

15. Introduction to Interstellar Chemistry

1. Background
2. Gas Phase Chemistry
3. Formation & Destruction of H₂
4. Formation & Destruction of CO
5. Other Simple Molecules

References

- Tielens, "Physics & Chemistry of the ISM" (2006), Ch. 4
- Duley & Williams, "Interstellar Chemistry" (1984)
- van Dishoeck & Blake, ARAA 36 317 (1998)
- van Dishoeck ARAA, 42 119 (2004)

Data Collections

<http://www.udfa.net> (UMIST)

<http://kinetics.nist.gov/kinetics/index.jsp/> (NIST)

1. Motivation for Interstellar Chemistry

Half the baryons in the ISM are in molecules ...

Interstellar chemistry began with the discovery of interstellar molecules. It now includes nano to micron sized *particles*, as well as molecules.

Some differences with terrestrial lab chemistry:

1. Much lower pressures
2. Extreme temperatures (cryogenic to hot)
3. External energy sources (UV, X-rays, CRs)
4. Time- and space-varying conditions (dynamics)

More than 145 molecules have been detected (not counting isotopes):

<http://aramis.obspm.fr/mol/list-mol.html>

Notice the many “exotic” species, e.g., small chains, unsaturated radicals, and ions.

Goals of Interstellar Chemistry

- (1) Model molecular diagnostics in terms of the physical conditions (temperature density, & ionization fraction).
- (2) Explore novel aspects of non-terrestrial chemistry and relate interstellar to pre-biotic chemistry.

Main Applications

- (1) **Interstellar Clouds:** Partially shielded diffuse and dense clouds, i.e., photon-dominated regions, and shocks
- (2) **Outflows from Evolved Stars & SNRs**
- (3) **Star-Formation:** Cloud cores, in-falling envelopes, disks & winds of young stellar objects
- (4) **Structure formation in the early universe**

2. Gas Phase Chemistry of Gas Clouds

Focus on cool ($T < 100$ K), low-ionization ($x_e < 10^{-3}$) gas with minimal attention to surface chemistry:

Diffuse Clouds and Exteriors of Molecular Clouds

Moderate density - typically 100 cm^{-3}

Low temperature - typically 50 K

Low ionization - mainly H^+ and C^+

Molecular Cloud Interiors

Intermediate density - typically 250 cm^{-3}

Low temperature - typically 20 K

Very low ionization - typically 10^{-7}

Historical Note: Interstellar chemistry developed rapidly c. 1973, strongly influenced by Salpeter et al. (e.g. Gould, Werner, Watson, Hollenbach & Draine). Other pioneering work emphasizing grain catalysis was by Bates & Spitzer (ApJ 113 441 1951) & Stecher & Williams (ApJ 146 88 1966).

Stimulating Chemical Activity

Few chemical reactions occur under the “mild” physical conditions of the gas just cited, e.g., the most abundant molecules in dense clouds, H_2 and CO , are unreactive.

- Even exothermic reactions may not proceed unless the collision energy is high enough to overcome some characteristic **activation energy** of order 1 eV.
- To activate cold chemistry, **energy has to be provided externally** in the form of UV or X-ray photons, cosmic rays, or mechanical energy (shocks).
- Chemistry in partially shielded quiescent regions is energized by **UV photons**, which dissociate molecules at rates $\sim 10^{-10}\text{s}^{-1}$ (i.e., on a time-scale as short as 300 yr). In shielded regions, **cosmic rays** and **X-rays** are invoked.

Generic Reaction Types

1. One-body



2. Two-body

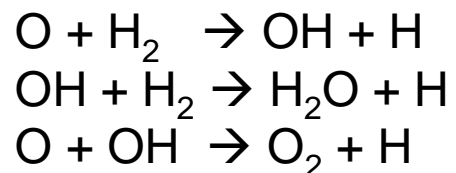


k is the reaction ***rate-coefficient***

- The rate coefficient is usually a function of T , as in reactions with activation energy, where it varies as $\exp(-T_a/T)$, possibly multiplied by a power of T .
- Three-body reactions are rare because of the low ISM density.
- ***Volumetric rates are sensitive to both T and n_{H} .***

Examples of Specific Types of Reaction

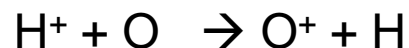
Neutral Radical – Warm regions ($> 300\text{ K}$); k up to $10^{-10}\text{ cm}^3\text{ s}^{-1}$.



