Microwave Rotational Spectroscopy

CHE 6416

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How does Microwave relate to other spectroscopies

- Different types of motion
  - Translational
  - Vibrational
  - Rotational.

What is Microwave Spectroscopy?

- Microwave stimulates Rotational translations
- Measures the rotational states of molecules
- *Gas Phase*
- Must have a dipole.

Applications of MW

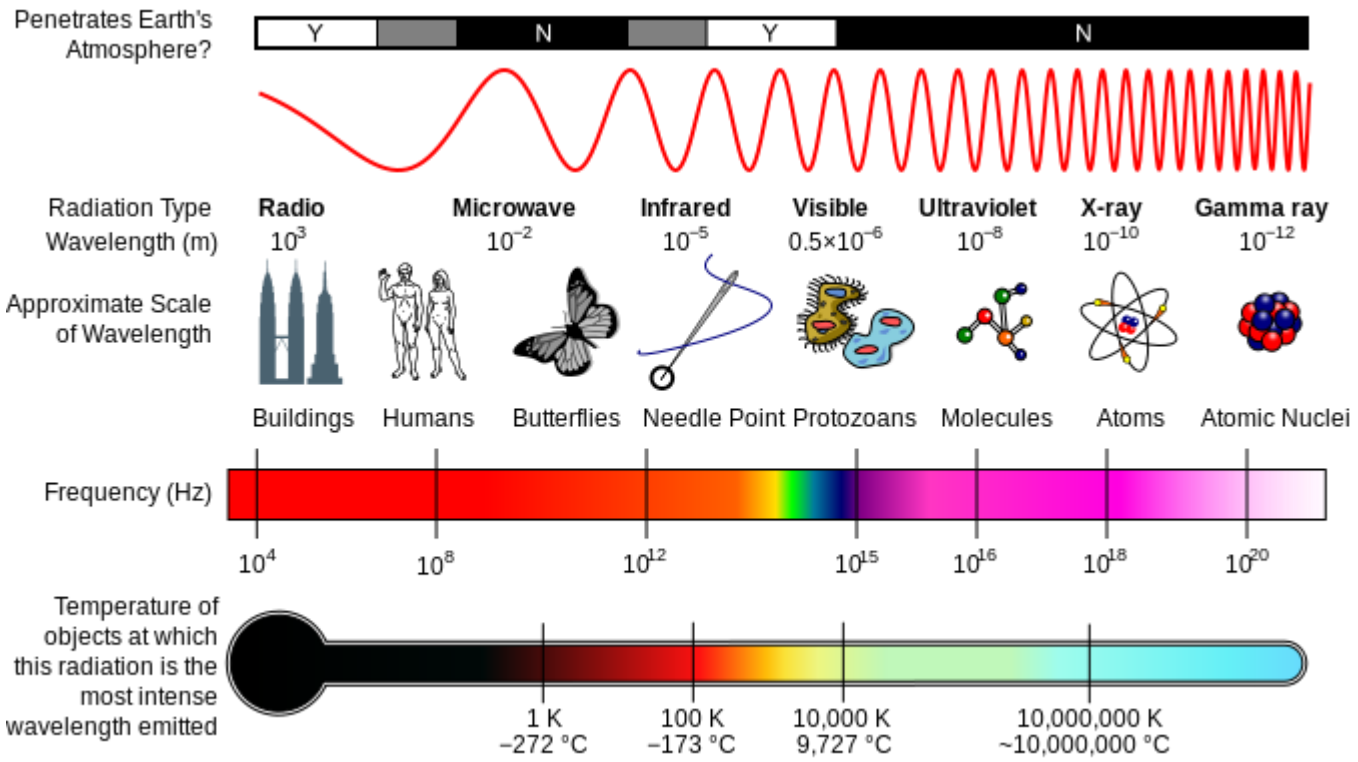
- Measurement of bond lengths
- Observation by radio telescopes for life precursors in interstellar clouds
- Precise observation of translating stereochemistries and confirmation verification

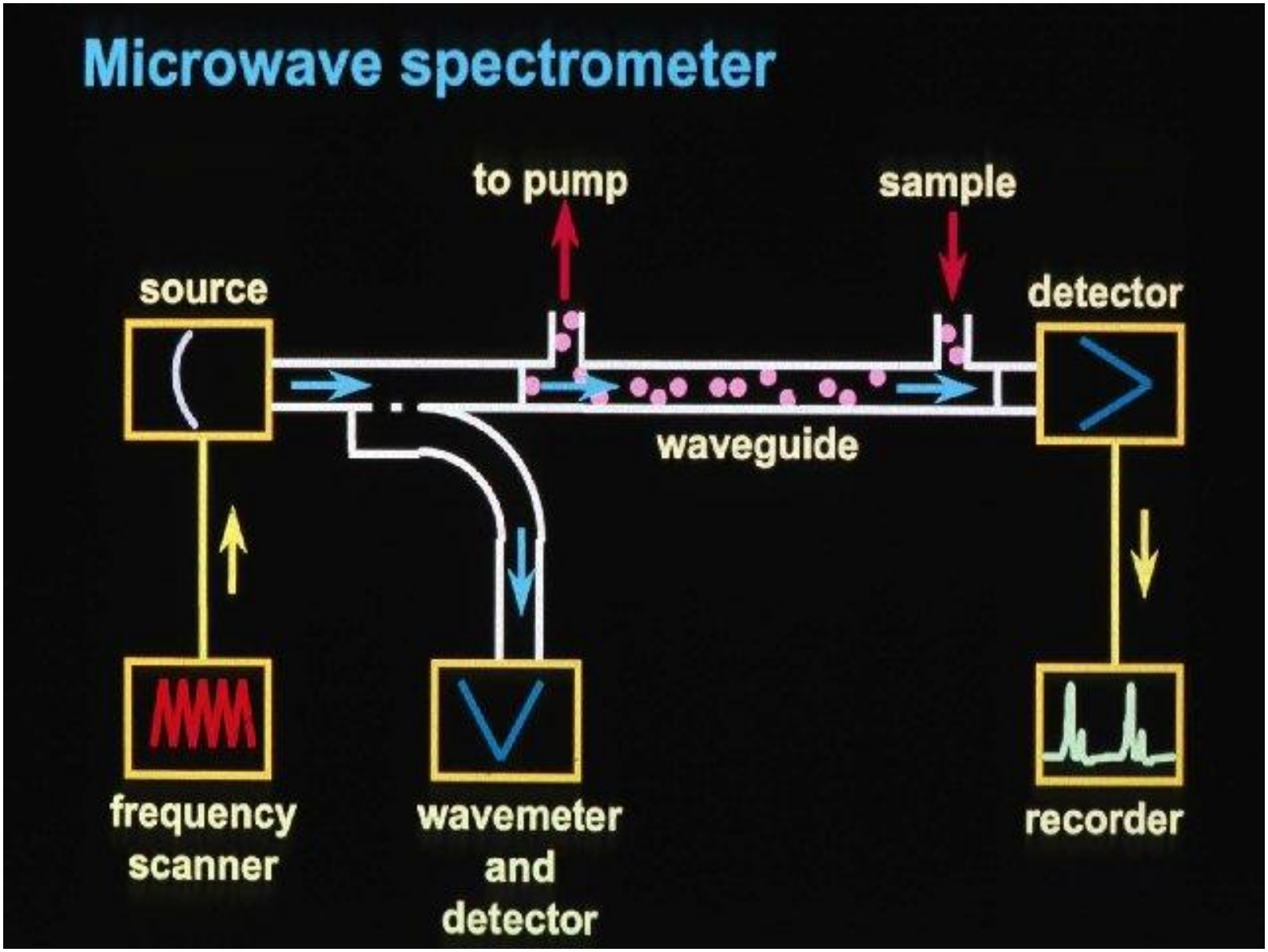
Microwave Spectroscopy

- RADAR was impetus for its invention
- 1948, Walter Gordy, first published review

Gordy, W., *Microwave Spectroscopy*, Reviews of Modern Physics, Volume 20, Number 4, October 1948,

Microwaves

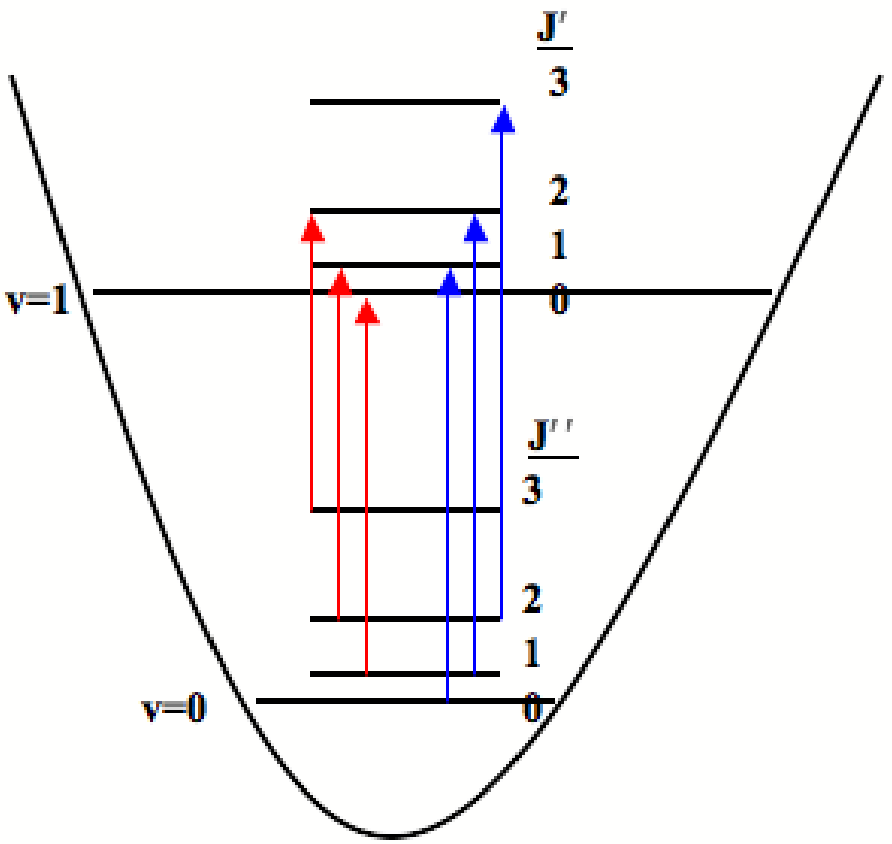

Penetrates Earth's Atmosphere?
Y
N
Y
N
Radiation Type
Wavelength (m)
Radio
10^{3}
Microwave
10^{-2}
Infrared
10^{-5}
Visible
0.5×10^{-6}
Ultraviolet
10^{-8}
X-ray
10^{-10}
Gamma ray
10^{-12}
Approximate Scale of Wavelength
Buildings
Humans
Butterflies
Needle Point
Protozoans
Molecules
Atoms
Atomic Nuclei
Frequency (Hz)
10^{4}
10^{8}
10^{12}
10^{15}
10^{16}
10^{18}
10^{20}
Temperature of objects at which this radiation is the most intense wavelength emitted
1 K
−272 °C
100 K
−173 °C
10,000 K
9,727 °C
10,000,000 K
~10,000,000 °C



http://www.chem.canterbury.ac.nz/research group/sarah_masters_group/rotational_spectroscopy.shtml

