Interstellar Molecules: From Hydrogen to Amino Acids

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Department of Physics and Astronomy
The University of Waterloo
“Hydrogen is the most important constituent of the Universe.”

G. Herzberg
In this talk

- Overview of Interstellar Space and Interstellar Molecules
  (ex) \( \text{H}_3^+ \) and \( \text{HCO}^+ \)
- Submillimeter-wave Spectroscopy and New Initiatives in Submillimeter Astronomy
  Multiply deuterated species in space
  Anions in the lab and in space
  Biological molecules in space
Cosmic Abundance

H

He

Others
21cm-Line of Hydrogen Atom

- van de Hulst (Leiden Observatory)
  1944 pointed out possibility of H 21cm line.

- Ewen, Purcell (Harvard University)
  Oort, Muller (Leiden Observatory)
  1951 detection of the line

- Christiansen, Hindman (Australia, AAO)

- Hydrogen Maser (N. F. Ramsey)
  1 420 405 751.786Hz
  21.10611405 cm
Discovery of Interstellar Molecules

- 1814 Fraunhofer lines
- 1904 Absorption lines of Ca,K against bright stars
- 1934 Discovery of 4 Diffuse Interstellar Bands (DIBS) Still remain unidentified.
- 1937-1941 Discovery of CH⁺,CH,CN 4230-4300 Å
- 1951 Bates, Spitzer: skeptical about interstellar molecules.
- 1955~ Townes, Shklovsky: Pointed out possibility of observing molecules with radio telescopes.

OH, NH₃, HCN, CO...............
Free radicals, ions.
Carbon chains
Cyclic molecules

\[
\text{H} = \text{C} \equiv \text{C} - \text{C} \equiv \text{C} - \text{C} \equiv \text{C} - \text{C} \equiv \text{C} - \text{C} \equiv \text{N}
\]

<table>
<thead>
<tr>
<th>Table 4.1: List of Interstellar Molecules Identified (as of May, 2004).</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Simple Hydrides, Oxides, Sulfides, Halogenated Compounds</strong></td>
</tr>
<tr>
<td>H$_2$(IR)</td>
</tr>
<tr>
<td>HF</td>
</tr>
<tr>
<td>HC$_2$</td>
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<tr>
<td>H$_2$O</td>
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<tr>
<td>N$_2$O</td>
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<tr>
<th><strong>Nitrylones, Acetylene Derivatives</strong></th>
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<tbody>
<tr>
<td>C$_2$H$_3$(IR)</td>
</tr>
<tr>
<td>C$_2$H$_3$(IR)</td>
</tr>
<tr>
<td>C$_2$O</td>
</tr>
<tr>
<td>C$_3$S</td>
</tr>
<tr>
<td>C$_4$Si$^+$</td>
</tr>
<tr>
<td>C$_5$N$_4$</td>
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<tr>
<td>C$_6$H$_6$</td>
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<thead>
<tr>
<th><strong>Aldehydes, Alcohols, Ethers, Ketones, Amides</strong></th>
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<tbody>
<tr>
<td>H$_2$CO</td>
</tr>
<tr>
<td>H$_2$CS</td>
</tr>
<tr>
<td>CH$_3$CHO</td>
</tr>
<tr>
<td>NH$_2$CHO</td>
</tr>
<tr>
<td>H$_2$COO</td>
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<tr>
<th><strong>Cyclic Molecules</strong></th>
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</thead>
<tbody>
<tr>
<td>c-C$_3$H$_2$</td>
</tr>
<tr>
<td>C$_8$H$_6$(IR)</td>
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</tbody>
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<tr>
<th><strong>Molecular Ions</strong></th>
</tr>
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<tbody>
<tr>
<td>CH$^+$ (IR)</td>
</tr>
<tr>
<td>HCS$^+</td>
</tr>
<tr>
<td>CO$^-$</td>
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<tr>
<td></td>
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<tr>
<th><strong>Free Radicals</strong></th>
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<tbody>
<tr>
<td>OH</td>
</tr>
<tr>
<td>CH</td>
</tr>
<tr>
<td>CH$_2$</td>
</tr>
<tr>
<td>CH$_3$(IR)</td>
</tr>
<tr>
<td>NH$_2$(UV)</td>
</tr>
<tr>
<td>NH$_2$</td>
</tr>
<tr>
<td>SH(IR)</td>
</tr>
</tbody>
</table>

Molecules identified other than radio are specified individually.