The first two have to overcome thermal activation barriers and are suppressed in cool clouds.

Ion-Molecule – Often $k \sim 10^{-9}\text{ cm}^3\text{ s}^{-1}$ and without activation energy for very exothermic reactions, and thus important for cool regions

charge exchange



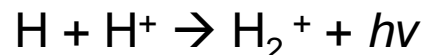
(H) abstraction



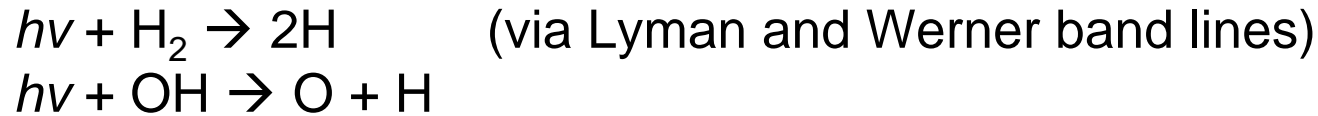
proton transfer



Radiative Association - Weak, but sometimes the only pathway, e.g., in the dark ages

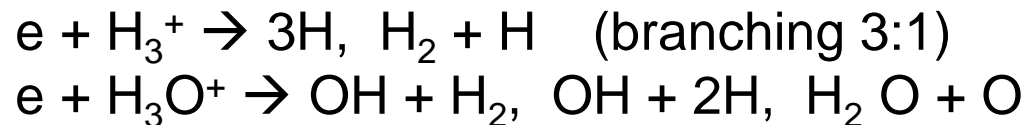


Photodissociation – Almost always important; typically $\sim 10^{-10} \text{ s}^{-1}$.

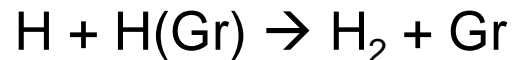


N.B. Many cross sections have not been measured accurately.

Dissociative Recombination - Always important; $k \sim 10^{-7} \text{ cm}^3 \text{ s}^{-1}$



Addendum on Surface Reactions – Important but poorly understood. One of the most important is grain synthesis of H_2 :



at close to the geometric rate (e.g., Hollenbach & Salpeter 1971) but still slow.

Additional processes: ***adsorption, desorption and catalysis*** are all not fully understood. See Tielens' book.

3. Formation and Destruction of H₂

A. Formation in Cool regions (T < 100-300 K)

The simplest process, radiative association of two H atoms,



is very weak (a ro-vibrational, quadrupole transition). For more than 40 years it has been generally assumed that **H₂ is formed on grains**, as in

$$\text{volumetric formation rate} = R n_{\text{H}} n(\text{H})$$

where, following Hollenbach & Salpeter (1971), R is essentially the rate at which H atoms strike the available grain surface area (per unit volume) with a “sticking factor” of 1/3,

$$R = 3 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1} (T/100\text{K})^{1/2}.$$

NB McKee (Lec19-2006) uses a value twice as large based on Bertoldi & Draine ApJ 468 269 1996

