Some Interstellar Molecules (129 in 2005)

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<th>CH4</th>
<th>HCN</th>
<th>HNO</th>
<th>CH3N</th>
<th>CH3OH</th>
<th>CH2N2</th>
<th>HC3N</th>
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<td>CNHCN</td>
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<td>HCN</td>
<td>CH3NH2</td>
<td>CH2NH</td>
<td>CH3NC</td>
<td>CH3NH2</td>
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<tr>
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Confirmed in Comet Wild-2 Stardust mission (2009)
Amino acid – glycine $\text{CH}_2\text{NH}_2\text{COOH}$?


$\text{ND}_3$ in Interstellar Clouds

Deuteration: deuterium species slightly more stable than hydrogen form


$\text{ND}_3/\text{NH}_3 = 8 \times 10^{-4}$, compared with $(\text{D}/\text{H})^3 \\
- 3 \times 10^{-15}$
DIB’s

The Diffuse Interstellar Bands

Interstellar Ices

Modest water ice
Substantial components:
- CO, CO₂, CH₃OH
Minor components:
- HCOOH, CH₃, H₂CO
5. Molecules in the ISM

- Simplest molecules
  - Linear, e.g., CO (carbon monoxide) [structured spectrum]
  - Symmetric top, e.g., NH$_3$ (ammonia) [more complex spectrum]
  - Asymmetric top, e.g., H$_2$O (water vapor) [forest]
- Linear molecules
  - Rotation, vibration, electronic
  - Symmetric top
    - Rotational
- Why are there any molecules?
  - Hard to form
  - Easy to destroy
- Reaction networks
  - Rate equations
  - Timescales

Linear molecules I

- Molecules (rigid rotators, linear molecules)
  - $J$ is rotational quantum number
  - $v$ is vibrational quantum number
  - $B$ is rotational constant
  - $I$ is moment of inertia
  - $D$ is centrifugal stretching term
  - $\omega_0$ is vibrational constant
- $E(J) = J(J+1)B - J^2(J+1)^2D + \frac{(v+1/2)\hbar\omega_0}{k}\]
Spectra: Frank Shu Vol 1 Radiation, Chap. 30

\[ E(J) = B J(J+1) + (v+1/2)\hbar\omega_0 \]

- frequency \((=\Delta E/h)\) for each rovibrational line with different initial and final vibrational quantum numbers
- for example \(J \rightarrow J-1\), and \(v=2 \rightarrow v=1\)
- i.e., \(v=\Delta E/h = B [J(J+1) - (J-1)J] + \omega_0 = 2JB + \omega_0\)
- line frequency increases with \(J\)
- lines are approximately equally spaced in frequency.

Population of rotational levels

Both \(\text{H}_2\) and CO have low critical densities, and the lower rotational levels are often in thermal equilibrium: we can use this fact to measure the molecular clouds temperatures.

\[
\frac{n_j}{n_0} = \frac{g_j}{g_0} \exp\left(-\frac{\Delta E_{j0}}{kT}\right) = \frac{(2J+1)}{(2J'+1)} \exp\left[-J(J+1)B/kT\right]
\]

Ratio of any two levels can be found directly, i.e.,

\[
\frac{n_j}{n_{j'}} = \frac{(2J+1)}{(2J'+1)} \exp\left[-J(J+1)B/kT\right] / \exp\left[-J'(J'+1)B/kT\right]
\]

Population distribution

To find the partition function we sum all \(n_j\) and when \(T \gg B/k\) we replace the discrete sum with integration over continuous values.

\[
n(\nu) = \sum_{J=0}^{\infty} (2J+1) \exp\left[-J(J+1)B/kT\right]
\]
Population distribution