* Indicates molecules observed only in Red Giants.

? Reported, however, not yet confirmed.
HC$_3$N
HC$_5$N
Formation of molecules in interstellar space

- Ion-molecule reactions
  \[ \text{H}_3^+ \quad \text{HCO}^+ \]

- Neutral molecule reactions
  \[ \text{CN} + \text{C}_2\text{H}_2 \rightarrow \text{HC}_3\text{N} + \text{H} \]

- Surface reactions on dust grains
  \[ \text{H}_2, \text{CO}, \text{CO}_2, \text{H}_2\text{CO}, \text{CH}_3\text{OH} \ldots \]
Fig. 1. X-ogen spectra observed for: a, W3 (OH); b, Orion; c, L134; d, Sgr A (NH₃A); and e, W51. Antenna temperature is in degrees Kelvin uncorrected for antenna efficiency (and dome attenuation in the case of Orion). Radial velocity is in km s⁻¹ corrected to the local standard of rest. Spectrum for L134 taken with 100 kHz filter spacing.
Ion-molecule reaction

\[
\begin{align*}
H_2 & \rightarrow H_2^+ + e^- \\
H_2^+ + H_2 & \rightarrow H_3^+ + H \\
H_3^+ + CO & \rightarrow HCO^+ + H_2 \\
H_3^+ + X & \rightarrow HX^+ + H_2
\end{align*}
\]
Particle density of standard atmosphere

\[ 3 \times 10^{19} \text{ /cm}^3 \]

Collision interval

\[ \sim 10^{-9} \text{ sec} \]

Molecular Clouds

\[ 10 \text{ /cm}^3 \]

Collision interval

\[ \sim 100 \text{ years} \]

---

**Fig. 4.1.** The physical regimes of the interstellar medium, as currently observed.

From B. E. Turner
$\text{H}_3^+$

- $\text{H}_3^+$ in the laboratories
- $\text{H}_3^+$ in Jupiter
- $\text{H}_3^+$ in Dark clouds
- $\text{H}_3^+$ in Diffuse clouds
- Dissociative recombination of $\text{H}_3^+$ with electrons
Discovery of $\text{H}_3^+$ spectra

Figure 2. The spectral pattern for the $\nu_2$ band of $\text{H}_3^+$ calculated by Watson for the rotational temperature of 200 K. Observed transitions are marked with asterisks (Oka 1980).

Figure 3. The intense and pure $\text{H}_3^+$ emission spectrum recorded on the southern hemisphere of Jupiter at 60° latitude and mean longitude 40° (Maillard et al. 1990).

H$_3^+$ in Jupiter
Detection of Interstellar H$_3^+$

**SN1987A**  Miller, Tennyson, Lepp, and Dalgarno (1992)

Dark cloud  Geballe and Oka (1996)

Diffuse cloud  Geballe, McCall, Hinkle, and Oka (1999)
Formation and destruction of $H_3^+$

$$H_2 \rightarrow H_2^+ : \zeta \sim 10^{-17} \text{s}^{-1}$$

$$H_2^+ + H_2 \rightarrow H_3^+ + H : k_1$$

In dark cloud

$$H_3^+ + CO \rightarrow HCO^+ + H_2 : k_2$$

$$[H_3^+] \sim \zeta [H_2] / k_2 [CO]$$

In diffuse cloud

$$H_3^+ + e^- \rightarrow 3H, H_2 + H : k_d$$

$$[H_3^+] \sim \zeta [H_2] / k_d [e^-]$$
In dark clouds

\[ [\text{H}_3^+] \sim \zeta [\text{H}_2]/k_2 [\text{CO}] \]
\[ \zeta = 3 \times 10^{-17} \text{ s}^{-1} \]
\[ k_2 = 1.8 \times 10^{-9} \text{ cm}^3\text{s}^{-1} \]
\[ [\text{CO}]/[\text{H}_2] = 1.5 \times 10^{-4} \]
\[ [\text{H}_3^+] = 1.1 \times 10^{-4} \text{ cm}^{-3} \]

