

# 21. Introduction to Interstellar Chemistry

1. Background
2. Gas Phase Chemistry
3. Formation and Destruction of H<sub>2</sub>
4. Formation and Destruction of CO
5. Other Simple Molecules

## References

- Tielens, "Physics and Chemistry of the ISM" (2006), Ch. 4 plus Secs. 8.8, 10.2, 10.4.4
- Duley & Williams, "Interstellar Chemistry" (1984)
- McKee, Lecture 19 (ay216-2006)
- 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)

ay216-09

1

## 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.**

ay216-09

2

## Goals of Interstellar Chemistry

- (1) Model molecular diagnostics in terms of the physical conditions (temperature density, and 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 and SNRs**
- (3) **Star-Formation:** Cloud cores, in-falling envelopes, disks and winds of young stellar objects
- (4) **Structure formation in the early universe**

ay216-09

3

## 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  $100 \text{ cm}^{-3}$

Low temperature - typically 50 K

Low ionization - mainly  $\text{H}^+$  and  $\text{C}^+$

### Molecular Cloud Interiors

Intermediate density - typically  $250 \text{ cm}^{-3}$

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. (i.e., Gould, Werner, Watson, Hollenbach & Draine) and by Dalgarno et al. Other pioneering work emphasizing grain catalysis was by Bates & Spitzer (ApJ 113 441 1951) and Stecher & Williams (ApJ 146 88 1966).

ay216-09

4

## Stimulating Chemical Activity

Little chemical activity occurs under the “mild” physical conditions of the gas just cited, e.g., the most abundant molecules in dense clouds, H<sub>2</sub> and CO, are unreactive.

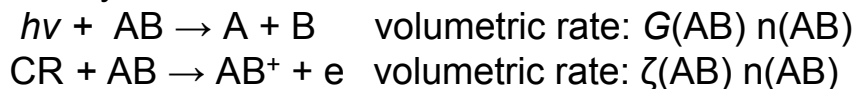
- Even exothermic reactions may not proceed unless the collision energy is high enough to overcome some characteristic **activation energy** of order 1 eV.
- To activate cold chemistry, **energy has to be provided externally** in the form of UV or X-ray photons, cosmic rays, or mechanical energy (shocks).
- 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.

ay216-09

5

## Generic Reaction Types

### 1. One-body



### 2. Two-body



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

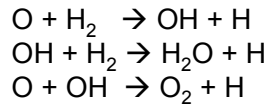
- The rate coefficient is usually a function of  $T$ , as in reactions with activation energy, where it varies as  $\exp(-T_a/T)$ , possibly multiplied by a power of  $T$ .
- Three-body reactions are rare because of the low ISM density.
- **Volumetric rates are sensitive to both  $T$  and  $n_H$ .**

ay216-09

6

## Examples of Specific Reaction Types

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

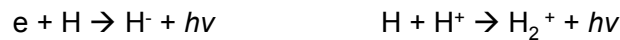


The first two have to overcome thermal activation barriers and are suppressed in cool clouds.

**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



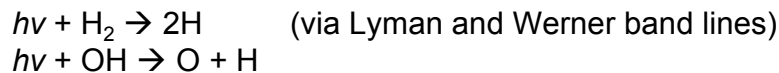
**Radiative Association** - Weak, but sometimes the only pathway, e.g., in the dark ages



ay216-09

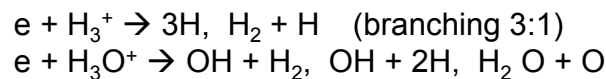
7

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

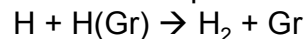


N.B. Many cross sections have not been measured accurately.

**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  $\text{H}_2$ :



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.

