Lecture 6: Dense molecular clouds

http://www.sron.nl/~vdtak/astrochem.html
Recap of Lecture 5

- **Shock basics; types of shocks**
  - ubiquity; Mach number; jump conditions
  - magnetic precursor; J- vs C-type
  - processes: high-$T$ gas phase; grain core/mantle erosion; photoreactions

- **Chemistry of J-type shocks**
  - collisional / photo-dissociation; two-step H$_2$ reformation
  - role of OH; SiO as diagnostic

- **C-type shocks**
  - non-dissociative; formation of OH, H$_2$O, CH$^+$, ...

- **Examples**
  - IC 443: mixed shock type; H$_2$O dissociation & depletion
  - Orion-KL: enhanced SO, SO$_2$, SiO
  - L1157: SiO & CH$_3$OH from grain mantles
# Course Schedule

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<th>Date</th>
<th>Topic</th>
<th>Literature</th>
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<td>17-05-2016</td>
<td>I. Basic chemical processes</td>
<td>Tielens 2013, Rev. Mod. Phys.</td>
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<tr>
<td>19-05-2016</td>
<td>II. Gas-phase and grain surface reactions</td>
<td>Smith 2011, ARAA</td>
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<td>24-05-2016</td>
<td>III. Early Universe chemistry</td>
<td>Galli &amp; Palla 2013, ARAA</td>
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<td>26-05-2016</td>
<td>IV. Diffuse interstellar clouds (09:00)</td>
<td>Snow &amp; McCall 2006, ARAA</td>
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<td>02-06-2013</td>
<td>VI. Dense interstellar clouds</td>
<td>Bergin &amp; Tafalla 2007, ARAA</td>
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<td>07-06-2016</td>
<td>VII. Star- and planet-forming regions</td>
<td>Herbst &amp; van Dishoeck 2009, ARAA</td>
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<td>17-06-2016</td>
<td>Presentations</td>
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Today's lecture

Introduction

Observations
  gas phase
  solid state

Models
  pure gas phase
  gas-grain models

Comparison with observations
  TMC-1 vs other cores
  pre-stellar cores

Conclusions
Some history

Gas-phase ion-molecule chemistry
- Herbst & Klemperer 1973: importance of IM reactions
- Watson 1976: isotope fractionation
- Black & Dalgarno 1977: include photoprocesses
- Prasad & Huntress 1980: time & depth dependence
- Millar et al 1991: UMIST database

Early years: comparison focused on TMC-1 cloud

Grain surface chemistry:
- Allan & Robinson 1977: basic processes
- Tielens & Hagen 1982: accretion-limited scheme
- d'Hendecourt et al 1985: coupling to gas phase
- Hasegawa & Herbst 1993: H$_2$ tunneling, CR-UV desorption
Observations of dark clouds

Conditions: $T = 10$ K, $n = 10^4 – 10^5$ cm$^{-3}$
strong mm-wave low-$J$ line emission

Prototype: TMC-1
~60 species found in 1980s, esp. long C-chains
recently: anions, saturated chains

Abundance variations between cores
Cirrus cores: Turner 2000

Recent focus: pre-stellar cores
prototypes: B68, L1544
centrally condensed, about to collapse
See Bergin & Tafalla 2007 for review
CO 1-0 survey of Taurus

Ungerechts & Thaddeus 1987
Carbon chains in TMC-1

$\text{H}_2\text{C}_n$, $\text{HC}_n\text{N}$, $\text{C}_n\text{H}$ up to $n=9$: Langer et al 1997
Anions & saturated chains

large species: high e- attachment rates
*Herbst 1981; McCarthy et al 2006*

Prop(yl)ene (CH$_2$CHCH$_3$) in TMC-1
*Marcelino et al 2007*
Solid state molecules

Mid-IR absorption against background stars
  broad feature without rotational substructure
  band position and width depends on composition

 Mostly simple saturated species
   H$_2$O, CO, CO$_2$

 Also more complex ones like HCOOH
   even in quiescent clouds

 Dark starless clouds: 10-50% of heavy elements
   centers of dense pre-stellar cores: up to 99% freeze-out

 Ices are key chemical component
Quiescent clouds

Probe clouds prior to star formation unaffected by heating and processing

See same features as toward protostars starlight does not change composition

Knez et al 2005; Chiar et al 2011

<table>
<thead>
<tr>
<th>Ice species</th>
<th>Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>1</td>
</tr>
<tr>
<td>CO</td>
<td>0.27 – 0.32</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.19 – 0.35</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>0.02 – 0.05</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>0.05 – 0.10</td>
</tr>
</tbody>
</table>
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Conclusions
Two types of models