Observed Column densities

\[ [\text{H}_3^+]L = 6 \times 10^{14} \text{ cm}^{-2} \quad \text{W33} \]
\[ = 4 \times 10^{14} \text{ cm}^{-2} \quad \text{GL2136} \Rightarrow L = 1 \sim 2 \text{ pc} \]
In diffuse clouds

\[ [\text{H}_3^+] \sim \zeta \frac{[\text{H}_2]}{k_d \text{[e-]}} \]

\( \zeta = 3 \times 10^{-17} \text{ s}^{-1} \)

\( k_d = 1.8 \times 10^{-7} \text{ cm}^3\text{s}^{-1} \) \( (4.6 \times 10^{-7}) \)

\( \frac{[\text{e-}]}{[\text{H}_2]} = 5.6 \times 10^{-4} \)

\( [\text{H}_3^+] = 1.1 \times 10^{-7} \text{ cm}^{-3} \)

Observed Column density

\( [\text{H}_3^+]L = 3.8 \times 10^{14} \text{ cm}^2 \) Cyg OB2 No.12

\( \Rightarrow L = 400 \sim 1200 \text{ pc} \)
High-resolution Spectroscopy of Negative ions

- OH\(^-\) (OD\(^-\))
  - IR, FIR
- SH\(^-\) (SD\(^-\))
  - IR, sub-mm
- FHF\(^-\), ClHCl\(^-\), NH\(_2\)\(^-\), NCO\(^-\), NCS\(^-\), N\(_3\)\(^-\)
  - IR
Mystery of “B1377”

  Detected a series of emission lines toward IRC+10216. Linear molecule of the rotational constant of 1376.86868 MHz.

- Aoki (2000)
  “Carrier of B1377 is very likely to be C₆H⁻.”

  Succeeded in the laboratory detection of B1377, and in astronomical detection in TMC-1.

  \[ C₅N⁻ \] (Cernicharo et al, 2008)
Waterloo sub-mm system

- The frequency range of 270-890 GHz is covered with four BWOs (Backward-wave oscillator) with ~1 mW power.
- The absorption cell is designed to detect positive ions.
- Mostly operated in extended negative glow discharge mode with longitudinal magnetic field of ~250 Gauss.
Double modulation sub-mm system at Waterloo
Submillimeter-wave system in Ibaraki

Now moved to Waterloo
Three types of discharges are tried for detection of anions:

- Glow discharge
- Hollow anode discharge
- Extended negative glow discharge
CN⁻ in “hollow anode” discharge
$\text{C}_4\text{H}^-$ in extended negative glow discharge

![Graph showing frequency vs. C$_4$H$^-$]
Sub-mm observations of C$_3$N$^-$

- Production:
  - $\text{C}_2\text{N}_2 \leq 1 \text{ mTorr} + \text{C}_2\text{H}_2 \sim 2 \text{ mTorr} + \text{Ar} 12 \text{ mTorr}$
  - in either “hollow anode discharge” or extended negative glow discharge of 4~10 mA, cooled to 210 K.
  - Freq. range $\sim 504 \text{ GHz}$

Thaddeus et al, HC$_3$N (20 %) + Ar (80 %) $\sim 15 \text{ mTorr}$
dc discharge current of 20 mA at 200 K.
Extended Negative Glow

\[ C_3 N^- \]

\[ J=39 \rightarrow 38 \]

- (a) 250 Gauss
- (b) 0 Gauss

Frequency/GHz

378.260 378.262 378.264 378.266 378.268
Hollow-anode discharge

\[ \text{C}_3\text{N}^- \]

\[ J=42 \rightarrow 41 \]
Frequency shift /kHz

Gottlieb et al

CN\(^-\) J=4 - 3
Density of negative charges is high in negative glow and anode glow.
Why sub-mm now?

