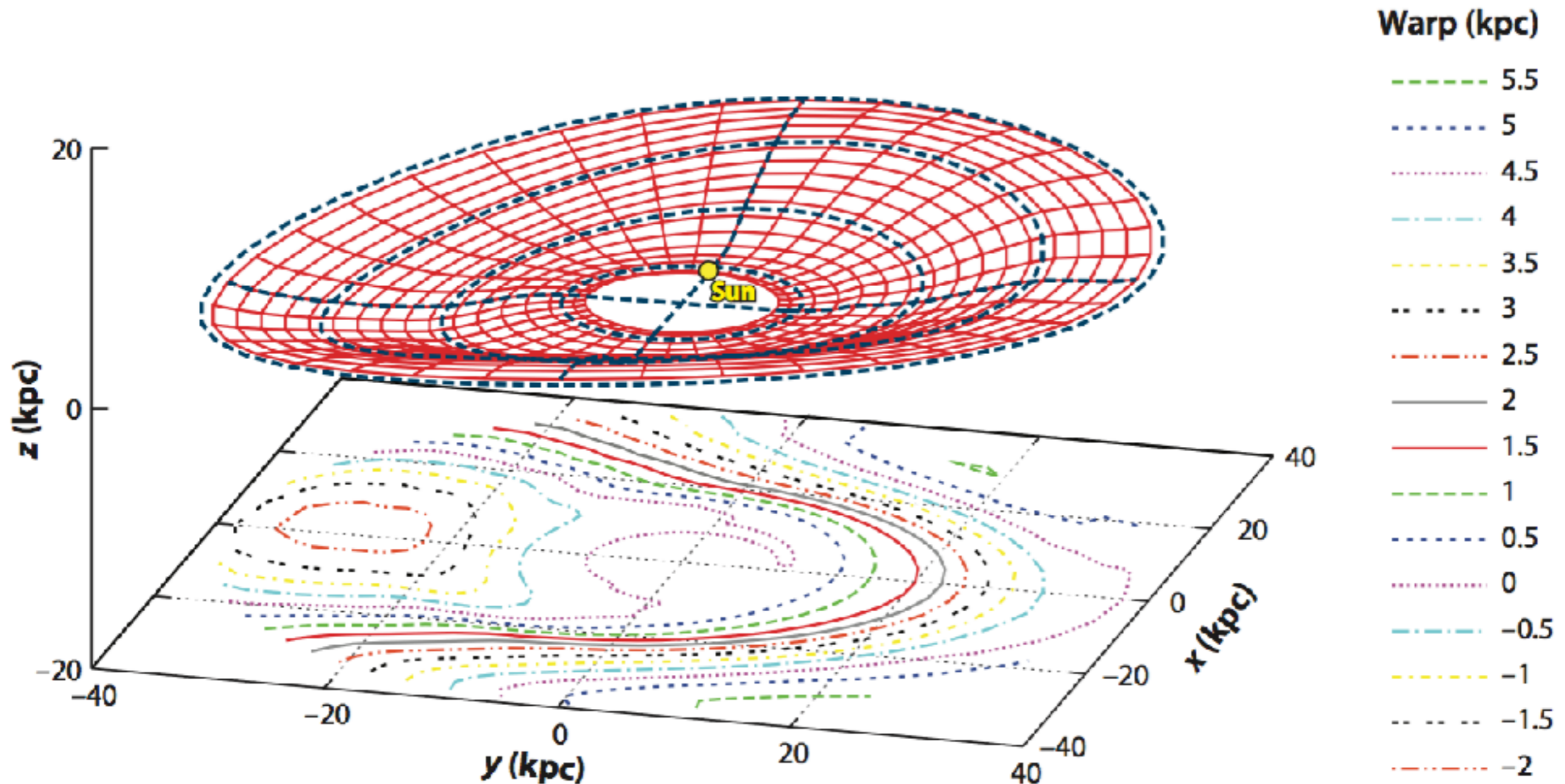
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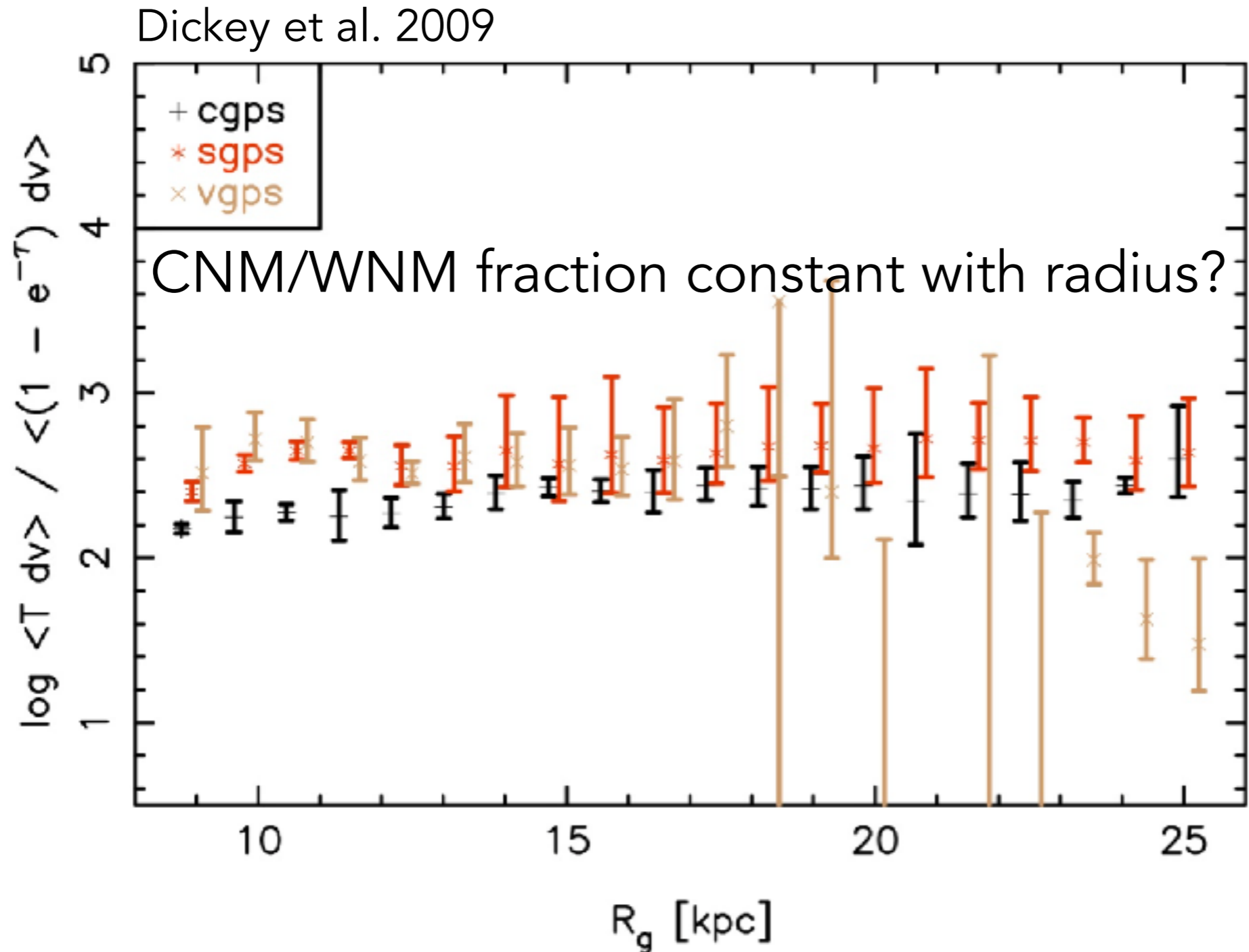


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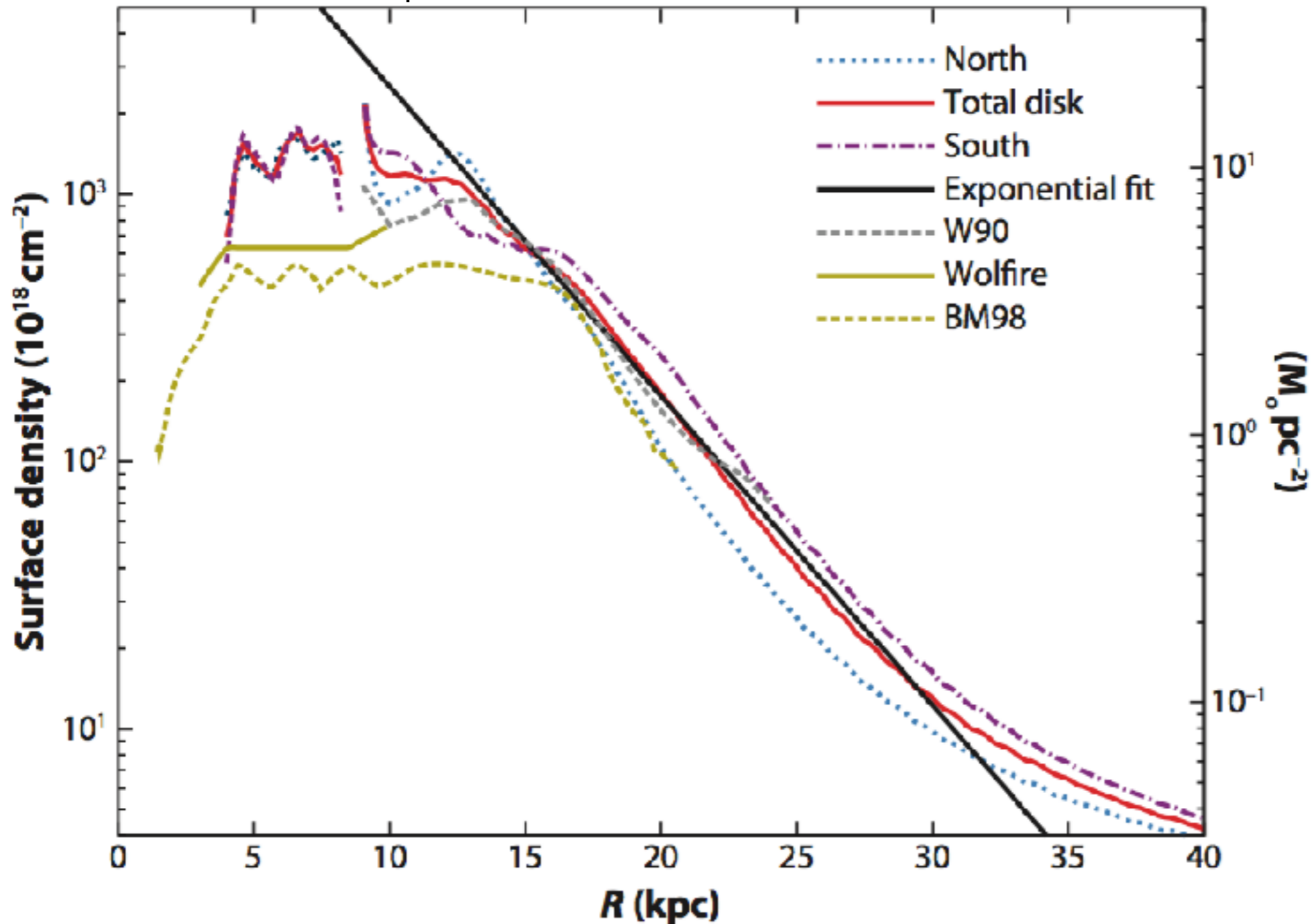


