Volatiles & Organics in the ISM

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The Grand Challenges of Astrochemistry

• What is the organic inventory of space, in particular in regions of star and planet formation and how does that relate to the prebiotic origin of life?

• What is the role of molecules in the evolution of the Universe?

• How can we use molecules to study the Universe?
Building the Solar System’s Organic Inventory

From small to big:
- Protective environment of dense clouds

From big to small:
- Stars as sooting candles
- UV and energetic particle processing

Chemical growth: a few atoms at a time
Building the Solar System’s Organic Inventory

CO reservoir

Gas:
- ion-molecule reactions
- cosmic-ray photolysis

PAH reservoir

Stars:
- soot chemistry
- shock chemistry

Ices:
- hydrogenation
- photolysis
- thermal polymerization
- ice-ion-molecule
- ice segregation

Asteroids:
- aqueous alteration

Comets:
- energetic processing

Hot core:
- ice evaporation
- ion-molecule reactions

Nebula:
- UV & X ray photolysis
- radical reactions
- hydrocarbon chemistry
- Fischer-Tropsch
- shocks, intermittent
- accretion, diffusion

Tielens 2011
### Table 9.2: The composition of dark clouds

<table>
<thead>
<tr>
<th>Species</th>
<th>TMC1</th>
<th>L134N</th>
<th>Species</th>
<th>TMC1</th>
<th>L134N</th>
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<td>1.7 (-9)</td>
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<td>3 (-10)</td>
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<tr>
<td>CO</td>
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<td>8.7 (-5)</td>
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<td>HCS(^{+})</td>
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<td>HCO</td>
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<td></td>
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<td>C(_3)S</td>
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<td>C(_5)N</td>
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<tr>
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<td>NH(_2)</td>
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<td>1.0 (-8)</td>
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<td>&lt; 5.0 (-11)</td>
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<td>C(_2)H</td>
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<td>C(_6)H</td>
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<td>c-C(_3)H(_2)</td>
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</table>

\(^{a}\) Abundance relative to H\(_2\). Taken from the compilation of [?], which should be consulted for the original references, and the studies by [? , ? , ?]. \(^{g}\) Measured in the warm carbon chain source L1527 [?].
Ion-molecule chemistry: Carbon forms small hydrocarbon radicals but the route to CH₄ is closed. Hence, carbon burns to CO. A small fraction flows to carbon chains through radical reactions.
Neutral neutral reactions with radicals flow to $N_2$. The ion-molecule or neutral routes to $NH_3$ are really closed.

If this were all, this meeting would be over as far as I am concerned.
Interstellar Ices

Boogert et al 2015, ARAA, 53, 541
(non) Hydrogen-bonding Ice

hydrogen bonding ices: $\text{H}_2\text{O}:\text{CO}_2:\text{CH}_3\text{OH}:\text{CO}=100:20:10:3$

