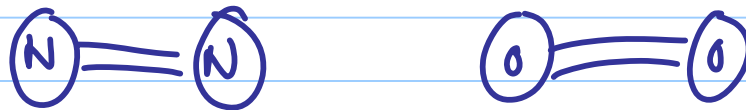
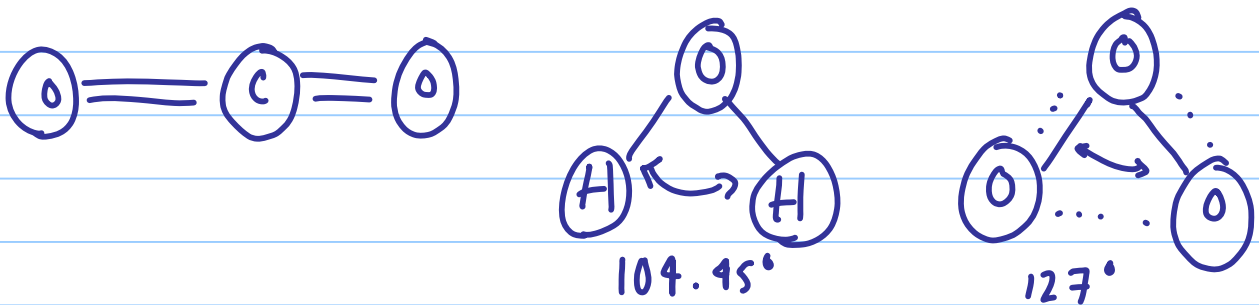


MOLECULAR ABSORPTION AND EMISSION

N_2 , O_2 are not IR active because they are homopolar molecules with no dipole moment.



Three molecules that are important in establishing radiative balance in Earth's atmosphere are H_2O , CO_2 , and O_3 . All three are IR-active.



For a simple diatomic molecule $A-B$, it can be shown that from quantum mechanics that the energy levels for rotation are

$$E_J = E_0 J(J+1) + \text{other terms}$$

where

J = rotational quantum number (integer)
 E_0 = ground state energy (J)

Rotational constant $B = \frac{E_0}{hc}$ (cm^{-1})

$$B = \frac{h}{8\pi^2 c I} \quad \text{with } I = \frac{m_1 m_2}{m_1 + m_2} r^2$$

m_1, m_2 are atomic masses

r = separation between the atoms

When the molecule changes state, the rotational quantum number must change by 1 so that

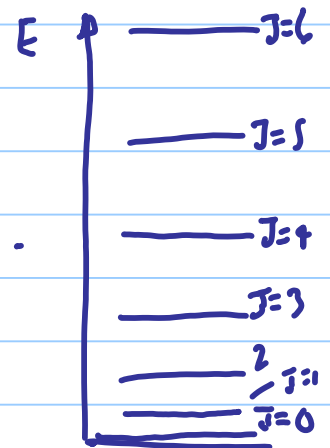
$$\Delta E = B [J'(J'+1) - J(J+1)] \quad \text{in } \text{cm}^{-1}$$

↪ scaled by hc

where $J' = J + 1$

$$\Delta E = 2B(J+1), \quad J = 0, 1, 2, \dots$$

(in cm^{-1})



Thus energy can only be absorbed or emitted at specific energies or wavenumbers.

↪ equally

These transitions form a regularly spaced spectrum in energy or wavenumber units because $\Delta E = hc\nu(J)$.

Becomes more complicated for real and larger molecules.

For CO_2 , due to its linear structure with oxygen atom at each end, it has no permanent dipole moment and behaves as a homopolar molecule wrt its pure rotation spectrum

$\Rightarrow \Delta J = \pm 1$ is forbidden

$\Rightarrow \text{CO}_2$ does not have a pure rotation spectrum

For H_2O , due to its "bent" shape, it can rotate about several axes to generate a complex rotational spectrum.