- Ground- and satellite-based astronomical and/or atmospheric observation platforms.
  Higher spatial resolution with shorter wavelength.
  Better sensitivity.
- Easy to use laboratory system.
  multipliers.
  BWOs.
Atmospheric Opacity in the submillimeter-wave region

Atmospheric Transmission versus Frequency for 0.5, 1.0 and 5.0 mm pwv

Transmission

Frequency (GHz)

200 300 400 500 600 700 800 900
ALMAは、日本・北アメリカ・ヨーロッパの3国が協力して、チリ・アンデス山中の標高5000mの高原に建設することを計画している。アタカマ大型ミリ波サブミリ波干涉計（Atacama Large Millimeter/submillimeter Array）の略称です。直径12mの高精度アンテナ64台と「ACAシステム」と呼ばれる超高精度アンテナ16台からなる、全部で80台のアンテナを干涉計方式で組み合わせ、ひとつの巨大な電波望遠鏡を合成します。電波の中で最も波長が短く、最高の周波数帯である「ミリ波・サブミリ波」を使って、ビッグバン後数年ないし宇宙初期における銀河の誕生、今も続くさまざまな惑星系の誕生、そして生命につながる物質の進化を解き明かします。

宇宙に一番近い場所

ALMAの望遠場所は、チリ共和国北部にあるアタカマ砂漠に近い、アンデス山中の標高約5000mの高原です。世界の気候帯を詳しく調査・比較した結果、乾燥した気候、高い標高、平坦な地形、そして安全で容易なアクセスという条件を満たす、この土地が選ばれました。
Getting the WHOLE picture

- An object can look radically different depending on the type of light collected from it:

Constitution Orion

left: visual wavelengths
right: far-infrared image

From NASA web page
- **Visible**: dark nebula, heavily obscured by interstellar dust
- **Near-IR**: dust is transparent, embedded proto-stars can be observed
- **Mid- and far-IR**: glow from cold dust is directly observable

From NASA web page
SOFIA SOFIA — The Next Generation

Airborne Observatory

- 2.5 meter telescope mounted in a 747-SP
- "First Light" expected winter 2004-2005
- 150 flights per year when fully operational
- First observatory designed to support E/PO

NASA/DLR
A RIGOROUS ATTEMPT TO VERIFY INTERSTELLAR GLYCINE

L. E. Snyder, F. J. Lovas, J. M. Hollis, D. N. Friedel, P. R. Jewell, A. Remijan, V. V. Ilyushin, E. A. Alekseev, and S. F. Dyubko

Received 2004 May 25; accepted 2004 October 7

ABSTRACT

In 2003, Kuan and coworkers reported the detection of interstellar glycine (NH$_2$CH$_2$COOH) based on observations of 27 lines in 19 different spectral bands in one or more of the sources Sgr B2(N-LMH), Orion KL, and W51 e1/e2. They supported their detection report with rotational temperature diagrams for all three sources. In this paper we present essential criteria that can be used in a straightforward analysis technique to confirm the identity of an interstellar asymmetric rotor such as glycine. We use new laboratory measurements of glycine as a basis for applying this analysis technique, both to our previously unpublished 12 m telescope data and to the previously published Swedish-ESO Submillimetre Telescope (SEST) data of Nummelin and colleagues. We conclude that key lines necessary for an interstellar glycine identification have not yet been found. We identify some common molecular candidates that should be examined further as more likely carriers of several of the lines reported as glycine. Finally, we illustrate that a rotational temperature diagram used without the support of correct spectroscopic assignments is not a reliable tool for the identification of interstellar molecules.