Depth-dependent models (Lecture 4):
1. diffuse/translucent clouds
   - low $n$; $T$ input or from heating / cooling
   - pure gas phase
2. dense PDRs
   - high $n$; $T$ from heating / cooling
   - pure gas phase
   - homogeneous / clumpy structure

Time-dependent models: today
1. pseudo-time-dependent models
   - low $T$; $T$ & $n$ constant
   - pure gas phase / gas-grain
2. dynamical models
   - low $T$; $T(t)$ & $n(t)$
   - pure gas phase / gas-grain
3. hot core models
   - high $T$; $T$ & $n$ constant
   - start from evaporated ices
Pure gas phase models

Basic networks: Lecture 4
  dense clouds: form more complex carbon species

Reactions with $C^+$, $C$, and $C_2H_2^+$

$$C^+ + CH_4 \rightarrow C_2H_3^+ + H / C_2H_2^+ + H_2$$
$$C^+ + C_2H_2 \rightarrow C_3H^+ + H$$
$$C + C_2H_2 \rightarrow C_3H + H$$
$$C_2H_2^+ + C_2H_2 \rightarrow C_4H_3^+ + H / C_4H_2^+ + H_2$$

Reactions with $CH_3^+$ also play a role (mostly RA)

e.g. $CH_3^+ + H_2O \rightarrow CH_3OHH_2^+ \rightarrow CH_3OH$

but experiments suggest DR yield of only a few %

cannot make observed amount of $CH_3OH$
Recent developments

Rates of ion-polar reactions enhanced at low $T$
  e.g., $\text{C}^+ + \text{OH} \rightarrow \text{CO}^+ + \text{H}$

Measure DR branching ratios
  e.g., $\text{H}_3\text{O}^+ \rightarrow \text{OH} / \text{H}_2\text{O}$

Cosmic-ray induced photodissociation
  interaction with $\text{H}_2$

Some neutral-neutral reactions are fast at low $T$
  e.g., $\text{CN} + \text{C}_2\text{H}_2$

Current models:
  \sim 4500 reactions between \sim 450 species with up to 13 atoms

Public resources:
  UMIST  http://www.udfa.net/
  KIDA    http://kida.obs.u-bordeaux1.fr/
Pseudo-time-dependent models

Most species need $10^5 - 10^6$ yr to reach equilibrium
solve chemical network as function of time
keep $T$ & $n$ constant (2 x $10^4$ cm$^{-3}$, 10 K)

Initial conditions:
usually H$_2$ molecular, CNO atomic
represents diffuse clouds

Main result:
conversion of C$^+$ $\rightarrow$ C $\rightarrow$ CO in $10^6$ yr

Consequence:
early-time / steady-state species
C-chains need C for formation

Markwick et al 2000
Pure gas-phase models: successes ...

Abundances protonated species
HCO$^+$, N$_2$H$^+$, HOCO$^+$ ...
Detection of interstellar H$_3^+$ is important confirmation

Abundances metastable species
HCN / HNC ratio

Abundances anions
primarily large C-chains

Isotopic fractionation
$^{12}$CO/$^{13}$CO, DCO$^+$/HCO$^+$
heavy isotope enhanced at low $T$ due to lower zero point vibration

Unsaturated molecules
reactions of many species with H$_2$ are endothermic
expect that molecules are H-poor
despite overabundance of H by $10^4$
... and problems

- Some species off by orders of magnitude even simple species

- Comparison with observations of TMC-1
  best fit: 80% of species within factor of 10
  indicates age of $\sim 10^5$ yr ... why so young?

- C-chains not well fit if $C_n + O$ and $C_n + N$ rapid
  even at early times

- Predict most oxygen in $O_2$ at late times
  but observed abundance is low

- Predictions sometimes ambiguous especially “bistability” phenomenon
Sensitivity analysis

- Vary rates of relevant reactions within uncertainty
  black area: range of possible predictions

*Wakelam et al 2010*
Methanol in cold clouds

Models with and without grain surface chemistry: need grains to make observed amount of methanol

Herbst & van Dishoeck 2009
Herschel detection of interstellar $O_2$

Multiple lines:
  first secure detection
  confirms hint from Odin

Low abundance:
  oxygen depleted onto grain surfaces

Goldsmith et al 2011; Liseau et al 2012
Bistability of networks

Low density
high ionization phase

High density
low ionization phase

Between: both!
location depends on $\zeta_{CR}$
and on specific rates ($H_3^+ DR$)
Disappears if grains dominate neutralization