Distribution of HI in the MW



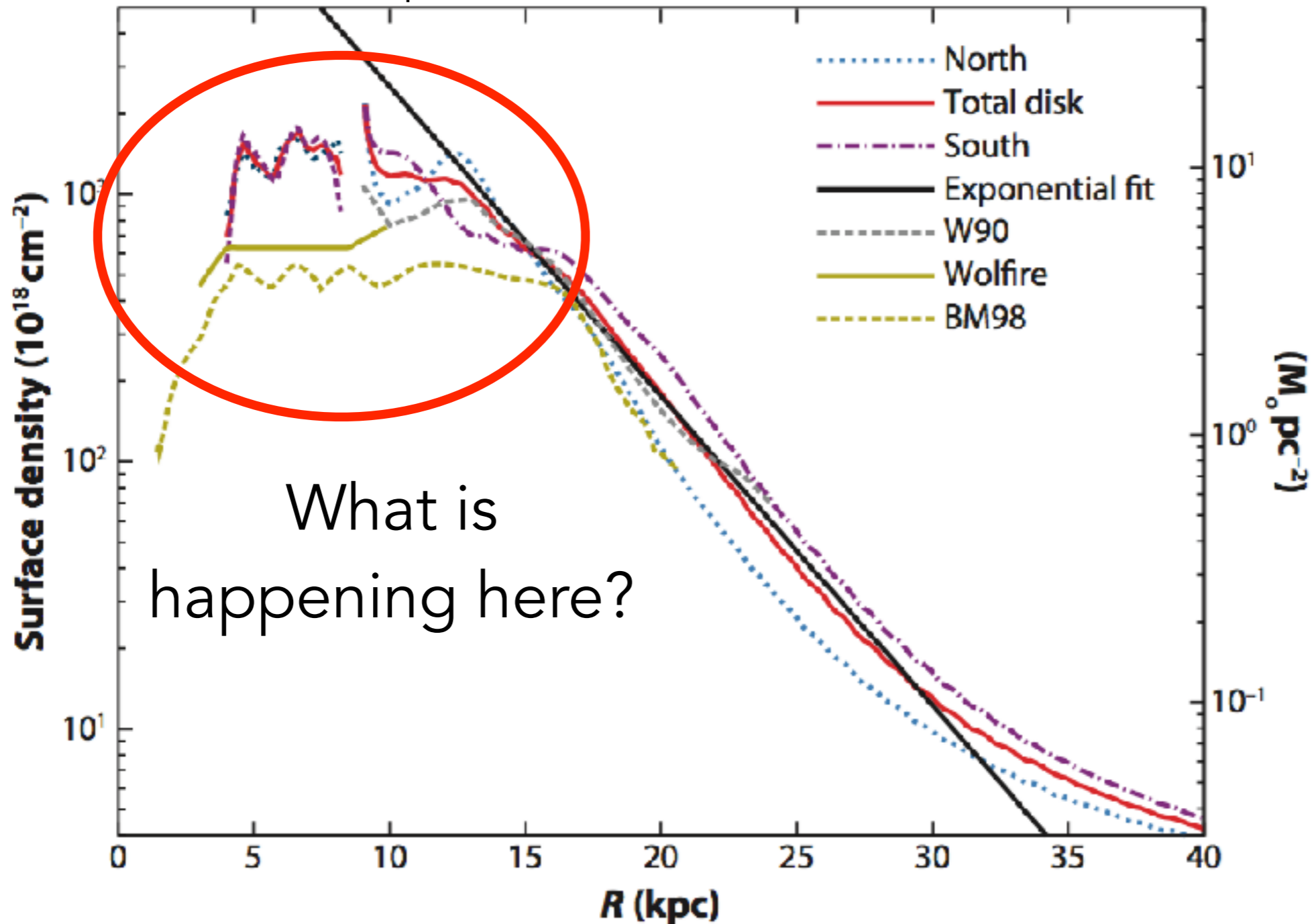
Distribution of HI in the MW

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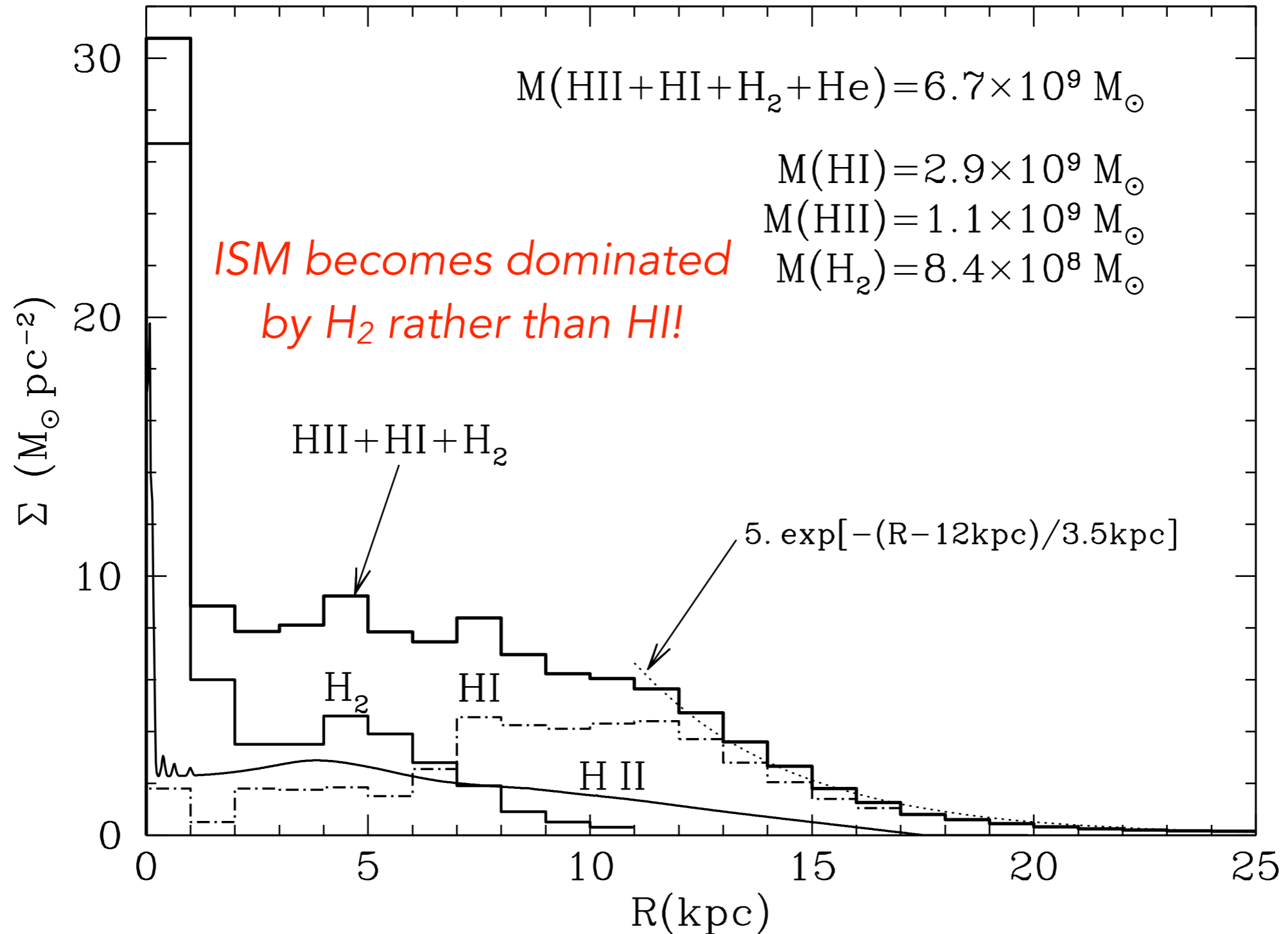


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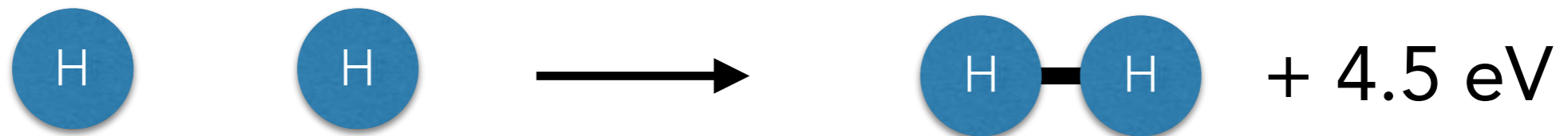


Distribution of HI in the MW



Forming H₂

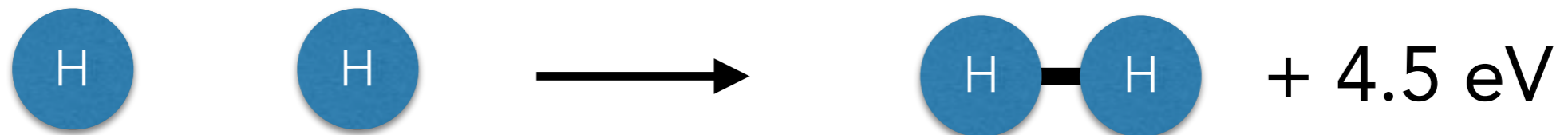
Formation of H₂ by gas-phase reactions is slow



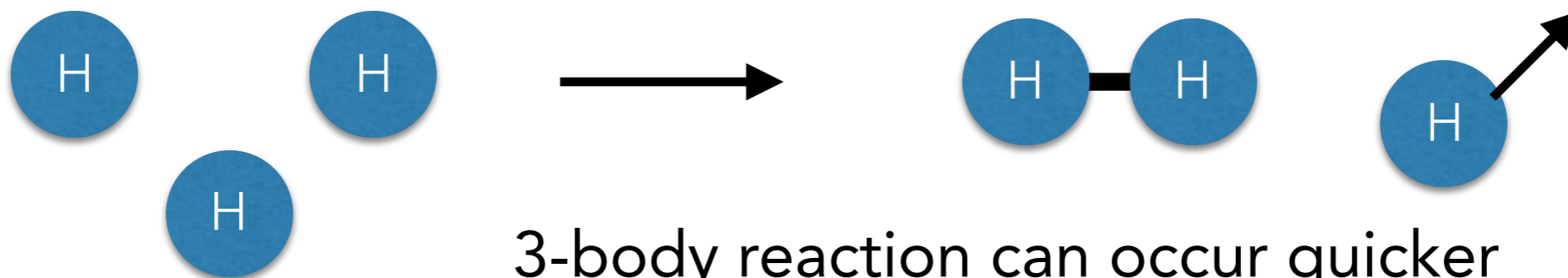
no effective way to carry away 4.5 eV worth of binding energy when two H bond, no dipole moment
negligible rate for this reaction

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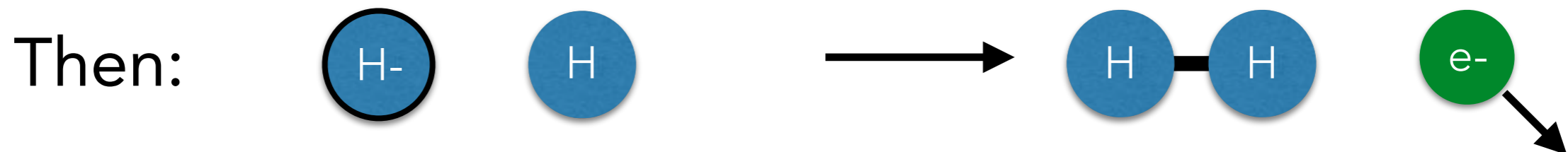
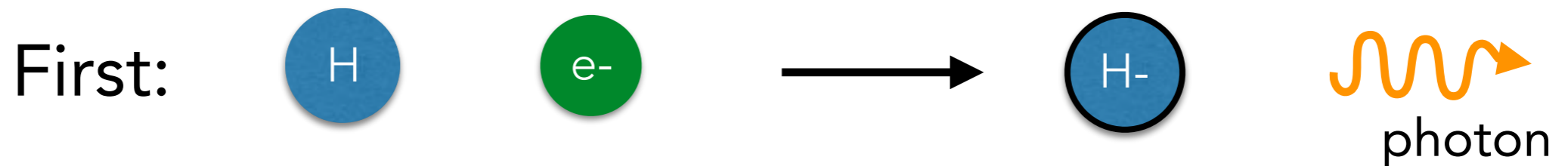


3-body reaction can occur quicker
but this is still very slow

Forming H₂

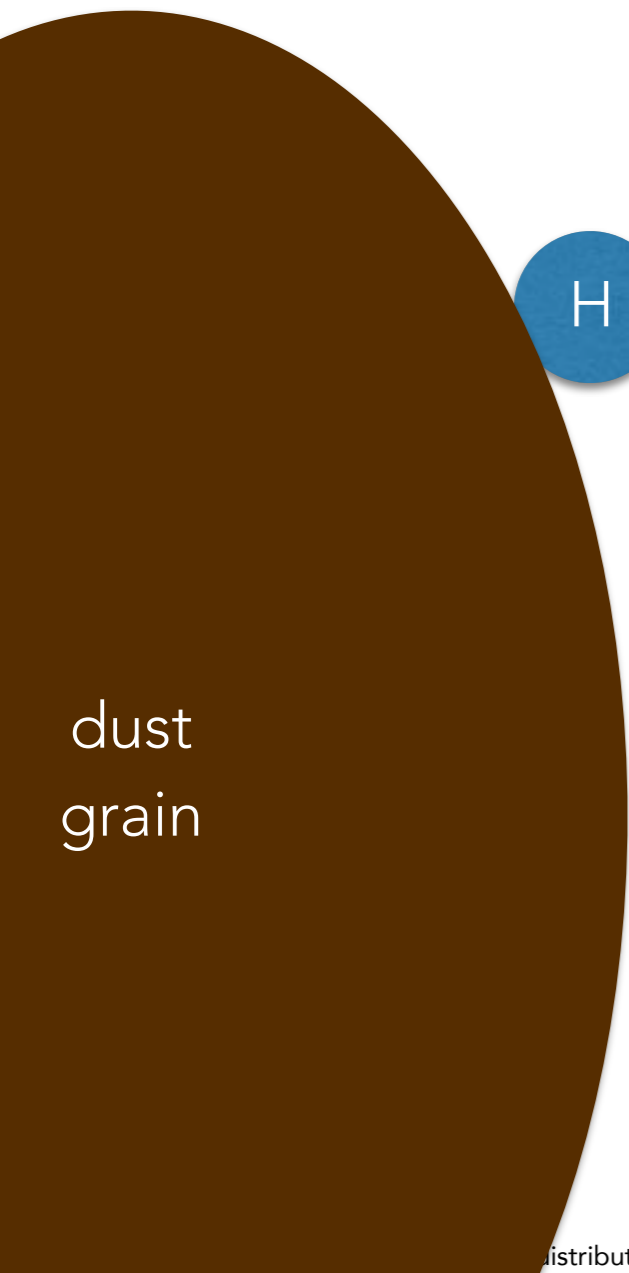
Formation of H₂ by gas-phase reactions is slow

Fastest gas-phase route is "associative attachment"



Forming H₂

Grain Surface H₂ formation is much faster if there is dust.

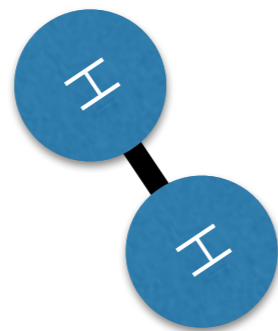


Depends on:
collision rate of H with grain (n, T)
available grain surface area
"sticking" probability



Forming H₂

Grain Surface H₂ formation is much faster if there is dust.



