Chemistry of the Interstellar Medium

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OUTLINE

Chemistry of the ISM I:

- “The Molecular Universe”: Introduction and motivations
- Environments where we detect molecules.

Chemistry of the ISM II:

- Basic notions, basic formation and destruction mechanisms of gas-phase molecules in different environments.
- And now put all of this in computer models…
Bibliography on interstellar chemistry

* “Physical Processes in the Interstellar Medium”

* “Interstellar Chemistry”

* “The Physics and Chemistry of the ISM”

* “Master in Astrochemistry”
  Ewine Van Dishoeck, 2010, Notes University of Leiden.

* “Physics of the Interstellar and Intergalactic Medium”
Molecules in the ISM?  Typical Scales

“Size” of a diatomic molecule, \( r \approx 2 \, \text{Å} = 2 \cdot 10^{-8} \, \text{cm} \)

Cross-section (surface) \( \sigma = \pi r^2 \approx 10^{-15} \, \text{cm}^2 \)

Typical speeds \( v \approx 0.1 \, \text{km} \, \text{s}^{-1} = 10^4 \, \text{cm} \, \text{s}^{-1} \)

Collision rate \( \Upsilon (\text{cm}^3 \, \text{s}^{-1}) = \sigma \cdot v = 10^{-11} \, \text{cm}^3 \, \text{s}^{-1} \)

\( \text{H}_2 \) density in dense clouds \( n(\text{H}_2) \approx 10^5 \, \text{cm}^{-3} \)

Time between collisions \( t (\text{s}) \approx 1 / (\Upsilon \, n) \approx 2 \) weeks !!

Distance between collisions \( d = v \, t \approx 100,000 \) km !!

**SLOW** chemistry, don’t expect many molecules…

But… interstellar clouds contain a very rich molecular content !!
Molecules in Space

Where? Which? How? Do they provide any astrophysical information?

• More than 180 different molecules found in Space (55 outside our Galaxy)

• Ordinary species on Earth: H₂O, NH₃, H₂CO, alcohols (CH₃OH…)

• Exotic molecules: ions (HCO⁺…), radicals (C₂H…), chains (HCCCCCN, …)
  (rare on Earth, e.g., very reactive, but very usual in space)
The number of C, N, O, S ... atoms represents < 0.1% of H atoms.

B. McCall 2001
(H$_2$) Molecular clouds  Typical Conditions

- Diffuse interstellar clouds (CNM): $T_{\text{kin}} \sim 100$ K  $n \sim 100$ cm$^{-3}$
- Dense molecular clouds: $T_{\text{kin}} \sim 10$-20 K  $n \sim 10^3$-$10^5$ cm$^{-3}$
- Star-forming: PDRs, Hot cores, outflows: $T_{\text{kin}} \sim 100$-1000 K  $n \sim 10^5$-$10^8$ cm$^{-3}$
- Compare with this room: $T_{\text{kin}} \sim 300$ K  $n \sim 10^{19}$ cm$^{-3}$ (!)
- Best laboratory ultra-vacuum chambers: $P = 2.5 \cdot 10^{-11}$ mbar  $\approx n \sim 10^5$ cm$^{-3}$

ISM = very low densities, often very low temperatures  $\rightarrow$ conditions very different compared to Earth !!

+ chemistry affected by presence of UV-photons, X-rays, Cosmic Rays, turbulence, magnetic fields...

$\rightarrow$ ISM is NEVER in thermochemical equilibrium  
(reaction kinetics needed)
Detecting molecules in Space: Spectroscopy

Rotation-Vibration-Electronic transitions

\[ E = E_{\text{el}} + E_{\text{vib}} + E_{\text{rot}} \]
High-resolution spectroscopy

- “Unresolved spectroscopy” → line blending in (spectrally) crowded regions integrated line intensities conserved but...

- High resolution → line profiles are “resolved” → accurate frequencies, shape, width, etc.

**HIFI (heterodyne) and SPIRE (FTS) spectral scans of Orion star-forming region**
(on board ESA’s *Herschel Space Observatory*)
INTERSTELLAR CLOUDS are COMPLEX

• The structure of molecular clouds is complex with strong gradients ($T_k$, $n_H$, UV field, ...) between different regions...

.. we don’t have exact laws to determine $T_k(x,y,z,t)$, $n(x,y,z,t)$..
* 1926 – A. Eddington

Existence and survival of molecules in the harsh conditions of the ISM is controversial…

* In 1930-1940 **three** molecules were observed in the line-of-sight towards slightly reddened stars in the **VISIBLE**: CN, CH and CH⁺.
Some history:

- Development of radio astronomy
  - H I 21 cm: Ewen & Purcell 1951; Oort & Muller 1951
  - OH 18 cm: Weinreb et al. 1963
  - NH₃ 1 cm: Cheung, Townes et al. 1968
    - First polyatomic molecule!
  - H₂O 1 cm (22 GHz): Cheung et al. 1969

- Development of UV astronomy
  - 1970: H₂

- Development of millimeter astronomy
  - 1970: CO
  - >1970: flood of new molecules
    (many with the IRAM-30m telescope!!)
Development of IR astronomy

1983: \textit{IRAS}
- First full-sky survey at 12, 25, 60 and 100 \textmu m
- Cirrus clouds and dust properties
- Presence of very small dust particles (10-100 Å), large molecules (PAHs)

1995 – 98: \textit{Infrared Space Observatory (ISO)}
- First complete 2-200 \textmu m spectra
- Nature and composition of grains (silicates, ices) and PAHs
- H$_2$O, OH, [O I] far-IR lines
- Symmetric molecules: C$_6$H$_6$, CH$_3$, C$_2$H$_4$, CO$_2$,…
- H$_2$ lines as probe of shocks and PDRs

2003-2009: \textit{Spitzer Space Telescope}
- High sensitivity imaging and mapping; limited spectroscopy
- Ices and silicates toward low mass protostars and disks

1980’s – now: \textit{Ground} and \textit{airborne} IR instruments

Last years: \textit{Herschel} \& \textit{ALMA}
Interesting detections in Space

- $\text{H}_2$ most abundant species, but actually not detected until 70’s
- $\text{H}_3^+, \text{H}_2\text{D}^+, \text{D}_2\text{H}^+$ key species ion-molecule chemistry
- $\text{OH}^+, \text{H}_2\text{O}^+, \text{CH}^+$ simple hydrides, first steps of ISM chemistry
  - $\text{C}_3, \text{C}_4, \ldots \text{HC}_3\text{N}, \text{HC}_5\text{N} \ldots$ linear carbon chains
- $\text{C}_6\text{H}_6$ benzene, simplest aromatic unit and $\text{C}_{60}, \text{C}_{60}^+$ (fullerenes)
- $\text{D}_2\text{CO}, \text{ND}_3, \text{CD}_3\text{OH}$ doubly and triply deuterated molecules
  - $\text{NaCl}, \text{AlCN}, \text{TiO} \ldots$ metal-containing molecules
- $\text{HCOCH}_2\text{OH}$ glycolaldehyde, simplest sugar
- $\text{NH}_2\text{CH}_2\text{COOH}$ glycine?, simplest aminoacid, but not detected!
Interesting competition…

- List not complete
- Some identifications challenged
- About 3 new species/yr for last 30 years!