Formation of H₂ on Grain Surfaces

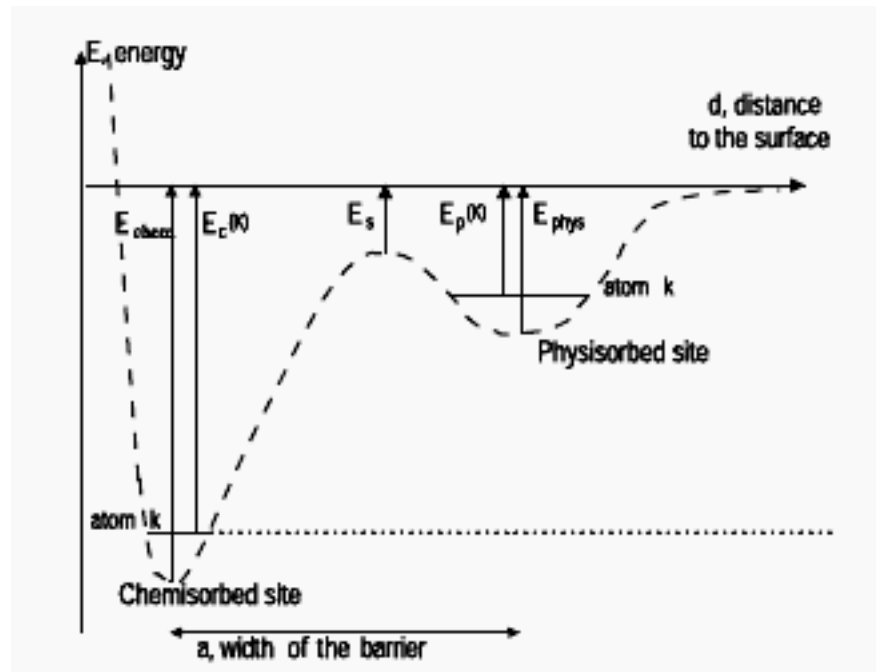


Figure from
Cazaux & Spaans
ApJ 611 40 2004

- Incident H atoms can be bound by long and short range forces, commonly called physisorption and chemisorption.
- When another H strikes, it diffuses on the surface until it combines with a bound H, forms H₂, and leaves the surface.
- The processes of adsorption, sticking, binding, diffusion, formation and desorption depend on the gas and dust temperatures and on grain surface.
- Cazaux & Tielens (ApJ 575 L29 2000, 604 222 2004) find that the formation efficiency is ~ 1 for $T < 30\text{K}$ and ~ 0.3 for $100 < T < 1000\text{ K}$.

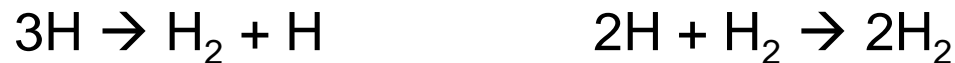
Additional H₂ Formation Processes

B. Formation in Warm Regions ($T > 300$ K) – **radiative association** of H ions of both signs



Typical applications are post-recombination and outflows from YSOs.

C. Formation in Very Dense Regions ($> 10^{12}$ cm³ s⁻¹) - **three-body** reactions. e.g.,



with rate coefficients $10^{-32} - 10^{-33}$ cm⁶ s⁻¹. Typical applications are cool stellar atmospheres, YSO disks and jets.

Photodissociation of H₂

Following Lecture 14, H₂ is dissociated in a two-step process where a far UV photon is absorbed in a Lyman or Werner transition below 1108 Å, and the excited molecule decays into the continuum of the ground electronic state with the emission of a photon in the 1300-1700 Å band.

With typical oscillator strengths of 0.03, the L-W lines easily become optically thick. For example, with a Doppler parameter $b = 3 \text{ km s}^{-1}$, the standard formula for optical depth at line center

$$\tau(0) = f_{lu} \frac{\pi e^2}{m_e c} \frac{N_l}{\sqrt{\pi} b}$$

yields $N(\text{H}_2) > 10^{14} \text{ cm}^{-2}$. Thus absorption occurs mainly in the damping wings of the Lyman and Werner lines.

NB The theory of H₂ photodissociation was developed by Salpeter et al., e.g., Hollenbach, Werner, & Salpeter (ApJ, 163, 166, 1971) and applied to the early Copernicus observations by Jura (ApJ 191 375 1974) and Federman, Glassgold & Kwan (ApJ, 227, 466, 1979; *FGK*). See Warin et al. A&A 308 535 1996 for a more complete theory.

Photodissociation of H₂ (cont'd)

FGK showed that, in the presence of H₂ absorbers, the transmitted dissociating radiation is given by the *derivative* of the equivalent width. The proof follows from considering the definition of equivalent width for the transition $j \rightarrow k$:

$$W_{jk} = \int_{-\infty}^{\infty} d\nu \varphi(\nu) \left[1 - \exp(-N_j s_{jk} \varphi(\nu)) \right]$$

Here $\sigma_{jk}(\nu) = s_{jk} \varphi(\nu)$ is the frequency dependent absorption cross section. Differentiation leads to:

$$\frac{\partial W_{jk}}{\partial(N_j s_{jk})} = \int_{-\infty}^{\infty} d\nu \varphi(\nu) \exp(-N_j s_{jk} \varphi(\nu)) = \frac{\int_{-\infty}^{\infty} d\nu s_{jk} \varphi(\nu) \exp(-N_j s_{jk} \varphi(\nu))}{\int_{-\infty}^{\infty} d\nu \varphi(\nu) s_{jk} \varphi(\nu)} = J_{jk}$$

where J_{jk} is the line self-shielding function. In practice, a sum over all of the dissociating transitions has to be carried out