Depends on:
collision rate of H with grain (n, T)
available grain surface area
"sticking" probability

dust
grain

Forming H₂

Grain Surface H₂ formation is much faster if there is dust.

$$\left(\frac{dn(\text{H}_2)}{dt}\right)_{\text{gr}} = R_{\text{gr}} n_{\text{H}} n(\text{H})$$

total density
of hydrogen in
any form

density of
H atoms

Forming H₂

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density of H atoms

total density of hydrogen in any form

$$R_{\text{gr}} = \frac{1}{2} \left(\frac{8kT}{\pi m_H}\right)^{1/2} \langle \epsilon_{\text{gr}} \rangle \Sigma_{\text{gr}}$$

v_{thermal} average "sticking" coeff for grain pop

Forming H₂

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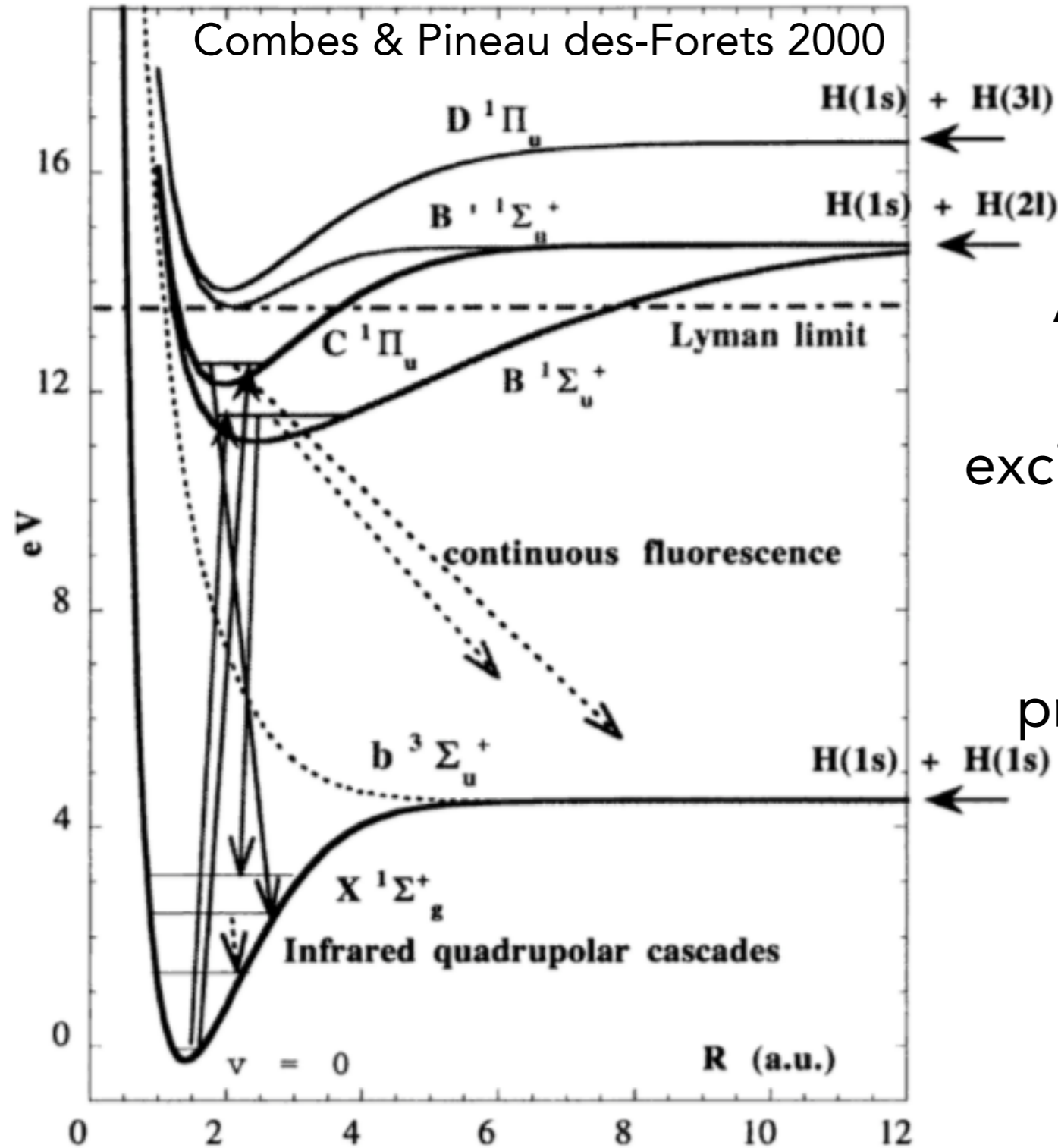
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V_{thermal} average "sticking" coeff for grain pop

Grain surface area

$$\Sigma_{\text{gr}} \equiv \frac{1}{n_H} \int \pi a^2 \frac{dn_{\text{gr}}}{da} da$$

Photodissociation of H₂



After H₂ absorbs a UV photon from ground to one of the excited levels (Lyman-Werner bands) has ~85% probability of radiative decay, ~15% probability of photo-dissociating

Lyman band = ground -> B
 Werner band = ground -> C

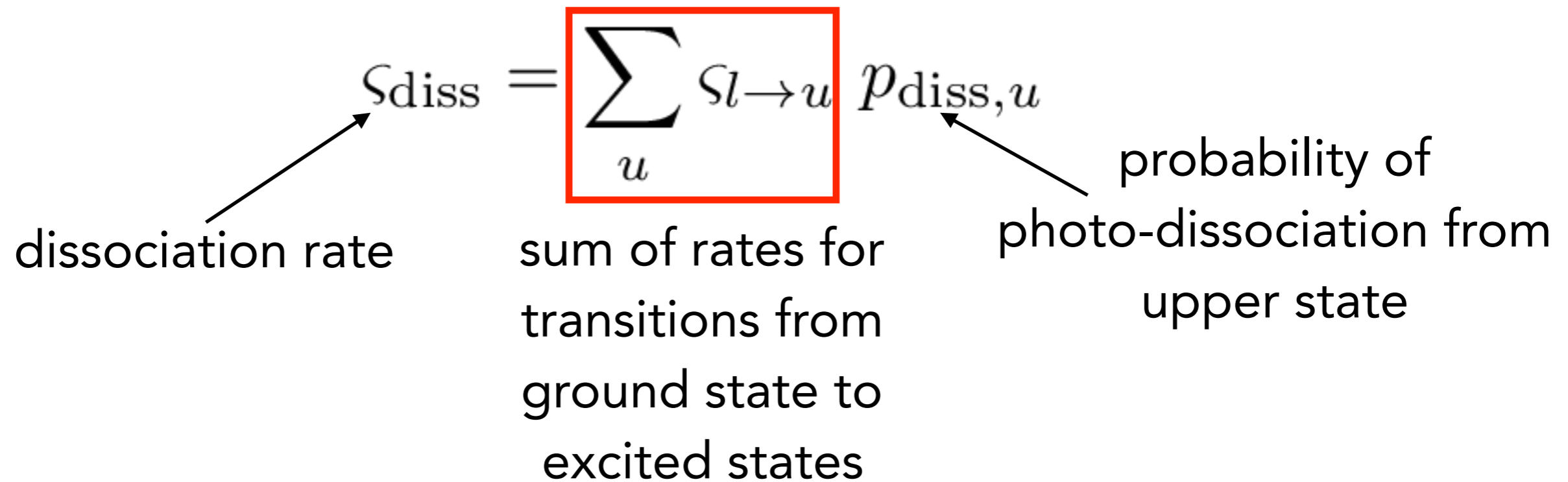
Photodissociation of H₂

$$S_{\text{diss}} = \sum_u S_{l \rightarrow u} p_{\text{diss},u}$$

dissociation rate

sum of rates for transitions from ground state to excited states

probability of photo-dissociation from upper state



Photodissociation of H₂

$$S_{\text{diss}} = \sum_u S_{l \rightarrow u} p_{\text{diss},u}$$

dissociation rate

sum of rates for transitions from ground state to excited states

probability of photo-dissociation from upper state

depends on quantum mechanics
and radiation field intensity at relevant wavelengths

H₂ Abundance

In steady state:

photo-
dissociation

$$\zeta_{\text{diss}} n(\text{H}_2) = R_{\text{gr}} n_{\text{H}} n(\text{H})$$

formation on
dust grains

For CNM conditions this is pretty small:

$$\frac{n(\text{H}_2)}{n_{\text{H}}} \approx 1.8 \times 10^{-5} \left(\frac{n(\text{H})}{30 \text{cm}^{-3}} \right) \left(\frac{R_{\text{gr}}}{3 \times 10^{-17} \text{cm}^3 \text{s}^{-1}} \right) \left(\frac{\zeta_{\text{diss}}}{5 \times 10^{-11} \text{s}^{-1}} \right)^{-1}$$

But we have left out an important component:
shielding

H₂ Abundance

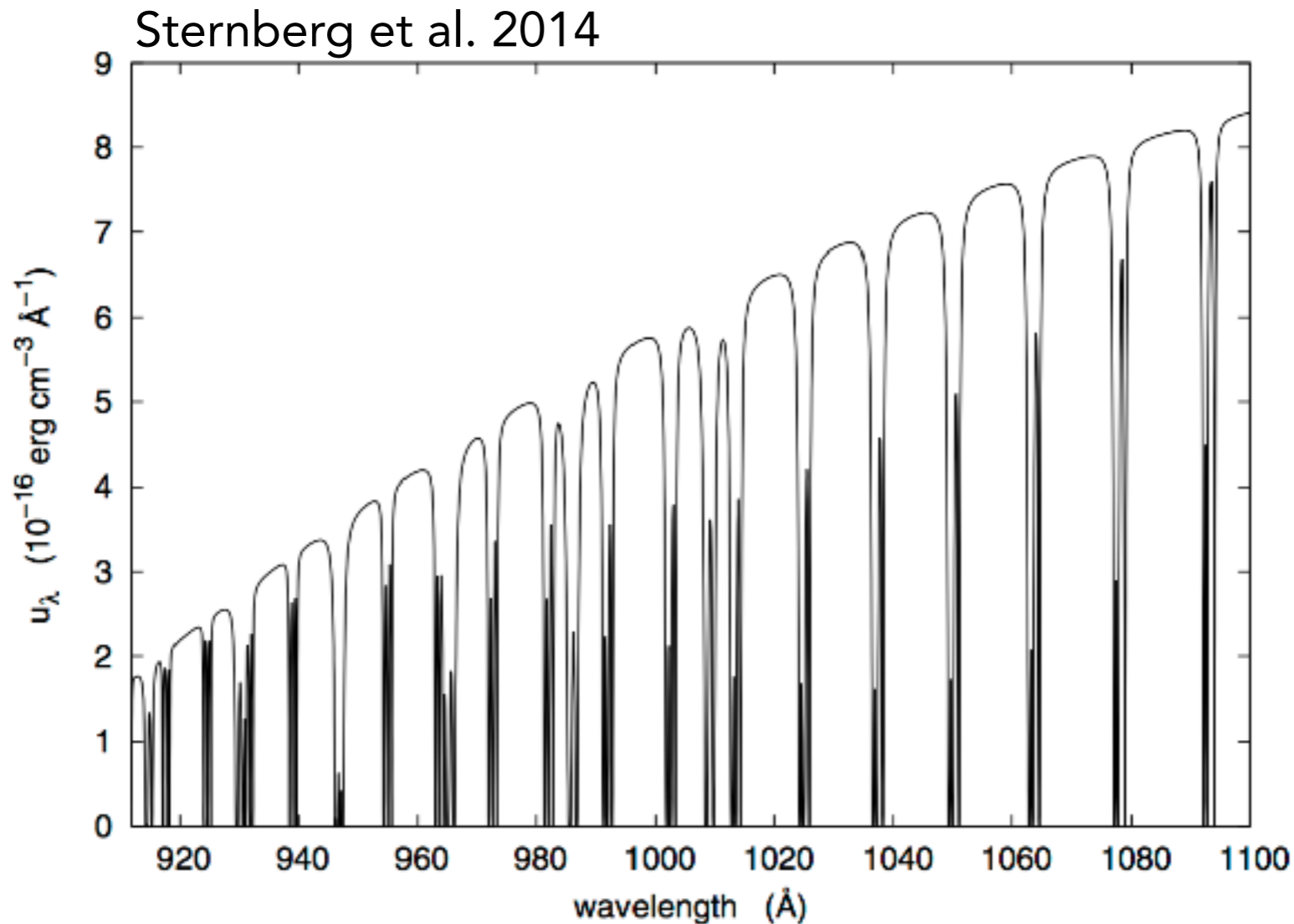
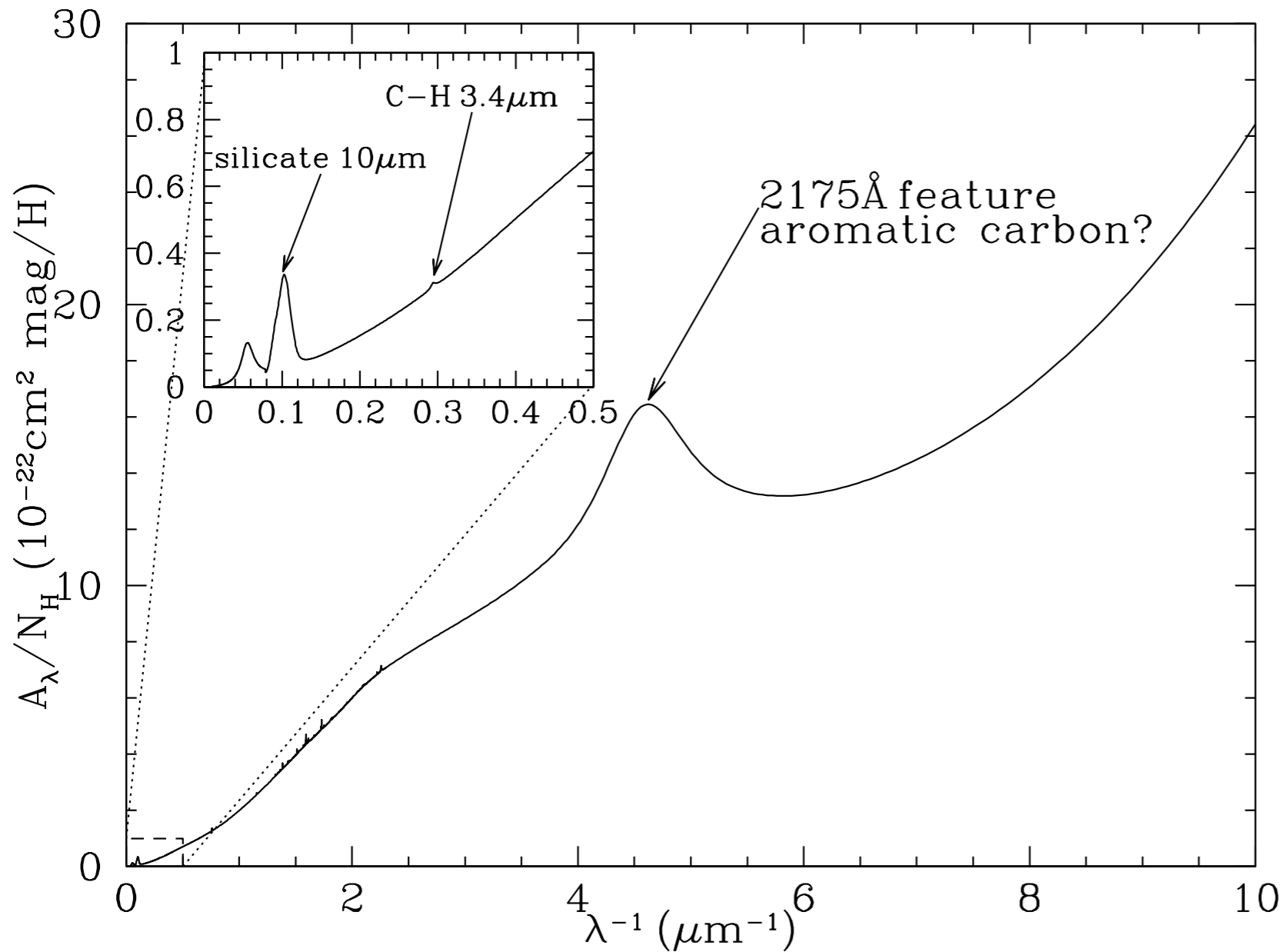