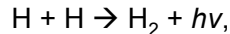
ay216-09

8

### 3. Formation and Destruction of H<sub>2</sub>

#### 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 **H<sub>2</sub> is formed on grains**, as in

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

where, following Hollenbach and 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) gives a somewhat different development of H<sub>2</sub> formation and destruction. He uses a value for  $R$  that is as large, based on Bertoldi & Draine (ApJ 468 269 1996).

ay216-09

9

### Formation of H<sub>2</sub> on Grain Surfaces

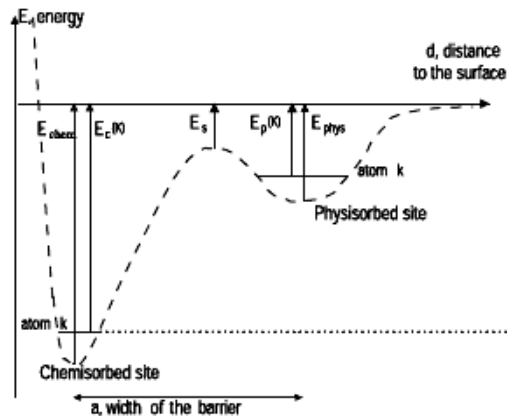


Figure from  
Cazaux & Spaans  
ApJ 611 40 2004

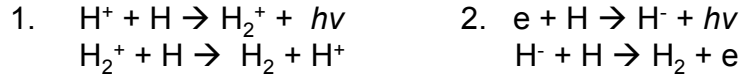
- Incident H atoms can be bound by long and short range forces, commonly called physisorption and chemisorption.
- When another H strikes, it diffuses on the surface until it combines with a bound H, forms H<sub>2</sub> and leaves the surface.
- The processes of adsorption, sticking, binding, diffusion, formation and desorption depend on the gas and dust temperatures and the grain surface.
- Cazaux & Tielens (ApJ 575 L29 2000; ApJ 604 222 2004) find that the formation efficiency is  $\sim 1$  for  $T < 30\text{K}$  and  $\sim 0.3$  for  $100 < T < 900\text{K}$ .

ay216-09

10

## Additional H<sub>2</sub> 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 (  $> 10^{12}$  cm<sup>3</sup> ) - *three-body* reactions. e.g.,



with rate coefficients  $10^{-33} - 10^{-32}$  cm<sup>6</sup> s<sup>-1</sup>. Typical applications are cool stellar atmospheres, YSO disks and jets.

ay216-09

11

## Photodissociation of H<sub>2</sub>

Following Lecture 19, H<sub>2</sub> 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  $b = 3$  km s<sup>-1</sup>, 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  $N(\text{H}_2) > 10^{14}$  cm<sup>-2</sup>. Thus absorption occurs mainly in the damping wings of the Lyman and Werner lines.

**NB** The theory of H<sub>2</sub> 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.

ay216-09

12

## Shielding of the Photodissociation

Absorption of the dissociating radiation by the H<sub>2</sub> lines themselves reduces the photo rate. FGK related this **self-shielding** effect to the familiar concept of equivalent width by showing that 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  $j \rightarrow k$ :

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

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

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

$J_{jk}$ , the **line self-shielding function**, is the mean absorption cross section averaged over the line shape, taking into account attenuation. **It specifies the transmission of the dissociating radiation.**

ay216-09

13

## The Line Self-Shielding Function

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

The line self-shielding function 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. In practice, a sum over all dissociating transitions needs to be carried out, leading to

$$G(\text{H}_2) = G_0 J$$

where  $G_0$  is the rate for  $N(\text{H}_2) = 0$  and  $J$  is the mean self-shielding, Function for finite  $N(\text{H}_2)$ , averaged over all lines .

ay216-09

14

## 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  $J$ :

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

The Lyman & Werner bands are usually very optically thick: *the dissociation rate decreases as the inverse square root of the  $H_2$  column density*. Without any shielding, the rate due to the interstellar radiation field is

$$G_0 \sim 6 \times 10^{-11} \text{ s}^{-1}$$

ay216-09

15

## Balancing $H_2$ Formation and Destruction

Balance the photodestruction rate  $G_0 J n(H_2)$  against the grain formation rate  $R n_H n(H)$  and require mass conservation,  $n_H = n(H) + 2n(H_2)$ . The photo rate involves the sum of all accessible Lyman & Werner band transitions. The fraction of  $H_2$  molecules can then be expressed approximately as:

$$f(H_2) = \frac{1}{1 + \varepsilon} \quad \varepsilon = \frac{G_0 J}{2 n_H R} \quad J \cong \sqrt{\frac{M}{N(H_2)}}$$

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

$\varepsilon$  is the ratio of the formation to the photodissociation time scale. For a slab,  $\varepsilon$  is large outside ( $J=1$ ), whereas inside  $J$  decreases with  $N(H_2)$  due to self-shielding until  $\varepsilon = 0$  and  $f(H_2) = 1$ .