Rotational vs. Vibrational

- Where J = rotational
  - –V= vibrational
- Observed from lowest vibration state



$$E(J) = B\,J(J+1)$$

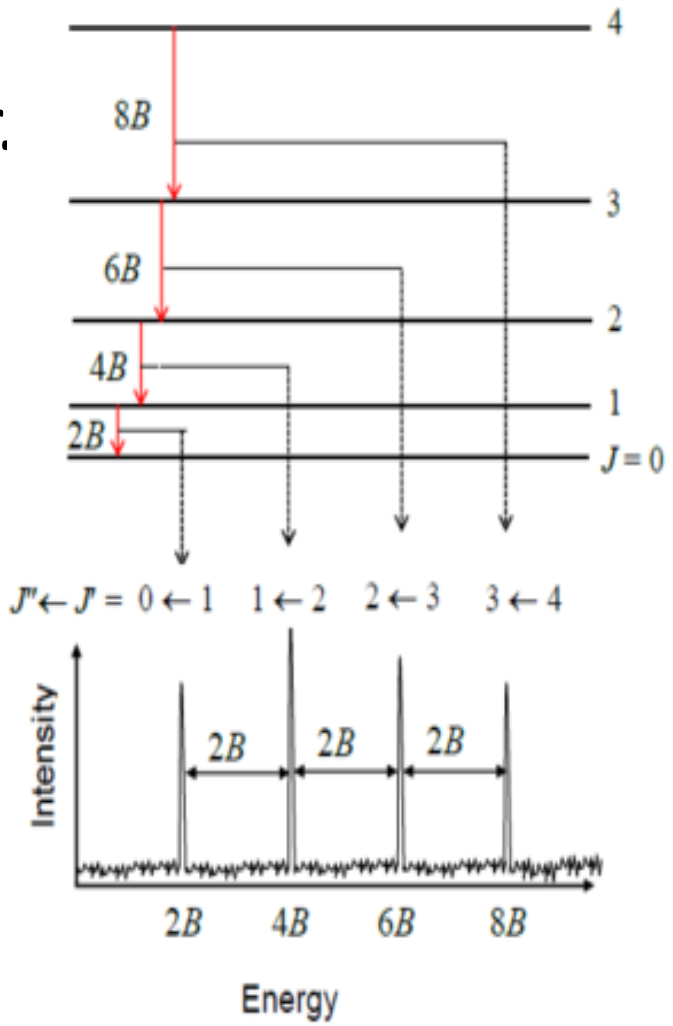
http://chemwiki.ucdavis.edu/Physical_Chemistry/Spectroscopy/Rotational_Spectroscopy/Rotational_Spectroscopy_of_Diatomic_Molecules

Motion of Rotation

- 3 Possible moments of inertia
  - I_a, I_b, I_c

Diatomic molecule

- Rotation E from Schrodinger.
- $I_a = I_b\ , I_c = 0$
- $B = \frac{h}{8Ic\pi^2}$
- $I = R^2\, u = \frac{(M_1 M_2)}{(M_1 + M_2)} R^2$
- Line spacing is 2B.



Theory of Microwave Spectroscopy

- Microwave wavelength photon
- Highest probability of transition
- Molecules with dipoles

How do we measure if it will translate?

- Probability of Transition=$\int \psi rot(F) \mu \hat{} \ \psi rot(I) \, d\tau$
  - Where: $\psi rot(F)$ is the complex conjugate of the final rotational state
  - $\psi rot(I)$ is the wave function of the initial rotational state
  - μ is the dipole moment operator with X, y, z coordinates.

  - The function is positive.
  - Only tells if is allowed.

But there are limits.

- Photons limited
  - Each photon has one unit of momentum

    $\Delta J \pm 1$

– Only one transition per

Is it available to translate?

- Boltzmann distribution

$$\frac{nJ}{n0} = e\left(-\frac{Erot(J)}{RT}\right) / \sum_{J=0}^{J=n} e\left(-\frac{Erot(J)}{RT}\right)$$

Where nJ=number of molecules excited

n0=number of molecules in ground state

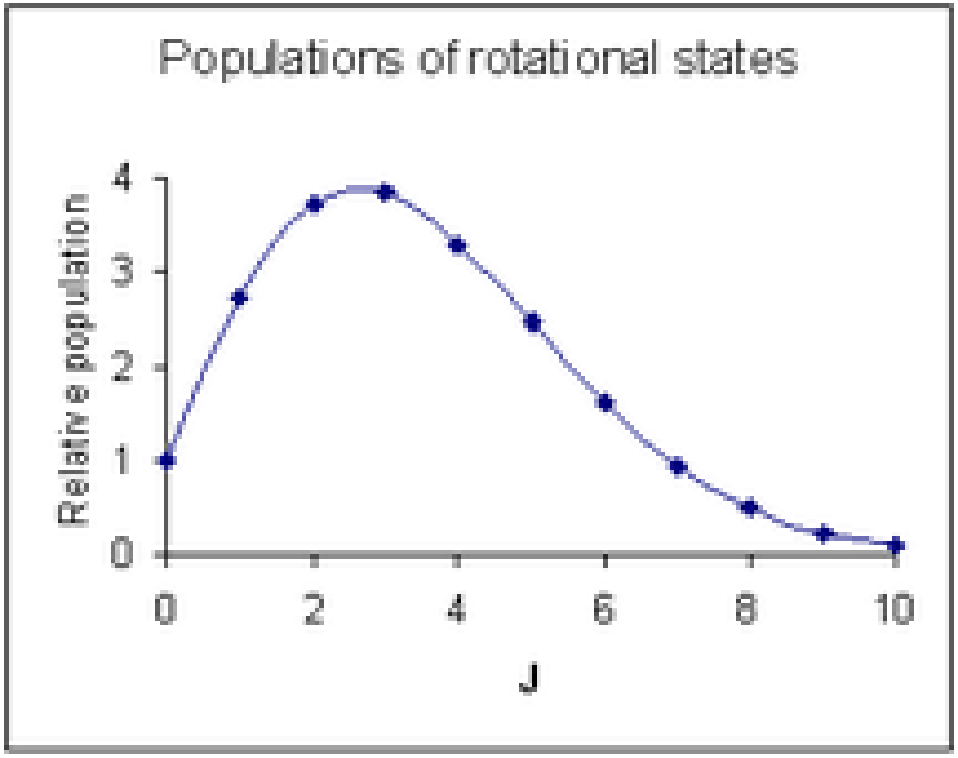
R=gas constant

T=temperature

ErotJ=molar energy of the rotational state

Plot of Probability

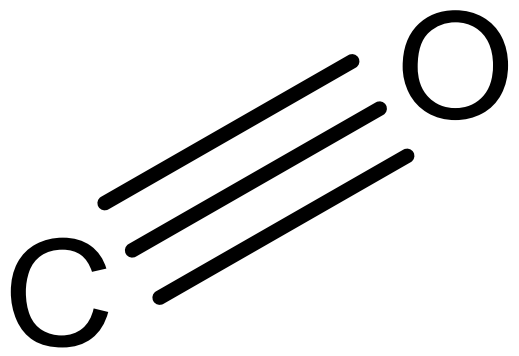
- Probability of Population
- Similar to spectra



http://http://en.wikipedia.org/wiki/Rotational_spectroscopy#Effect_of_rotation_on_vibrational_spectra