$\text{HCl} \rightarrow$ good example of a simple linear diatomic molecule

$$r = 0.13 \text{ nm}$$

$$m_1 = 1$$

$$m_2 = 35.5$$

} line spacing $\sim 20 \text{ cm}^{-1}$

HCl does have a pure rotation spectrum.

Calculation of the shape of the spectrum requires consideration of the population of states, which depend on

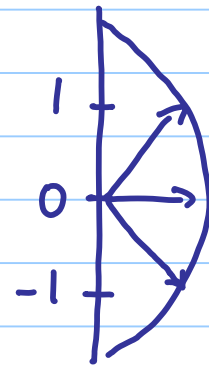
- ① temperature
- ② energy above the ground state
- ③ degeneracy of the state

For a diatomic molecule, the degeneracy is $2J+1$, which is the number of possible projections of J onto some fixed axis.

degeneracy = existence of two or more energy states

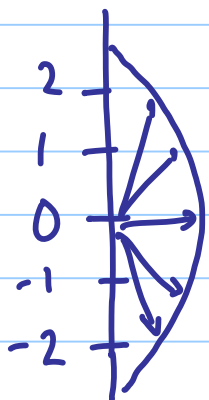
Unless an external electric or magnetic field is applied, these degenerate energy levels are equal.

If $J=1$, then $2J+1=3$



three degenerate orientations of the angular momentum vector

If $J=2$, then $2J+1=5$



five degenerate orientations for $J=2$



All of the molecules A-B are distinguishable particles, so Boltzmann statistics apply.

The population of the J^{th} state is

$$n_J = (2J+1) \exp \left[-\frac{Bhc}{kT} J(J+1) \right]$$

Because every molecule must be in some state, the total population is

$$n = \sum_{J=0}^{\infty} n_J = \sum_{J=0}^{\infty} (2J+1) \exp\left[-\frac{Bhc}{kT} J(J+1)\right]$$

If the levels are closely spaced such that J can be considered a continuous variable, then the sum can be transformed into a solvable equation (integrate over J) to get

$$n = \frac{kT}{Bhc} = \frac{kT}{E_0} \quad (\text{stat mechanics})$$

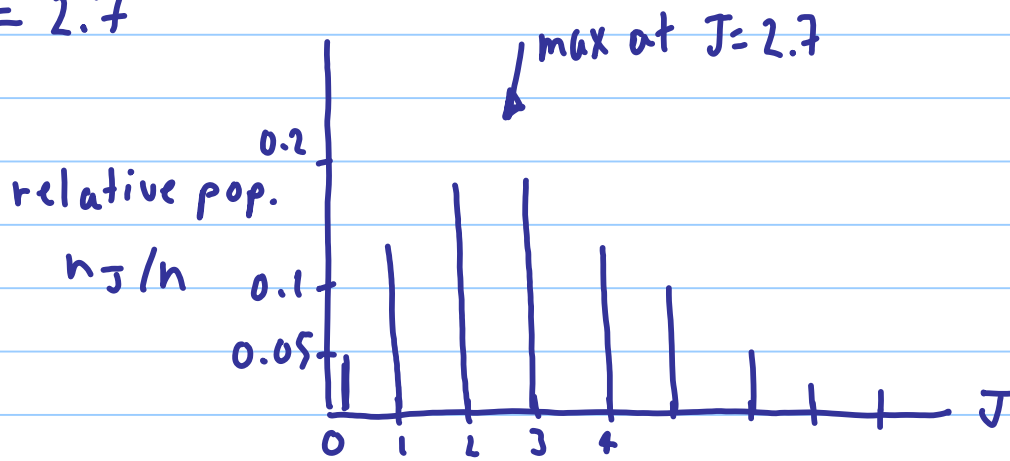
The population of any state is

$$\frac{n_J}{n} = \frac{Bhc}{kT} (2J+1) \exp\left[-\frac{Bhc}{kT} J(J+1)\right]$$

