Bridging the molecular divide between molecular clouds and biology, a spectroscopist's view of detectability

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What we know and would like to know

- **More than 130 uniquely identified molecules**

  – **Most identified from rotational spectra**

  – **More complex molecules most abundant in warm (or hot) environments**
    - **Star (and planet) formation regions**

  – **Grains play a significant role**
    - **Chemical production of complex molecules**
    - **Freeze out of gas phase when cold enough**
    - **Evaporate from grain mantels when warm enough**

  – **Complex is 6+ atoms**

- **Complex molecules in biology are thousands of atoms**

  – **Three orders of magnitude in complexity divide biology and astrophysics**

- **How complex can interstellar molecules be?**

  – **What role if any did ISM chemistry play in biology?**

- **What might we be able to detect?**

Molecular Physics

- **Einstein A Coefficient**

$$A_{m \leftarrow n} = \frac{64\pi^4 \nu_{mn}^3}{3hc^3} S_{mn} \mu^2$$

- **Partition Functions**

$$Q = Q_{el} Q_{vib} Q_{rot} Q_{spin}$$

$$Q_{rot} \cong \left(\frac{5.34 \times 10^6}{\sigma} \right) \left(\frac{T^3}{ABC} \right)^{1/2}$$

$$Q_{vib} = \left(\sum_{v_1} e^{-v_1 h\omega_1 / kT} \right) \left(\sum_{v_2} e^{-v_2 h\omega_2 / kT} \right) \left(\sum_{v_3} e^{-v_3 h\omega_3 / kT} \right) \dots$$

Implications for Detection

- ◆ A coefficients favorable for detection

  - Higher frequency transitions v^3 (Bad for big molecules)

  - Big dipole moments μ^2 (possible even probable)

- ◆ Partition function favorable for detection

  - Low temperature $T^{3/2}$ (possible)

  - Large rotational constants (Bad for big molecules)

  - High lying vibration states (Bad for big molecules)

- ◆ Big molecules loose on 3 of 5

  - Temperature requires some further exploration

What We Know

		dipole	MP	BP	A	B	C
CH3CN	methyl cyanide	3.9	-45.7C	81.6C	158099	9199	9199
CH3NC	methyl isocyanide	3.9	-45C	~80C	157151	10053	10053
CH3CH2CN	ethyl cyanide	4	-87C	97C	27663	4714	4235
CH3OH	methy alcohol	1.7	-93.9C	65C	127484	24679	23740
CH3CH2OH	ethyl alcohol	1.5	-117.3C	78.5C	34891	9350	8135
CH3CHO	Acetaldehyde	2.7	-121C	20.8C	56609	10162	9100
CH2CHCHO	Propenal	3.1	-86.9C	52.5C	47353	4659	4243
CH3CH2CHO	Propanal	2.5	-81C	48.8C	16669	5893	4599
CH2(OH)CHO	Glycolaldehyde	2.4	**97C**	**hot**	18446	6525	4969
CH3OCHO	Methyl formate	1.8	-100C	32C	19986	6915	5304
HCOOCH3	Acetic Acid	1.7	16.6C	117.9C	11324	9494	5326
(CH3)2CO	acetone	2.9	-95.4C	56.2C	10165	8515	4910
(CH3)2O	dimethyl either	1.3	-138.5C	-25C	38788	10057	8887
CH3CH2OCH3	ethyl methyl either	1.2	~-80C	10C	27992	4159	3891
(CH2OH)2	ethylene glycol	2.3	-12C	196.3C	15361	5588	4614
CH3NH2	methyl amine	1.3	-93.5C	-6.3C	105976	22608	21723
CH3CONH2	acetamid	??	**82.3C**	**221.2C**	13291	9326	5175
CH3SH	methyl mercaptan	1.5	-123C	6.2C	102691	12947	12386

MP=Melting Point

BP=Boiling Point (1atm)

Acetamid and Glycolaldehyde? are high others are similar

Temperature Effects

◆ Lower temperature results in smaller partition function

- Absorption probably easier for detection

- But, low frequency is normally required

◆ Vapor pressure is important

- Water is known to freeze below 100K

- Few saturated molecules in cold regions suggestive of the same physics

- More elaborate physics is required to get sticky molecules off grains

  - Gas phase formation
  - Mechanical removal (e.g. shock)

- Confirming detection of low vapor pressure molecule requires great care!

