Astrochemistry in high-mass Star-Forming regions

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Low-mass star formation

1- PRE- STELLAR PHASE: SIMPLE MOLECULES

2- PROTOSTELLAR PHASE: COMPLEX MOLECULES

3- PROPLYDS PHASE: SIMPLE + COMPLEX

4- PLANETS FORMATION CONSERVATION + DELIVERY: LIFE (?)

chemical sequence!

Shu, Adams & Lizano 1987
Caselli & Ceccarelli 2012
High-mass star formation

Tentative evolutionary sequence

![Diagram of star formation stages](image)

- IRDC
- HMPO
- HMC
- UCH II

\[ T \sim 10 - 20 \text{ K} \quad T \sim 20 - 100 \text{ K} \quad T \geq 100 \text{ K} \]

- Huge distances (d>1 kpc)
- Rare objects
- Strong feedback
- Variations in a shorter time

**chemical sequence?**
Presentation outline

1. Main (astro)chemical processes in Star-Forming regions
2. Chemistry of InfraRed-Dark Clouds
3. Chemistry of High-Mass Protostellar Objects, and Hot Molecular Cores
4. Isotopic ratios: are they evolutionary indicators?
Gas-phase processes

Neutral-neutral: \( A + BC \rightarrow AB + C \)

Minimum energy to brake bonds: \( E \sim 0.01-1 \text{ eV} \)

Energy released by the formation of the new bond:

\[ k_b T \sim 0.01 \text{ eV} \quad @ \quad 100 \text{ K} \]

in cold molecular clouds cannot overtake the Barrier...

Dominant in warm (\( T > 100 \text{ K} \)) gas

e.g. Duley & Williams 1984, “Interstellar chemistry”
Van der Tak 2005
Gas-phase processes

Ion-neutral: $A^+ + BC \rightarrow AB^+ + C$

Exothermic ion-molecule reactions can occur even in very cold $(T<90 \text{ K})$ gas because the ACTIVATION BARRIER is OVERTAKEN by the energy of the long-range attractive interaction between the ion and the dipole moment induced in the neutral particle.

$V(R) = -\alpha e^2/2R^4$

Dominant in cold $(T < 100 \text{ K})$ gas

e.g. Herbst & Klemperer 1973; Anicich & Huntress 1986
Grain-surface processes

(1) A particle that impacts on a dust grain can be adsorbed (i.e. it remains on the surface) if the temperature is low ($T \leq 30$ K): ACCRETION.

(2) If many particles are adsorbed, i.e. if the density is high ($n \geq 10^4$ cm$^{-3}$): SURFACE DIFFUSION → MOLECULE FORMATION

(3) When the temperature increases ($T > 30 - 90$ K) above the evaporation threshold: DESORPTION

e.g. Duley & Williams 1984, Caselli+1997, Herbst 2005
In this way one can form efficiently on cold surfaces:

\[
\begin{align*}
H & \rightarrow H_2 \\
O & \rightarrow OH \rightarrow H_2O \\
C & \rightarrow CH \rightarrow CH_2 \rightarrow CH_3 \rightarrow CH_4 \\
N & \rightarrow NH \rightarrow NH_2 \rightarrow NH_3 \\
CO & \rightarrow HCO \rightarrow H_2CO \rightarrow H_3CO \rightarrow CH_3OH
\end{align*}
\]

Chemistry of Infrared-dark clouds

• Extinction features against the bright mid-IR Galactic background
• detected ~15 years ago by ISO (then by MSX, Spitzer, and Herschel)
• Cold (T < 25 K); dense ($N_{H_2} > 10^{23} \text{ cm}^{-2}$); massive ($10^2 M_{\text{sun}} \leq M \leq 10^4 M_{\text{sun}}$)

Typical low-T high-n chemistry

1) dominant species: $N_2H^+$, HCO+, HCN, HNC, $C_2H$...
   Vasyunina+11, Sanhueza+12, Henshaw+13, Miettinen14