**Grain formation of  $H_2$  is slow: the formation time at 100 K is:**

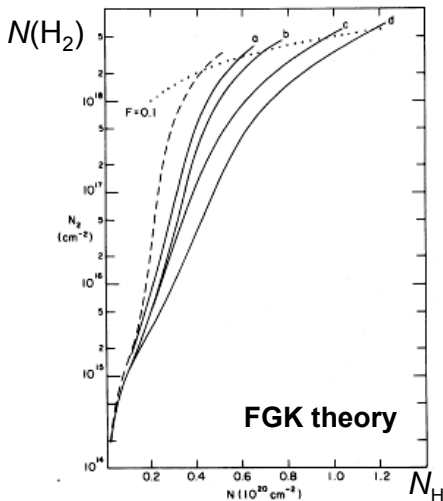
$$1/Rn_H \approx 1 \text{ Gyr} \left( \frac{\text{cm}^{-3}}{n_H} \right)$$

ay216-09

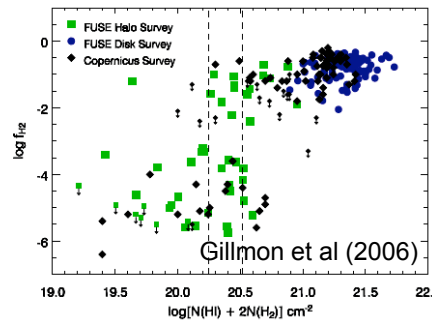
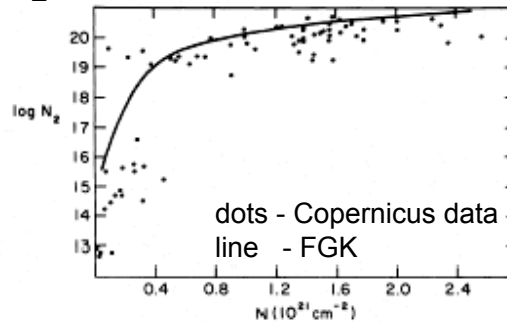
16



## The H-H<sub>2</sub> Transition



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



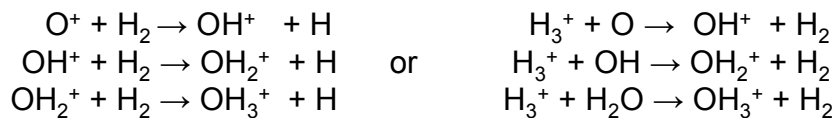
FUSE data from Gillmon et al (2006)  
somewhat similar to theory.

ay216-09

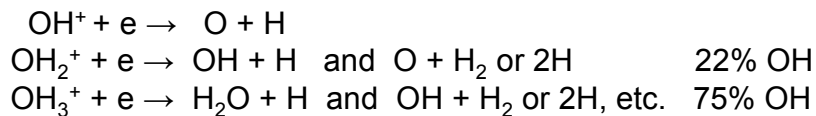
17

## 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*,  $\beta \sim 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  :



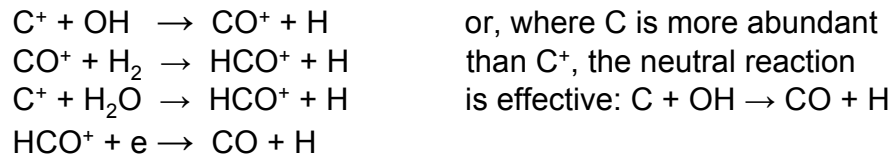
- The synthesis of OH is driven by the ions  $\text{O}^+$  and  $\text{H}_3^+$ .
- This scheme also produces  $\text{H}_2\text{O}$  and other O-bearing molecules.
- OH is a crucial intermediary in the formation of CO; it requires  $\text{H}_2$  as a precursor.