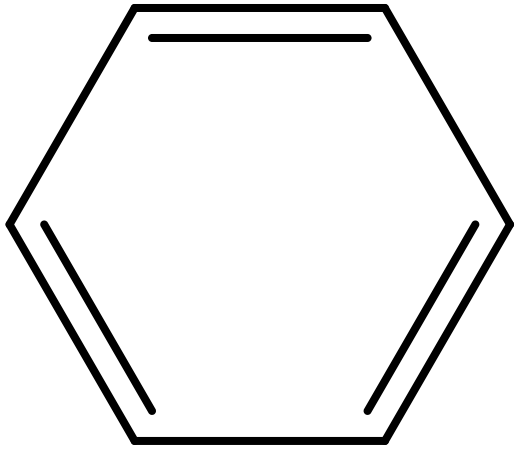
Types of Molecules that are MW-Active

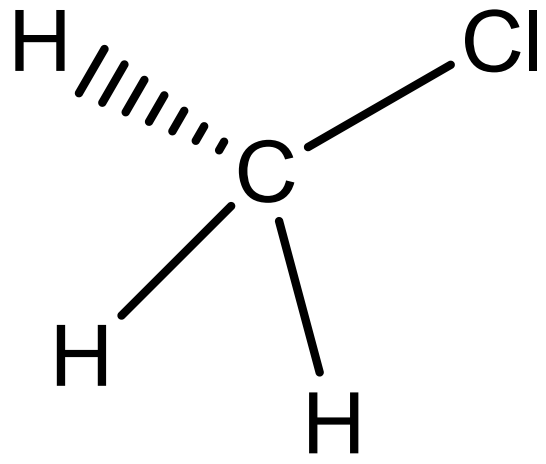
- Linear



Types of Molecules that are MW-Active

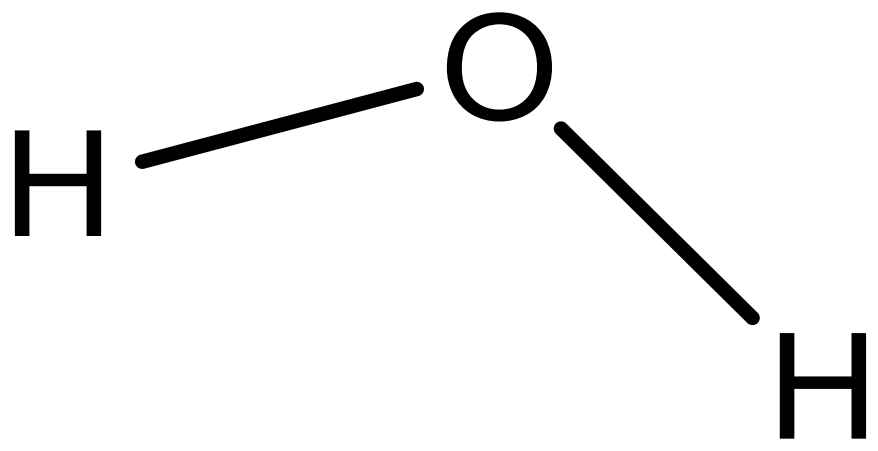
- Symmetric Tops





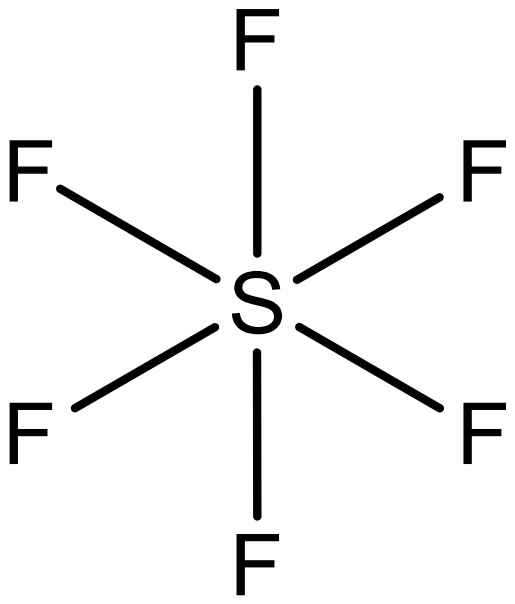
Types of Molecules that are MW-Active

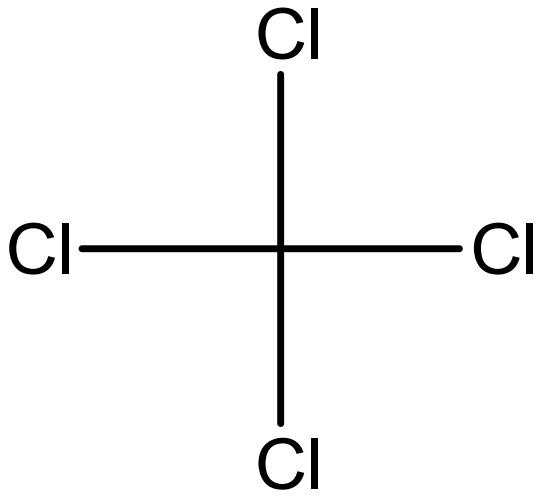
- Antisymmetric tops



Types of Molecules that are MW-Active

- Spherical tops-*Not active*

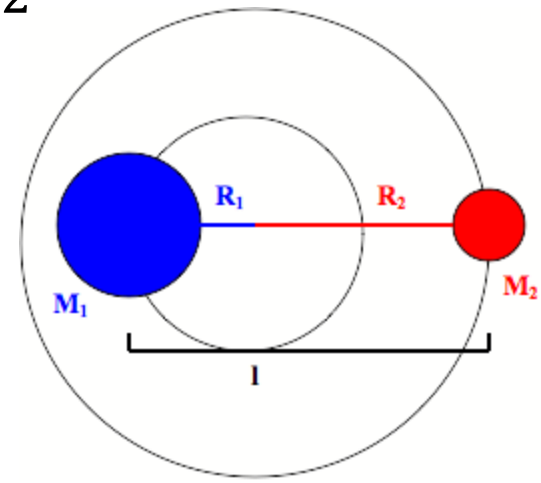




Linear Molecules.

- Linear molecules(Rigid rotors)
- Bond length directly calculated
- $I_a = I_b\ , I_c = 0$

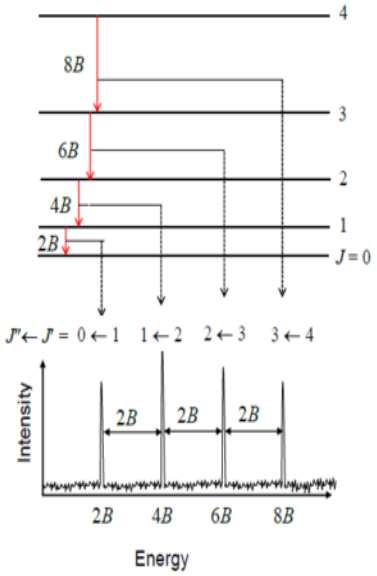
$$I = R^2\, u = \frac{(M_1 M_2)}{(M_1 + M_2)} R^2$$



http://chemwiki.ucdavis.edu/Physical_Chemistry/Spectroscopy/Rotational_Spectroscopy/Microwave_rotational_spectroscopy

Linear Molecules.

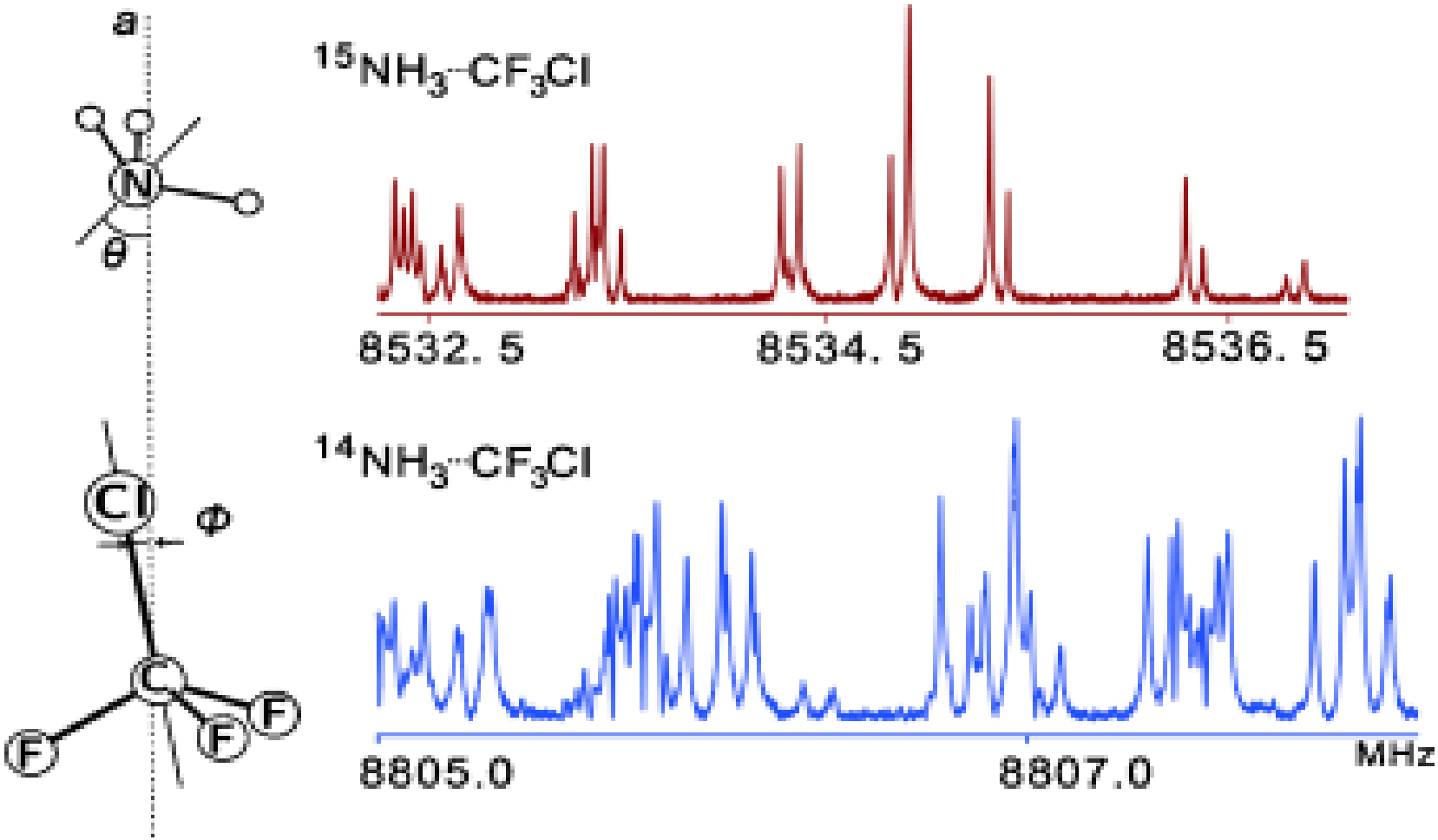
- Linear molecules(Rigid rotors)
- $\Delta J = J' - J'' = \pm 1$
- $v_{J' \leftrightarrow J''} = E(J') - E(J'') = 2B\left(J^{"} + 1\right)$
  - Where $J'' = Lower\ level$
    - $J' = Upper\ Level$



Symmetric Tops (Rotors)

- Two rotational axes same, one different
- Oblate
  - $I_a \neq I_b = I_c$
  - Oblate.
  - Benzene, XeF_4
- Prolate
  - $I_a = I_b \neq I_c$
  - Prolate.
  - CH_3Cl, NH_3

Symmetric Top Spectra



Fengm G., Evangelisti, L, Gaspartini, N., Caminati, W., *On the Cl···N Halogen Bond: A Rotational Study of CF_3Cl···NH_3,* Chemistry-A European Journal, Vol 18, #5 pg 1364-1368

Why more complicated?

