

Rotational Populations

(neglecting ortho - para effects, which exist!)

$$P(E_{J,K_a}) = \frac{g_{K_a} (2J+1) e^{-E_{J,K_a}/kT}}{q_{rot}}$$

$$g_{K_a} = \begin{cases} 2 & |K_a| \neq 0 \\ 1 & K_a = 0 \end{cases} \quad q_{rot} \approx \left(\frac{kT}{hA}\right)^{1/2} \left(\frac{kT}{hB}\right)^{1/2} \pi^{1/2}$$

Stark Effect (1st order)

$$E^{(1)} = -\mu_{a,c} E_z M_J K_{a,c} / J(J+1) \quad J \neq 0$$

Asymmetric Tops

$$I_a < I_b < I_c$$

$$A > B > C$$

No simple formula for quantum mechanical energies for all J

For each J, must diagonalize matrix. (n solve secular determinant)

Approach: $\psi_{J,M_J} = \sum_{K_a} a_{J,K_a} \psi_{J,K_a}(r) (\theta, \phi, \chi)$

K no longer good quantum no. (no symmetry axis)

determine these by matrix diagonalization for each J

$\Delta K_a = 0, \pm 2$
matrix elements

Characteristics of Energy Levels

$$E = E(A, B, C)$$

$$\text{asymmetry parameter } K = \frac{2B - A - C}{A - C}$$

$$-1 \leq K \leq +1$$

prolate limit
 $A > B = C \quad K = -1$

← B changes →

oblate limit
 $A = B > C \quad K = +1$

$$H_r \psi = E \psi \quad H_r = h (A \hat{J}_a^2 + B \hat{J}_b^2 + C \hat{J}_c^2)$$

$$H_r \sum_{K_a} a_{J, K_a} |J K_a\rangle = E \sum_{K_a} a_{J, K_a} |J, K_a\rangle$$

$\langle J K_a' |$:

$$\sum_{K_a} a_{J, K_a} \langle J K_a' | H_r | J K_a \rangle = E \sum_{K_a} a_{J, K_a} \underbrace{\langle J K_a' | J K_a \rangle}_{\delta_{K_a' K_a}}$$

$$\sum_{K_a} a_{J, K_a} \left\{ \langle J K_a' | H_r | J K_a \rangle - E \delta_{K_a' K_a} \right\} = 0$$

$\Delta K_a = 0, \pm 2$ ONLY

To avoid trivial solution:

$$\left| \begin{array}{c} H_r - E \delta_{K_a' K_a} \end{array} \right| = 0$$

K_a, K_a' go from
 $-J$ to J
 $(2J+1) \times (2J+1)$

sketchend for

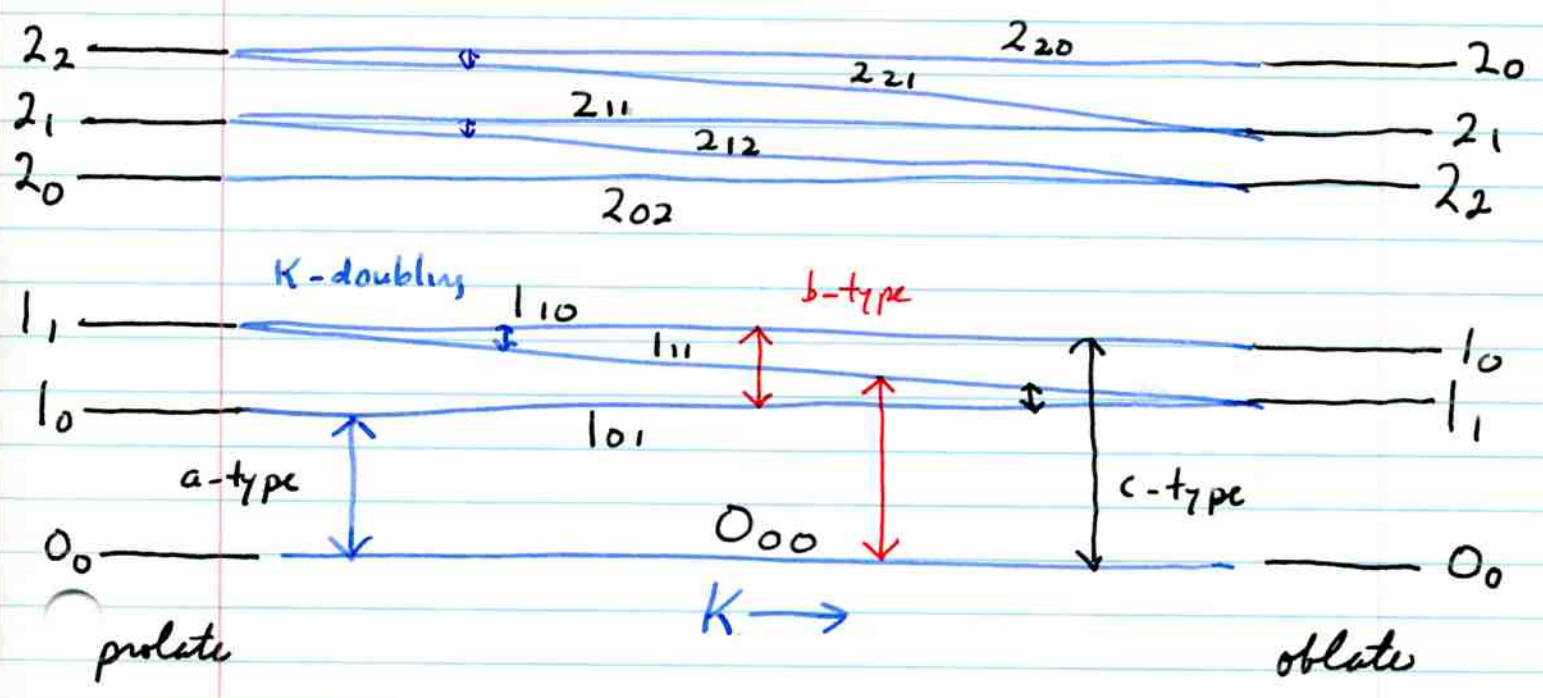
$$\left| \begin{array}{c} \langle J - J | H_r | J - J \rangle - E \dots \dots \dots \\ \vdots \\ \dots \dots \dots \end{array} \right| = 0$$

get $2K_a+1$ roots for each $J =$ energies
 With E 's can go back and obtain a_{J, K_a} 's
 + wave functions. Functions of A, B, C .

$$J_{K_a K_c} : J_{K_1 K_1} \quad J_{K_p K_0}$$

designates energy levels based on symmetric top limits + a correlation diagram.

(assuming no J overlap)



2x degeneracy important

alternative designation $J_{\tau} \quad -J \leq \tau \leq J$

Selection Rules + Spectroscopy

$\mu_a \mu_b \mu_c$ may all be non-zero.

$$\langle \Psi_{J' K_a' K_c'} | \mu_Z | \Psi_{J'' K_a'' K_c''} \rangle \neq 0 \text{ if } \Delta J = 0, \pm 1$$

$K_a K_c$ rules more relaxed (strongest below)

a-type ($\mu_a \neq 0$)

$$\Delta K_a = 0$$

$$\Delta K_c = \pm 1$$

b-type ($\mu_b \neq 0$)

$$\Delta K_a = \pm 1$$

$$\Delta K_c = \pm 1, \pm 3$$

c-type ($\mu_c \neq 0$)

$$\Delta K_a = \pm 1$$

$$\Delta K_c = 0$$

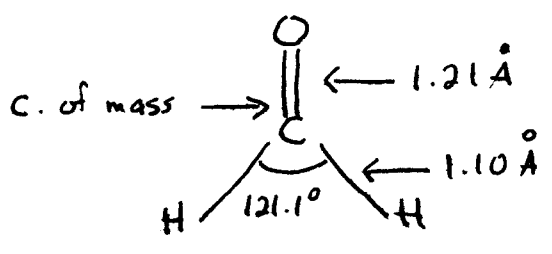
often associated with near prolate tops

often associated with near oblate tops

(More rigorous selection rules: $\Delta K_a \Delta K_c$ even n odd)

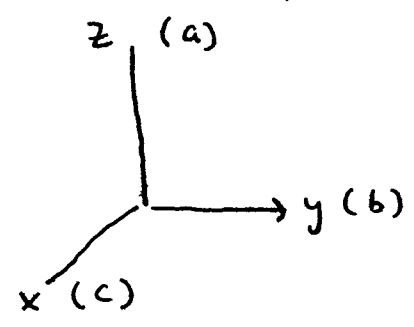
An Example: H_2CO (formaldehyde)