ay216-09

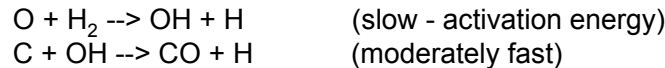
18

## B. Gas-Phase Synthesis of CO

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



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



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 any theory for CO. Klemperer had earlier identified an unknown mm transition with HCO<sup>+</sup> (ApJ 188 255 1974) and was responsible for the idea that this easily detected ion is the surrogate for the primary and difficult to detect molecular ion H<sub>3</sub><sup>+</sup>

ay216-09

19

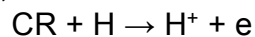
## C. The Role of Cosmic Rays

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

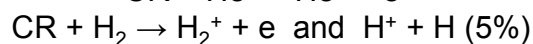
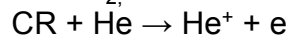
The cosmic ray ionization rate in the solar neighborhood from demodulated satellite observations out to 42 AU is:

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

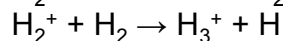
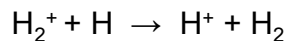
This is for atomic H, i.e.,



Similar rates apply to He and H<sub>2</sub>,



But H<sub>2</sub><sup>+</sup> is very reactive:



and leads to H<sub>3</sub><sup>+</sup>, the primary ion in ion-molecule chemistry.

The O<sup>+</sup> in ion-molecule chemistry comes from charge exchange with the cosmic ray produced H<sup>+</sup> ion.

ay216-09

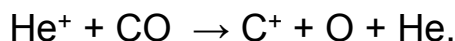
20

## D. Destruction of CO

1. In partially UV-shielded regions, photo-dissociation occurs via the same two-step line process that operates for H<sub>2</sub>, with the following changes:

- $G_0 = 2 \times 10^{-10} \text{ s}^{-1}$  (for the mean UV radiation field),
- self-shielding is reduced since usually  $x(\text{CO}) \ll x(\text{H}_2)$ .
- mutual shielding occurs in the 912-1108 Å band by H<sub>2</sub> and even by lines of atomic H
- mutual shielding of the isotopes <sup>13</sup>CO and C<sup>17</sup>O by the lines of <sup>12</sup>CO and H<sub>2</sub> also occurs

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



ay216-09

21

## E. Summary of CO Synthesis

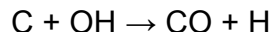
The chemically active ions are generated from neutral atomic O:

**O<sup>+</sup>** (by charge exchange of H<sup>+</sup>)

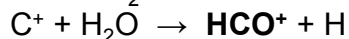
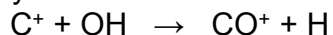
**OH<sup>+</sup>** (by proton transfer of H<sub>3</sub><sup>+</sup>).

These ions are then hydrogenated by H<sub>2</sub>, producing the series **OH<sub>n</sub><sup>+</sup>** with n=1,2,3, but mainly **OH<sub>3</sub><sup>+</sup>** (if the abundance of H<sub>2</sub> is large).

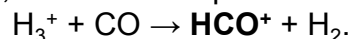
Recombination of OH<sub>3</sub><sup>+</sup> leads to O, OH and H<sub>2</sub>O; CO is made from the neutral reaction:



or by ionic reactions:



Once CO is formed, HCO<sup>+</sup> can be produced directly from CO with H<sub>3</sub><sup>+</sup>:



Since H<sub>3</sub><sup>+</sup> and H<sub>3</sub>O<sup>+</sup> are spherical rotors and HCO<sup>+</sup> is linear (with a large dipole moment), **HCO<sup>+</sup> is considered a strong signature of ion-molecule interstellar chemistry.**

ay216-09

22

## F. Caveats on 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  $\zeta_{CR}/n_H$ .

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<sub>2</sub> 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.

ay216-09

23

## 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<sub>2</sub> and CO<sub>2</sub>:



Chemical models had predicted full association of oxygen into H<sub>2</sub>O and O<sub>2</sub> in shielded regions, as described above. This conclusion is *not* supported by SWAS and ISO.

**SWAS** (4' beam) did not detect O<sub>2</sub> at 487 GHz (616 microns), giving upper abundance limits of 10<sup>-6</sup>. It did detect the lowest rotational transition of H<sub>2</sub>O at 547 GHz (538 microns), giving H<sub>2</sub>O/H<sub>2</sub> ~10<sup>-8</sup>, and ten times higher for Orion and the Sgr B2 cloud (galactic center).