- With more axis, more complicated
  - Symmetrical molecules gain 2 terms
  - K = vector about the symmetry axis
    - Must be between –J and +J
  - M = rotational momentum about a external field
    - Also between –J and +J
    - 0 if no external field

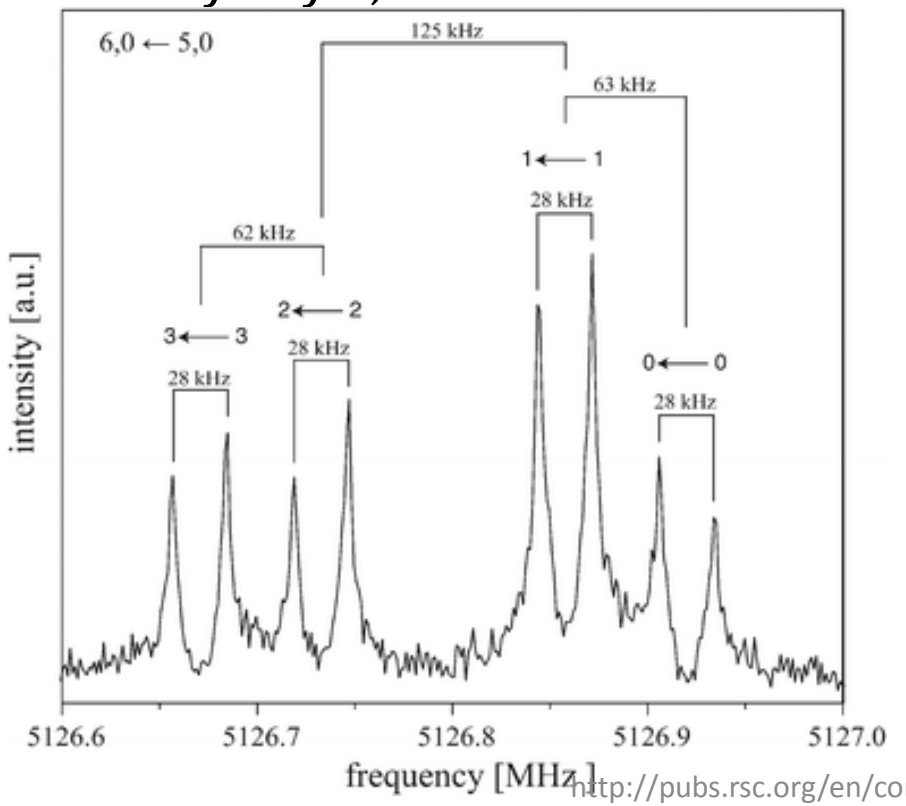
Why more complicated?

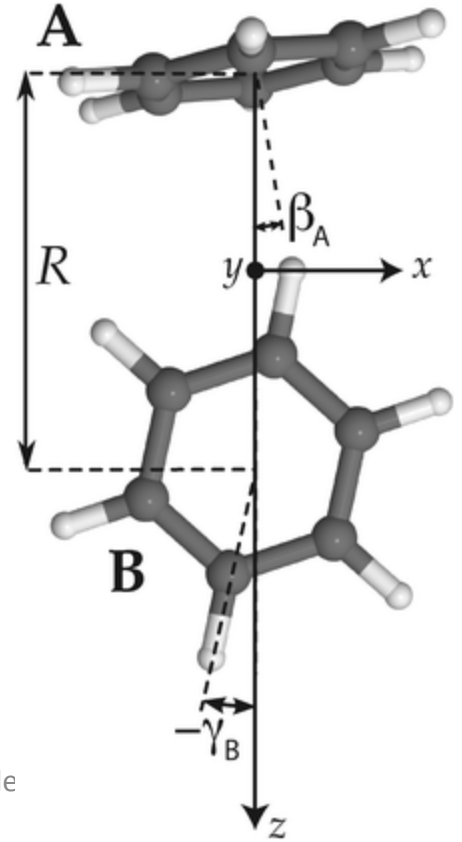
- With more axis, more complicated
  - $E(J,K) = BJ(J+1) + (A-B)K^2$
    - Where B= $\frac{h}{8\pi^2 c I_b}$
    - A= $\frac{h}{8\pi^2 c I_a}$, Prolate
    - A= $\frac{h}{8\pi^2 c I_c}$, Oblate

Why more complicated?

- Which leads to Lines at:

$$-\nu_{J'\leftrightarrow J'',K} = E(J',K) - E(J'',K) = 2B\left(J^{"}+1\right)$$





http://pubs.rsc.org/en/content/article2013/cp/c3cp51181b

Why more complicated?

- With more axis, more complicated
  - Stark Effect
  - Hyperfine splitting

Stark Effect

- Similar to Zeeman effect
- Lifts level degeneracy
- Due to external electric field
- 1rst Order-Linear
- 2^{nd} Order-Quadratic

Stark Effect

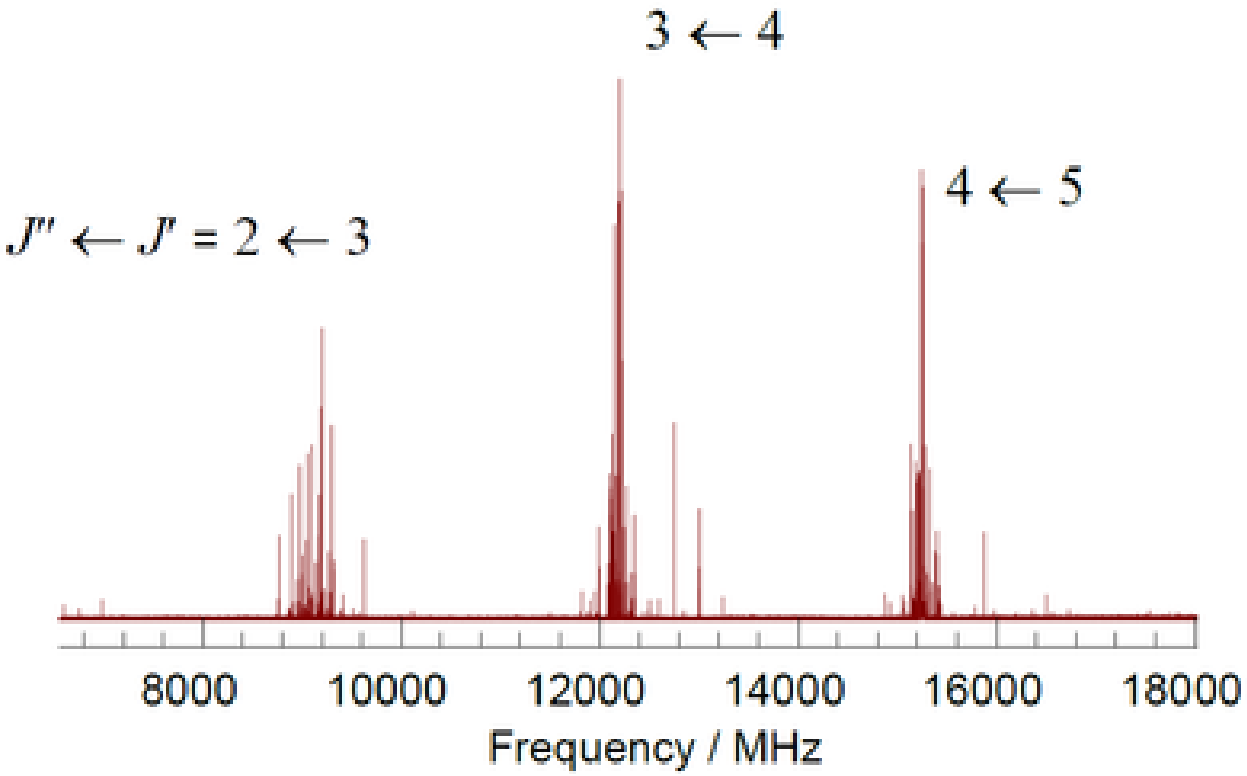
- $E_{Stark}(J, K, M) = -\frac{uEKM}{J(J+1)}$
- M = 0, no stark
- K, M $\neq 0$ splitting occurs
  - -M inc, + M dec

Hyperfine Splitting

- Coupling of Nuclear spin and molecular rotation.
  - If $J > l$, $2l+1$ levels
  - If $J < l$, $2J+1$ levels.