Figure 2. Absorbed far-UV spectrum showing partially overlapping Lyman–Werner band absorption lines, for beamed radiation into a cloud, at a total hydrogen gas column density of $3.74 \times 10^{20} \text{ cm}^{-2}$, for a free-space radiation intensity $I_{\text{UV}} = 35.5$, gas density $n = 10^3 \text{ cm}^{-3}$, and metallicity $Z' = 1$ ($\alpha G/2 = 1$).

H₂ Lyman-Werner bands can become optically thick and shield interior H₂ from being dissociated.

H₂ Abundance

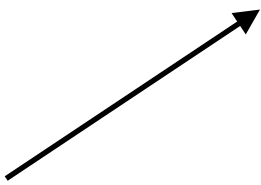


At UV wavelengths
even small A_V
corresponds to
substantial amounts
of UV extinction.

H₂ Abundance

$$\zeta_{\text{diss}} \approx \zeta_{\text{diss},0} f_{\text{shield}} e^{-\tau_{d,1000}}$$

dissociation rate
with no shielding



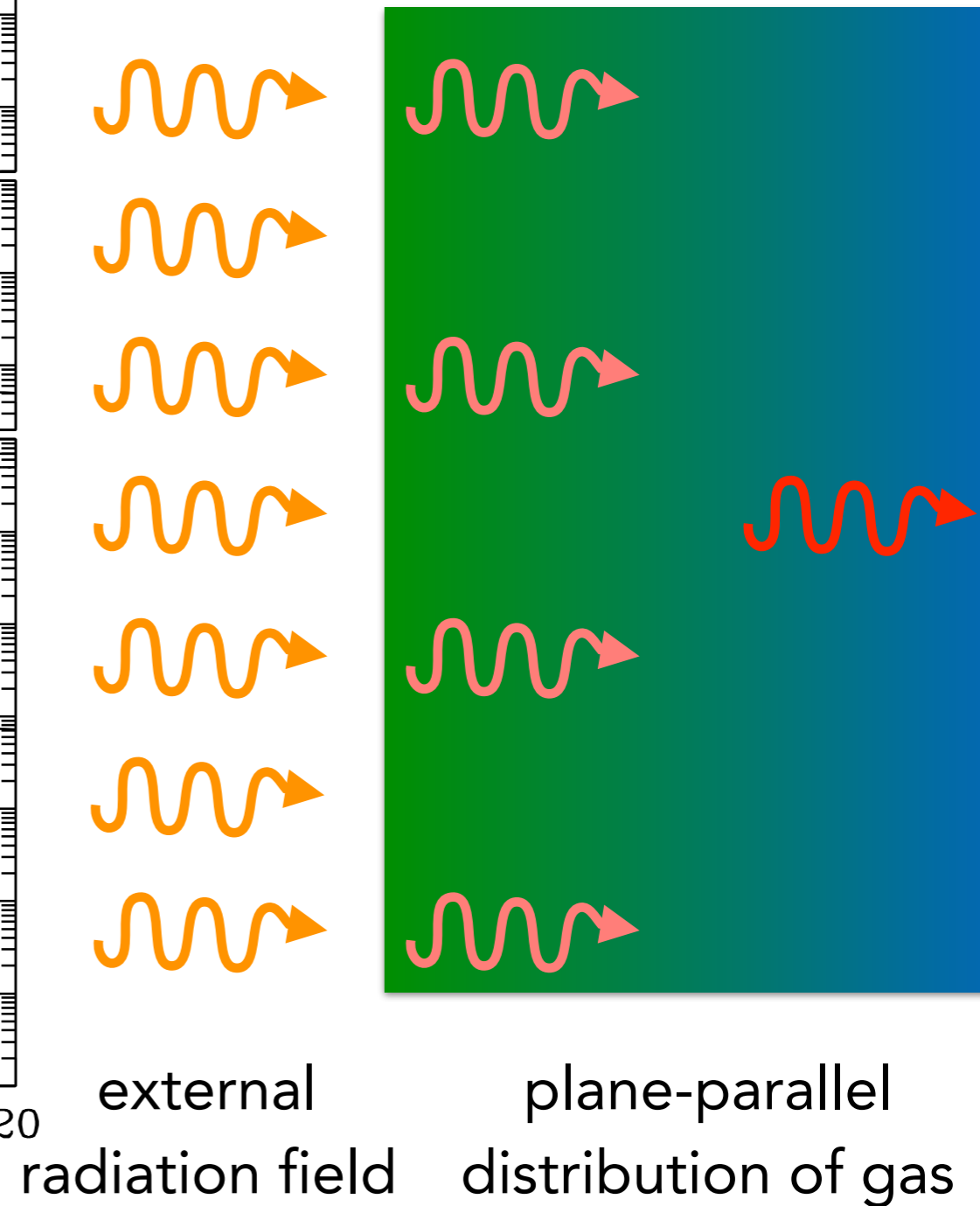
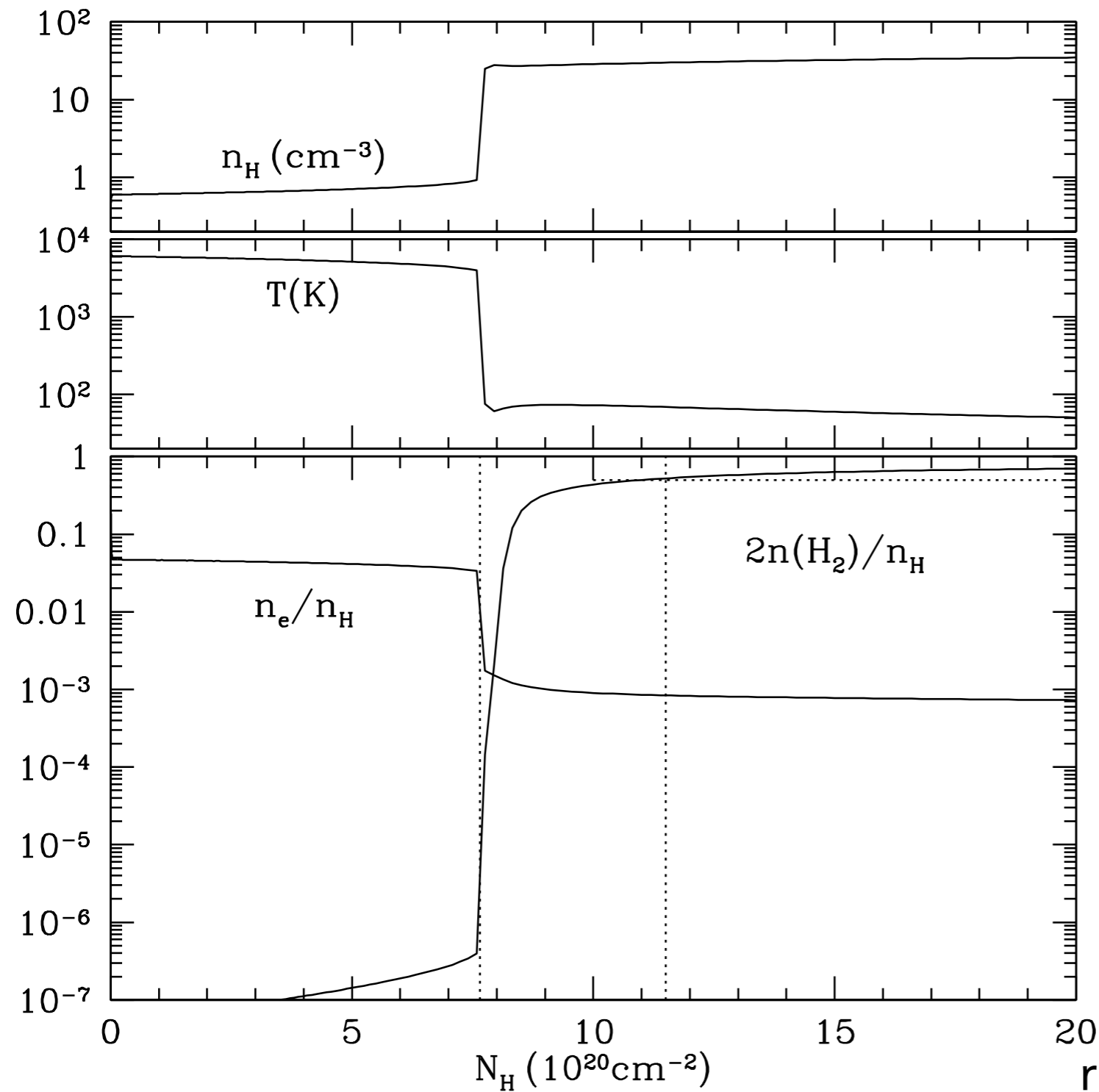
self-shielding
factor



dust extinction
at 1000 Å

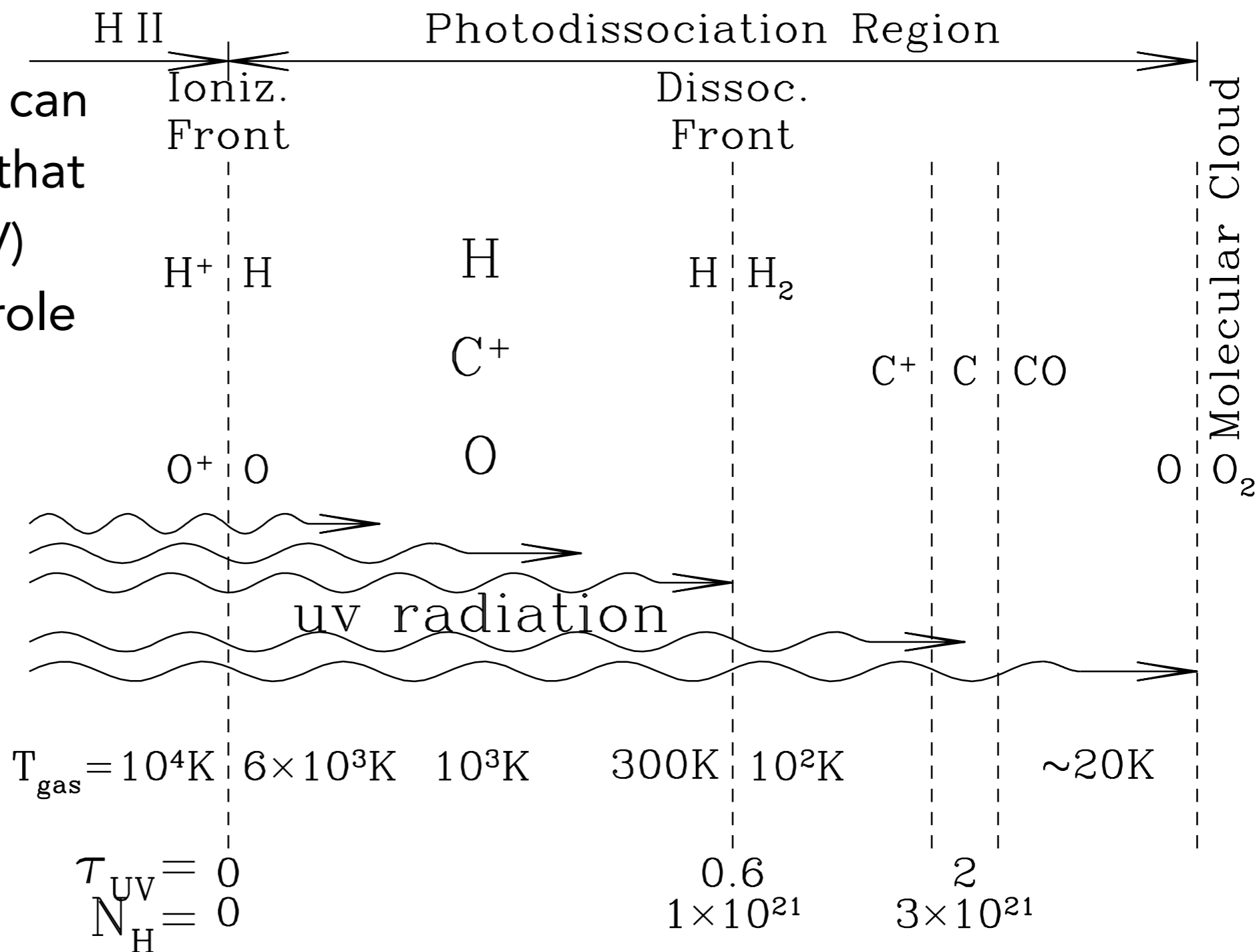


H₂ Abundance



Photodissociation Regions

Very general term, can refer to anywhere that far-UV (<13.6 eV) photons play key role in chemistry, ionization, etc.