(e.g. http://wwwastrochymist.org)
Chemical complexity (high-mass protostars)

Orion hot core
(Tercero and cols.)

Rotational spectroscopy in the mm and submm domain
Unidentified infrared bands due to PAHs

Seen everywhere where UV photons are present (star formation tracers!)

Puget, Leger…
Allamandola, Tielens…
Ice grain mantles
(solid-state spectroscopy)

• **Grain surface chemistry:** formation of complex molecules
  *e.g.*  
  \[ \text{CO} \rightarrow \text{HCO} \rightarrow \text{H}_2\text{CO} \rightarrow \text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH} \]
Where do we see these molecules?

Fig. 3.—A section of the umbral spectrum from 12.636 to 12.674 \( \mu \text{m} \) from atlas 4. The unidentified lines in this region are probably \( \text{H}_2\text{O} \). The telluric lines were divided out with a penumbral reference spectrum similar to a photospheric spectrum.
CO$_2$-ice

Mars
North Polar Cap

January 1997

October 1996

CO gas

PRC97-15b • ST ScI OPO • May 20, 1997
P. James (Univ. Toledo), T. Clancy (Space Science Inst.), S. Lee (Univ
In Comets ...

Comet 73P/Schwassmann-Wachmann 3
NASA / JPL-Caltech / W. Reach (SSC/Caltech)


The interstellar life-cycle of gas and dust
Diffuse & translucent clouds...
Simple molecules in diffuse ISM

High-resolution (heterodyne) rotational spectroscopy (< 1 km/s resolution)
Far-IR and submm domain: \( J=1-0 \) transition of light molecules

\[ f = \left(1 - \frac{v_{s,r}}{c}\right)f_0 \]

(Gerin et al. 2010, Neufeld et al., 2010... PRISMAS Herschel-KP)
\( E > 13.6 \text{ eV photons ionize H} \quad \text{Only } E < 13.6 \text{ eV photons penetrate} \)

\[ N_H (\text{cm}^{-2}) \approx 10^{21} A_V = n_H (\text{cm}^{-3}) \times \text{length (cm)} \]
“Imaging” high-mass star-forming regions

Example: Orion A (M42)
Chemical complexity in SFRs (submm band)

Orion KL/BN

(Bergin et al. 2010, A&A)
LABORATORY AND ASTRONOMICAL IDENTIFICATION OF THE NEGATIVE MOLECULAR ION \( \text{C}_6\text{H}^- \)

M. C. McCarthy, C. A. Gottlieb, H. Gupta, and P. Thaddeus

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ABSTRACT

The negative molecular ion \( \text{C}_6\text{H}^- \) has been detected in the radio band in the laboratory and has been identified in the molecular envelope of IRC +10216 and in the dense molecular cloud TMC-1. The spectroscopic constants derived from laboratory measurements of 17 rotational lines between 8 and 187 GHz are identical to those derived from the astronomical data, establishing unambiguously that \( \text{C}_6\text{H}^- \) is the carrier of the series of lines with rotational constant 1377 MHz first observed by K. Kawaguchi et al. in IRC +10216. The column density of \( \text{C}_6\text{H}^- \) toward both sources is 1%–5% that of neutral \( \text{C}_6\text{H} \). These surprisingly high abundances for a negative ion imply that if other molecular anions are similarly abundant with respect to their neutral counterparts, they may be detectable both in the laboratory at high resolution and in interstellar molecular clouds.

Subject headings: ISM: molecules — line: identification — molecular data — molecular processes — radio lines: ISM
Importance of molecules:

- Exotic chemistry and unique laboratory
- Chemical abundances evolve with $t$
- Molecules as physical diagnostics ($T_{\text{kin}}, n, v, B, \zeta_{\text{CR}}, \text{age}, \ldots$)
- Gas thermodynamics: gas coolants

Radiation escapes from cloud $\rightarrow$ net energy lost $\rightarrow$ gas is cooled
(example: critical to allow gravitational collapse and star formation)
Molecules in Star-forming environments

Changes in $n, T_k \rightarrow$ chemistry changes

Class 0

Cloud collapse $t=0$

Class II

Formation planets $t=10^7$ yr

Class I

Rotating disk $t=10^5$ yr

Solar system $t>10^8$ yr

Hogerheijde 1998, after Shu et al. 1987
Low-mass stars formation: protostars & outflows

Looney, Tobin & Kwon 2007
Low-mass stars formation: protostars & outflows

Kristensen et al. 2012

$\mathrm{o-H_2O\ 1_{10}-1_{01} @ 557\ GHz}$
Low-mass stars formation: protostars & outflows

Looney, Tobin & Kwon 2007
Kristensen et al. 2012
Protoplanetary disks
(chemistry when planets form...)

Haro 6-5B

IRAS 04302+2247
HL Tau
Protoplanetary disk (35mas resolution)

Dust continuum emission with ALMA

MWC 480 disk
Complex cyanides with ALMA
Öberg et al. 2015, Nature
Fig. 3.— Top left: ice features toward edge-on disk CRBR 2422.8-3423. Some absorptions arise in the cold foreground core (Pontoppidan et al., 2005). Top right: silicate emission at 10 and 20 μm toward EC 82 (Kessler-Silacci et al., 2006); inset, gas-phase CO v=1-0 emission (Blake and Boogert, priv. comm.). Bottom right: PAH features toward RR Tau (Geers et al., 2006, in prep.); Bottom left: gaseous C_2H_2, HCN and CO_2 toward IRS 46 in Oph (Lahuis et al., 2006);
Fig. 2.—Spectra of the $1_{00} \rightarrow 1_{01}$ transition of o-H$_2$O, the $^3 P_1 \rightarrow ^3 P_0$ transition of C$^+$, and the $J = 5 \rightarrow 4$ transition of $^{13}$CO obtained with SWAS toward IC 443C. Also shown are the spectra of the $J = 1 \rightarrow 0$ transition of $^{12}$CO and the $J = 1 \rightarrow 0$ transition of HCO$^+$ convolved to the SWAS angular resolution from data obtained at FCRAO toward IC 443G. The coordinates of IC 443C are $\alpha = 6^h17^m44^s2$ and $\delta = 22^\circ21'49''1$ (J2000.0).
Chemistry in (Sun-like) evolved stars 
(dust grain factories)
IRC+10216 (or CW Leo)  C-rich AGB
Dust formation and Mass-loss into ISM
IRc+10216 (or CW Leo)  C-rich AGB
From AGB to Planetary Nebulae

Dusty Eye of the Helix Nebula (NGC 7293) - Spitzer Space Telescope
NASA / JPL-Caltech / K. Su (University of Arizona)

Hourglass Nebula - MyCn18 - HST - WFPC2
PRC96-07 - ST ScI OPO - January 16, 1996
R. Sahai and J. Trauger (JPL), the WFPC2 Science Team and NASA

CO with ALMA (Maercker et al.)
Molecules in distant galaxies?