Hyperfine splitting

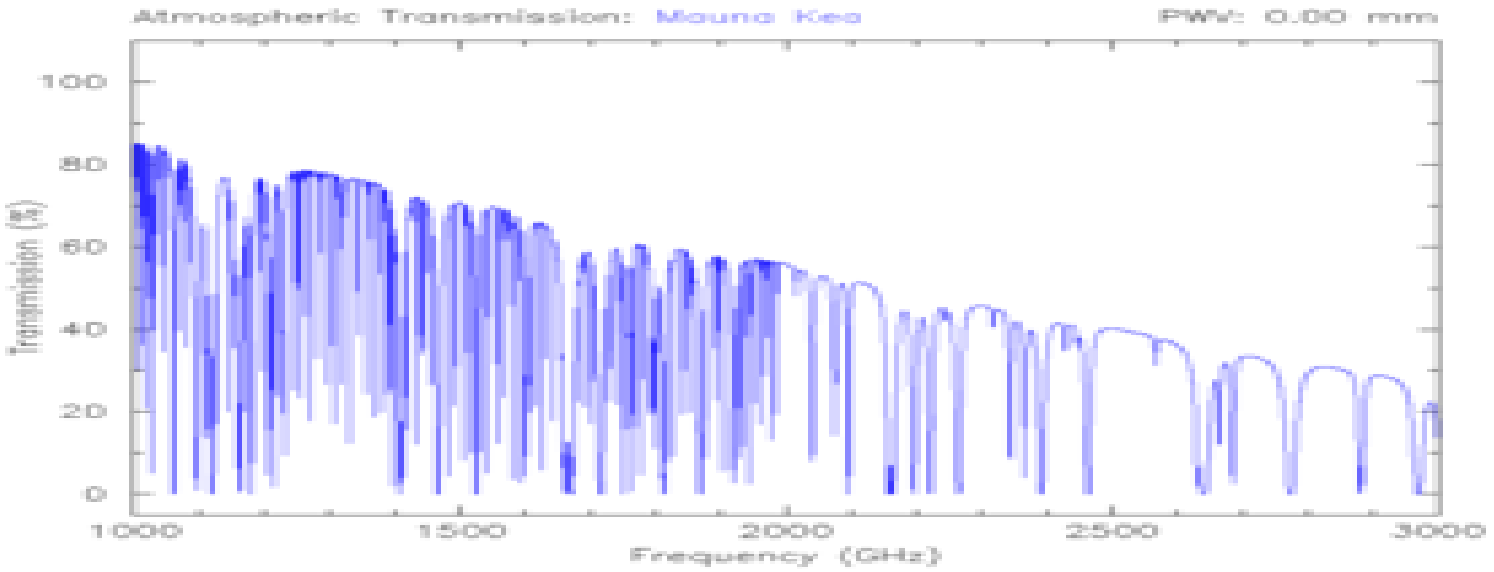
- CF_3I, Splitting due to ^{127}I



http://en.wikipedia.org/wiki/Rotational_spectroscopy

Asymmetrical Tops

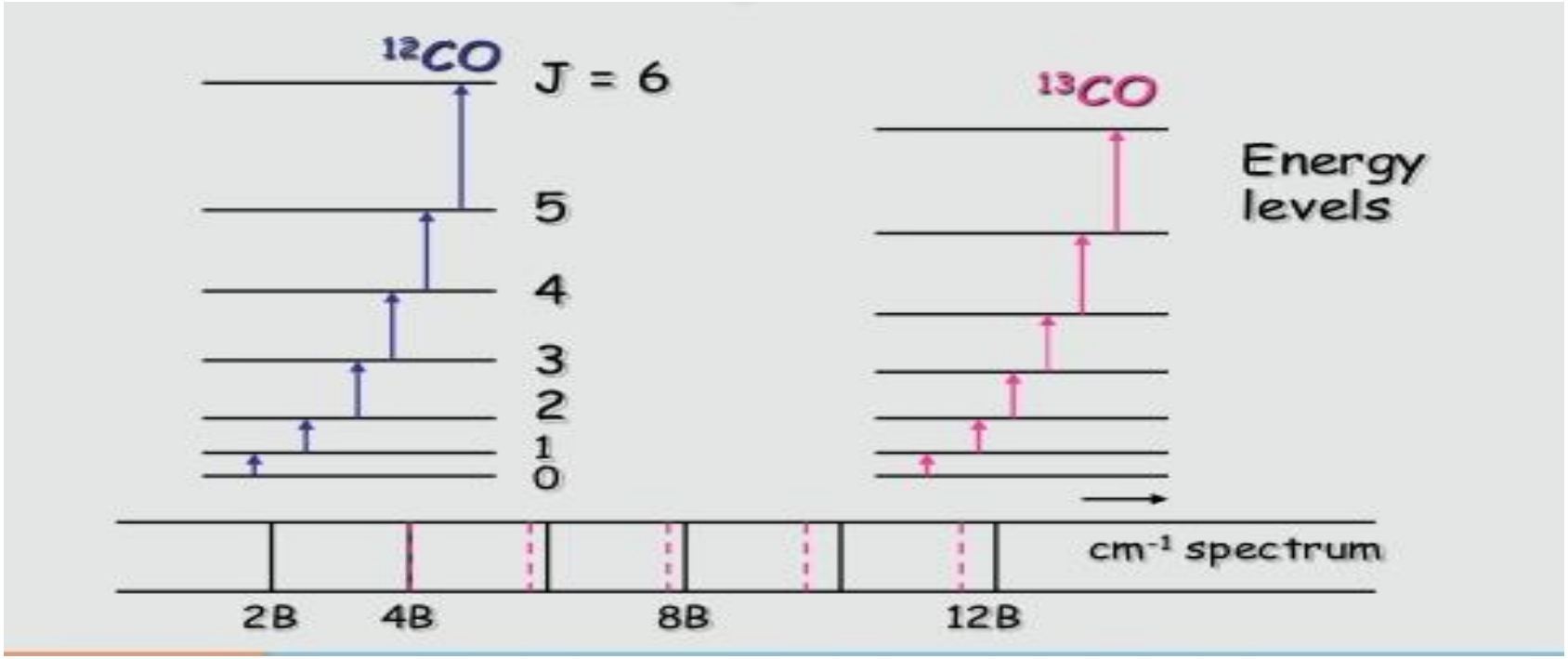
- Three different axes, 3 different inertias
- Most molecules.
- Very complex spectra.



http://en.wikipedia.org/wiki/Rotational_spectroscopy#Asymmetric_top

Effect of Isotope Substitution

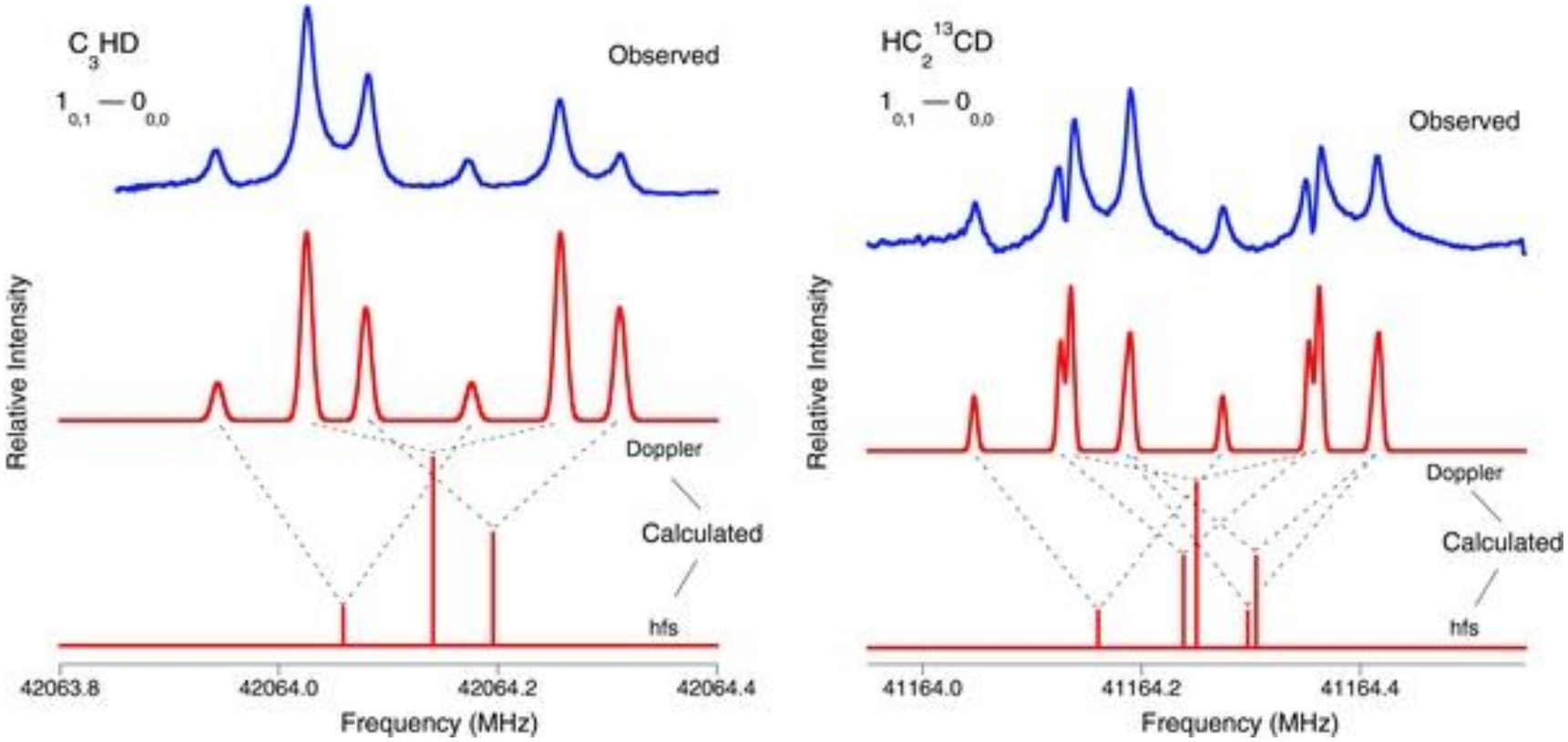
- $^{12}C^{16}O \rightarrow {}^{13}C^{16}O$, mass ↑, B ↓ (~1/I), E ↓.



http://www.slideshare.net/khemendrabhardwaz/rotational-spectra-microwave-spectroscopy_group/rotational_spectroscopy.shtml

Isotope splitting

- ***c*-C_3HD**



http://http://iopscience.iop.org/0067-0049/200/1/1/article

Isotopic Substitution

- As Isotopic Mass ↑, Energy ↓

Example (CO)