Photodissociation Regions

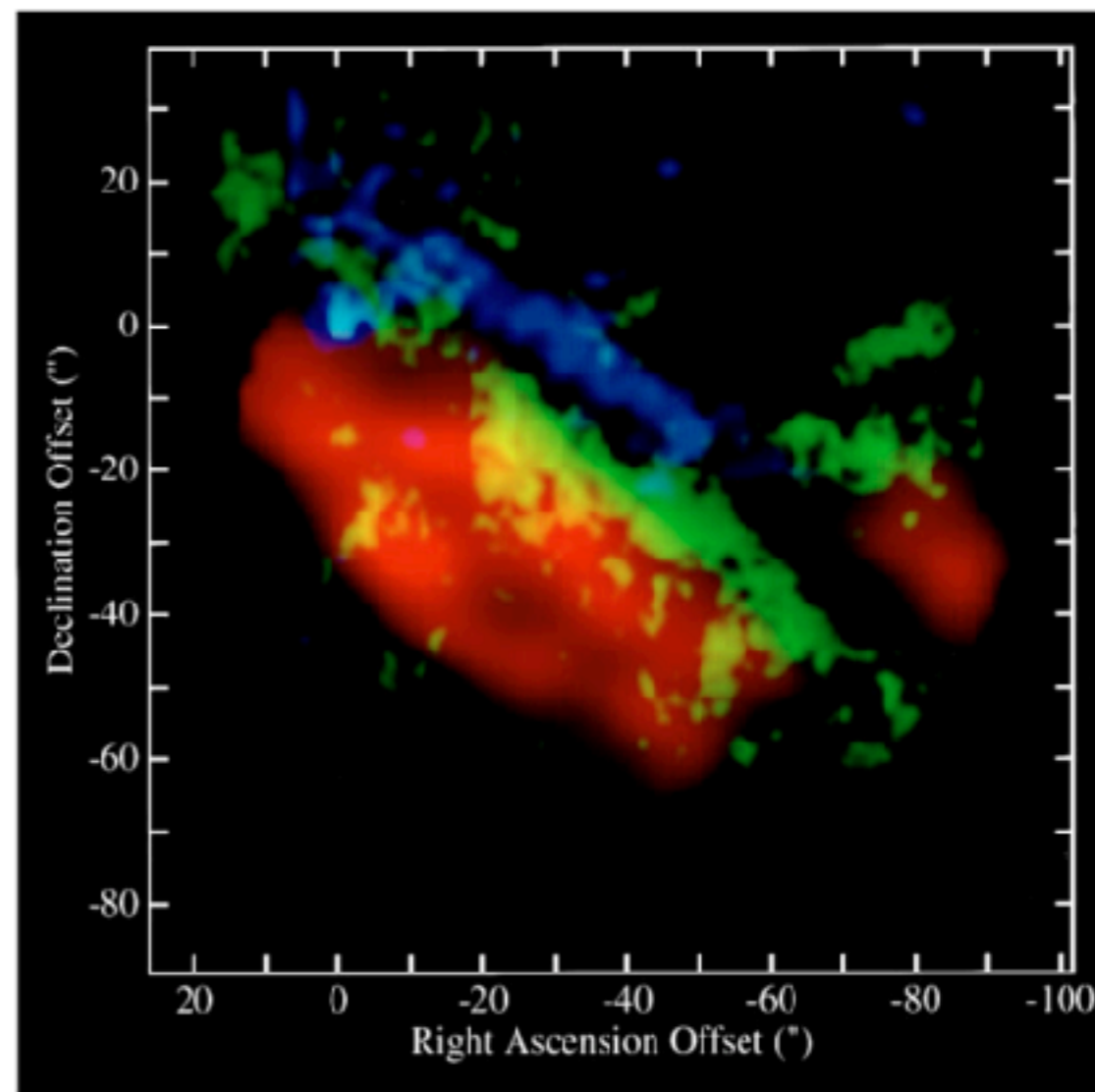


FIG. 2. (Color) The Orion Bar region mapped in the $3.3\text{-}\mu\text{m}$ PAH feature (blue), H_2 $1\text{-}0$ S(1) emission (yellow), and $\text{CO } J=1\text{-}0$ emission (red; Tielens *et al.*, 1993). The (0,0) position corresponds to the (unrelated) star θ^2 A Ori. The illuminating source, θ^1 C Ori, and the ionized gas are located to the northwest (upper right). For all three tracers, the emission is concentrated in a bar parallel to but displaced to the southeast from the ionization front. The PDR is seen edge on; a separation of $\approx 10''$ is seen between the PAH emission and the H_2 emission, and between the H_2 emission and the CO emission, as predicted by PDR models (see text).

Image: NASA/C. R. O'Dell & S. K. Wong (Rice Univ.)

Hollenbach & Tielens 1999 Review

Photodissociation Regions

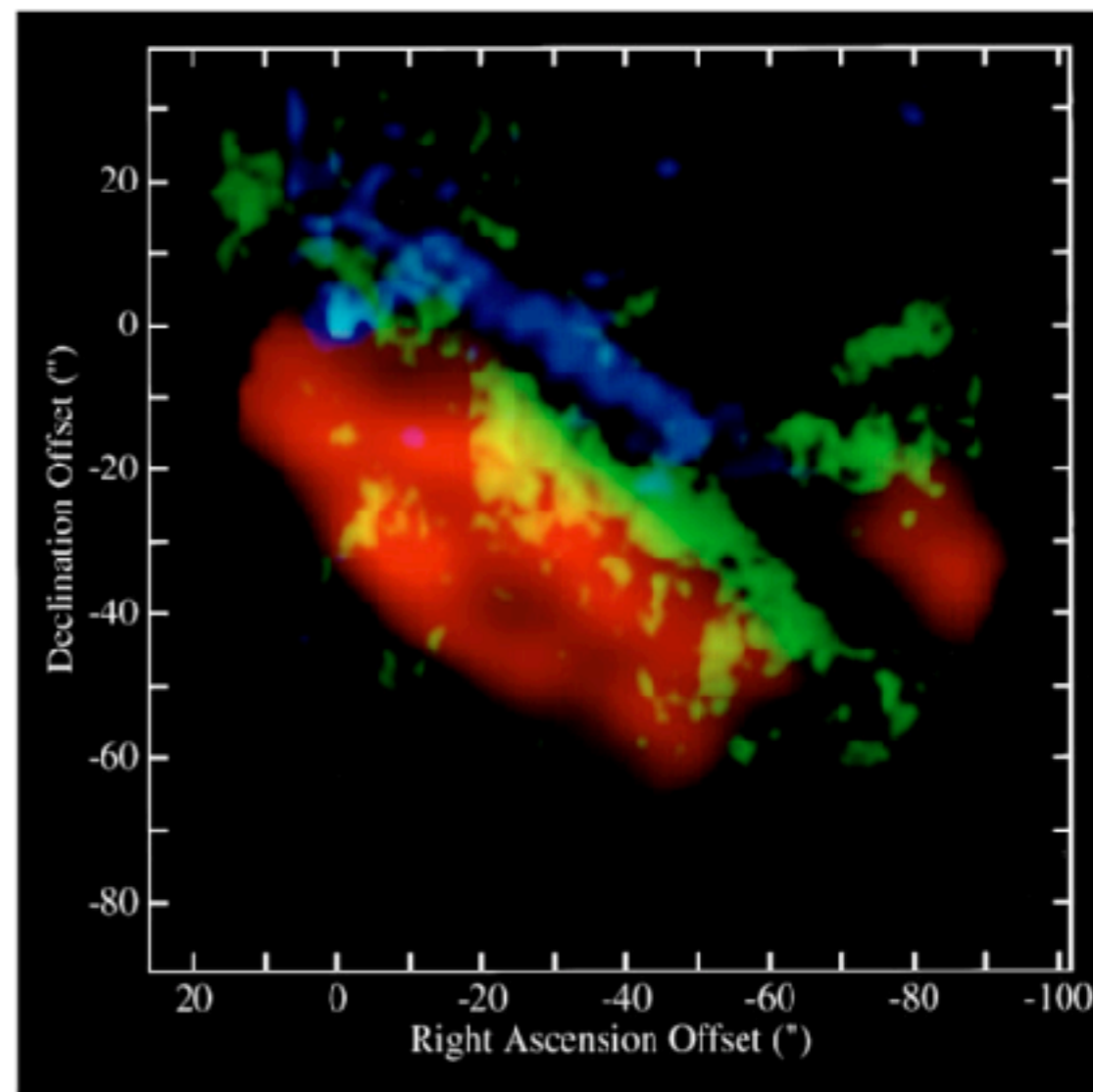
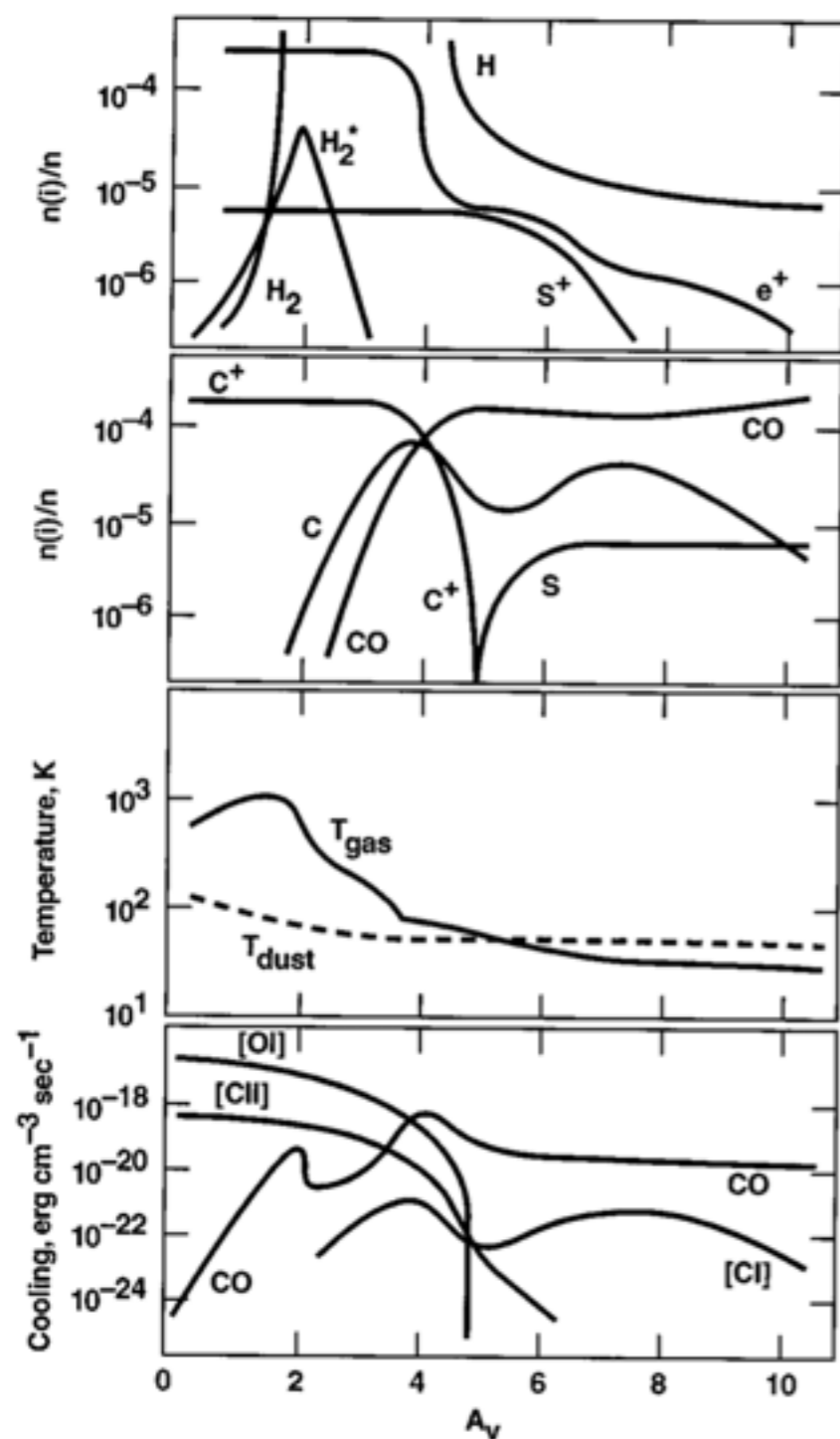