Le Bourlot et al 1995; Boger & Sternberg 2006
Beyond pseudo-time-dependence

**Dynamical models**
- $n$ & $T$ vary with time
- e.g. protostellar collapse
  - *Gerola & Glassgold 1978, Tarafdar et al 1985*

**Depth-dependent models**
- $\approx$ PDRs with low UV field
- photodissociation limits build-up of large molecules
  - *Viala et al 1988, Lee et al 1996*

**Turbulent mixing models**
- gas cycles diffuse $\leftrightarrow$ dense clouds
- increase C hence complex molecules in dense phase
  - *Boland & de Jong 1982, Willacy et al 2002*
Today's lecture

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Gas-depletion timescale: $2 \times 10^9 \, y_S^{-1} \, n_H^{-1} \, \text{yr}$

with $y_S = \text{sticking coefficient} \sim 1$ at 10 K

at $n_H > 10^4 \, \text{cm}^{-3}$, gas-grain collisions change the chemistry

**Pure grain models**

molecules accrete & react in isolation


**Gas-grain models**

molecules accrete, react, and return to gas phase


**Only consider diffusive mechanism here**
A day in the life of an interstellar grain

A few atoms / molecules land on the surface
H, He, C, O, CO, N, N₂
All species but He stick with $y_s \approx 1$

Light species migrate over surface
- tunneling: only H & H₂
- thermal hopping: H, C, N, O
- maybe: CH, NH, OH, NH₂, CH₂, CH₃

Reactions occur if barrier low enough
- 4500 K for H₂
- 3500 K for H
- 450 K for C, N, O
## Time scales at 10 K

<table>
<thead>
<tr>
<th>Species</th>
<th>$E_D$ (K)</th>
<th>$t_{\text{des}}$ (s)</th>
<th>$t_{\text{hop}}$ (s)</th>
<th>$t_{\text{acc}}$ ($10^{12}$ s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>350</td>
<td>500</td>
<td>10^{-12}</td>
<td>7</td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>450</td>
<td>$10^7$</td>
<td>$4 \times 10^{-12}$</td>
<td>5</td>
</tr>
<tr>
<td>C</td>
<td>800</td>
<td>$10^{22}$</td>
<td>$10^{-2}$</td>
<td>2</td>
</tr>
<tr>
<td>$\text{CH}_4$</td>
<td>2600</td>
<td>...</td>
<td>...</td>
<td>1</td>
</tr>
</tbody>
</table>

*Lecture 2; Tielens, Chapter 4.2*
Gas-grain interaction

Low gas-phase density
large H abundance
mainly *hydrogenation*
H$_2$O, CH$_4$, NH$_3$, ...

High gas-phase density
large O abundance
mainly *oxidation*
CO$_2$, O$_2$, ...

*Tielens 1989*
Formation of complex molecules

Formation routes $\text{H}_2\text{O}, \text{CH}_3\text{OH}$
see Lecture 2

Setup of experimental tests
see Lecture 2

Larger species: pure theory
HCNO addition scheme

Dashed: detected in gas
Solid: detected in ice

Tielens & Charnley 1997;
Bisschop et al 2007
Desorption mechanisms

- **Thermal evaporation**
  - depends on type of surface (silicate / ice)
  - apolar species (CO, N₂, O₂): $T > 20$ K
  - polar (H-bonding) species (H₂O): $T > 100$ K

- **Cosmic-ray spot heating**
  - $t \sim 4 \times 10^6 - 10^7$ yr

- **Explosive desorption**
  - exothermic reactions between radicals
  - induced by cosmic rays: $t \sim 10^5$ yr

- **Gas-grain collisions in shocks** (Lecture 5)
  - sputtering of ice mantle

- **Energy liberated by reactions**
  - efficient locally or for small grains ($\sim 100$ Å)

Non-thermal mechanisms only efficient for apolar ice
Herschel detection of H$_2$O in L1544

- Cold pre-stellar core
  - $\sim$10 K: expect H$_2$O frozen
- Detect $1_{10}-1_{01}$ line at 557 GHz
  - ground state of o-H$_2$O
  - needs space mission
- Chemistry:
  - cosmic-ray desorption of ice mantle
- Dynamics: infall
  - infall = start of star formation

*Caselli et al 2012*
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Comparison with observations: TMC-1

Large carbon chains are abundant indicator of young age
~$10^5$ yr since diffuse cloud stage

Surveys of dark cores:
good correlation between carbon chains but not with NH$_3$ or N$_2$H$^+$

Use C$_2$S / NH$_3$ and C$_2$S / N$_2$H$^+$ ratios as age indicator
Chemical gradient across TMC-1 = age gradient?