The Line Self-Shielding Function

$$J_{jk} = \frac{\int_{-\infty}^{\infty} dv s_{jk} \varphi(v) \exp(-N_j s_{jk} \varphi(v))}{\int_{-\infty}^{\infty} dv \varphi(v) s_{jk} \varphi(v)}$$

J_{jk} the absorption cross section averaged over the line shape, taking into account attenuation. It may be considered a function of the optical depth at line center

$$\tau(0) = N_j s_{jk} \varphi(0) = f_{jk} \frac{\pi e^2}{m_e c} \frac{N_l}{\sqrt{\pi} b} \quad (\text{for Doppler broadening})$$

J_{jk} is a decreasing function of optical depth (or column), starting from unity at zero optical depth. From the dependence of *the* equivalent width W on optical depth, the dependence of J_{jk} can be obtained by differentiation:

Curve of Growth and Line Self-Shielding

There are three regimes of equivalent width, depending on optical depth at line center:

$\tau_0 \ll 1$	linear	$\sim \tau_0$
$\tau_0 > 1$	flat or logarithmic	$\sim \log \tau_0^{1/2}$
$\tau_0 \gg 1$	square-root	$\sim \tau_0^{1/2}$

Differentiating W gives the corresponding behavior for J :

$\tau_0 \ll 1$	$J = 1$
$\tau_0 > 1$	$J \sim 1/\tau_0$
$\tau_0 \gg 1$	$J \sim \tau_0^{-1/2}$

In practice, the Lyman & Werner bands are usually very optically thick: ***the dissociation rate decreases as the inverse square root of the H_2 column density***

Balancing H₂ Formation and Destruction

Balance the photodestruction rate $G_0 J n(\text{H}_2)$ against the grain formation rate $R n_{\text{H}} n(\text{H})$ and satisfy mass conservation, $n_{\text{H}} = n(\text{H}) + 2n(\text{H}_2)$. The photo rate is calculated summing all accessible Lyman & Werner band transitions.

$$x(\text{H}_2) = \frac{1}{1 + \varepsilon} \quad \varepsilon = \frac{G_0 J}{2 n_{\text{H}} R} \quad J \cong \sqrt{\frac{M}{N(\text{H}_2)}}$$

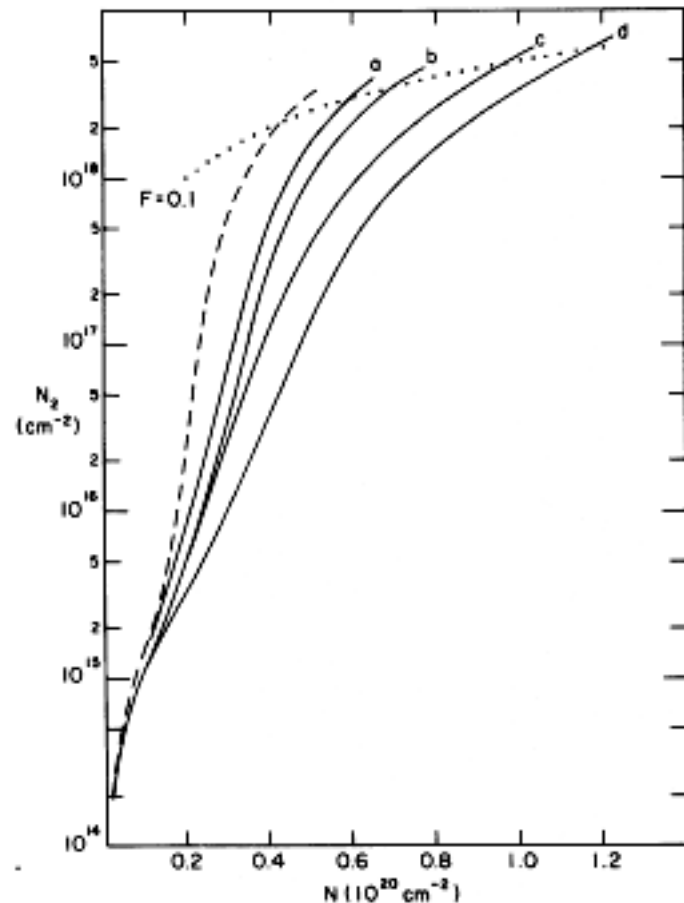
$$M = 6.75 \times 10^{11} \text{ cm}^{-2}, R = 3 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1} (T / 100 \text{ K})^{1/2}, G_0 = 6 \times 10^{-11} \text{ s}^{-1}$$