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Hollenbach & Tielens 1999 Review

Chemistry in Molecular Gas

List of molecules that have been detected in the ISM:

2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	>12 atoms
H ₂	C ₃ [*]	<i>c</i> -C ₃ H	C ₅ [*]	C ₅ H	C ₆ H	CH ₃ C ₃ N	CH ₃ C ₄ H	CH ₃ C ₅ N	HC ₉ N	<i>c</i> -C ₆ H ₆ [*]	HC ₁₁ N
AlF	C ₂ H	<i>l</i> -C ₃ H	C ₄ H	<i>l</i> -H ₂ C ₄	CH ₂ CHCN	HC(O)OCH ₃	CH ₃ CH ₂ CN	(CH ₃) ₂ CO	CH ₃ C ₆ H	<i>n</i> -C ₃ H ₇ CN	C ₆₀ [*]
AlCl	C ₂ O	C ₃ N	C ₄ Si	C ₂ H ₄ [*]	CH ₃ C ₂ H	CH ₃ COOH	(CH ₃) ₂ O	(CH ₂ OH) ₂	C ₂ H ₅ OCHO	<i>l</i> -C ₃ H ₇ CN	C ₇₀ [*]
C ₂ ^{**}	C ₂ S	C ₃ O	<i>l</i> -C ₃ H ₂	CH ₃ CN	HC ₅ N	C ₇ H	CH ₃ CH ₂ OH	CH ₃ CH ₂ CHO	CH ₃ OC(O)CH ₃	C ₂ H ₅ OCH ₃ ?	C ₆₀ ^{**}
CH	CH ₂	C ₃ S	<i>c</i> -C ₃ H ₂	CH ₃ NC	CH ₃ CHO	C ₆ H ₂	HC ₇ N				
CH ⁺	HCN	C ₂ H ₂ [*]	H ₂ CCN	CH ₃ OH	CH ₃ NH ₂	CH ₂ OHCHO	C ₈ H				
CN	HCO	NH ₃	CH ₄ [*]	CH ₃ SH	<i>c</i> -C ₂ H ₄ O	<i>l</i> -HC ₆ H [*]	CH ₃ C(O)NH ₂				
CO	HCO ⁺	HCCN	HC ₃ N	HC ₃ NH ⁺	H ₂ CCHOH	CH ₂ CHCHO (?)	C ₈ H ⁻				
CO ⁺	HCS ⁺	HCNH ⁺	HC ₂ NC	HC ₂ CHO	C ₆ H ⁻	CH ₂ CCHCN	C ₃ H ₆				
CP	HOC ⁺	HNCO	HCOOH	NH ₂ CHO	CH ₃ NCO 2015	H ₂ NCH ₂ CN	CH ₃ CH ₂ SH (?)				
SiC	H ₂ O	HNCS	H ₂ CNH	C ₅ N		CH ₃ CHNH					
HCl	H ₂ S	HOCO ⁺	H ₂ C ₂ O	<i>l</i> -HC ₄ H [*]							
KCl	HNC	H ₂ CO	H ₂ NCN	<i>l</i> -HC ₄ N							
NH	HNO	H ₂ CN	HNC ₃	<i>c</i> -H ₂ C ₃ O							
NO	MgCN	H ₂ CS	SiH ₄ [*]	H ₂ CCNH (?)							
NS	MgNC	H ₃ O ⁺	H ₂ COH ⁺	C ₅ N ⁻							
NaCl	N ₂ H ⁺	<i>c</i> -SiC ₃	C ₄ H ⁻	HNCHCN							
OH	N ₂ O	CH ₃ [*]	HC(O)CN								
PN	NaCN	C ₃ N ⁻	HNCNH								
SO	OCS	PH ₃	CH ₃ O								

<http://www.astro.uni-koeln.de/cdms/molecules>

KCl	HNC	H ₂ CO	H ₂ N ₂ CN	<i>l</i> -HC ₄ N
NH	HNO	H ₂ CN	HNC ₃	<i>c</i> -H ₂ C ₃ O
NO	MgCN	H ₂ CS	SiH ₄ ⁺	H ₂ CCNH (?)
NS	MgNC	H ₃ O ⁺	H ₂ COH ⁺	C ₅ N ⁻
NaCl	N ₂ H ⁺	<i>c</i> -SiC ₃	C ₄ H ⁻	HNCHCN
OH	N ₂ O	CH ₃ ⁺	HC(O)CN	
PN	NaCN	C ₃ N ⁻	HNCNH	
SO	OCS	H ₃ ⁺	CH ₃ ⁺	
SO ⁺	SO ₂	HCNO	NH ₄ ⁺	
SiN	<i>c</i> -SiC ₂	HOCN	H ₂ NCO ⁺ (?)	
SiO	CO ₂ ⁺	HSCN	NCCNH ⁺ 2015	
SiS	NH ₂	H ₂ O ₂		
CS	H ₃ ⁺ (*)	C ₃ H ⁺		
HF	SiCN	HMgNC		
HD	AlNC	HCCO 2015		
FeO ?	SiNC			
O ₂	HCP			
CF ⁺	CCP			
SiH ?	AlOH			
PO	H ₂ O ⁺			
AlO	H ₂ Cl ⁺			
OH ⁺	KCN			
CN ⁻	FeCN			
SH ⁺	HO ₂			
SH	TiO ₂			
HCl ⁺	C ₂ N			
TiO	Si ₂ C 2015			
ArH ⁺				
NO ⁺ ?				

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Chemistry in Molecular Gas

Abundance of molecules is set by rates of formation & destruction.

Formation

- gas-phase reactions
 - neutral-neutral
 - ion-neutral
 - radiative association
- grain surface reactions

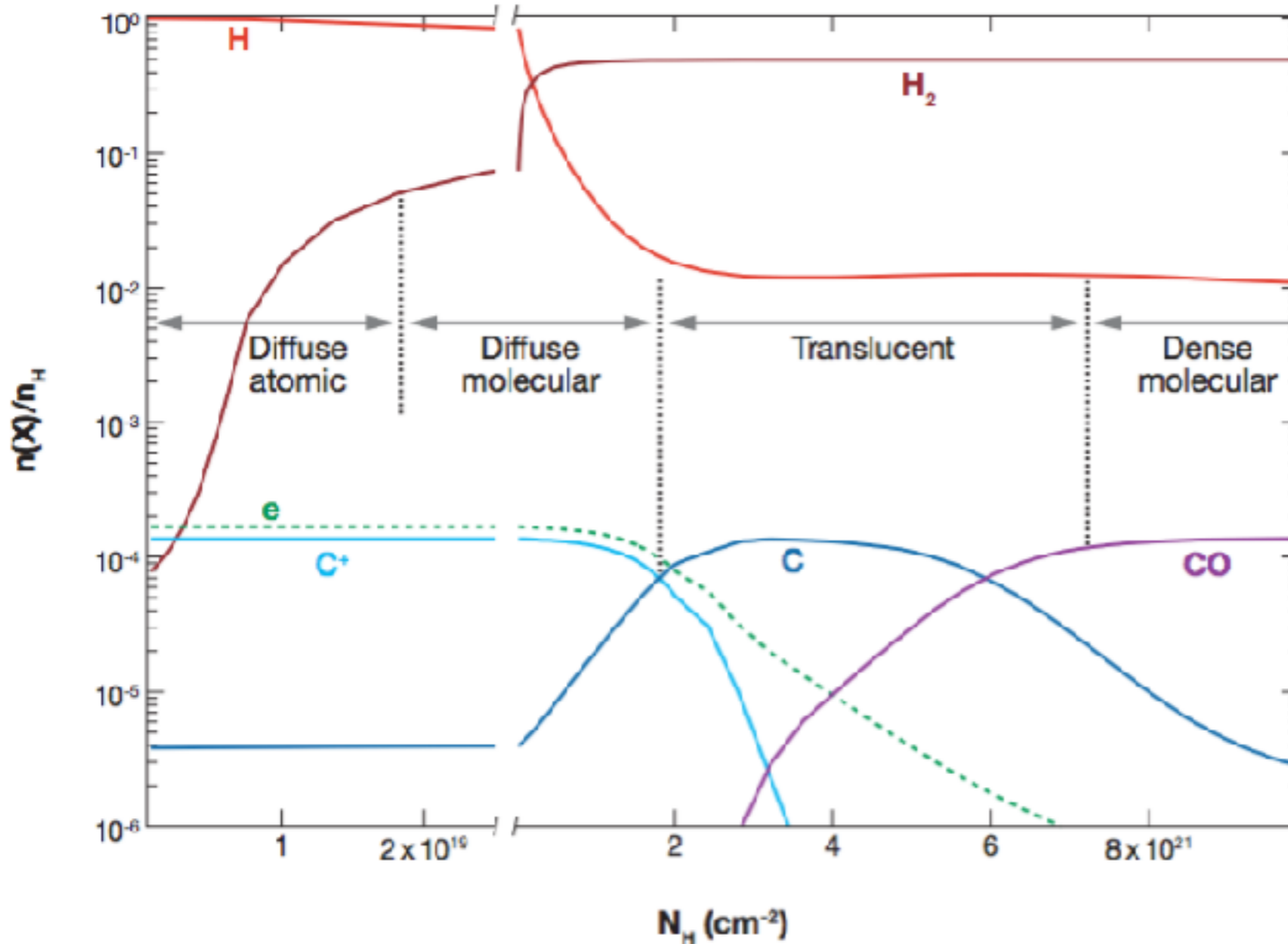
Destruction

- photoionization
- photodissociation
- incorporation into other molecular species

Dense gas, shielded from UV, but still with ions & dust is ideal for chemistry.

Chemistry in Molecular Gas

Snow & McCall 2006



Chemistry happens in diffuse phases,

(& is very interesting - intermittent turbulent dissipation, shattering of dust grains, grain surface reactions, etc)

...but things really get going when H_2 forms.

Figure 1

Results from photodissociation region model [with $n_H = 100 \text{ cm}^{-3}$ and $\chi_{UV} = 1$] from Neufeld et al. (2005), illustrating the revised definitions of cloud types.

Chemistry in Molecular Gas

Astrochemistry is really interesting!

The time scale to reach steady state in the interstellar medium is longer than the dynamical time scale of the physical condition evolution in most regions; as a consequence, the chemical composition depends on the initial conditions (initial chemical composition). For example, under dense cloud conditions (typical temperature of 10 K, density of a few 10^4 cm^{-3} , and a visual extinction A_V of 30 magnitudes¹⁰⁴), the typical time to reach the steady state for a reservoir molecule such as CO is approximately 10^9 yr if both gas-phase chemistry and gas-grain interactions are considered, whereas the typical lifetime of such objects is 10^7 yr or shorter.^{105,106} Since most chemical models of dense clouds do not take into account the formation of the cloud itself, the computed chemical composition depends on the initial conditions.

Agundez & Wakelam 2013 - arXiv:1310.3651

Chemistry is not in thermochemical equilibrium -
governed by "chemical kinetics".

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Chemistry in Molecular Gas

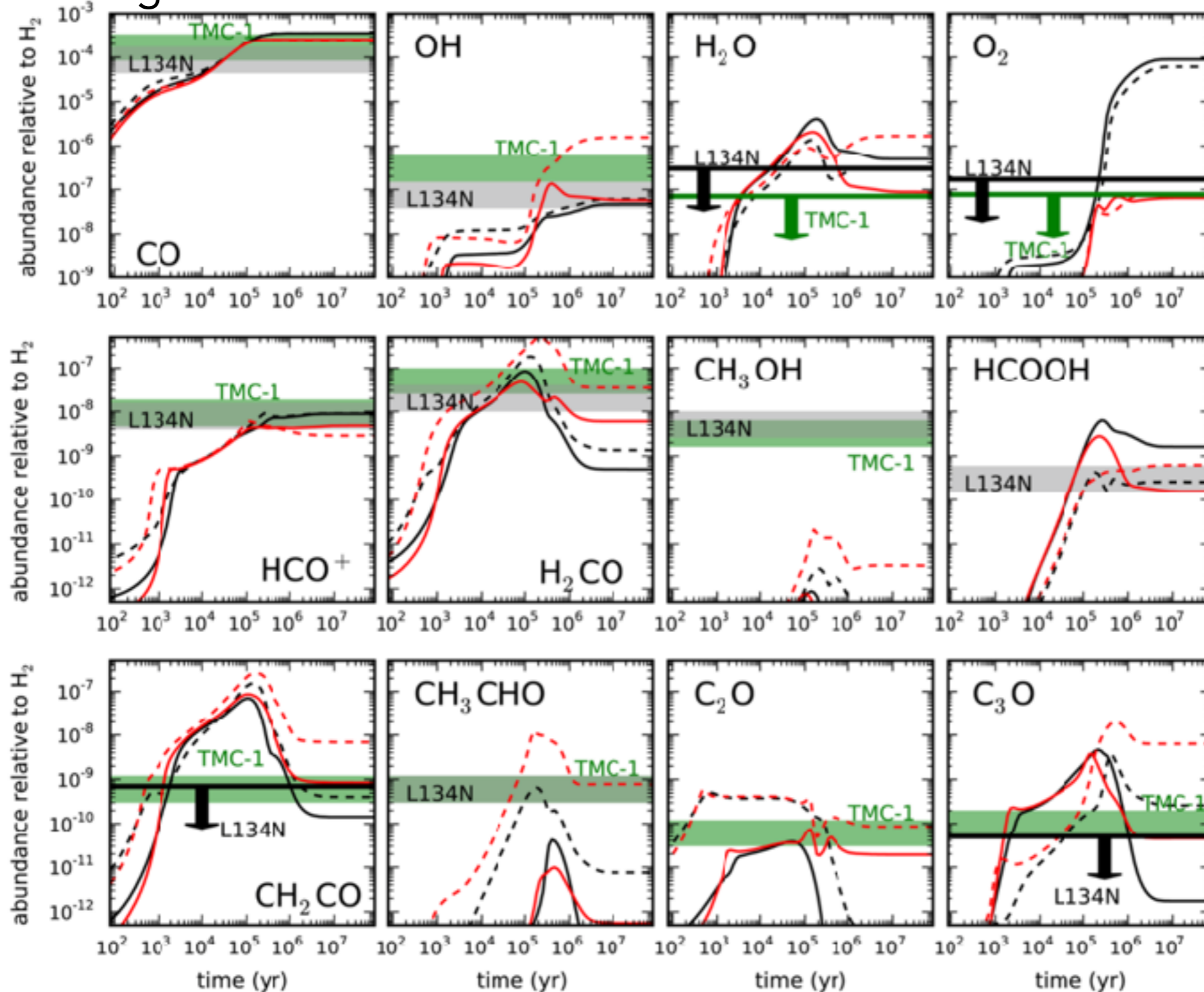
Evidence of non-equilibrium chemistry:

CO is the most abundant molecule after H₂

Chemical equilibrium models at $T=10$ K would predict most carbon in CH₄ and most oxygen in H₂O.