PEP GOODS-S 113+113h
70+100+160μm
≈800 sources
Extragalactic ISM clouds
Extragalactic line-surveys with the 30m
S. Martín, et al.
How are molecules formed in the interstellar and circumstellar media?
THE NATURE OF THE PROBLEM OF INTERSTELLAR CHEMISTRY

1) Low Temperatures:

Gas phase temperatures from $\sim 10$ K (dark, starless clouds) to $\sim 100-1000$ K (UV/shocks…)

2) Low Volume Density:

From $\sim 100$ cm$^{-3}$ (diffuse clouds) to $\sim 10^{5-6}$ cm$^{-3}$ (dense clouds)

3) The Formation of H$_2$ in gas phase NOT possible (H + H),
   - How is H$_2$ formed?
   - How does interstellar chemistry start?
Which are the key processes in ISM chemistry?

1) Need to form the basic molecule, $\text{H}_2$, how?

2) We need atomic or molecular ions ($\text{H}_2 + \text{O}^+ \rightarrow \text{OH}^+ + \text{H}$):
   - UV-photons near stars
   - But inside dense molecular clouds?

3) Cold gas ($T < 100 \text{ K}$) $\rightarrow$ only exothermic reactions work?
Because of the low temperatures and densities, interstellar chemistry is NOT in thermochemical equilibrium (UV photons, cosmic-ray particles affect the chemistry…) but controlled by 2-body gas-phase reactions

(A + B = C + D) \rightarrow \text{chemical kinetics}
BIMOLECULAR REACTIONS (ISM)

\[ A + B \xrightarrow{k} M + N \]

A, B = atoms, molecules or electron
M = molecule
N = molecule, atom or photon

\[ M + h\nu \xrightarrow{\beta} \ldots \]

“number density” of molecule “M”? 

\[ N(M) = \text{density of “M” molecules} \]

\[ [n(M)] = \text{(molecules)} \, \text{cm}^{-3} \]

\[ k = k(T) \quad \text{“rate coefficient”} \]

\[ [k] = \text{cm}^3 \, \text{s}^{-1} \sim \sigma \, \text{(cm}^2) \cdot v(\text{cm} \, \text{s}^{-1}) \]

\[ \beta = \text{“UV photodissociation rate”} \]

\[ [\beta] = \text{(molecules)} \, \text{s}^{-1} \]

**typical** \[ \beta \approx 10^{-10} \, \text{s}^{-1} \rightarrow \text{molecule lifetime} \]

in diffuse ISM = \[ 1/\beta \approx 300 \, \text{yr}! \] (photochemistry is fast...)
BIMOLECULAR REACTIONS (ISM)

A + B $\xrightarrow{k} M + N$

A, B = atoms, molecules or electron
M = molecule
N = molecule, atom or photon

M + hν $\xrightarrow{\beta} \ldots$

Formation rate of M = $k \ n(A) \ n(B) \ [cm^{-3} \ s^{-1}]$

Destruction rate of M = $\beta \ n(M) \ [cm^{-3} \ s^{-1}]$

n(M) as function of time?

$\frac{d}{dt} \ n(M, t) = Formation - Destruction = k \ n(A, t) \ n(B, t) - \beta \ n(M, t)$
\[ A + B \xrightarrow{k} M + N \quad M + h\nu \xrightarrow{\beta} \ldots \]

\[ \frac{d}{dt} n(M) = \text{Formation} - \text{Destruction} = k \, n(A) \, n(B) - \beta \, n(M) \]

**Steady-state** → \( \frac{d}{dt} \, n(M) = 0 \) → \( n(M) = \frac{F}{\beta} = k \, n(A) n(B) / \beta \)

*Time-scale* \( \sim 1/\beta \)

**PROBLEM:** \( k = k (T) ?? \quad \beta \) (cloud position) ??

- \( k \) and \( \beta \) can only be determined from quantum calculations and/or through sophisticated laboratory measurements

\[ k(T) = A(T) \exp \left( -\frac{E_a}{kT} \right) \quad \text{“Arrhenius law”} \quad [\text{cm}^3 \text{ s}^{-1}] \]

\[ \beta (A_V) \approx \beta_0 \exp \left( -\alpha A_V \right) \quad [\text{s}^{-1}] \]
HOW DO WE FORM MOLECULE “AB” IN SPACE?

\[ A + B \rightarrow AB^* \quad AB^* + Z \rightarrow AB + Z \]

In all chemical processes the interaction between two species (atoms or molecules) produces an activated complex \((AB^*)\) that has to loss energy in a very short time period, often similar to the vibration time of the molecule nuclei. There are many ways for the activated complex to loss energy. But, while in terrestrial laboratories catalysers or a third body are available, we will see that in space three body collisions are very uncommon (WHY?).
Let us consider the reaction

$$A + B \rightarrow AB^* \quad (k_1)$$

It may happen that $AB^*$ interacts with a third body (catalyser=$Z$) to remove the energy excess, $\Delta E_k(A+B)$, produced in the formation of the activated complex. However, $AB^*$ can also dissociate into the initial particles $A$ and $B$

$$AB^* + Z \rightarrow AB + Z \quad (k_2)$$

$$AB^* \rightarrow A + B \quad (k_3)$$

$k_1 \approx 10^{-11} \text{ cm}^3 \text{ s}^{-1}$

$k_2 \approx 10^{-10} \text{ cm}^3 \text{ s}^{-1}$

$k_3 \approx 10^{+11} \text{ s}^{-1}$

*Potential energy surface (PES)*
EXAMPLE: The simplest trimolecular reaction (H₂ formation)

Let us consider an atomic cloud without dust grains and without radiation field. For \( t=0 \) the density of atomic hydrogen is \( n=n(H) \) and that of molecular hydrogen is \( n(H_2)=0 \). The formation of H₂ occurs through the reaction

\[
H + H + H = H_2 + H
\]

with a \( k \) rate of \( 10^{-32} \text{ cm}^6 \text{ s}^{-1} \)

The formation rate of H₂ is given by

\[
\frac{dn(H_2, t)}{dt} = k n^3_H(t)
\]

\[
f(t) = \frac{2 n_{H_2}(t)}{n(H)(t) + 2 n_{H_2}(t)}
\]

\[
\frac{df(t)}{dt} = 2k n^2 (1 - f(t))^3
\]

Time to reach \( f=0.5 \) ??
EXAMPLE

(Earth at sea level  density ~ $10^{19}$ cm$^{-3}$)

(ultra-high vacuum chamber  density ~ $10^5$ cm$^{-3}$)

\[ f(t_0) = 0.5, \quad t_0 =? \]

<table>
<thead>
<tr>
<th>$n_H$(cm$^{-3}$)</th>
<th>$10^5$</th>
<th>$10^{10}$</th>
<th>$10^{12}$</th>
<th>$10^{15}$</th>
<th>$10^{16}$</th>
<th>$10^{18}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_0$ (years)</td>
<td>$6 \times 10^{14}$</td>
<td>$6 \times 10^4$</td>
<td>$6$</td>
<td>$6 \times 10^{-6}$</td>
<td>$6 \times 10^{-8}$</td>
<td>$6 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