ε is the ratio of the formation to the photodissociation time scales. H₂ formation on grains is a slow process, e.g., the formation time at 100 K is

$$1 / R n_{\text{H}} = 10 \text{ Gyr} \left(\frac{\text{cm}^{-3}}{n_{\text{H}}} \right)$$

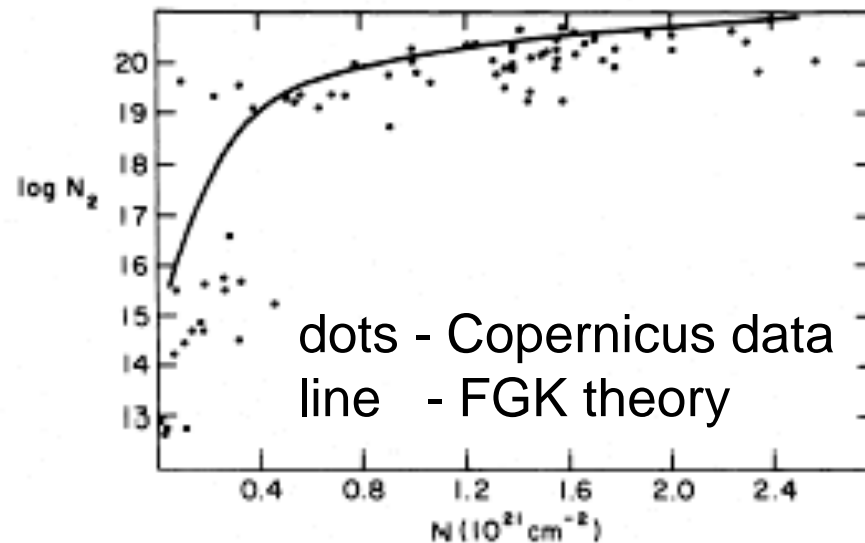
The H-H₂ Transition

$N(\text{H}_2)$



N_{H}

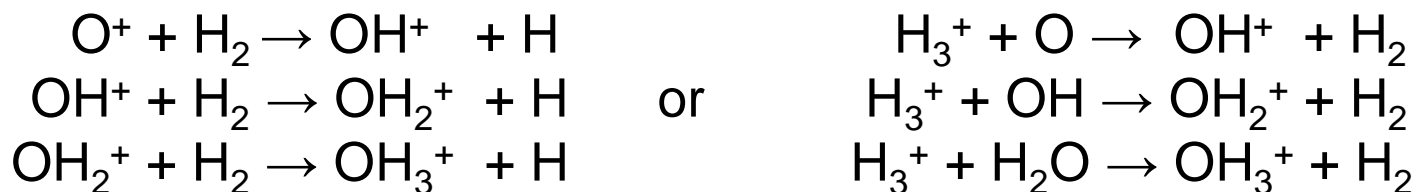
dashed curve HWS
 a. FGK theory (only ground state)
 b. with dust
 c. thermal level population
 d. collisional-radiative population
 dotted-curve: 10% conversion



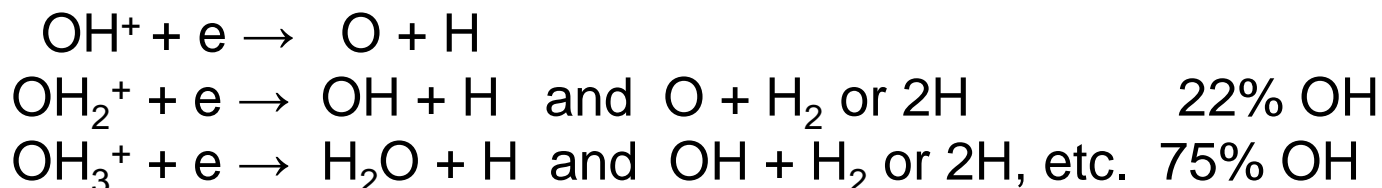
Limited observational support for the theory of H₂ formation & destruction