Subject headings: ISM: abundances — ISM: clouds — ISM: individual (Sagittarius B2(N-LMH), Orion Kleinmann-Low, W51 e1/e2) — ISM: molecules — radio lines: ISM
Fig. 1. Orion KL spectra from 113323 to 113355 MHz (centered at 113339 MHz) observed with the hybrid spectrometer on the NRAO 12 m telescope. The spectral positions of the negative results for the nearly fourfold degenerate $J = 19-18$ glycine lines are marked by the four vertical lines centered at 113336 MHz. U113326 is on the left, and CH$_3$OD is on the right. The ordinate is in units of mK on the $T^*_R$ scale. The abscissa is rest frequency calculated with respect to $V_{LSR} = 9$ km s$^{-1}$ (for the Orion compact ridge), except for the CH$_3$OD rest frequency, which is with respect to $V_{LSR} = 5.6$ km s$^{-1}$ (representative of the Orion hot core). The rms noise level for the spectral region between U113326 and CH$_3$OD is 3.7 mK.

Glycine in Comet Tail

Glycine has been identified in a dust sample collected by the Stardust Spacecraft from the tail of Comet Wild 2.

http://www.newscientist.com/article/dn17628-found-first-amino-acid-on-a-comet.html

http://scientificinquiry.suite101.com/article.cfm/comet_tail_with_glycine_amino_acid_amazes_all
In future

- Sub-mm astronomical observations with very high spatial resolution.
  
  ALMA

- In the process of star and planet formation, what kind of molecules can survive and be entrained into the planetary system? Life related molecules?

- Lab. data are essential in such identifications.
“To understand hydrogen is to understand all of physics, chemistry, and biology.”

Victor Weisskopf
Hydrogen, light colorless odorless gas, which given enough time turns into human being

氫，輕質量 無色 無味的氣體，如果給它足夠的時間，它會逐漸演變成今天的人類
Discovery of multiply deuterated species in space

\[ [\text{D}]/[\text{H}] \sim 1.5 \times 10^{-5} \]

- \( \text{D}_2\text{CO} : \text{Turner}(1990) \)  \( \text{Ori-KL} \)  \( 0.3\% \)
- \( \text{Ceccarelli et al (1998)} \)  \( \text{IRAS 16293-2422} \)  \( 5\% \)
- \( \text{Loinard et al (2001)} \)  \( 16293\text{E} \)  \( 26\% \)

\( \text{NHD}_2 \) (2000), \( \text{ND}_3 \) (2002)

\( \text{CHD}_2\text{OH} \) (2002), \( \text{CD}_3\text{OH} \) (2004)

\( \text{D}_2\text{S} \) (2003)
Formation of Deuterated Species

- H/D exchange reactions of $\text{H}_3^+$ with HD are exothermic.
  
  \[
  \text{H}_3^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ + \text{H}_2 + 230 \text{ K}
  \]
  
  \[
  \text{H}_2\text{D}^+ + \text{HD} \rightarrow \text{D}_2\text{H}^+ + \text{H}_2 + 180 \text{ K}
  \]
  
  \[
  \text{D}_2\text{H}^+ + \text{HD} \rightarrow \text{D}_3^+ + \text{H}_2 + 230 \text{ K}
  \]

- Under liquid-$\text{N}_2$ cooled environment, such reactions become dominant.
Spectroscopy of H$_2$D$^+$ and D$_2$H$^+$

IR

- Shy, Farley, Wing (1981): Ion beam
- Amano & Watson (1984), Amano (1985): $\nu_1$ band (H$_2$D$^+$)
- Lubic & Amano (1984): $\nu_1$ band (D$_2$H$^+$)
- Foster et al. (1986): $\nu_2$ /$\nu_3$ bands (H$_2$D$^+$)
- Foster, McKellar, Watson. (1986): $\nu_2$ /$\nu_3$ bands (D$_2$H$^+$)
- Polyansky & McKellar (1990): All available data were fitted together to improve molecular constants. (D$_2$H$^+$)
- Fárník et al. (2002):
  - Molecular beam experiments of vibrational overtone and combination bands ($2\nu_2$, $2\nu_3$, $\nu_2+\nu_3$).
mm-, sub-mm, FIR