Structure:



a) determine I_a, I_b, I_c

Start with:



2-fold symmetry

Smart choice: $I_{xy} = I_{xz} = I_{yz} = 0 \therefore x, y, z$ principal axes

$I_{xx} = I_c \quad I_{yy} = I_b \quad I_{zz} = I_a$

$I_a < I_b < I_c$

b) Switch to A, B, C (here refer to ground vibrational state)

$A_0 = 278,668 \text{ MHz}$

$B_0 = 38,662.6 \text{ MHz}$

$K = -0.96$

$C_0 = 33,952.0 \text{ MHz}$

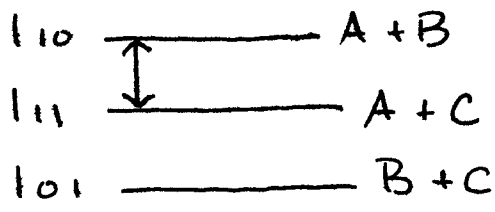
"near prolate top"

c) Now determine $E(J_{K_a K_c}) = E(A, B, C)$

d) Finally, with selection rules, can determine spectrum.

$J = 1$

3 x 3 determinant



$\nu = B - C$

a-type

$\mu = \mu_a$
(see structure)

More normal approach:

Spectrum \rightarrow Molecular Structure

1. Assign spectrum

2. Determine $A, B, C \rightarrow I_a, I_b, I_c$

$$3. \quad I_a = \sum_i m_i (b_i^2 + c_i^2)$$

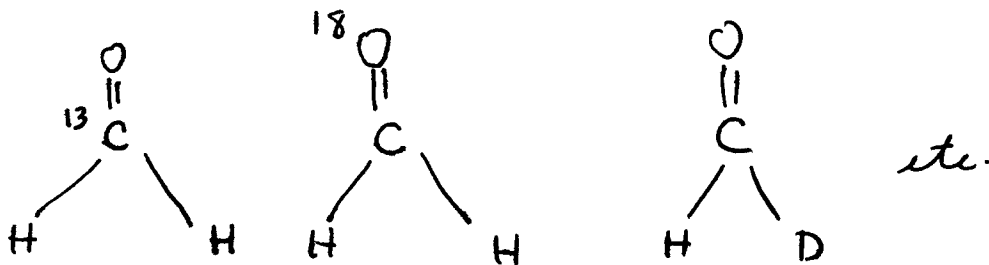
$$I_b = \sum_i m_i (a_i^2 + c_i^2)$$

$$I_c = \sum_i m_i (a_i^2 + b_i^2)$$

a_i, b_i, c_i positions
of nuclei

Clearly the measurement of I_a, I_b, I_c does not determine all the coordinates.


Trick: use isotopic substitution (changes I 's and m_i 's) assuming that the structure remains the same.



Spectroscopy From Space

- main tool used by astronomers to study atmospheres of stars and interstellar matter.

Diffuse Interstellar Matter

* $h\nu$ → 

← 1-10 LY →

absorption in visible/UV by gas
scattering by tiny dust particles

$n \sim 10^{2-3} \text{ cm}^{-3}$ $T \sim 50 \text{ K}$ mainly atoms $\text{H} > \text{C}^+, \text{O}, \dots$
except for lots of H_2

Dense Interstellar Matter

- often part of larger, more diffuse, associations known as giant molecular clouds.

- * - dark in visible due to dust particles
- studied at longer wavelengths
- contrast IR and radio (from ground)

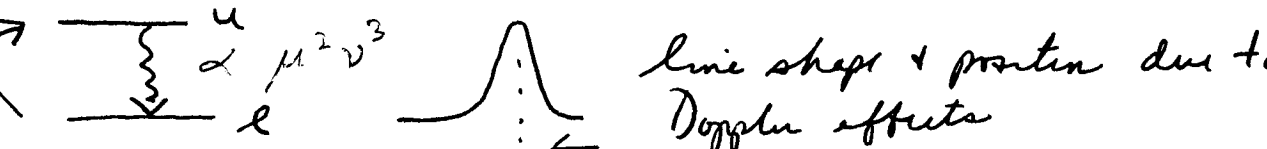
Black cloud

overall physical characteristics: $n \sim 10^{4-6} \text{ cm}^{-3}$
(all H_2) + molecules $T \sim 10-20 \text{ K}$ (T_{kinetic})

- sites of collapse to form stars + planets

Some Radioastronomy (rotational spectroscopy)

- * - lines seen in emission, normally collisionally excited - 'many' per molecule

n_{crit} 

line shape + position due to Doppler effects

← intensity measured by $T_b(\nu)$; $\int T_b(\nu) d\nu$; equivalent of black body at temperature T .