non hydrogen bonding ices: $\text{CO}_2:\text{CO}=3:20$
<table>
<thead>
<tr>
<th>Species</th>
<th>Quiescent cloud$^b$</th>
<th>Low mass protostar$^c$</th>
<th>High mass protostar$^d$</th>
<th>Comets$^e$</th>
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<td>H$_2$O</td>
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<td>100</td>
<td>100</td>
<td>100</td>
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<td>CO (total)</td>
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<td>5</td>
<td>13</td>
<td>23</td>
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<tr>
<td>CO (H$_2$O-ice)</td>
<td>3</td>
<td>10</td>
<td>6</td>
<td>–</td>
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<tr>
<td>CO (pure CO)</td>
<td>22</td>
<td>4</td>
<td>3</td>
<td>–</td>
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<tr>
<td>CO$_2$ (total)</td>
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<td>19</td>
<td>13</td>
<td>6</td>
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<tr>
<td>CO$_2$ (H$_2$O-ice)</td>
<td>18</td>
<td>(10)$^f$</td>
<td>9</td>
<td>–</td>
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<tr>
<td>CO$_2$ (CO-mix)</td>
<td>3</td>
<td>(10)$^f$</td>
<td>2</td>
<td>–</td>
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<tr>
<td>CO$_2$-CH$_3$OH complex</td>
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<td>–</td>
<td>1.2</td>
<td>–</td>
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<tr>
<td>CO$_2$ (pure crystalline)</td>
<td>–</td>
<td>–</td>
<td>1.0</td>
<td>–</td>
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<tr>
<td>CH$_4$</td>
<td>&lt; 3</td>
<td>&lt; 1.4</td>
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<td>0.6</td>
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<td>30</td>
<td>18</td>
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<td>H$_2$CO</td>
<td>–</td>
<td>–</td>
<td>6</td>
<td>1.1</td>
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<tr>
<td>HCOOH</td>
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<td>&lt; 1</td>
<td>7</td>
<td>0.09</td>
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<td>OCS</td>
<td>&lt; 0.2</td>
<td>&lt; 0.1</td>
<td>0.2</td>
<td>0.4</td>
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<td>NH$_3$</td>
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<td>&lt; 11</td>
<td>15</td>
<td>0.7</td>
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<td>OCN$^-$</td>
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<td>&lt; 0.2</td>
<td>3.5</td>
<td>0.1$^g$</td>
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Grain Surface Reactions

• Hydrogenation & oxidation
• Tunneling
• Deuteration

$H_2CO/CH_3OH/CO_2/CO$


$H_2O$


Gas-Grain Interaction is at the core of interstellar chemistry

- Depletion in dense cores (i.e., B68, L1489)
- Interstellar ice
- H$_2$O & surfaces of molecular clouds
- Gas phase HO$_2$ & H$_2$O$_2$ (i.e., ρ Oph)
- High deuterium abundances of CH$_3$OH/H$_2$CO in protostellar envelopes
- Hot Core composition &

Parise et al 2012
Ceccarelli et al,
Deuterium Chemistry

High atomic D/H in the accreting gas
Tunneling abstraction reactions

Hama & Watanabe, 2013, Chem Rev, 113, 8783
Simple Organic Molecules ("SOM")

- Warm dense gas with rich organic inventory: of relatively simple organic molecules
  - CH$_3$OH, CH$_3$CH$_2$OH, CH$_3$OCH$_3$, H$_2$CO, CH$_3$CHO, HCOOH, NH$_2$CHO, ...
  - HCN, CH$_3$CN, CH$_3$CH$_2$CN, ...
- Large deuterium fractionations
- Driven by evaporation of ice mantles formed in cold phase

Ceccarelli et al, 2007, PPV, 47
Origin of “SOM”

Deuterium fractionation implies formed from cold-reservoir-progenitors

- Surface chemistry in cold regions
- Photolysis of ices
- Evaporation followed by gas phase reactions
- Ion molecule chemistry in ices


Grain surface chemistry: Charnley & Rodgers 2007 Bioastronomy


“SOM” molecules require ‘free’ carbon
Dark clouds: $C/CO \approx 6 \times 10^{-3}$
Evaporating Ices

- Evaporating ice molecules drive rich chemistry
- Protonated methanol & methyl transfer
- Issues:
  - Experimental studies disagree
  - Formation of intermediaries inhibited
  - Recombination leads to fragmentation
  - Role of ammonia as proton scavenger
- Chemical clock $\sim3 \times 10^4$ yr incompatible with hot corinos?