4. Formation and Destruction of CO

A. Oxygen hydride formation by fast ion-molecule reactions ($k \sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$)



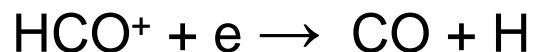
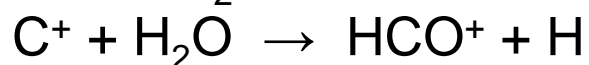
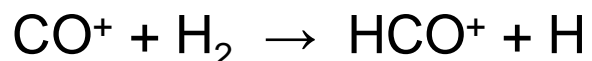
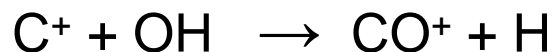
and fast **dissociative recombination**, $\beta \sim 10^{-7} \text{ cm}^3 \text{ s}^{-1}$:



- OH is a crucial intermediary in the formation of CO; it requires H_2 as a precursor.
- The synthesis of OH is driven by the ions O^+ and H_3^+ .
- This scheme also produces H_2O and other O-bearing molecules.

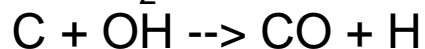
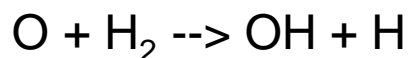
B. Gas-Phase Synthesis of CO

CO is rapidly produced from OH by fast reactions, e.g.,



or, where C is more abundant than C^+ , the neutral reaction is effective: $\text{C} + \text{OH} \rightarrow \text{CO} + \text{H}$

NB. In warm regions, radical reactions take the place of ion-molecule reactions:



(slow - activation energy)

(moderately fast)

NB: The idea of using ion-molecule reactions to initiate low-temperature interstellar chemistry is due to Watson (ApJ 183 L17 1973) and Herbst & Klemperer (ApJ 185 505 1973), although the latter did not give the correct theory for CO. Klemperer had earlier identified an unknown mm transition with HCO^+ (ApJ 188 255 1974) and was responsible for the idea that easily detected ion is the surrogate for the primary and difficult to detect molecular ion H_3^+

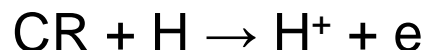
C. The Role of Cosmic Rays

The progenitor ions of the ion-molecule chemistry in cool regions are presumed to come from cosmic rays.

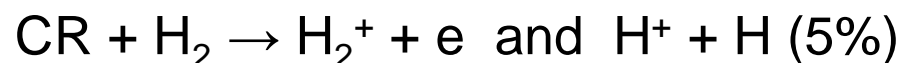
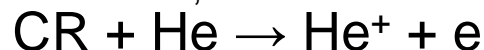
We estimated (Lec09) that the cosmic ray ionization rate in the solar neighborhood (from demodulated satellite observations out to 42 AU):

$$\zeta_{\text{CR}}(> 2 \text{ MeV}) \approx 5 \times 10^{-17} \text{ s}^{-1}$$

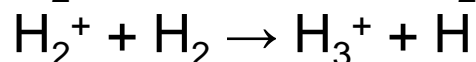
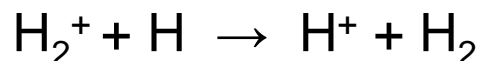
This is for atomic H, i.e.,



Similar rates apply to He and H₂,



But H₂⁺ is very reactive:



and leads to **H₃⁺**, the **primary ion in ion-molecule chemistry**.