2) high CO depletion factors
   Pillai+07, Zhang+09, Hernandez+11, Fontani+12

3) high abundances of D-molecules
   (D/H $>> 10^{-5}$)
   Fontani+2011, Tan+2013, Pillai+2012,
   Kong+2015, Gerner+2015

\[ N_2 + H_3^+ \rightarrow N_2H^+ + H_2 \]
\[ CO + H_3^+ \rightarrow HCO^+ + H_2 \]
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**Typical low-$T$ high-$n$ chemistry**

1) Dominant species: $N_2H^+$, $NH_3$, $HCO^+$, $HCN$, $HNC$, $SiO$
   
   Vasyunina+11, Sanhueza+12, Henshaw+13, Miettinen14

2) High CO depletion factors ($f_{CO}>5-10$)
   
   Pillai+07, Zhang+09, Hernandez+11, Fontani+12

3) High abundances of D-molecules
   
   ($D/H>>10^{-5}$)
   

**At a resolution of ~27`` (or ~0.4pc)**

*Mean deuterium fraction = 0.04*
CO depletion and D-fractionation

If $T$ is low

\[ \text{H}_3^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ + \text{H}_2 + 230K \]

If $n(\text{H}_2)$ is high

\[ \text{H}_2\text{D}^+ + \text{CO} \rightarrow \text{DCO}^+ \]

\[ \text{H}_2\text{D}^+ + \text{N}_2 \rightarrow \text{N}_2\text{D}^+ \]

\[ \text{H}_2\text{D}^+ + \text{CN} \rightarrow ... \rightarrow \text{DNC} \]

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

\[ \text{H}_2\text{D}^+ + \text{H}_2\text{CO} \rightarrow ... \rightarrow \text{HDCO} \]

$D_{\text{frac}} = \frac{N(\text{XD})}{N(\text{XH})} >> 10^{-5}$

(e.g. Crapsi et al. 2005, Emprechtinger et al. 2009, Gerner et al. 2015)

If $T < 20$ K

\[ n(\text{H}_2) > 10^5 \text{ cm}^{-3} \]

High CO (and CS) DEPLETION FACTOR

\[ f_D = \frac{X(\text{CO})^T}{X(\text{CO})^O} > 1 \]

(e.g. Caselli et al. 1999, 2002, Tafalla et al. 2004)
Chemistry of H-M Protostellar Objects

- Accreting protostars with $M \geq 8 \, M_{\text{sun}}$, mid-Infrared-luminous;
- Warm ($T \sim 20 - 100 \, K$); associated with powerful outflows

**Intermediate-T high-n chemistry**

1) Dominant species: CO, $^{13}\text{CO}$, $\text{N}_2\text{H}^+$, HCO$^+$, H$^{13}\text{CO}^+$
   + saturated Molecules: CH$_3$CCH, CH$_3$OH, H$_2$O
   Beuther+07,+09, Herpin+12, Foster+11, Gerner+14

2) Lower CO dep. factors ($f_{\text{CO}} < 10$)
   ~high abundances of D-molecules
   Fontani+06,+11 Giannetti+14
   Miettinen+11, Gerner+2015

3) Outflow/shock tracers:
   CO wings, SiO, SO$_2$

Cyganowski et al. 2011
G19.01-0.03 (SMA + IRAC)
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Beuther et al. 2009
Chemistry of Hot Molecular Cores

- Molecular “cradles” of newly born OB stars
- Hot ($T > 100$ K); dense ($n_{H_2} > 10^{6-7}$ cm$^{-2}$); luminous ($L > 10^4$ L$_{\odot}$)
- Rich in complex molecules and saturated species

**Typical high-$T$ high-$n$ chemistry**

1) Dominant species: CH$_3$CN, OCS, Complex Organic Molecules
   + shock tracers: SiO, SO, SO$_2$
   Beuther+07,+09, Beltrán+07,+14
   Oberg+13, Sanchez-Monge+14