(600 s)           (6s)           (0.0006s)

3-body reactions are only efficient for densities > $10^{12}$ cm$^{-3}$
(not in the ISM)

\[ H + H + H = H_2 + H \quad \text{DOES NOT WORK!} \]

BUT $H_2$ HAS BEEN DETECTED IN SPACE…
AN INTERSTELLAR GRAIN

$M_{\text{gas}}/M_{\text{dust}} \sim 100$ (ISM)
Cooling a gas of H atoms and dust grains

FORMATION OF MOLECULAR HYDROGEN ON AMORPHOUS WATER ICE: INFLUENCE OF MORPHOLOGY AND ULTRAVIOLET EXPOSURE

J. E. Roser, G. Manicò, V. Pirronello, and G. Vidali

Received 2002 April 26; accepted 2002 August 14

ABSTRACT

In this paper, we report on the formation of molecular hydrogen on different types of amorphous water ice. We show that mass spectra of desorbing molecules upon formation are sensitive to the way in which ice is deposited on a cold substrate, to its thermal history, and to the action of UV photons. Implications that these results bear on H₂ formation in dense quiescent clouds are presented and discussed.

Subject headings: astrochemistry — dust, extinction — ISM: molecules — methods: laboratory — molecular processes

H atoms are adsorbed and form H₂ in the surface

T typical of cold ISM!
**H$_2$** sublimates and leaves the surface!

**H$_2$** sublimates and leaves the surface!

**CO** sublimates at $T_d \sim 20$-30 K

**H$_2$O** sublimates at $T_d \sim 80$-100 K

**T** typical of ISM!

---

Fig. 4.—Desorption rate ($dN_{HD}/dT$) vs. ramp temperature after adsorption of H and D for 4 minutes on high-density amorphous water ice at $\sim$10 K before (filled circles) and after (open circles) UV exposure for 15 minutes. Traces have been scaled to yield the same area.
\[ H_2 \text{ formation rate} \approx 0.5 \beta_0 \cdot \frac{f}{n} \approx 3 \times 10^{-17} \, \text{cm}^3 \, \text{s}^{-1} \]

(e.g. Le Bourlot et al. 2012, Bron et al. 2014)

Weakly bound molecules: “diffusion” = “Langmuir-Hinshelwood” mechanism
H₂ is formed on the surface of the dust grains. How do we form other gas-phase molecules?

H₂ + (C, C⁺, O, O⁺, N, Si, Si⁺, S, S⁺) → ???

A + B → AB ??

let us consider the following reaction;

A + B → AB + hv (radiative association)

is it possible?
is it fast enough to be efficient in the ISM?
Radiative Association

\[ X + Y \xrightarrow{\tau_c} XY^* \xrightarrow{\tau_r} XY + h\nu \]

- Energy conservation → photon must be emitted, which is a very slow process

\[ \tau_r = 10^{-2} - 10^{-3} \text{ s vibrational transition} \]
\[ \tau_{c,d} = 10^{-13} \text{ s collision time} \]

\[ \Rightarrow \text{Molecule formation occurs only 1:}10^{10} \text{ collisions} \]

Bond probability = \( \text{tau}_{\text{diss}} / \text{tau}_{\text{radiate}} \)
Radiative Association

- Process becomes more efficient if electronic states available

\[ \tau_r = 10^{-8} \text{ s} \quad \text{electronic transition} \]
\[ \tau_{c,d} = 10^{-13} \text{ s} \quad \text{collision time} \]

\[ \Rightarrow \text{Efficiency increased to } 1:10^5 \]

Slow, anyway...
The reaction will occur if the change of energy is positive to account for the low temperatures of the interstellar medium (in general, reactions in the ISM should be exothermic!!)

For example, let us consider the reaction:

\[ \text{C}^+ + H_2 \rightarrow \text{CH}_2^+ + h\nu \rightarrow \text{slow} \]

what about: \( \text{C}^+ + H_2 \rightarrow \text{CH}^+ + H \)?
D(products) – D (reactants) > 0 → exothermic
< 0 → endothermic

The dissociation energy of H\(_2\) is 4.48 eV and that of CH\(^+\) is 4.09 eV

The reaction will be produced if we add 0.39 eV to the system (about 4600 K).

This reaction is endothermic and has little probability to occur in the ISM as we need \(T_{\text{gas}} > 4000\) K
**Letter to the Editor**

**CH⁺ (1–0) and ¹³CH⁺ (1–0) absorption lines in the direction of massive star-forming regions**, **(Dissipation of turbulence)**

Shocks in diffuse ISM?

*(Dissipation of turbulence)*

See Falgarone et al. Godard et al. ("TDR models")
The reaction

\[ S^+ + H_2 \rightarrow SH^+ + H \]

Has even fewer chances to occur in the ISM

\[ D(H_2)=4.49 \text{ eV} \quad \text{and} \quad D(SH^+)=3.5 \text{ eV} \]

(endothenmic by \(~10,000 \text{ K})
However, the reaction

\[ \text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+ + \text{H} \]

can occur because \( D(\text{H}_2) = 4.49 \text{ eV} \), \( D(\text{OH}^+) = 5.1 \text{ eV} \) and it is exothermic by 0.61 eV!

The reaction rate has been measured in the laboratory and is rather fast, \( k \approx 1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \).
Herschel/HIFI: observations of interstellar OH$^+$ and H$_2$O$^+$ towards W49N*: a probe of diffuse clouds with a small molecular fraction


(Affiliations can be found after the references)
### Hydride molecule formation \((X + H_2\) and \(X^+ + H_2\))

<table>
<thead>
<tr>
<th>Element</th>
<th>Ionization Potential (eV)</th>
<th>Endothermicity (Kelvin equivalent = (\Delta E/k_B)) for (X + H_2 \rightarrow XH + H)</th>
<th>Endothermicity (Kelvin equivalent = (\Delta E/k_B)) for (X^+ + H_2 \rightarrow XH^+ + H)</th>
<th>Endothermicity (Kelvin equivalent = (\Delta E/k_B)) for (X + H_3^+ \rightarrow XH^+ + H_2)</th>
<th>Driver</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>24.587</td>
<td>No reaction</td>
<td>Exothermic, but primary channel is to (He + H + H^+)</td>
<td>29000</td>
<td>Warm gas</td>
</tr>
<tr>
<td>C</td>
<td>11.260</td>
<td>11000</td>
<td>4300</td>
<td>[✅]</td>
<td>Cosmic rays</td>
</tr>
<tr>
<td>N</td>
<td>14.534</td>
<td>15000</td>
<td>230</td>
<td>[✅]</td>
<td>Warm gas or cosmic rays</td>
</tr>
<tr>
<td>O</td>
<td>13.618</td>
<td>940</td>
<td>[✅]</td>
<td>[✅]</td>
<td>None needed</td>
</tr>
<tr>
<td>F</td>
<td>17.423</td>
<td>[✅]</td>
<td>10000</td>
<td>[✅]</td>
<td>Cosmic rays</td>
</tr>
<tr>
<td>Ne</td>
<td>21.564</td>
<td>No reaction</td>
<td>Exothermic, but primary channel is to (Ne + H + H^+)</td>
<td>27000</td>
<td>None needed</td>
</tr>
<tr>
<td>Si</td>
<td>8.152</td>
<td>17000</td>
<td>15000</td>
<td>[✅]</td>
<td>Warm gas</td>
</tr>
<tr>
<td>P</td>
<td>10.487</td>
<td>19000</td>
<td>13000</td>
<td>[✅]</td>
<td>Warm gas</td>
</tr>
<tr>
<td>S</td>
<td>10.360</td>
<td>10000</td>
<td>10000</td>
<td>[✅]</td>
<td>Warm gas</td>
</tr>
<tr>
<td>Cl</td>
<td>12.968</td>
<td>450</td>
<td>[✅]</td>
<td>[✅]</td>
<td>UV with (hv &gt; 12.97) eV</td>
</tr>
<tr>
<td>Ar</td>
<td>15.760</td>
<td>No reaction</td>
<td>[✅]</td>
<td>[✅]</td>
<td>Cosmic rays</td>
</tr>
</tbody>
</table>