Chemistry in Molecular Gas

Agundez & Wakelam 2013



Chemistry in Molecular Gas

Key Elements of Gas Phase Chemistry in Dense Clouds:

Chemistry in Molecular Gas

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1. Hydrogen is dominantly **molecular** (H_2 formation on grain surfaces).

Chemistry in Molecular Gas

Key Elements of Gas Phase Chemistry in Dense Clouds:

1. Hydrogen is dominantly **molecular** (H_2 formation on grain surfaces).
2. **Cosmic rays** provide ionization even in very dense clouds, UV absorbed in outer layers of cloud. H_2^+ quickly reacts with H to form H_3^+ , a key reactant.

Chemistry in Molecular Gas

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3. H_3^+ easily donates protons to neutral species, leads to quick reactions:
$$\text{H}_3^+ + \text{X} \rightarrow \text{XH}^+ + \text{H}_2.$$

Chemistry in Molecular Gas

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$$\text{H}_3^+ + \text{X} \rightarrow \text{XH}^+ + \text{H}_2.$$
4. Exothermic reactions with no activation barrier are strongly preferred due to low temperatures. **Ion-neutral reactions** are the most efficient path in these conditions - drive chemical networks.

Chemistry in Molecular Gas

Some key gas phase reaction types:

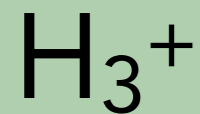
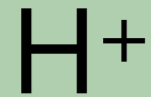
Type	Example	Notes	typical rate coefficient (k)
Neutral-Radical	$O + H_2 \rightarrow OH + H$	some have thermal activation barriers	$\sim 10^{-10} \text{ cm}^3 \text{ s}^{-1}$
Ion-Molecule	$H^+ + O \rightarrow O^+ + H$ $O^+ + H_2 \rightarrow OH^+ + H$ $H_3^+ + O \rightarrow OH^+ + H_2$	<- charge exchange <- H abstraction <- proton transfer	$\sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$
Radiative Association	$H + H^+ \rightarrow H_2^+ + h\nu$	only important if other pathways lacking	very low
Photodissociation	$h\nu + OH \rightarrow O + H$	always important	$\sim 10^{-10} \text{ cm}^3 \text{ s}^{-1}$
Dissociative Recombination	$e + H_3^+ \rightarrow 3H, H_2 + H$ (branching 3:1)	always important	$\sim 10^{-7} \text{ cm}^3 \text{ s}^{-1}$

info from A. Glassgold Ay216 at Berkeley

Chemistry in Molecular Gas

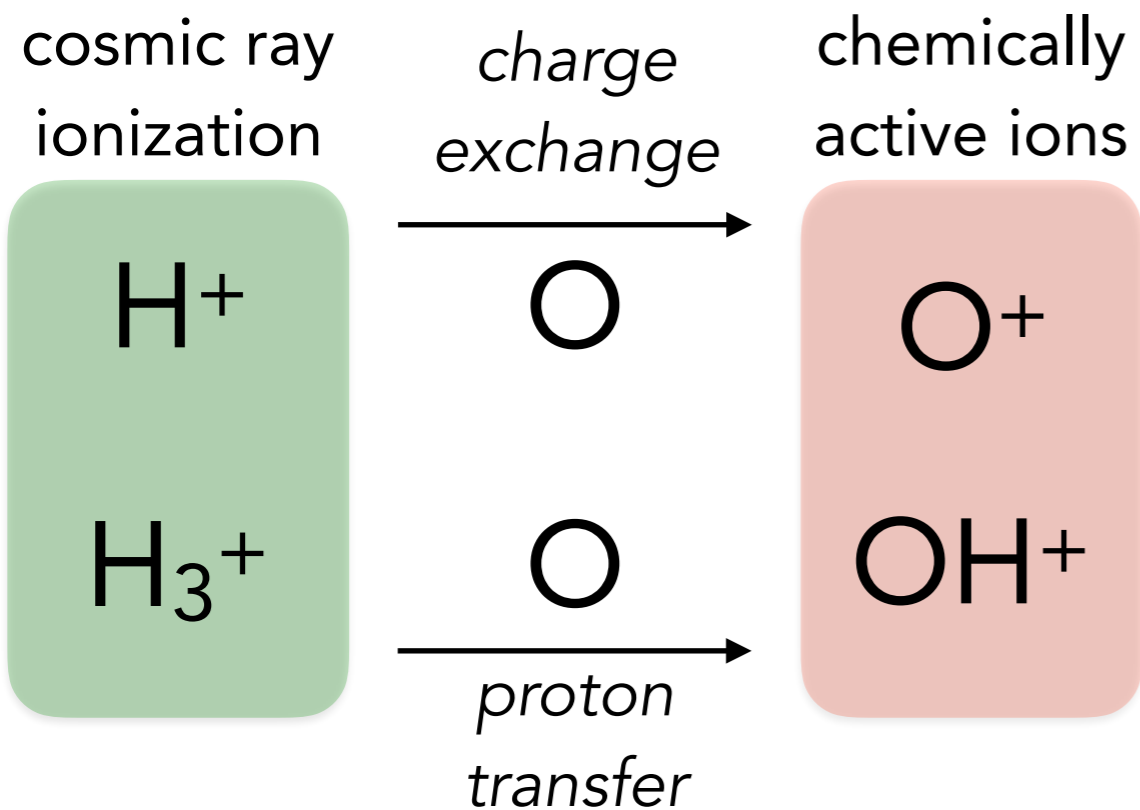
Carbon Monoxide - most abundant molecule after H₂