The Unhappy State of Affairs

◆ **Big molecules have big partition functions**

  – Often have multiple conformers (factors of 2-4 in Q)

  – Often have multiple low lying vibrational states (factors of 2 in Q)

  – Always have small rotational constants (factors of 5-1000 in Q)

◆ **Big molecules also generally have higher melting points**

  – Harder to get and keep off grains

  – There are some interesting exceptions

    • Big dipoles often mean higher melting points!

How to Manipulate Physics

◆ Detection of Big molecules in absorption

   – Allows for partition function to be largely collapsed

       • Does not work if freeze out onto grains is effective

       • Does not solve low frequency weak line strength

◆ Look at transitions sampling low energy levels at high Frequency

   – Ro-Vibrational, Ro-Torsional, Ro-electronic

   – Emission possible if

       • Q is small enough

       • Dipole is big enough

   – Absorption is better for detection

       • Does not work if freeze out onto grains is effective

       • Dipole moment is no longer the rotational dipole moment

Dipoles in Vibrational Transitions

- The dipole in a Ro-vibrational transition is a dipole derivative

$$\mu = \mu_e + \left(\frac{\partial \mu}{\partial \vec{R}}\right)$$

  - **Typically <10% of the rotational dipole**

- The dipole in a Ro-Torsional transition is the rotational dipole

$$\mu = \mu_{\parallel} + \sum_n \mu_{\perp} \cos^n \gamma + \sum_n - \mu_{\perp} \sin^n \gamma$$

$$\langle \mu \rangle_{RT} = \mu_{\perp} \langle \psi_l | \cos^n \gamma | \psi_m \rangle - \mu_{\perp} \langle \psi_l | \sin^n \gamma | \psi_m \rangle$$

  - **Overlap integrals can be nearly unity (Inversion of NH_3)**

  - **Perpendicular part of dipole can be major moment (~1.4 Debye in CH_2DOH)**

Strong dipoles

◆ Motion (larger the amplitude the better) of the rotational dipole

   – Inversion (change of sign)

   – Quasi linearity

   – Internal rotation (large dipole component off of internal rotation axis)

   – Puckering of ring (Quasi Planarity)

◆ Electronic Transitions

   – Generally a significant fraction (~½) rotational dipole

What to look for

◆ **Molecules with large amplitude motion of highly polar group**

    – Internal Rotation

    – Inversion

    – Conformational transitions

◆ **Molecules with large dipole moments**

◆ **Molecules with low melting and boiling points**

◆ **Preferably in absorption to reduce partition functions**

Truth in Advertising

◆ Nearly nothing is known about such species!

  – Detailed physics is incomplete for asymmetric-top asymmetric-frame internal motions

  – Almost no laboratory data exists
    • Some low resolution THz
    • Some Raman data (also low resolution)

◆ Plenty of confusing lines exist

  – [13]C substituted large molecule are almost all unknown

  – D substitute (especially in CH_3 rotors) are almost all unknown

  – Even Methanol at higher excitation is insufficient for ALMA and Herschel

How to confirm detection

◆ Measure and Cataloged all the known species

   – Must include isotopomers (probably doubly substituted)

   – Must include all the vibrational states observable

      • Vibrational energy required can be calculated from ground state signal-to-noise and excitation temperature

   – Transitions frequencies should be 10 time more accurate than observation resolution

◆ Potential detection molecules must be known

   – Transitions should be 10 times more accurate than observation

   – Extrapolated transitions should never be used

   – Astronomical sources that have well understood abundances should be used

      • At a minimum it gives a confusion limit

◆ A few lines are not enough

   – Whole series of clean detection are required

Grim Prospects

- **Herschel and ALMA will detect thousands of U-lines**
  - Most will be transitions of well known molecules

- **Laboratory work and Quality catalogs will make or break the identification of exciting large molecules**

- **In US only NASA has a laboratory astrophysics program**
  - About 10 awards a year (typically $100K/year for 3 years) across all wavelengths
  - NASA is not funding any atomic/molecular catalogs