Hydride detections in diffuse clouds (*Herschel, SOFIA...*)

Figure 6

Absorption spectra observed toward W31C. Left panel from top to bottom: spectra of \( \text{H}_2 \text{S} \) at 168.8 GHz (based on data published by Neufeld et al. (2015a)); \( \text{CH}_2 \Pi_3/2 \text{J}=3/2 \) at 32.7/536.8 GHz (Gerin et al. 2010a); \( \text{SH}_2 \Pi_3/2 \text{J}=5/2 \) at 1381 GHz (Neufeld et al. 2015a); \( \text{HF} \) \( \text{J}=1 \) at 1232 GHz; \( \text{H}_2 \text{O} \) \( \text{J}=111 \) at 1113 GHz (Neufeld et al. 2010); \( \text{NH} \) \( \text{J}=21/10 \) at 974.5 GHz; \( \text{NH}_3 \) \( \text{J}=21/10 \) at 1215.2 GHz (Persson et al. 2010). Right panel from top to bottom: \( \text{H}_i \) \( 21 \) cm (Winkel et al. in preparation); \( \text{CH}_+ \) \( \text{J}=1 \) at 835.1 GHz; \( \text{CH}_+ \) \( \text{J}=1 \) at 830.2 GHz (Godard et al. 2012); \( \text{ArH}^+ \) \( \text{J}=1 \) at 617.5 GHz (Schilke et al. 2014); \( \text{OH}^+ \) \( \text{J}=3/2 \text{J}=5/2 \) at 971.8 GHz; \( \text{H}_2 \text{O}^+ \) \( \text{J}=111 \) at 485.4 GHz (Neufeld et al. 2012). For species with a partially-resolved hyperfine splitting (SH, NH, \( \text{OH}^+ \), \( \text{H}_2 \text{O}^+ \)), black histograms show the observations and color histograms show the hyperfine-deconvolved spectra. For clarity, the spectra are separated by vertical offsets. The \( \text{ArH}^+ \) spectrum is expanded by a factor 4 (in addition to being translated) so that the relatively weak absorption is clearer.

In Table 2, we summarize the typical hydride abundances derived for the diffuse ISM. In the case of molecular ions (with the exception of \( \text{H}_3 \text{O}^+ \)), these are shown relative to atomic hydrogen, whereas for neutral molecules, they are shown relative to \( \text{H}_2 \). In both cases, the corresponding abundances are also given relative to the gas-phase abundance of the relevant heavy element. The values shown in Table 2 indicate that most hydride molecules in diffuse gas are only minor reservoirs of the heavy element they contain, with most heavy elements remaining overwhelmingly in atomic or singly-ionized form.

Are all ion-neutral reactions fast enough?

\[ A^+ + BC \rightarrow AB^+ + C \]
The formation rate of the product $AB^+$ is given by

$$A^+ + BC \rightarrow AB^+ + C$$

Formation rate ($AB^+$) = $k \, n(A^+) \, n(BC)$

Does $k \, [\text{cm}^3 \, \text{s}^{-1}]$ depend on the gas temperature?

**Laboratory:**
For most of these reactions (exothermic and BC non-polar):

- $k$ does not depend on the temperature
- and is of the order of $10^{-9} \, \text{cm}^3 \, \text{s}^{-1}$ (high!)

**Why?**
Start with the classical treatment of the “collision capture” problem.
Let BC be a non-polar molecule.

$A^+$ induces a dipole moment in BC during the collision process.
The energy produced in the collision reorders the orbitals and overcome any possible activation barrier.

\[ A^+ + BC \rightarrow AB^+ + C \]

The collisional cross section \( \sigma \) is \( \pi b_0^2 \) (area) and the reaction rate is given by

\[ k = \sigma \cdot v = \pi b_0^2 v = \ldots = 2\pi e (\alpha/m)^{1/2} \quad [\text{cm}^3 \text{s}^{-1}] \]

and does not depend on \( T \), only on the polarizability and on the reduced mass of the system !!!

This reaction rate is known as “The Langevin rate” (1905)
Example:

\[ \text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+ + \text{H} \]

Langevin value \( 1.6 \cdot 10^{-9} \text{ cm}^3\text{s}^{-1} \)
Experimental value \((1-2) \cdot 10^{-9} \text{ cm}^3\text{s}^{-1}\)

The other reaction “channel”:

\[ \text{O}^+ + \text{H}_2 \rightarrow \text{OH} + \text{H}^+ \]

is slightly endothermic

D(H\(_2\))=4.48 eV \ y \ D(\text{OH})=4.39 eV

and thus less probable than the OH\(^+\) formation
What happens in ion-neutral reactions if the BC molecule is polar?

Rate coefficients for ion-polar reactions may be factors of 10-100 larger than Langevin values at low T, because $V(R) \propto R^{-2}$

Example:

$$C^+ + OH \rightarrow CO^+ + H$$

A classical treatment of the problem ("ADO" = Averaged Dipole Orientations) of the dipole interaction

$$k_{ADO} = 2 \pi e (\alpha^{1/2} + c \mu_D (2/ \pi kT)^{1/2})$$

Where $\mu_D$ is the dipole moment of the molecule, $T$ is the gas temperature and $c$ is a function of $\mu_D/\alpha^{1/2}$
Reaction rate $k$ depends on the gas temperature inversely (ion – polar neutral).

Fig. 3.2 Plot of the constant $c$ against $\mu_D/\alpha^2$ for temperatures of 150–500 K at intervals of 50 K, and for a temperature of 650 K. (T. Su and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.*, 1975, 17, 211.)
But keep in mind that…

**Maybe** at low temperatures these simple “semi-classical” theories are just approximations (low velocities and hence long interaction times between the particles, quantum calculations & lab. experiments are needed).

Close interactions between **physico-chemists** (both laboratory and quantum calculations) and **astronomers** needed!!
Which are the key processes in ISM chemistry?