$T_\nu \ll 1$ $\int T_b(\nu) d\nu = \frac{8\pi^3 \nu_{ue}^2}{3ck} |\mu_{ue}|^2 N_e$

integrated brightness temperature (n_z, n_{crit} - see below) N_e column density (cm⁻²) in lower state

measure many lines → get n_i, T_{rot}, n_{TOTAL} n_e · l if homogeneous; otherwise $\int_0^L n_e(x) dx$

Example (map)

CO $\mu_{1-0} = 0.04$ Debye $\int T_b(\nu) d\nu = 100$ K-MHz

⇒ $N_0 = 2.3 \times 10^{17}$ cm⁻²

$L \sim 10$ LT YR = 10^{19} cm [1.26×10^{19} cm really] × (9.46×10^{18} cm)

⇒ $n_0 = 0.0185$ cm⁻³ $T_{rot} \sim 10$ K

$g_{rot} = \frac{kT}{hB} = 3.6 \Rightarrow n = 0.066$ cm⁻³

$\frac{n_0}{n} = \frac{1 e^{-E_0/kT}}{g_{rot}}$ (lower limit since optically thick)

$n \sim 1$ cm⁻³ correct

Typically $n_{TOTAL} \sim n_{H_2} \sim 10^4$ cm⁻³

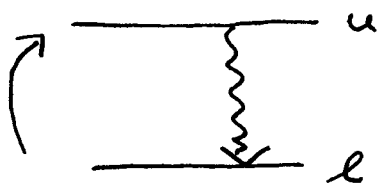
∴ $f_{CO} \gtrsim 10^{-5}$

* LIST OF MOLECULES

neutral molecules, molecular ions, radicals, isomers, isotopomers

examples CH₃OH, HCO⁺, C₈H, HNC, DCO⁺
Glycine!

Minimum Density Needed For Detection



no continuum background

Rate of excitation upward via collisions

$$= k_{u \leftarrow l} n_{H_2}$$

rate coefficient
(rate constant)
 $cm^3 s^{-1}$

gas density (cm^{-3})

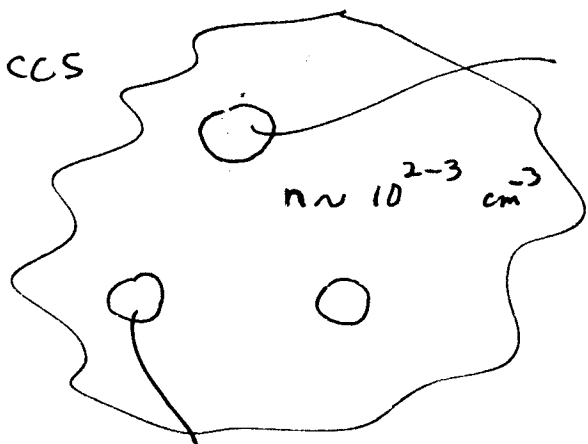
$$k_{u \leftarrow l} = v_{rel} \sigma_{u \leftarrow l} (cm^2) \sim 10^{-10} - 10^{-11} cm^3 s^{-1}$$

Rate of de-excitation (relaxation) per molecule: $A_{u \rightarrow l} (s^{-1})$

To detect emission: $k_{u \leftarrow l} n_{H_2} \gg A_{u \rightarrow l} \propto v_{rel}^3 |y_{ul}|^2$

The higher the frequency, the higher the permanent dipole, the higher the gas density needed for excitation.

* CCS



dense "core" $n \sim 10^4 cm^{-3}$

CO low μ
 $J=1 \rightarrow 0$ $n \gg 10^{2-3} cm^{-3}$

HCN high μ
 $J=1 \rightarrow 0$ much higher n

maps out dense clumps

sites of star formation