This function has a maximum when

$$(2J+1)^2 = \frac{2kT}{Bhc} \rightarrow \text{function of temperature}$$

For HCl at room temperature, this gives $J=2.7$

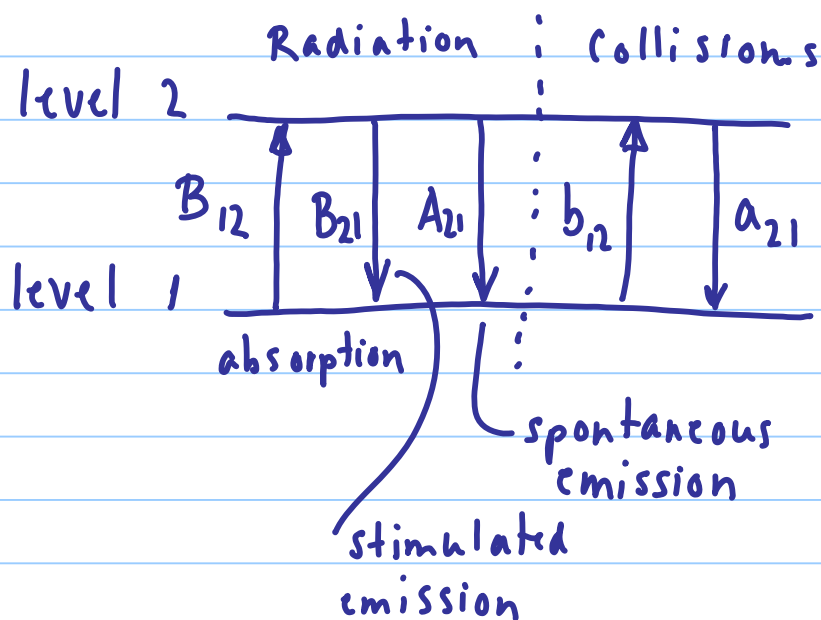


The more molecules there are in a given initial state, the greater the interaction with radiation.

Want to determine how strong that interaction is and how it varies with J .

→ need quantum mechanics to calculate the strength of this interaction.

Recall two-level atoms with Einstein coefficients:



The interaction of a beam of radiation with this matter is given by Beer's Law

$$dI = -I k n dx$$

where k is not Boltzmann's constant

n = molecular density

We want to find k for a particular transition of...

... photon energy $hc\bar{\nu}$.

In quantum mechanical terms, this equation would be

$$dI = \frac{hc\bar{\nu}}{c} \left(\underbrace{B_{21} n_2}_{\text{stimulated emission}} - \underbrace{B_{12} n_1}_{\text{absorption}} \right) I d\nu$$

Now reconsider the matter in a blackbody field for which

$$(1) \quad B_{12} n_1 \alpha = n_2 (A_{21} + B_{21} \alpha) \quad \begin{array}{l} \text{radiation} \\ \text{only, no} \\ \text{collisions} \end{array}$$

where α is the blackbody radiation density

$$\alpha = \frac{4\pi \bar{I}}{c} = \frac{4\pi B_{\bar{\nu}}}{c} \quad \begin{array}{l} \text{where } \bar{I} = \text{avg intensity} \\ B = B_{\bar{\nu}} \end{array}$$

$$= \frac{4\pi}{c} \left(\frac{2hc^2 \bar{\nu}^3}{\exp\left(\frac{hc\bar{\nu}}{kT}\right) - 1} \right)$$

$$(2) \quad \alpha = \frac{8\pi hc \bar{\nu}^3}{\exp\left(\frac{hc\bar{\nu}}{kT}\right) - 1}$$

The state populations must be given by Boltzmann statistics:

$$\textcircled{3} \quad \frac{n_2}{n_1} = \frac{g_2}{g_1} \exp\left(-\frac{hc\bar{\nu}}{kT}\right)$$

where g_1, g_2 are degeneracies of the states

Combining $\textcircled{1}$, $\textcircled{2}$ and $\textcircled{3}$, we get

$$g_2 B_{21} = g_1 B_{12}$$

$$A_{21} = 8\pi hc\bar{\nu}^3 B_{21}$$

Using quantum mechanics, it is possible to show (with some difficulty) that

$$B_{12} = \frac{2\pi^2}{3h^2 \epsilon_0} \frac{\sum |R(1,2)|^2}{g_1}$$

where

the sum is over all degenerate states of levels 1 and 2 of matrix elements $R(1,2)$ for the transitions

These are molecular properties independent of the physical state of the molecule.