To find the partition function we sum all $n_j$ and when $T \gg B/k$ we replace the discrete sum with integration over continuous values

$$n(\nu) = \sum_{J=0}^{J_{\text{max}}} (2J+1) \exp[-J(J+1)B/kT]$$

$$= \int (2J+1) \exp[-J(J+1)B/kT] dJ = kT/B$$

Which gives is an expression for the relative populations

$$\frac{n_J(\nu)}{n(\nu)} \approx \frac{(2J+1)B}{kT} \exp[-J(J+1)B/kT]$$

LTE internal energy

The mean contribution to the rotational internal energy per molecule

$$\sigma_{\text{rot}} = \sum_{J=0}^{J_{\text{max}}} (J+1)B \frac{n_J(\nu)}{n(\nu)}$$

$$= \int (J+1)B \exp[-J(J+1)B/kT] \frac{2J+1}{kT} dJ$$

$$= kT$$

So when $T \gg B/k$ there is equipartition of $kT/2$ for each of the two independent axes of rotation.
Symmetric top

- Molecules (nonlinear molecules)
  - $J$ is total angular momentum
  - $K$ is projection on symmetry axis
  - $A, B, C$ are rotational constants
  - $I_A, I_B, I_C$ are the moment of inertia,
    - prolate (cigar) $I_A < I_B = I_C$ (e.g., propyne $\text{CH}_3\text{C}≡\text{CH}$)
    - oblate (disk) $I_A = I_B < I_C$ (e.g., benzene $\text{C}_6\text{H}_6$)

- Prolate $E(J) = J(J+1)B + (A-B)K^2$
- Oblate $E(J) = J(J+1)B + (C-B)K^2$
- Selections rule $\Delta K = 0$
  - series of equal frequency separation lines

Symmetric top Ammonia ($\text{NH}_3$)

- Oblate symmetric top
  - 22$\implies$23 GHz (1.3 cm)
  - inversion transitions:
  - Thermometer of ISM dense molecular clouds [credit John Bally]
Formation – the problem

- Collisions (A+B)
  - No time to “relax” to energetic stable state
    - i.e., remove energy during collision
    - interaction time is about $10^{-13}$ s
  - the fastest “relaxation” electronic rate is $10^8$ s$^{-1}$
  - So only 1 in 100,000 collisions may remove energy and lead to a molecule = radiative association
  - Alternatively a 3-body reaction may carry away energy
    - need all 3 to collide at once: A+B+C
    - rate $\approx 10^{-44}$ m$^6$s$^{-1}$ when A+B are interacting: ISM $n\approx 10^7$ m$^{-3}$
    - this might work on/near in a star/circumstellar disk ($n\approx 10^{17}$ m$^{-3}$)
      - but not in the space between stars
    - = collisional association

Grain surface reactions

- Langmuir-Hinshelwood
  - surface diffusion

- Eley-Rideal
  - direct hit

Destruction

- Electronic photo-dissociation in the galactic ultraviolet
- Example from course book (Dyson & Williams)
  - Cross-section $10^{-21}$m$^2$ over 10 nm band
  - Number of UV photons $10^{10}$ m$^{-2}$ s$^{-1}$ nm$^{-1}$
  - Lifetime of $10^9$s = 300 years
Destruction

- Electronic photo-dissociation in the galactic ultraviolet
- Example from course book (Dyson & Williams)
  - Cross-section $10^{-16}$ m$^2$ over 10 nm band
  - Number of UV photons $10^{39}$ m$^{-2}$ s$^{-1}$ nm$^{-1}$
  - Lifetime of $10^{9}$s = 300 years

Formation: chemical reaction $A^+ {+} B \rightarrow C^+ {+} D^+$

- Reactions between ions and molecules are rapid, e.g.,
  - $O^+ {+} H_2 \rightarrow OH^+ {+} H$ ion-molecule
  - $O + H^+ \rightarrow O^+ + H$ (ion-atom version) = charge exchange
  - Rate coefficient of $10^{-15}$ m$^3$ s$^{-1}$ per molecule
  - Turns out to be a typical rate: let us see why as it applies to more than that chemical cross-sections

Neutral exchange

- Neutral exchange reactions (exothermic)
  - Final state is energetically favourable, e.g.,
    - $CH + O \rightarrow CO + H$
    - 7.6 eV
  - Departing atom carries excess energy
  - Rate coefficient of $10^{-17}$ m$^3$ s$^{-1}$ per molecule (100 weaker than ion-molecule)
  - Rate depends on short range forces (van der Waals)
  - Activation energy – a problem in the very cold ISM