1) $\text{H}_2$ is formed on dust grain surfaces
2) We need atomic or molecular ions (ok for diffuse ISM $\rightarrow$ UV)

But, how are atoms/molecules ionized deeply inside clouds?

With cosmic rays !!! (e.g. high speed $p^+$, He nuclei with E~100-1000 MeV)

\[
\text{CR} + \text{H} \rightarrow \text{H}^+ + \text{e}^- + \text{CR}
\]

\[
\text{CR} + \text{H}_2 \rightarrow \text{H}_2^+ + \text{e}^- + \text{CR} \text{ (unimolecular)}
\]

\[
\text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}
\]

and $\text{H}_3^+$ a key molecule !!  

Formation_rate($\text{H}_3^+$) = $\zeta_{\text{CR}} n(\text{H}_2)$

with $\zeta_{\text{CR}} \approx 10^{-16} - 10^{-17}$ s$^{-1}$ “CR ionization rate”

$\text{H}_3^+$ does not react with $\text{H}_2$, ionization source for other species
Ionization is produced in dense clouds by cosmic rays sufficiently energetic to penetrate the interior. Since H$_2$ and He are the dominant species, the major initial ions produced are H$_2^+$, H$^+$ (Solomon and Werner 1971), and He$^+$. The exothermic reaction H$_2^+$ + H$_2$ $\rightarrow$ H$_3^+$ + H is rapid (Bowers, Elleman, and King 1969), but the highly exothermic reaction of He$^+$ with H$_2$ does not occur for kinetic reasons (Fehtenfeld et al. 1966b). Thus He$^+$, unlike H$_2^+$, will exist in appreciable concentration. Having an electron affinity of 24 eV, He$^+$ ionizes most neutral species other than H$_2$ rapidly. The reactions of the primal ions—H$^+$, H$_3^+$, He$^+$—with abundant neutral species such as CO, O, N, O$_2$, and N$_2$ produce secondary ions such as C$^+$, N$^+$, O$^+$, N$_2^+$, O$_2^+$, HCO$^+$, and HN$_2^+$.

\[
\begin{align*}
\text{CR} + \text{H}_2 & \rightarrow \text{H}_2^+ + e^- + \text{CR} \\
\text{H}_2^+ + \text{H}_2 & \rightarrow \text{H}_3^+ + \text{H}
\end{align*}
\]
The role of $\text{H}_3^+$ ...

**PROTON TRANSFER**

$\text{H}_2$ has a low proton affinity and the reactions of $\text{H}_3^+$ with neutral species (B) will always produce $\text{BH}^+$ (molecular ions!)

$$\text{H}_3^+ + \text{B} \rightarrow \text{BH}^+ + \text{H}_2$$

if the reaction is exothermic (proton transfer).
### PROTON AFFINITIES

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2.69</td>
<td>O₂</td>
<td>4.34</td>
</tr>
<tr>
<td>H₂</td>
<td>4.34</td>
<td>CO</td>
<td>6.20</td>
</tr>
<tr>
<td>He</td>
<td>1.82</td>
<td>NO</td>
<td>4.99</td>
</tr>
<tr>
<td>O</td>
<td>5.03</td>
<td>C₂</td>
<td>7.20</td>
</tr>
<tr>
<td>C</td>
<td>6.46</td>
<td>CN</td>
<td>4.99</td>
</tr>
<tr>
<td>N</td>
<td>4.21</td>
<td>N₂</td>
<td>5.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CS</td>
<td>7.57</td>
</tr>
</tbody>
</table>

H₃⁺ will transfer protons to all atoms (except N, H, and He) and to most molecules.

E.g., \( H_3^+ + CO \rightarrow HCO^+ + H_2 \)
RADIATIVE RECOMBINATION  [SLOW!]

\[ X^+ + e^- \rightarrow X + h\nu \] (reverse of photoionization)

These mechanisms produce neutral species from a chemistry based on ion-neutral reactions.

In this reaction the energy excess of the system is released as radiation.

e.g. (deep in molecular clouds) \[ Fe^+ + e^- \rightarrow Fe + h\nu \]
IP = 7.9eV

Typical reaction rates are slow \[ k_{RR} \approx 10^{-12} \text{ cm}^3 \text{ s}^{-1} \]

Molecular ions recombine much faster through other mechanism…
Molecular ions: $XY^+ + e \rightarrow XY + hv$

$\rightarrow X + Y$

Radiative: slow

Dissociative: rapid at low T

Need curve crossing between $XY^+$ and repulsive $XY$ potential for reaction to proceed fast
DISSOCIATIVE RECOMBINATION

Molecular positive ions recombine with electrons to dissociate into neutral species (not by radiating a photon)

\[ \text{ABC}^+ + e^- \rightarrow \text{BC} + \text{A} \]

Reaction rates have a \( T^{-1/2} \) dependence!

Typical values for the dissociative recombination rate are

\[ k_{DR} \approx 10^{-6} - 10^{-7} \text{ cm}^3 \text{ s}^{-1} \text{ (fast)} \]

\[ \text{e.g. } \text{HCO}^+ + e^- \rightarrow \text{CO} + \text{H} \]

These reactions are very important in ISM even if \( n(e^-)/n_H \sim 10^{-4} - 10^{-8} \) (ionization fraction)
NEUTRAL-NEUTRAL REACTIONS

\[ A + BC = AB + C \]

* Long-range attraction weak: van der Waals interaction \( \sim 1/R^6 \)
* Strong temperature dependence has been found for many of these reactions + activation energy barriers \( E_a \)
**NEUTRAL-NEUTRAL REACTIONS** (Energy Barriers)

\[ k(T) = A(T) \exp \left( -\frac{E_a}{kT} \right) \]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( A(\text{cm}^3\text{s}^{-1}) )</th>
<th>( E_a(\text{K}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H} + \text{H}_2\text{CO} = \text{H}_2 + \text{HCO} )</td>
<td>(2.7 \times 10^{-11})</td>
<td>1300</td>
</tr>
<tr>
<td>( \text{H} + \text{H}_2\text{S} = \text{H}_2 + \text{SH} )</td>
<td>(1.3 \times 10^{-11})</td>
<td>860</td>
</tr>
<tr>
<td>( \text{H} + \text{O}_2 = \text{OH} + \text{O} )</td>
<td>(3.7 \times 10^{-10})</td>
<td>8500</td>
</tr>
<tr>
<td>( \text{O} + \text{H}_2 = \text{OH} + \text{H} )</td>
<td>(1.0 \times 10^{-11})</td>
<td>5700</td>
</tr>
<tr>
<td>( \text{O} + \text{H}_2\text{S} = \text{OH} + \text{SH} )</td>
<td>(6.6 \times 10^{-13})</td>
<td>900</td>
</tr>
<tr>
<td>( \text{OH} + \text{CO} = \text{H} + \text{CO}_2 )</td>
<td>(5.1 \times 10^{-13})</td>
<td>300</td>
</tr>
</tbody>
</table>