**ISO** (1.3' beam) detected a variety of molecules in emission and absorption, giving a large range of H<sub>2</sub>O abundances:

$$H_2O/H_2 \sim 10^{-8} - 10^{-4}.$$

**ODIN - ?**

ay216-09

24

## Conclusions on Oxygen Chemistry

Observations of O<sub>2</sub> and H<sub>2</sub>O 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 and 145 μm.

SWAS may have emphasized cool regions where H<sub>2</sub>O is frozen out onto grains or where the OH radical chemistry is inoperative due to activation energies ( $T_a \sim 3000$  K).

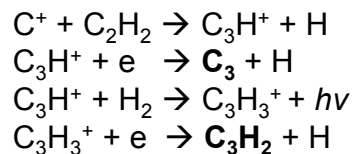
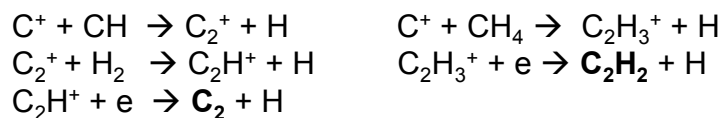
ISO detections of H<sub>2</sub>O in warm regions probably arise from thermally desorbed H<sub>2</sub>O or OH radical chemistry, with heating by outflow shocks

**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<sub>2</sub>O, CH<sub>4</sub>, NH<sub>3</sub>, and CH<sub>3</sub>OH 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<sub>2</sub><sup>+</sup>, C<sub>3</sub><sup>+</sup>, C<sub>2</sub>H<sub>2</sub> and C<sub>3</sub>H<sub>2</sub> can be made with gas-phase reactions:

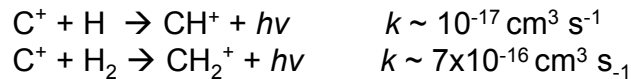


N.B. Not all routes and branches have been shown.

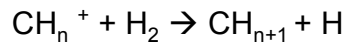
Compared to the mono-carbon species (CH, CH<sup>+</sup>, CH<sub>4</sub>), the **gas phase chemistry of multi-carbon species is quite promising.**

Mono-carbon species are hard to synthesize by gas-phase reactions, e.g.,  $\text{CH}_n$   $n=1-4$  and  $\text{CH}^+$ :

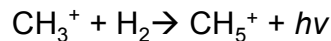
Problem #1:  $\text{C}^+ + \text{H}_2 \rightarrow \text{CH}^+ + \text{H}$  is endothermic by 0.4 eV. One possibility is *radiative association*



Problem #2: The sequence of abstraction reactions is broken at  $\text{CH}_3^+$ .



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:

***$\text{CH}_4$  is probably formed by hydrogenation on grains.***

ay216-09

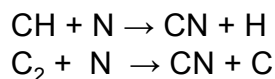
27

## C. Nitrogen Chemistry

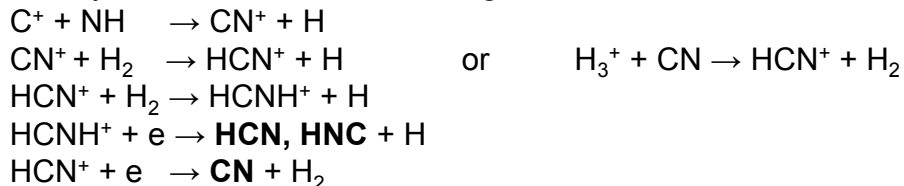
- IP(N) = 14.5 eV: The most abundant nitrogen species in diffuse regions is atomic N.
- $\text{NH}_3^+$  and  $\text{NH}_4^+$  interact weakly or not at all: standard ion-molecule sequence ends at  $\text{NH}_2$ .

**Ion-molecule chemistry doesn't work as well for N as for C and O:  $\text{NH}_3$  is probably made on grains in cool regions.**

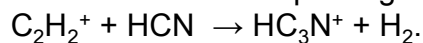
- CN can be made by *neutral reactions* from carbon radicals, e.g.,



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



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



ay216-09

28