- **Bogey et al. (1984):** $1_{10}-1_{11}$ $\text{H}_2\text{D}^+$ (372.4 GHz)
- **Warner et al. (1984):**
- **Saito, Kawaguchi, Hirota (1985):** $2_{20}-2_{21}$ $\text{H}_2\text{D}^+$ (156.0 GHz)
- **Jennings, Demuynck, Banek, Evenson (unpublished):**
  - $1_{01}-0_{00}$ $\text{H}_2\text{D}^+$ (1370.1 GHz)
  - $1_{11}-0_{00}$ $\text{D}_2\text{H}^+$ (1476.6 GHz)
  - $2_{20}-2_{11}$ $\text{D}_2\text{H}^+$ (1370.1 GHz)
- **Hirao & Amano (2003):** $1_{10}-1_{01}$ $\text{D}_2\text{H}^+$ (691.7 GHz)
- **Amano & Hirao (2005):** $3_{21}-3_{22}$ $\text{H}_2\text{D}^+$ (646.4 GHz)
Energy Level Diagram of $H_2D^+$

ortho-$H_2D^+$

$K_a$ = 1

para-$H_2D^+$

$K_a$ = 0

648.3 GHz

156.0 GHz

372.4 GHz

1370 GHz
Energy Level Diagram of $D_2H^+$

- $\mu \sim 0.48$D
- $1476$GHz
- $1370$GHz
- $2_{20}$, $2_{11}$, $2_{02}$, $2_{12}$, $1_{11}$, $1_{10}$, $1_{01}$, $3_{13}$, $3_{03}$, $2_{21}$
- $K_a = 2, 1, 0, 0$
Experimental Details

- Extended negative glow discharge source.
  (Magnetic field: 200G).
- Double modulation.
- $\text{H}_2/\text{D}_2/\text{Ar} = 3/2/17\ \text{mTorr},\ I = 8\ \text{mA},\ T \sim 77\ \text{K}$

Search around 691.705 (90) GHz.
(Polyansky and McKellar)
$D_2H^+$ has been detected in space!!!

C. Vastel, T. G. Phillips, and H. Yoshida


16293E pre-stellar core

$[D_2H^+] \sim [H_2D^+]$
Slight difference in observed vLSR between H2D+ and D2H+. They suggested that H2D+ rest frequency might not be accurate enough. Bogey et al. [372421.34(20) MHz] and Warner et al. [372421.380(100) MHz] prompted us to remeasure H2D+ line.

Table 1. Results of Gaussian fits to the H2D+ and D2H+ spectra.

<table>
<thead>
<tr>
<th>Line</th>
<th>ν (GHz)</th>
<th>T_a (K)</th>
<th>Δv (km s⁻¹)</th>
<th>V_LSR (km s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2D⁺ (1₁₀₋₁₁₁)</td>
<td>372.42134(20)ᵃ</td>
<td>1.31</td>
<td>0.36 ± 0.04</td>
<td>3.55 ± 0.02</td>
</tr>
<tr>
<td>D2H⁺ (1₁₀₋₁₀₁)</td>
<td>691.660440(19)ᵇ</td>
<td>0.34</td>
<td>0.29 ± 0.07</td>
<td>3.76 ± 0.03</td>
</tr>
</tbody>
</table>

ᵃMeasured frequency by Bogey et al. (1984).
bMeasured frequency by Hirao and Amano (2003).

⇒ Prompted us to remeasure H2D⁺ line.
Fig. 1.—Observation at 372.672 GHz. The spectra have been averaged in the four positions 20″ off the dust peak.

Fig. 1. (Top) The $\text{H}_2\text{D}^+ (1_{10}-1_{11})$ line at the dust peak of L1544 (RA(1950) = 05:01:13.1, Dec(1950) = 25:06:35.0). The black curve is the Gaussian fit (see Table 1). (Bottom) The $\text{H}_2\text{D}^+ (1_{10}-1_{11})$ spectrum averaged in the four positions 20″ off the dust peak.