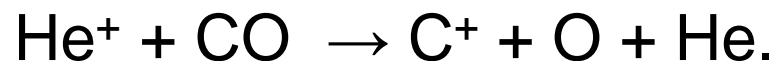
D. Destruction of CO

1. In partially UV-shielded regions, photo-dissociation occurs via the same two-step line process that operates for H₂, with the following changes:

- a. $G_0 = 2 \times 10^{-10} \text{ s}^{-1}$ (for the mean UV radiation field),
- b. self-shielding is reduced since usually $x(\text{CO}) \ll x(\text{H}_2)$.
- c. mutual shielding occurs in the 912-1108 Å band by H₂ and even by lines of atomic H
- d. mutual shielding of the isotopes ¹³CO and C¹⁷O by the lines of ¹²CO and H₂ also occurs

2. In well-shielded (thick) clouds, CO is destroyed by the

fast ion-molecule reaction



E. Summary of CO Synthesis

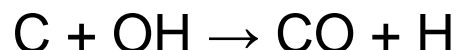
The chemically active ions are generated from neutral atomic O:

O⁺ (by charge exchange of H⁺)

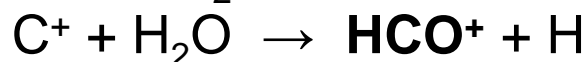
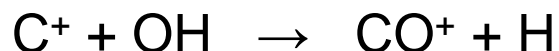
OH⁺ (by proton transfer of H₃⁺).

These ions are then hydrogenated by H₂, producing the series **OH_n⁺** with n=1,2,3, but mainly **OH₃⁺** (if the abundance of H₂ is large).

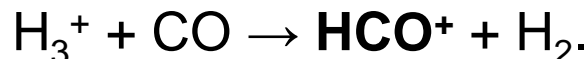
Recombination of OH₃⁺ leads to O, OH & H₂O; CO is made from the neutral reaction:



or by ionic reactions:



Once CO is formed, HCO⁺ can be produced directly from CO with H₃⁺:



Since H₃⁺ and H₃O⁺ are spherical rotors and HCO⁺ is linear (with a large dipole moment), ***HCO⁺ is considered a strong signature of ion-molecule interstellar chemistry.***

Caveats on the Ion-Molecule Synthesis of CO

The ion-molecule reactions for CO synthesis are fast, but the ions may be in short supply in dense shielded regions because their abundance depends on $\zeta_{\text{CR}}/n_{\text{H}}$.

In lightly shielded regions the time scales are short, but only a small fraction of carbon goes into CO because of strong photodissociation.

Slow formation of H_2 may be the limiting factor in the synthesis of CO in atomic regions.

Cloud conditions can be critical: geometry, proximity to and strength of the stellar FUV radiation, temperature, and age of the cloud.

5. Other Simple Molecules

A. Review of the Oxygen Chemistry

OH is the precursor of many molecules via moderately fast radical reactions e.g., O_2 and CO_2 :



Chemical models had predicted full association of oxygen into H_2O & O_2 in shielded regions, as described above. This conclusion is *not* supported by SWAS & ISO.

SWAS (4' beam) did not detect O_2 at 487 GHz (616 microns), giving upper abundance limits of 10^{-6} . It did detect the lowest rotational transition of H_2O at 547 GHz (538 microns), giving $\text{H}_2\text{O}/\text{H}_2 \sim 10^{-8}$, & 10 higher for Orion & the Sgr B2 cloud (galactic center).

ISO (1.3' beam) detected a variety of molecules in emission & absorption, giving a large range of H_2O abundances:

$$\text{H}_2\text{O}/\text{H}_2 \sim 10^{-8} - 10^{-4}.$$

Conclusions on Oxygen Chemistry

Observations of O_2 and H_2O suggest that the dominant gas phase oxygen species is often ***atomic oxygen***, consistent with limited observations of the OI fine-structure emission lines at 63 & 145 μm .

SWAS may have emphasized cool regions where H_2O is frozen out onto grains or where the OH radical chemistry is inoperative due to activation energies ($T_a \sim 3000$ K).

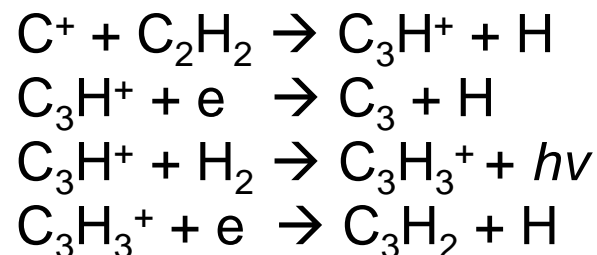
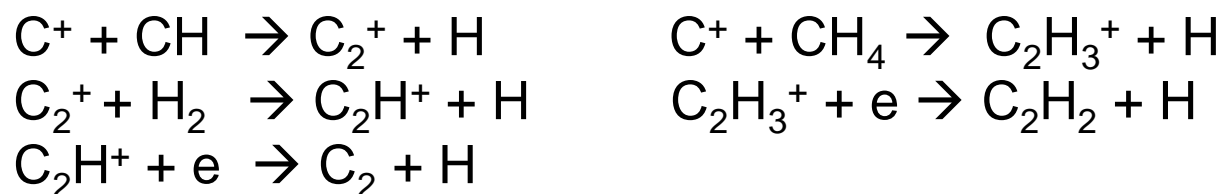
ISO detections of H_2O in warm regions probably arise from thermally desorbed H_2O or OH radical chemistry, with heating by outflow shocks