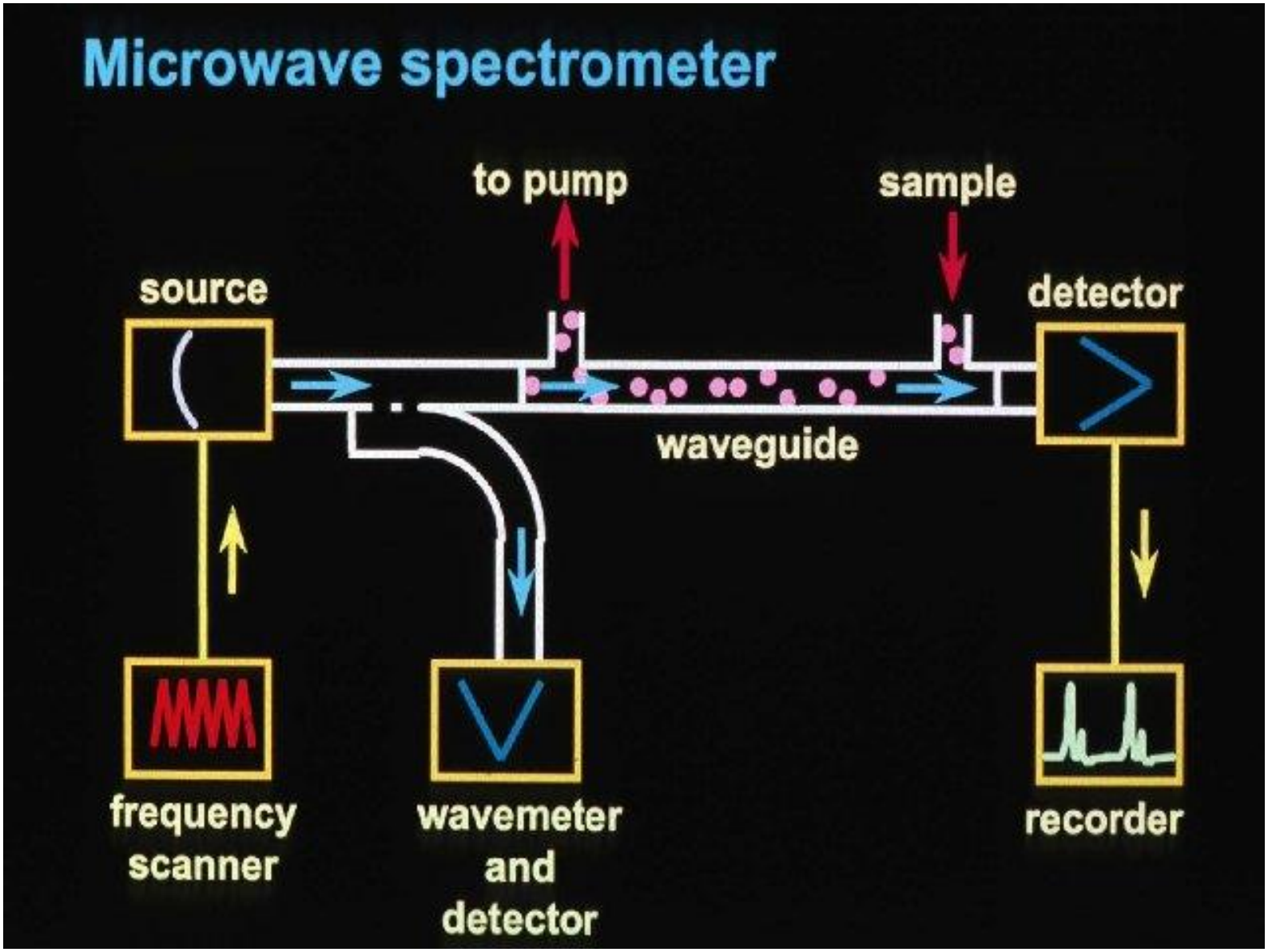
^{12}CO	J=0->J=1	@ 3.84235 cm^{-1}
^{13}CO		@ 3.67337 cm^{-1}

Instrumentation

- Most homemade.
- Two types spectrometers.
- Stark Modulated
- Fortier Transform Microwave Spectroscopy
  - Similar in concept to FTIR

Stark Modulated MW Spectrometer

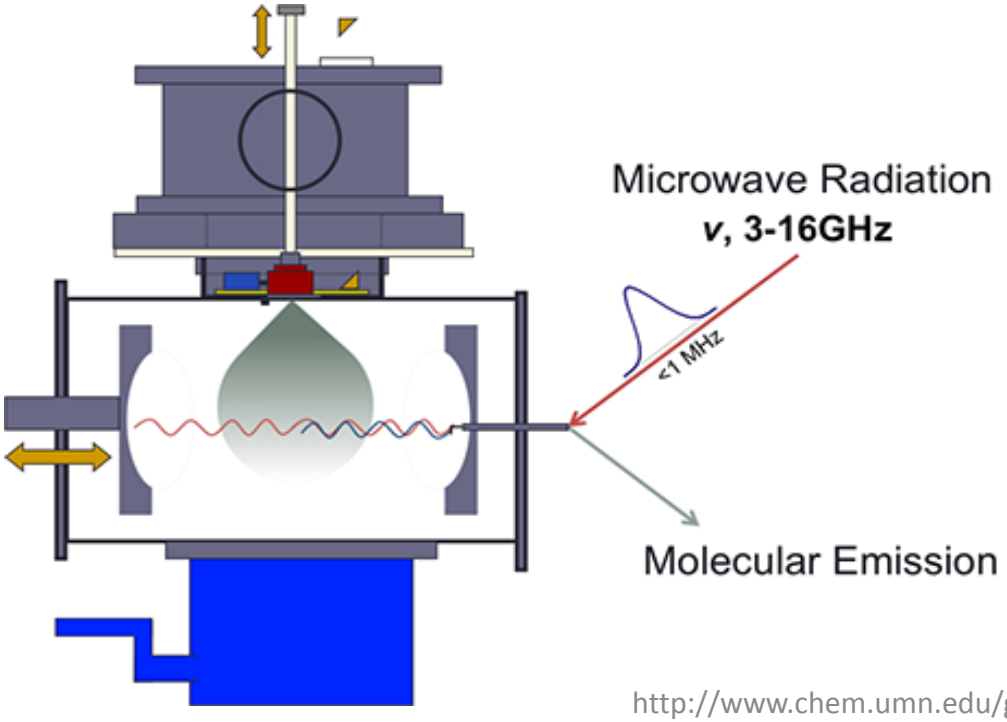
- Samples introduced as a gas.
- Can be heated.
- Generally high vacuum.



http://www.chem.canterbury.ac.nz/research group/sarah_masters_group/rotational_spectroscopy.shtml

FTMW Spectrometer

- Similar in principle to FTIR
- Broader Frequency, Greater Precision

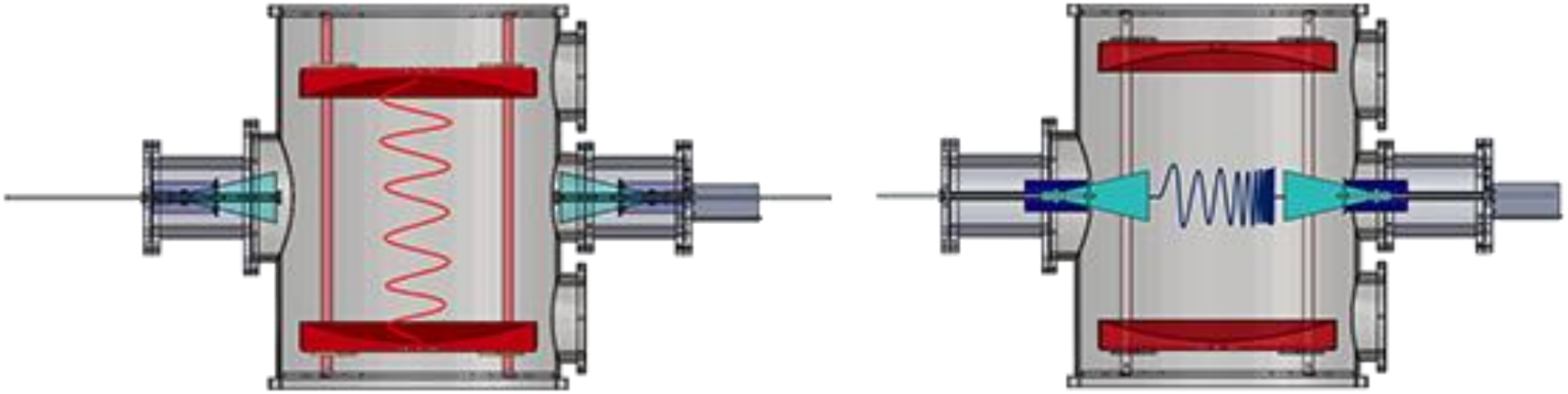


http://www.chem.umn.edu/groups/kleopold/instrumentation.html

Chipped Pulse FTMW

- Add waveform generators
- Widens Bandwidth several 1000x
- Decreases spectral search time