- **Majority of needed laboratory work is not interesting to chemical physics**
  - Funding is nearly impossible through normal channels (e.g. NSF chem)
  - Astronomical technology now exceeds previous laboratory spectroscopy ranges

- **A dedicated laboratory/catalog program is absolutely necessary**
  - White paper for US support is available

Take Home Picture
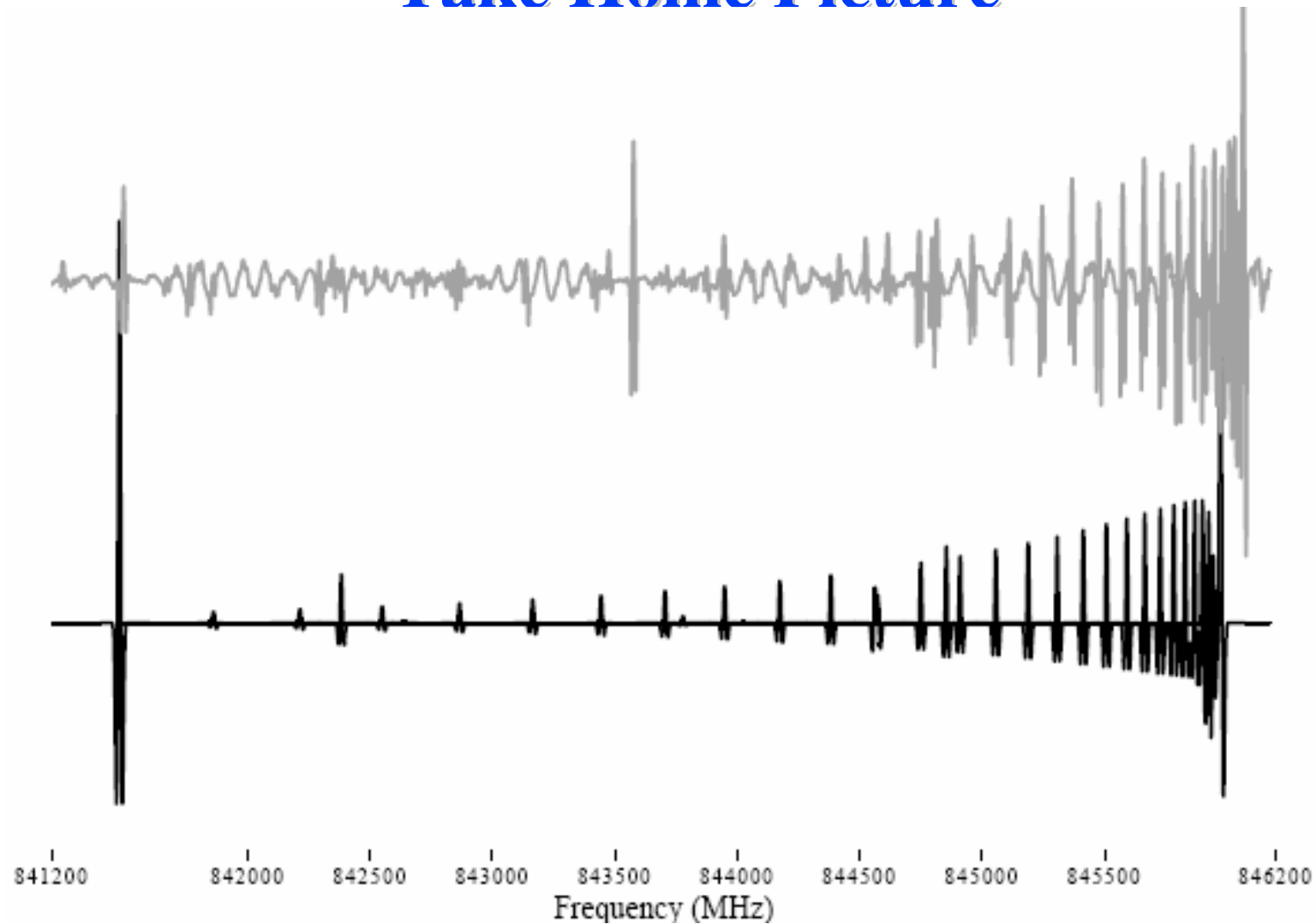
Ground state dimethyl either Q branch near 845 GHz Grey is lab spectra Black is JPL catalog.