**ISM:** need high temperature conditions
(e.g., shocks in protostellar outflows)
**State-to-state chemical reactions**

*(Vibrationally excited H\textsubscript{2})*

“Non-thermal reactions” may overcome endothermicities or activation energy barriers $E_a$

$H_2 (v=0) + C^+ \rightarrow CH^+ + H$ (endothermic by 0.39 eV or 4600 K)

The $H_2 (v=1)$ level has an energy of $\sim0.5$ eV ($\sim5800$ K)

- In some particular cases the $H_2 (v>0)$ levels can be significantly populated e.g. by absorption of UV photons in Photodissociation Regions.
State-to-state chemical reactions
(effects of UV-pumped vibrationally excited H₂)

THE CHEMISTRY OF VIBRATIONALLY EXCITED H₂ IN THE INTERSTELLAR MEDIUM

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H₂ (v ≥ 1) + C⁺ → CH⁺ + H (exothermic !!)
State-to-state chemical reactions (effects of UV-pumped vib. excited $H_2$)

$H_2$ v=1-0
Orion Bar PDR
Photodissociation region

$H_2^*$ 2.1$\mu$m
Spitzer 8$\mu$m
DUST 850$\mu$m
Non-thermal reactions may overcome endothermicities or activation energy barriers $E_a$.

Effect of $H_2 (v \geq 1) + C^+ \rightarrow CH^+ + H$
CH⁺, SH⁺ in the Orion Bar

Confirmation of UV-pumped H₂ (ν ≥ 1) reactions with C⁺ and S⁺


UV photodissociation and photoionization (PDRs)

The main path to destroy molecules in UV illuminated gas is photodissociation and photoionization

What do we need to know?

1) The electronic, vibrational and rotational levels of each molecule

2) The far-UV radiation field >911 Å (<13.6eV) (higher E photons ionize H atoms in HII regions)

- Experiments available for stable molecules, but not for radicals or ions
- Small molecules: quantum chemical calculations of potential surfaces of excited states + transition dipole moments, followed by nuclear dynamics to obtain cross sections
Photodissociation (PDR) models

Where physics and chemistry are driven by FUV photons (13.6-6 eV)

UV-PROCESSES:

1) FUV flux attenuation
   (dust extinction but also H$_2$ lines)

2) Chemistry
   (photochemistry)

3) Gas heating and cooling $\rightarrow T_{\text{gas}}$
   (photoelectric effect, line cooling, ...)

DETAILED PDR MODEL: Meudon PDR CODE

Review: Hollenbach & Tielens 1999

http://pdr.obspm.fr/PDRcode.html
Templates to understand the emission from distant/unresolved UV-regulated environments.

$\chi \sim \text{a few } 10^4$

Orion Bar PDR

$\chi \sim 100$

Horsehead PDR

Proplyd

Starburst galaxy
Inside “neutral” clouds:
Only <13.6 eV UV photons

“Photoionization”

\[
AB + hv \rightarrow AB^+
\]

\[
C + hv \rightarrow C^+
\]
Direct Photodissociation

$AB + hv \rightarrow A + B$

Internuclear distance

Energy

$H_2O, OH, CH, CH_2...$

“Direct Photodissociation”

$AB + hv_{\beta} \rightarrow A + B$
“Photo-Predisociation”

$$AB + hv \rightarrow AB^* \rightarrow A + B$$
“Dissociation via fluorescent emission”

\[ AB + h\nu \xrightarrow{\beta} A + B \]
\[ \text{H}_2(X^1\Sigma_g^+ , v^\prime\prime = 0) + h\nu \rightarrow \text{H}_2(B^1\Sigma_u^+ , v') \quad \lambda < 1109\text{Å} \]
\[ \rightarrow \text{H}_2(C^1\Pi_v) \quad \lambda < 1109\text{Å} \]

“Lyman and Werner bands”

There are not allowed electric dipole transitions from \( X^1\Sigma_g^+ \) to repulsive electronic states with energies <13.6 eV !

\[ \text{H}_2(B^1\Sigma_u^+ , v') \rightarrow \text{H}_2(B^1\Sigma_g^+ , v^\prime\prime) + h\nu \]
\[ \rightarrow \text{H} + \text{H} + h\nu \]

and

\[ \text{H}_2(B^1\Pi_u^+ , v') \rightarrow \text{H}_2(B^1\Sigma_g^+ , v^\prime\prime) + h\nu \]
\[ \rightarrow \text{H} + \text{H} + h\nu \]

90% of absorptions into B and C states are followed by emission back into bound vibrational levels of the X state 10% of the absorptions are followed by emission into the unbound vibrational continuum, leading to dissociation
FLUORESCENT MOLECULAR HYDROGEN EMISSION IN IC 63: FUSE, HOPKINS ULTRAVIOLET TELESCOPE, AND ROCKET OBSERVATIONS

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Received 2005 February 28; accepted 2005 April 6

Fluorescent H₂ emission in the FUV
Interstellar radiation field

Figure 5. The intensity of the interstellar radiation field as a function of wavelength cf. Draine (1978) (full line), Mathis et al. (1983) (long–dashed line), Gondhalekar et al. (1980) (short–dashed line) and Habing (1968) (dash–dotted line).

Average radiation provided by young O + B stars
far-UV field $I = I(\lambda)$ decreases with $A_V$

$A_V = 1.086 \cdot \tau_V$
(dust attenuation)

**Fig. 4.4** The interstellar radiation flux $F(E)$ photons cm$^{-2}$s$^{-1}$eV$^{-1}$ster$^{-1}$ in un-obscured regions of the interstellar medium, in a typical diffuse cloud with $\tau_V \approx 0.5$, and in a denser cloud with $\tau_V \approx 2$.

FUV photons are mainly absorbed by dust grains
$\kappa_{pd}$ photodissociation rate (complex calculation)

$$\beta = \kappa(A_V) = 4\pi \int_0^{13.6\text{eV}} I(E, A_V) \sigma_{PD}(E) dE$$

Goicoechea & Le Bourlot 2007, A&A

$\sigma_{PD} =$ molecule photodissociation cross-section [cm$^{-2}$]
\[ \kappa_{pd} = \beta_0 \exp(-\alpha A_V) \ (\text{s}^{-1}) \]