Chipped Pulse FTMW



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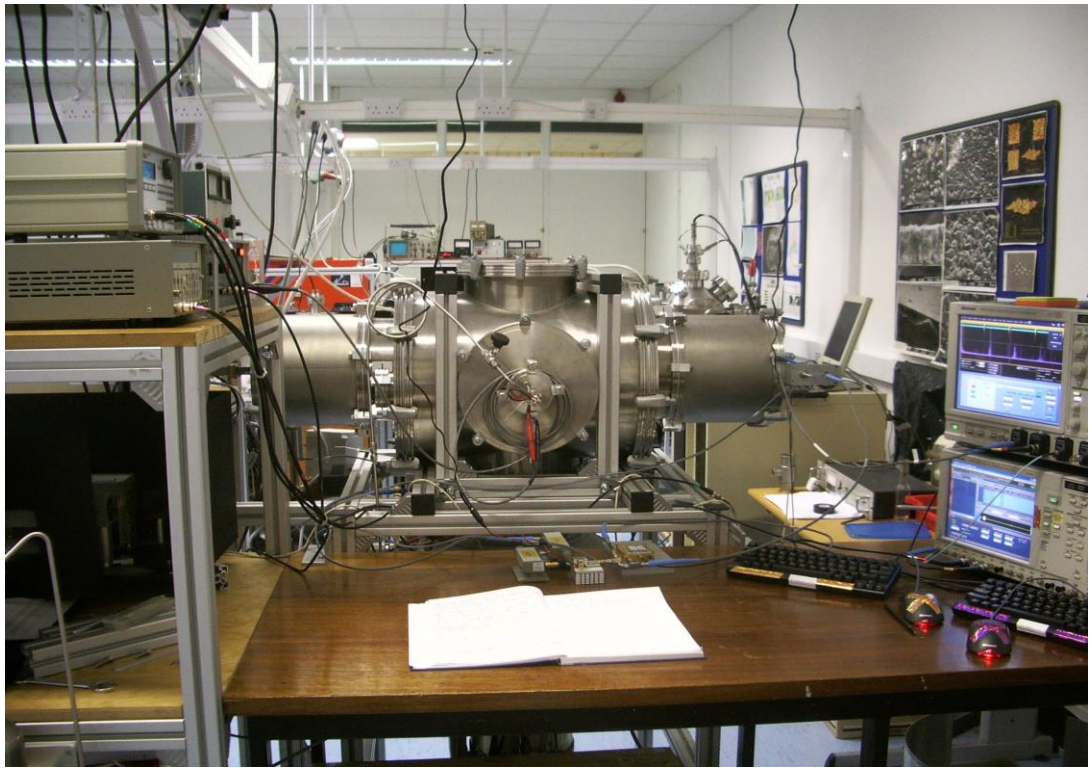
FTMW Spectrometer

- Typical setup

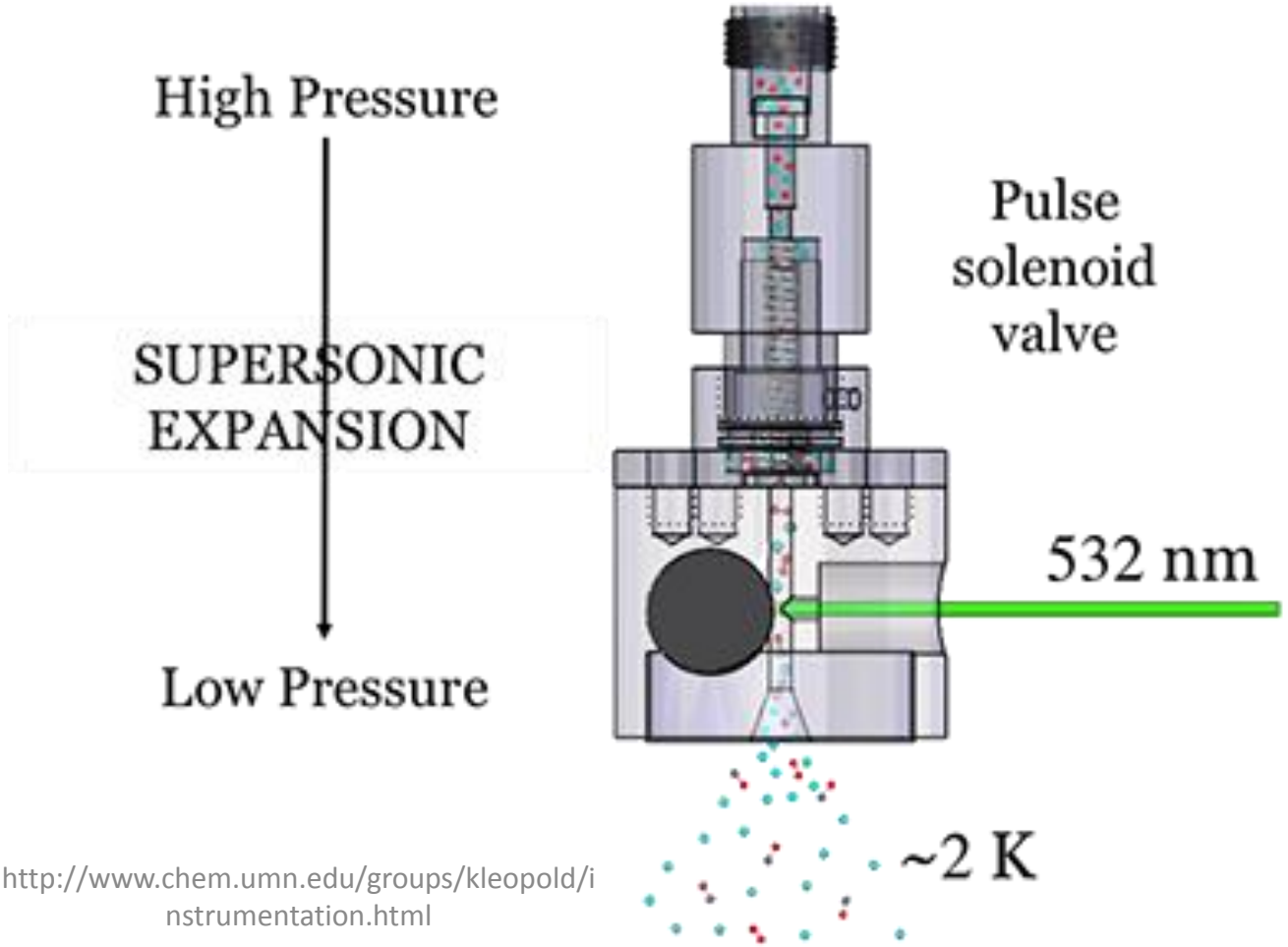


http://www.chm.bris.ac.uk/~chnrw/CPFTMW.htm

Sample Preparation/Introduction

- Gas samples
  - As is
  - As a diluted analyte in a non-MW reactive gas such as Neon
- Solids
  - Laser abatement
  - Vaporization
- Liquids
  - Vaporization
  - Supersonic Expansion

Supersonic Expansion/Laser Ablatement



http://www.chem.umn.edu/groups/kleopold/instrumentation.html

Applications of MW

- Measurement of bond lengths
- Observation by radio telescopes for life precursors in interstellar clouds
- Precise observation of translating stereochemistries and confirmation verification

Measuring Bond Length.

- For example, we will use the easiest case, a diatomic molecule, HCL.

cm^{-1}	J->J+1	R(nm)
83.03	3-4	.1288
103.73	4-5	.1288
124.3	5-6	.1289
145.03	6-7	.1289
165.51	7-8	.1290
185.86	8-9	.1291
206.38	9-10	.1292
226.5	10-11	.1293

Calculation example (HCL)

$$B = \frac{h}{8Ic\pi^2}$$

$$R = \sqrt{\frac{h}{8\pi^2 cBu}}$$

$$R = \sqrt{\frac{6.626e{-}34\ J.S}{8(3.14)^2\ (2.99792458e10\ cm.s)(\frac{35.5}{36.5} * 1.661x10{-}27\ kg)(10.3\ cm^{-1})}}$$

R=1.29x10^{-10} M or 0.129 nm

Problem

- Calculate bond length for CO
- Given=
  - $2B = 3.8626\ cm^{-1}$
  - $h = 6.626 \times 10^{-34}\ J \cdot S$
  - $c = 2.998 \times 10^{10}\ cm \cdot s$
  - Amu to kg = $1.661 \times 10^{-27}\ kg$

Calculation example (CO)

$$B = \frac{h}{8Ic\pi^2}$$

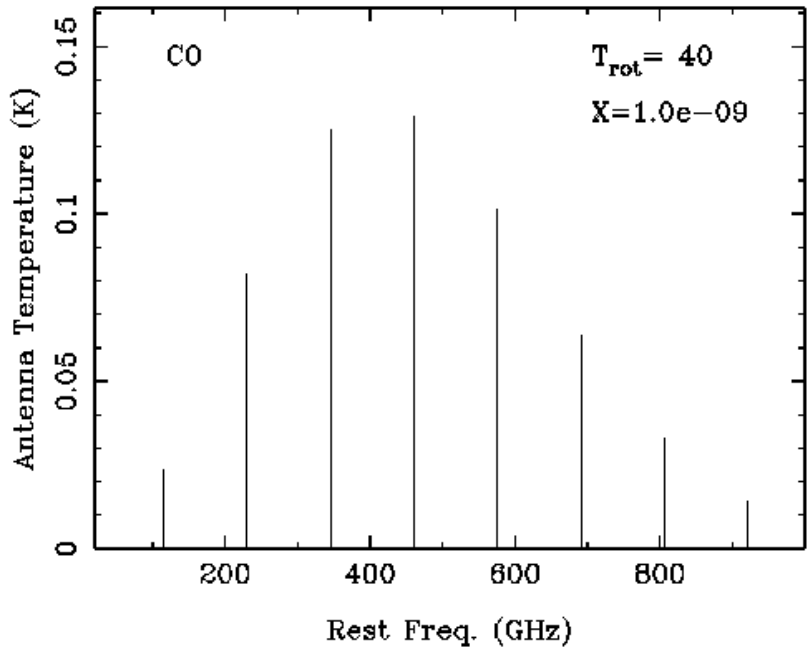
$$R = \sqrt{\frac{h}{8\pi^2 cBu}}$$

$$R = \sqrt{\frac{6.626e{-}34\ J.S}{8(3.14)^2\ (2.99792458e10\ cm.s)(\frac{48}{7}) * 1.661x10{-}27\ kg)(1.9313\ cm^{-1})}}$$