cosmic ray
ionization



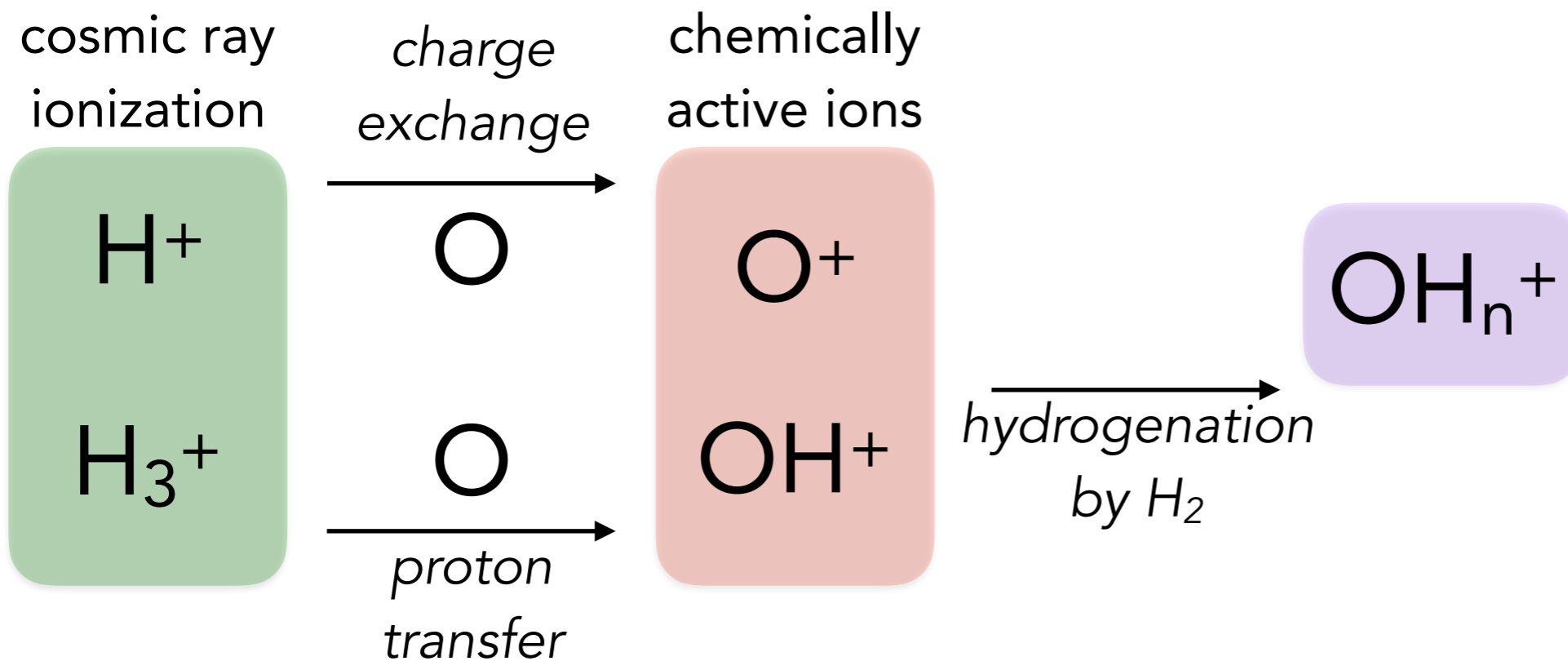
Chemistry in Molecular Gas

Carbon Monoxide - most abundant molecule after H_2



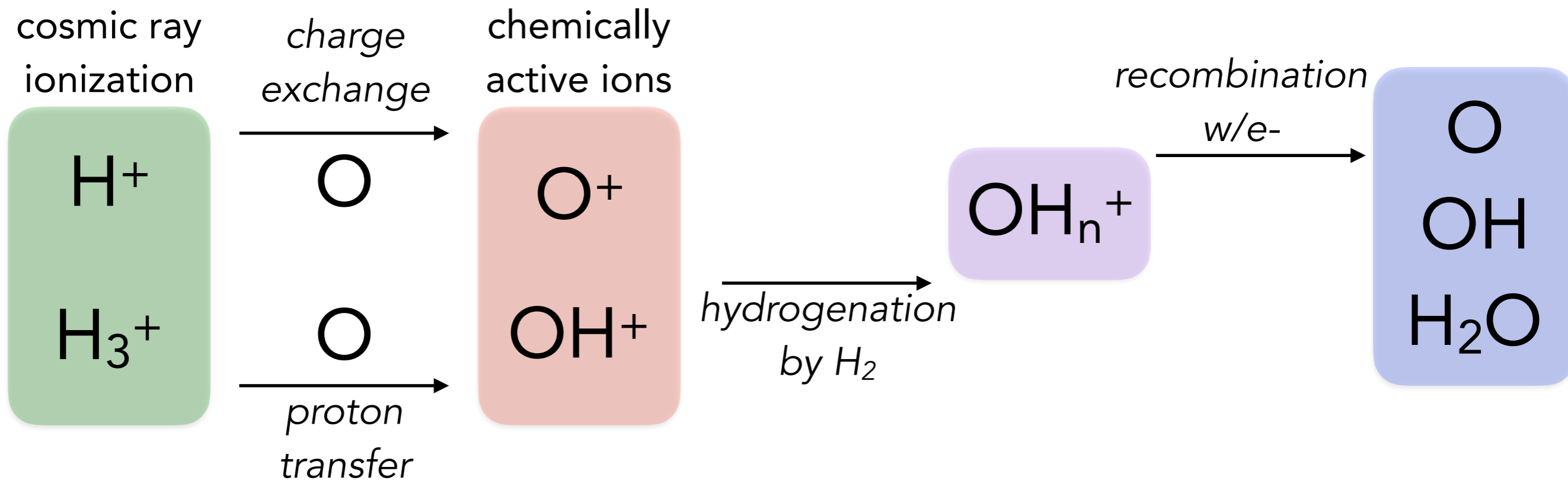
Chemistry in Molecular Gas

Carbon Monoxide - most abundant molecule after H_2



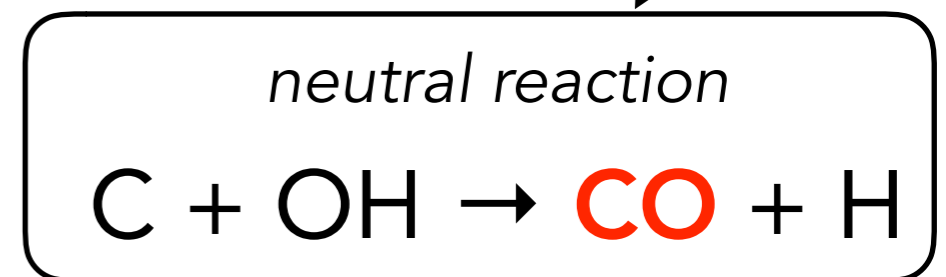
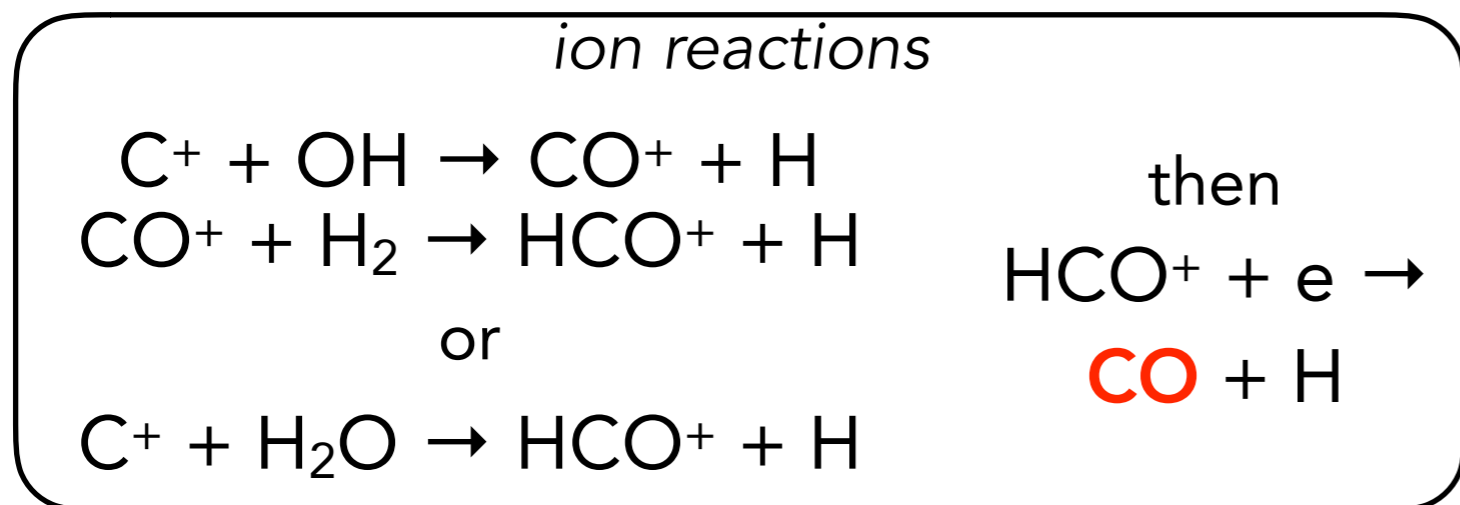
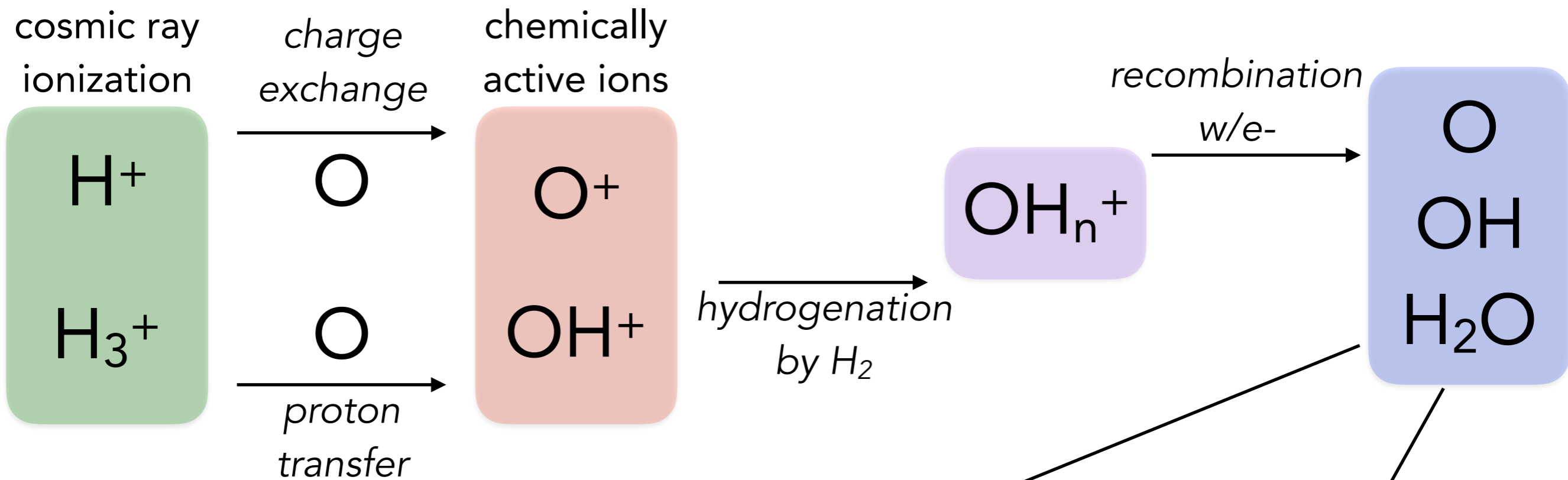
Chemistry in Molecular Gas

Carbon Monoxide - most abundant molecule after H_2



Chemistry in Molecular Gas

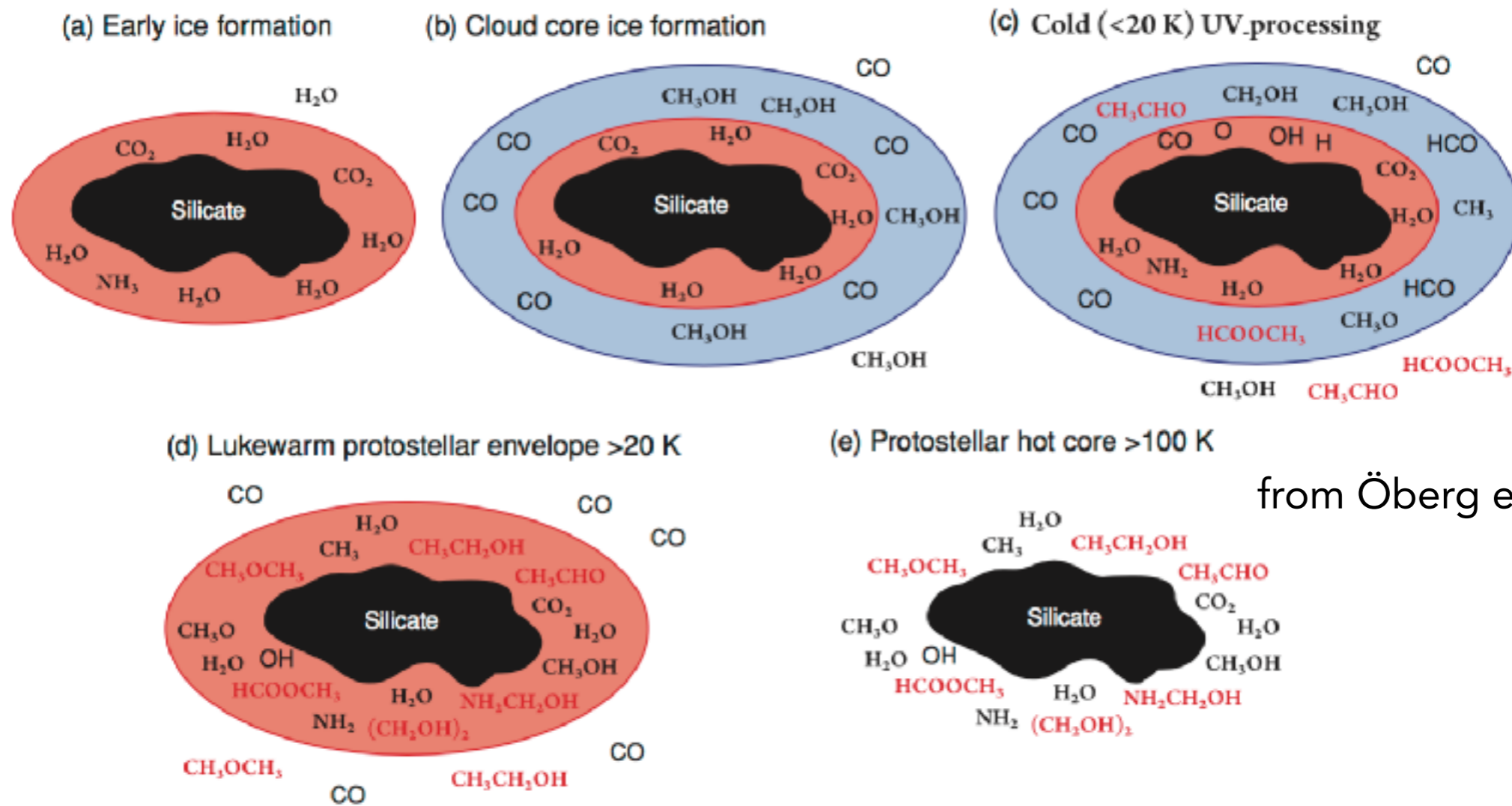
Carbon Monoxide - most abundant molecule after H₂



Chemistry in Molecular Gas

In dense parts of clouds

CO can "freeze out" to form ice on grains.

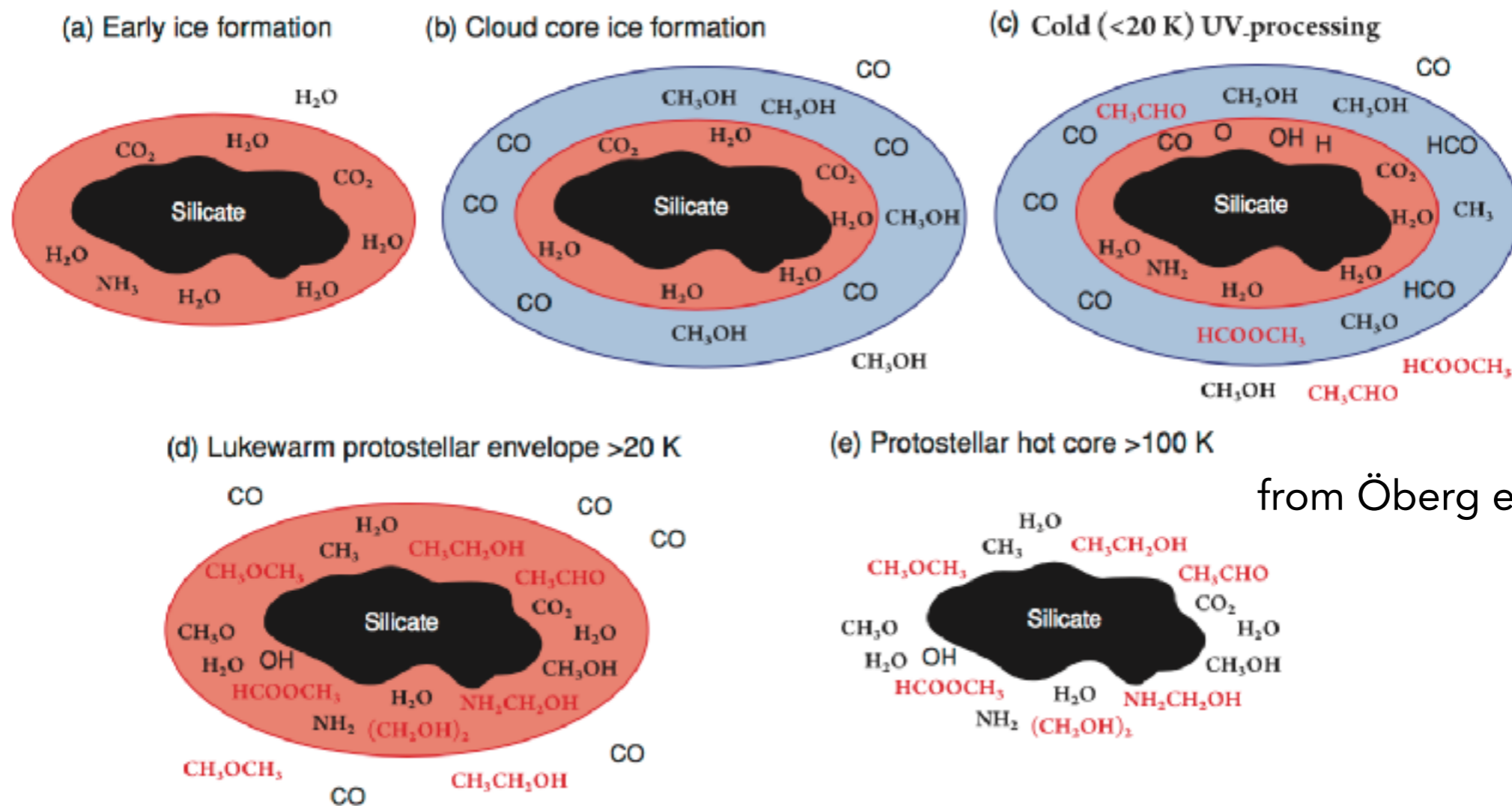


from Öberg et al. 2010

Figure 7. Suggested evolution of ices during star formation. Pink indicates an H₂O-dominated ice and blue a CO-dominated ice. At each cold stage a small amount of the ice is released non-thermally. Early during cloud formation (a) an H₂O-rich ice forms. Once a critical density and temperature is reached CO freezes out catastrophically (b), providing reactants for CH₃OH ice formation. Far away from the protostar (c), photoprocessing of the CO-rich ice results in the production of, e.g., HCOOCH₃. Closer to the protostar (d), following sublimation of CO, other complex molecules become abundant. Finally, all ice desorb thermally close to the protostar >100 K (e).

Chemistry in Molecular Gas

Grain surface chemistry + Ice mantle chemistry
can lead to complex molecules!



from Öberg et al. 2010

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