Geppert et al, Faraday discussions, 133, 177
Photolyzed Ices

UV photolysis/ion bombardment & warm up

- Radical production (CH$_3$ & others)
- Recombination
- Issues:
  - Polymerization
  - Chemical specificity
  - Simple photolysis products (HCO) not observed

Charged Ices

Ion-molecule Chemistry in Ices

- Ices are charged & charges are localized:
  - Na, PAHs
  - OCN⁻
- Polarization charge
- Warm-up leads to segregation
- H-bonding
- Stereochemistry
- Methanol drives chemistry
- Near evaporation, “droplets” may conduce methyl transfer without fragmentation

Building the Solar System’s Organic Inventory

From small to big
Protective environment of dense clouds

Chemical growth: a few atoms at a time

Comets

Asteroids

From big to small
Stars as sooting candles

UV and energetic particle processing

Tielens 2011
The incredibly rich spectrum of interstellar PAHs

Orion
PAHs in Orion
PAHs in the Protoplanetary Disk of HD 97048

PAHs and Herbig Stars

Interstellar Disk

Active Chemistry in disk environments

<table>
<thead>
<tr>
<th>Source</th>
<th>Sp T</th>
<th>Size</th>
<th>Location</th>
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</thead>
<tbody>
<tr>
<td>TY Cra</td>
<td>B7-B9</td>
<td>~2000 AU</td>
<td>HAeBe in cloud</td>
</tr>
<tr>
<td>HD 97048</td>
<td>B9-A0</td>
<td>~100-1000 AU</td>
<td>HAeBe cloud edge</td>
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<tr>
<td>HD 100546</td>
<td>B9</td>
<td>~150 AU</td>
<td>isolated HAeBe star</td>
</tr>
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</table>

PAH Variations in Regions of Star Formation

- Peak position of the 6.2 & 7.7 µm bands vary depending on local characteristics
- Aromatic versus aliphatic hydrocarbons
- N-incorporation
- PAH size

Active chemistry:
Key is strength of the radiation field
Key is stability

NGC 2023: The Movie

Stills from the Movie

Two Components:
6.2, G7.6, & G8.6 versus G7.8, G8.2 & 11.2

The 11.2/3.3 µm ratio

The Largest Molecule in Space: $C_{60}$

$C_{60}^+$ & the DIBs

$C_{60}$ in the PNe, TC1

Campbell et al, 2015, Nature, 523, 322

Cami et al, 2010, Science, 329, 1180
PAHs & C\textsubscript{60} in NGC 7023

Berne & Tielens, 2012, PNAS, 109, 401
PAHs & $C_{60}$ abundance

Berne & Tielens, 2012, PNAS, 109, 401
PAH photolysis

- Dehydrogenation & isomerization
- Stable intermediaries: cages & fullerenes
- Fragmentation products: hydrocarbon chains & radicals
- Relevant for hydrocarbon reservoir in PDRs?

Berne & Tielens, 2012, PNAS, 109, 401
From Graphene to $\text{C}_{60}$

Transformation of graphene to $\text{C}_{60}$, driven by electron irradiation
Multiphoton absorption leads to fragmentation in a laser pulse
Many pulses strip the molecule down
Loss of all H followed by loss of C₂ and C units (magic numbers)
From PAHs to $C_{60}$

$\lambda = 356\text{nm}$
From PAHs to $C_{60}$
UV Processing in Space

PAH destruction & fullerene formation

PAHs & Soot

PAH “Formation” in (Interstellar) Shocks

Shattering of carbon soot produces PAHs galore

Summary

• Bottom-up chemistry (~10% of elemental C)
  • Gas inventory: Largely CO (~99.5%), small amounts of hydrocarbon chains: ion-molecule & neutral-neutral radical chemistry
  • Icy inventory: H$_2$O dominated with CO, CO$_2$ & CH$_3$OH at 10-25%: Hydrogenation “activates” CO
  • Hot Cores Inventory: Largely CO (~98%), small amounts of methanol and its “daughter” products; Origin of SOM: methanol ice released to the gas

• Top-down chemistry (~10% of elemental C)
  • Largely aromatic
  • Produced in stellar outflows & shattering in interstellar shocks
  • Photochemistry: PAHs —>GrandPAHs—>Graphene—>C$_{60}$