Now compare two forms of Beer's Law to find an expression for k

$$dI = -Ikn dx = \frac{hc\bar{\nu}}{c} (B_{21}n_2 - B_{12}n_1) I dx$$

$$\begin{aligned}
 k &= -\frac{hc\bar{\nu}}{cn} (B_{21}n_2 - B_{12}n_1) \\
 &= h\bar{\nu} B_{12} \left(1 - \frac{g_1 n_2}{g_2 n_1}\right) \left(\frac{n_1}{n}\right) \quad \text{using eqn 3} \\
 &= h\bar{\nu} \left[\frac{2\pi^2}{3h^2 \epsilon_0} \sum \frac{|R_{(1,2)}|^2}{g_1} \right] \left(1 - e^{-hc\bar{\nu}/kT}\right) \left(\frac{n_1}{n_2}\right)
 \end{aligned}$$

Calculation of the exact value of $\sum |R|^2$ for a molecule is difficult, so in general, the absolute value of this function for any transition cannot be exactly determined.

However, for a diatomic molecule, the dependence of $\sum |R|^2$ on J can be determined \Rightarrow as $J[+1]$ where.

J = lower energy state

+1 is used when $\Delta J = +1$ and

+1 is omitted when $\Delta J = -1$

We can express relation in terms of J and constants:

$$\begin{aligned}
 k &\propto (J+1) \left(\frac{J[+1]}{2J+1} \right) \left(1 - \exp\left[-\frac{2E_0(J+1)}{kT}\right] \right) \\
 &\quad \times \left(\frac{2J+1}{kT} \right) \left(\exp\left[-\frac{EJ(J+1)}{kT}\right] \right)
 \end{aligned}$$

$$k \propto (J+1) (J+1) \left(1 - \exp\left[-\frac{2E_0 (J+1)}{kT}\right] \right) \\ \times \frac{1}{kT} \left(\exp\left[-\frac{E_0 J (J+1)}{kT}\right] \right)$$