R=1.13x10^{-10} M or 0.113 nm

Identification of Organics in Interstellar Space

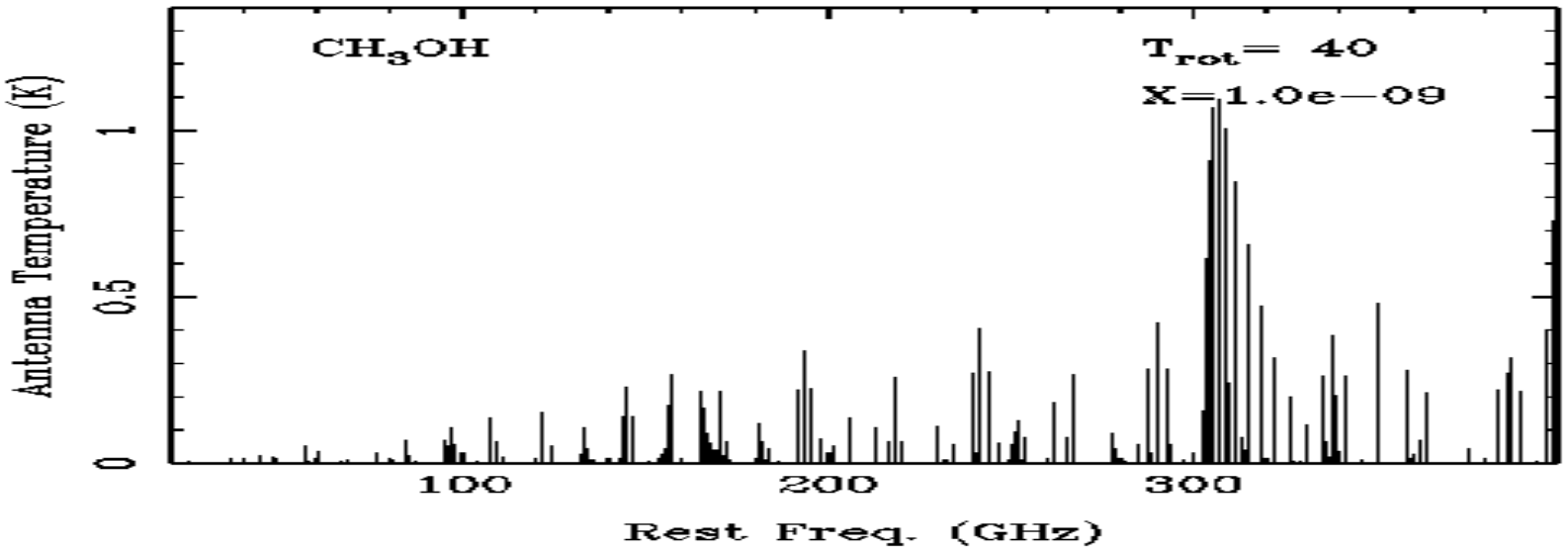
- Gas phase molecules and radicals
- Observed using a radio telescope.
- Linear molecule
  - Simple spectra



http://homepages.spa.umn.edu/~larry/PPT/MPS0306/molecules.html

Identification of Organics in Interstellar Space

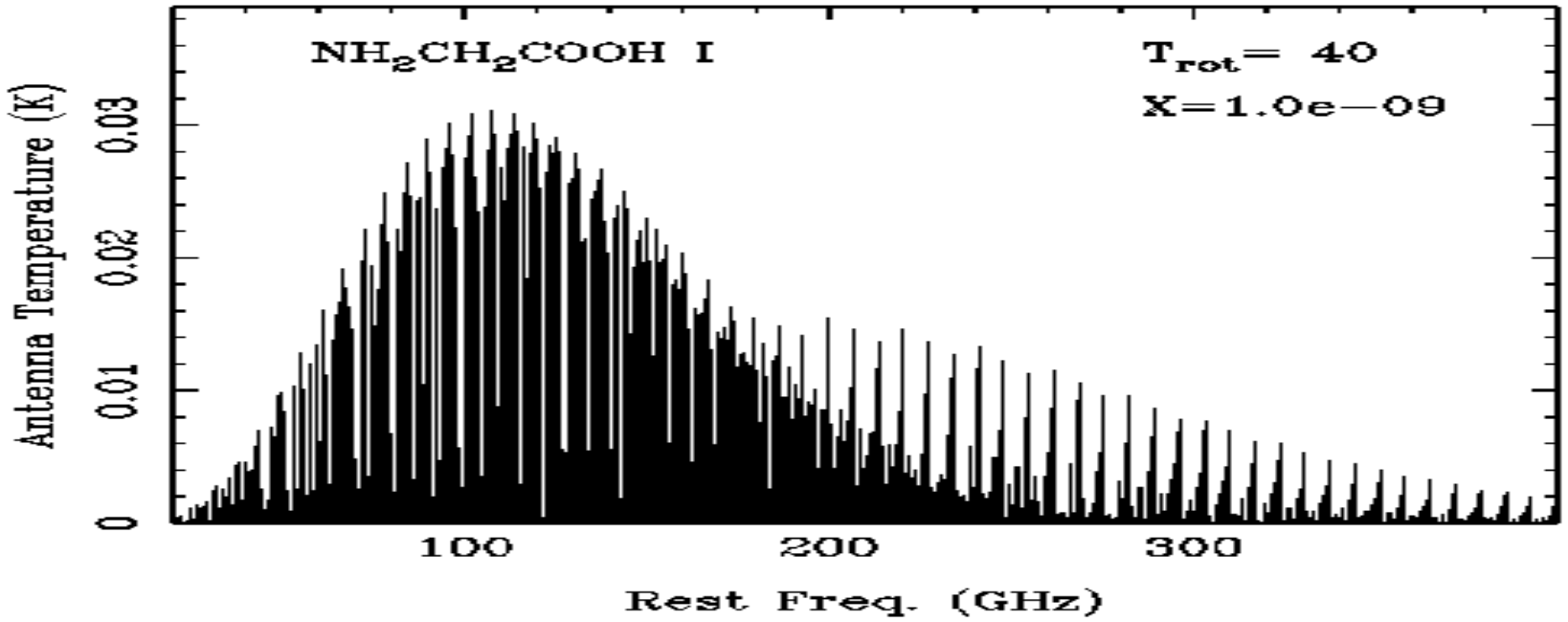
- Symmetric Molecule
  - Complicated due to symmetric top
  - Many more possible states



http://homepages.spa.umn.edu/~larry/PPT/MPS0306/molecules.html

Glycine? in interstellar clouds

- Other more complicated molecules may be observed
- Data too complicated



http://homepages.spa.umn.edu/~larry/PPT/MPS0306/molecules.html

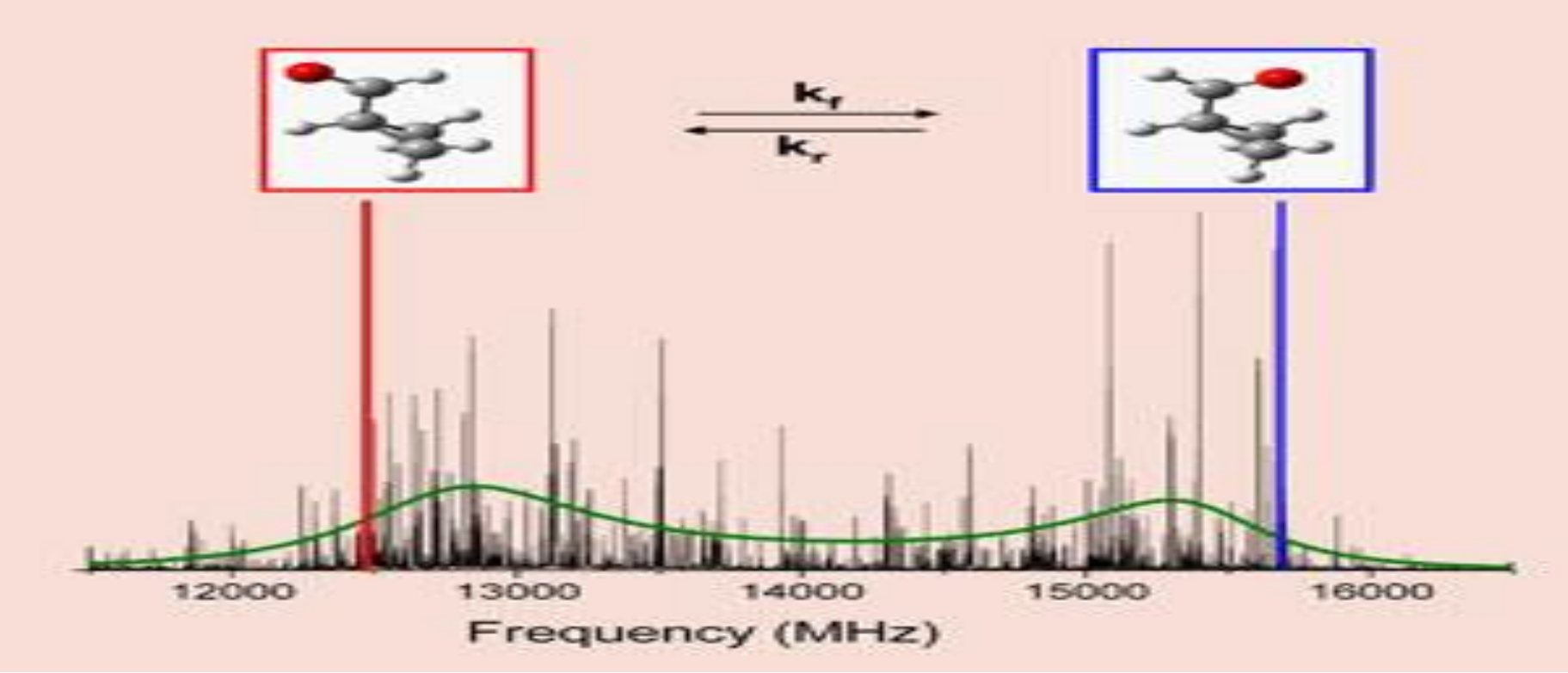
Molecular Confirmation

- Resolve rapidly interchanging conformers.
- 17000 scans/52 hrs.
- 27 yrs on standard unit.

B C Dian et al, Science, 2008, 320, 924 (DOI: 10.1126/science.1157668

Conformers

Cyclopropane carboxaldehyde



http://www.rsc.org/chemistryworld/News/2008/May/16050801.asp

Conclusion

- Useful for Gas Molecules
- Can determine bond length.
- Diverse usages for the technique.