2) Low CO depletion factors
   ($f_{CO} \sim 1$)
   Low abundance of D-molecules
   Fontani+07,+11,+15, Miettinen+11, Gerner+2015

Beuther et al. 2009
Hot-core G31.41 with ALMA

**COMPLEX ORGANIC MOLECULES**

- **7 atoms**
  - Acetaldehyde = CH$_3$CHO
  - Vinyl Cyanide = C$_2$H$_3$CN
- **8 atoms**
  - Methyl formate = CH$_3$OCHO
  - Glycolaldehyde = CH$_2$(OH)CHO
- **9 atoms**
  - Dimethyl ether = CH$_3$OCH$_3$
  - Ethanol = C$_2$H$_5$OH
  - Ethyl cyanide = C$_2$H$_5$CN
- **10 atoms**
  - Ethylene glycol = (CH$_2$OH)$_2$
  - Acetone = CH$_3$COCH$_3$

Courtesy of m. Beltrán
D-molecules: evolutionary tracers?

\[
\frac{N_2H^+}{D}: \text{sharp decrease } \text{HMSC} \rightarrow \text{HMPO}
\]

\[
\frac{HNC}{D}: \text{slight decrease } \text{HMSC} \rightarrow \text{HMPO}
\]

\[
\frac{NH_3}{D}: \approx \text{constant}
\]

\[
\frac{CH_3OH}{D}: \text{increase (sharp?) } \text{HMSC} \rightarrow \text{HMPO}
\]

Dfrac(N_2H^+) is the best (unique?) tool to identify High-Mass starless cores!

GAS

GRAINS

D-\text{molecules: evolutionary tracers?}

\text{Dfrac}(N_2H^+): \text{sharp decrease } \text{HMSC} \rightarrow \text{HMPO}

\text{Dfrac}(HNC): \text{slight decrease } \text{HMSC} \rightarrow \text{HMPO}

\text{Dfrac}(NH_3): \approx \text{constant}

\text{Dfrac}(CH_3OH): \text{increase (sharp?) } \text{HMSC} \rightarrow \text{HMPO}

\text{Dfrac}(N_2H^+) \text{ is the best (unique?) tool to identify High-Mass starless cores!}

\text{Fontani+15}
Formation of $^{15}$N-molecules

e.g. Terzieva & Herbst 2000; Charnley & Rodgers 2002; Rodgers & Charnley 2008; Hily-Blant et al. 2013; Roueff et al. 2015

**If T is low**

$^{15}$N + N$_2$H$^+$ $\rightarrow$ $^{15}$NNH$^+$ + N + 36K

N$^{15}$NH$^+$ + N + 28K

$^{15}$N + HCNH$^+$ $\rightarrow$ HC$^{15}$NH$^+$ + N + 36K

![Chemical network showing the main reactions responsible for $^{15}$N enhancement in nitriles and ammonia.](image)

*Figure 1.* Chemical network showing the main reactions responsible for $^{15}$N enhancement in nitriles and ammonia.
$^{15}\text{N}$-molecules: evolutionary tracers?

Main results:

1) Huge range of $^{14}\text{N}/^{15}\text{N}$ in $\text{N}_2\text{H}^+$

2) NO statistical separation between the evolutionary groups

→ time does not seem to play a role in $^{15}\text{N}$ fractionation
NO statistical separation between HMSCs / HMPOs / UCHIIIs, But overall faint anti-correlation (similar to L1544!!):
Spearman’s $\rho \sim -0.5$
Kendall’s $\tau \sim -0.6$
Summary and (some) open questions

1) Chemical complexity increases as in low-mass Star Formation. But how (and when) are COMs forming?

2) D-fractionation is (overall) an evolutionary indicator. But what is the contribution of surface chemistry?

3) $^{15}$N-fractionation is still mysterious... is it dependent on core evolution?
H and N isotopic anomalies

Caselli & Ceccarelli 2012, A&Arv (and references therein)