*Olano et al 1988, Markwick et al 2000*
[CI] 492 GHz map of Taurus

C peaks South of C$^{18}$O
fresh carbon mixed into TMC-1
origin of abundant carbon chains?

Maezawa et al 1999
C$_2$S shows trend with HC$_3$N but not with NH$_3$

in starless and in protostellar cores

_Suzuki et al 1992_
Production of C$_2$S; proposed evolutionary scheme

Main evolution C$^+$ → C → CO
trapped by C$_2$S → NH$_3$
Not all arrows represent single-step reactions

Suzuki et al 1992
Pre-stellar cores: L1498

Centrally condensed structure ... on the verge of gravitational collapse?

Strong chemical differentiation
- $\text{C}_2\text{S}$: clumpy atomic C-rich outer part
- $\text{NH}_3$ peaks in inner dense core
- $\text{C}^{18}\text{O}$ avoids densest part: depletion
- High D fractionation: $\text{DCO}^+/\text{HCO}^+ \approx 0.1$

*Willacy et al 1998*
Chemical differentiation

Dense core center:
traced by dust
$\text{NH}_3$ & $\text{N}_2\text{H}^+$ follow

CO & CS avoid center:
depleted onto grains

Extreme cases:
>90% of CNO gas frozen out

Physical structure

Left: $M = 1 \, M_0$, $G_0 = 1$
Right: $M = 1.6 \, M_0$, $G_0 = 10$

Galli et al 2002
Chemical structure

Toward center:
- CO freezes out
- D- and N-bearing species increase
- $\text{H}_2\text{D}^+$, $\text{N}_2\text{H}^+$ destroyed by CO

Aikawa et al 2005
Ionization and deuterium fractionation

$\text{H}_3^+$ is main ion
carries 20% of charge
rest in more complex ions

Strong fractionation:
$\text{D}_3^+ / \text{H}_3^+ \approx 0.1$
enhanced by $10^{14}$

*Maret & Bergin 2006*
H$_2$D$^+$ and D$_2$H$^+$ observations

From the ground

Stark et al 1999; Caselli et al 2003; Vastel et al 2006; Parise et al 2011
Triply deuterated CH$_3$OH & NH$_3$

Lis et al 2002;
Van der Tak et al 2002;
Parise et al 2004
Origin of strong deuteration

\[
\begin{align*}
\text{H}_3^+ + \text{HD} & \rightleftharpoons \text{H}_2\text{D}^+ + \text{H}_2 \\
\text{H}_2\text{D}^+ + X & \rightleftharpoons \text{XD}^+ + \text{H}_2
\end{align*}
\]

- Forward reaction exothermic by 230 K
  more rapid at low \( T \)
- **Reason**: zero point vibration of \( \text{H}_2\text{D}^+ \) lower than \( \text{H}_3^+ \)
- Proton affinity of \( \text{H}_2 \) low
  deuteration passed on to other species (CO, \( \text{N}_2 \), ...)
- Freeze-out of CO enhances deuteration
  main destroyer of \( \text{H}_2\text{D}^+ \) gone
Summary

- **Starless cores**: abundant carbon chains indicates young ageatomic C available

- **Pre-stellar cores**: centrally condensed
  
  CO freeze-out in center
  
  N- and D-species enhanced

Grain chemistry essential
Exercise: CH$_3$OH rotation diagram

Many lines of CH$_3$OH have been observed toward the young protostar IRAS 16293. The table on the course website lists for each line the frequency ($\nu$ in GHz), the upper level energy ($E_u$ in K), the Einstein A coefficient ($A_{ij}$ in s$^{-1}$), the upper state degeneracy ($g_u$), and the observed line flux ($W$ in K*km/s) with its rms error.

1. Make a plot of $\ln(N_u/g_u)$ versus $E_u$, using $\frac{N_u}{g_u} = C \frac{\nu^2 W}{A_{ul} g_u}$, with $C = 1942.75$

2. Fit a linear function to the data, using e.g. Python, Matlab, or IDL.

3. Find the rotation temperature $T_{rot}$ from the slope of the line, using $\frac{N_u}{g_u} = \frac{N}{Q(T_{rot})} e^{-E_u/T_{rot}}$

4. Find the partition function $Q(T_{rot})$ at this temperature, interpolating (in the log) from the values you find at the CDMS website.

5. Find the total CH$_3$OH column density $N$ from the intercept of the line, using Eq. 2.

6. Overplot the predictions from the on-line RADEX calculator for these lines under these conditions. Discuss the difference with the observations.