Table 4.1 Dissociation rates, \( \beta_0 \), and \( \alpha \) [equation (4.14)] for simple molecules exposed to the unshielded interstellar radiation field. (S. S. Prasad and W. T. Huntress, Jr, Astrophysical Journal Supplement Series, 1980, 43, 1.)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( \beta_0 ) (s(^{-1}))</th>
<th>( \alpha )</th>
<th>Molecule</th>
<th>( \beta_0 ) (s(^{-1}))</th>
<th>( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 )</td>
<td>( 5 \times 10^{-11} )</td>
<td>—</td>
<td>( \text{HCN} )</td>
<td>( 1 \times 10^{-10} )</td>
<td>1.8</td>
</tr>
<tr>
<td>( \text{HD} )</td>
<td>( 5 \times 10^{-11} )</td>
<td>—</td>
<td>( \text{HCO} )</td>
<td>( 8.8 \times 10^{-10} )</td>
<td>1.6</td>
</tr>
<tr>
<td>( \text{CH} )</td>
<td>( 1.4 \times 10^{-10} )</td>
<td>1.5</td>
<td>( \text{H}_2\text{CO} )</td>
<td>( 8.8 \times 10^{-10} )</td>
<td>1.6</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>( 5 \times 10^{-12} )</td>
<td>3.0</td>
<td>( \text{NH}_3 )</td>
<td>( 5.5 \times 10^{-10} )</td>
<td>2.0</td>
</tr>
<tr>
<td>( \text{CN} )</td>
<td>( 5 \times 10^{-11} )</td>
<td>1.7</td>
<td>( \text{H}_2\text{O} )</td>
<td>( 3.2 \times 10^{-10} )</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \text{CH}_3^+ )</td>
<td>( 2 \times 10^{-9} )</td>
<td>1.7</td>
</tr>
</tbody>
</table>
Cosmic-ray induced radiation
(UV “secondary photons” in cloud interiors)

\[ G_0 = 10^{-4} \, G_{\text{ISM}} \Rightarrow \text{no } UV\text{-dark environment exists} \]
Astrochemical models
• Astrochemical models contain thousands of reactions but only a few type of different reaction types:

**Formation of bonds**  \( \text{reaction rate } k(T): \)
- Radiative association: \(10^{-13} \text{ cm}^3\text{s}^{-1}\)  \(X^+ + Y \rightarrow XY^+ + h\nu\)
- Associative detachment  \(X^- + Y \rightarrow XY + e\)
- Grain surface: \(10^{-17} \text{ cm}^3\text{s}^{-1}\)  \(X + Y:g \rightarrow XY + g\)

**Destruction of bonds**
- Photo-dissociation: \(10^{-9}-10^{-12} \text{ s}^{-1}\)  \(XY + h\nu \rightarrow X + Y\)
- Dissociative recombination: \(10^{-6} \text{ cm}^3\text{s}^{-1}\)  \(XY^+ + e \rightarrow X + Y\)
- Collisional dissociation:  \(XY + M \rightarrow X + Y + M\)

**Rearrangement of bonds**
- Ion-molecule reactions: \(10^{-9} \text{ cm}^3\text{s}^{-1}\)  \(X^+ + YZ \rightarrow XY^+ + Z\)
- Charge-transfer reactions: \(10^{-9} \text{ cm}^3\text{s}^{-1}\)  \(X^+ + YZ \rightarrow X + YZ^+\)
- Neutral-neutral reactions: \(10^{-12} \text{ cm}^3\text{s}^{-1}\)  \(X + YZ \rightarrow XY + Z\)
Astrochemical reaction data bases

Mainly gas-phase:

~5000 reactions between ~450 species up to 13 atoms

http://udfa.ajmarkwick.net (UMIST-UDFA, T. Millar et al.)

http://www.physics.ohio-state.edu/~eric/research.html (OSU, E. Herbst et al.)

http://kida.obs.u-bordeaux1.fr (KIDA-Bordeaux, Wakelam et al.)

http://home.strw.leidenuniv.nl/~ewine/photo/ (Photo-rates, E. van Dischoeck)

\[ k(T)=a(T/300)^b \exp\left(-c/kT\right) \text{ [cm}^3\text{s}^{-1}] \]

\[ k_{ph}(A_v)=a \exp\left(-c A_v\right) \text{ [s}^{-1}] \]
Computational chemistry

\[ A + B \xrightarrow{k_{AB}} X + Y \]
\[ X + C \xrightarrow{k_{XC}} D + E \]
\[ X + \hbar \nu \xrightarrow{\beta_X} \text{products} \]

(on grains: \( A_{\text{grain}} + B_{\text{grain}} \rightarrow X_{\text{grain}} + Y_{\text{grain}} \); \( X_{\text{grain}} + \hbar \nu / T \rightarrow X \))

One differential equation per species in the network: (non-linear, stiff problem)
\[ \frac{d}{dt} n_X = F - D = \sum_A \sum_B k_{AB} n_A \ n_B - (\sum_C k_{XC} n_C + \beta_X) \ n_X \ (\text{only gas}) \]

+ Conservation equations:

Carbon \( n_C = n(C^+) + n(C) + n(CO) + n(CH)\ldots + 2n(C_2) + 2n(C_2H) + \ldots \)

... 

Charge \( n_e = n(C^+) + n(H^+) + n(H_3^+) \ + \ldots \)

SOLVED ITERATIVELY

(eg. Newton-Raphson techniques when \( dn/dt = 0 \) steady-state)
Astrochemical codes: e.g., Meudon PDR code, Cloudy...

- **Input** radiation field (UV) \( \rightarrow \) **output** radiation field (atomic/molecular line emission)
- Thermodynamics (heating and cooling) \( \rightarrow \) \( T_{\text{gas}}, T_{\text{dust}} \)
- Chemical kinetics (gas + grain) \( \rightarrow \) atomic/molecular abundances

Several iterations needed

But remember, rates are sometimes uncertain…,
\( \rightarrow \) Model predictions are uncertain (factors \( \sim \)2 to 10)

See e.g. Wakelam et al. 2005

Diffuse clouds

Low densities, warm gas
UV dissociation, CR ionization, turbulence...

Simple hydrides: OH\(^+\), CH\(^+\) ...
Seen in absorption

Dense clouds

High densities, cold gas
Depletion, CR ionization...

Heavier molecules: \(N_2H^+\) ...
Deuterated isotopologues: \(N_2D^+\) ...
**Shocks**

High-Temperature chemistry
Grain sputtering

\( \text{H}_2\text{O, OH, SiO and hot CO} \ldots \)

**Hot Cores**

Ice-mantle evaporation
Warm-temperature chemistry

\( \text{CH}_3\text{OH, NH}_3, \text{complex organics} \ldots \)
Circumstellar envelopes around evolved stars

High densities, dust formation

with metals: NaCl...
refractory: TiO, SiC...

UV-irradiated clouds (PDRs)

Photochemistry, Ion-molecule chemistry

PAHs, C⁺, O,
reactive ions (CO⁺, HOC⁺…),
hydrocarbons (C₃H⁺…)

Chemistry is not in thermochemical equilibrium but controlled by 2-body gas-phase reactions:

\[ X^+ + H_2 \rightarrow XH^+ + H \]

reaction kinetics

Gas-phase molecules are (predominantly) synthesised in exothermic reactions in the gas and on the surfaces of tiny dust grains.

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**Summary:**

Which are the key processes in ISM chemistry?

1) Need to form the basic molecule, H₂ in grain surfaces.

2) We need atomic or molecular ions (H₂ + O⁺ \(\rightarrow\) OH⁺ + H):
   - far-UV photons (<13.6 eV) near stars
   - Cosmic-ray particles in shielded clouds

and we prefer exothermic reactions…

- Chemistry is **not** in thermochemical equilibrium but controlled by 2-body gas-phase reactions (\( X^+ + H_2 \rightarrow XH^+ + H \)) \(\rightarrow\) reaction kinetics