Grains are important: In addition to incorporating O (as oxides of Si etc.), volatile gases freeze out on grains (as shown by ISO); grains may also catalyze chemical reactions.

Grain chemistry is poorly understood, but it is generally accepted that grains can hydrogenate the abundant heavy elements and synthesize H_2O , CH_4 , NH_3 , and CH_3OH among others (see Tielens 2006).

B. Complex Carbon Species

More than half of the interstellar molecules are polyatomic hydrocarbons. The most promising route is by “insertion reactions” (c.f. early work by Suzuki), e.g. C_2 , C_3 , C_2H_2 & C_3H_2 can be made with gas-phase reactions:

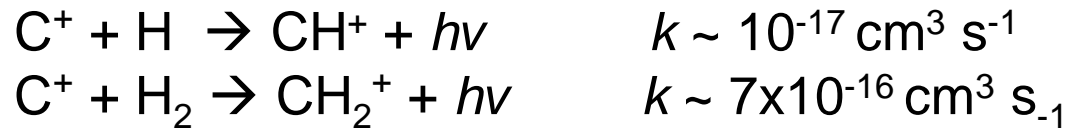


N.B. Not all routes and branches have been shown.

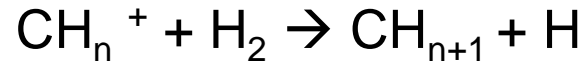
Compared to the mono-carbon species (CH , CH^+ , CH_4), the ***gas phase chemistry of multi-carbon species is quite promising.***

Mono-carbon species are hard to synthesize by gas-phase reactions, e.g., CH_n $n=1-4$ & CH^+ :

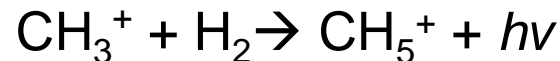
Problem #1: $\text{C}^+ + \text{H}_2 \rightarrow \text{CH}^+ + \text{H}$ is endothermic by 0.4 eV. One possibility is *radiative association*



Problem #2: The sequence of abstraction reactions is broken at CH_3^+ .



Again radiative association has been invoked:



Radiative association is difficult to measure (de-excitation by a 3rd body occurs) and the theory is unreliable by 1-2 dex:

CH_4 is probably formed by hydrogenation on grains.

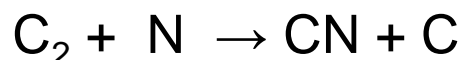
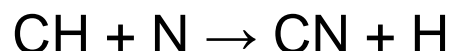
C. Nitrogen Chemistry

- $IP(N) = 14.5 \text{ eV}$: The most abundant nitrogen species in diffuse regions is atomic N.
- NH_3^+ and NH_4^+ interact weakly or not at all: standard ion-molecule sequence ends at NH_2 .

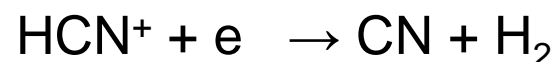
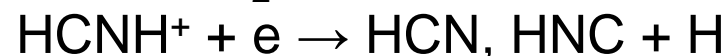
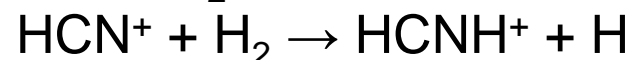
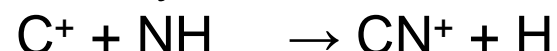
Ion-molecule chemistry doesn't work as well for N as for C & O.

NH_3 is probably made on grains in cool regions.

- CN can be made by *neutral reactions* from carbon radicals, e.g.,



And by ion-molecule reactions, e.g.,



- Polyacetylene chains can be built up along these same lines, e.g.,