where

J = lower state for a given transition

$$\Delta E = hc\bar{\nu}$$

$$= 2E_0 (J+1)$$

$$= hcB (J+1)$$

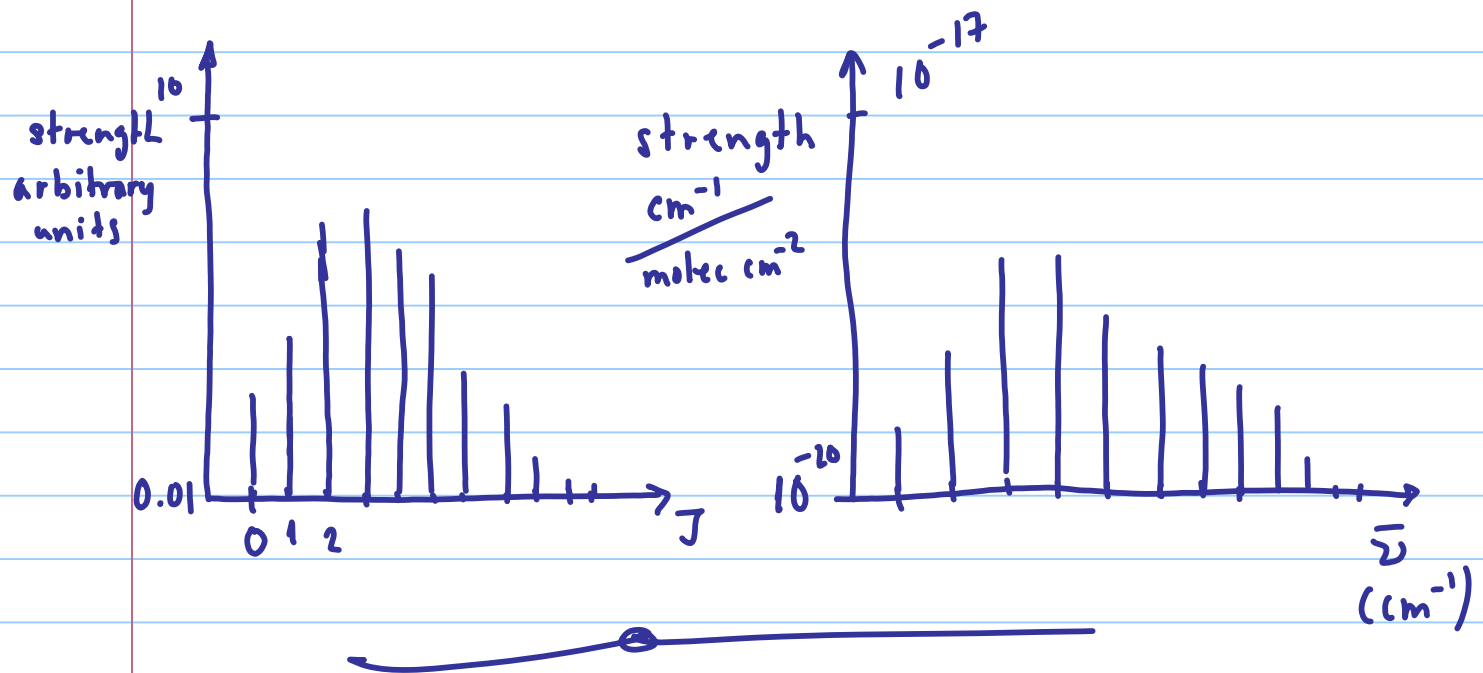
This term k is actually the strength of the transition, "S".

So the strength of a rotational transition depends on J in a complex way.

For pure rotational spectra, ΔJ is always ± 1 so the $[+1]$ is included (but left it in as the more general expression).

Although the exact strength of any rotational line cannot be calculated, if the strength of one line at one temperature can be measured, then the strengths of other lines at other temperatures can be determined from the proportionality conditions above.

Example: HCl



VIBRATION - ROTATION SPECTRA

Vibration and rotation effects are loosely coupled, mainly by selection rules

(1 rotation $\sim 10^{-11}$ sec / 1 vibration $\sim 10^{-14}$ sec)

The energy of a simple vibrating molecule is

$$E = E_v (v + \frac{1}{2}) \quad \rightarrow \text{comes from QM}$$

where

E_v = energy between the states (also ω)

v = vibrational quantum number

So for a vibrational-rotational transition in a diatomic molecule, the total energy is

$$E = E_v \left(v + \frac{1}{2} \right) + E_0 J (J+1) + \text{other terms}$$

or in cm^{-1} :

$$\frac{E}{hc} = \omega \left(v + \frac{1}{2} \right) + B J (J+1) + \text{other terms}$$

Selection rules: $\Delta v = \pm 1, \pm 2, \pm 3 \dots \pm n$
 $\Delta J = \pm 1$

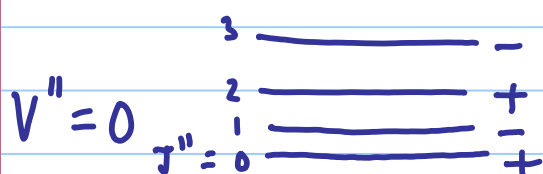
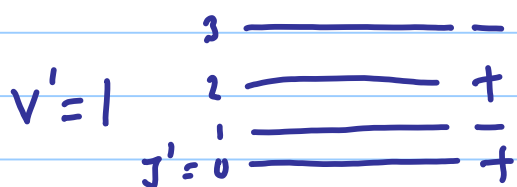
Diatomic molecules cannot make a vibrational transition without also making a rotational transition.

One more selection rule:
 parity $+ \leftrightarrow -$

Each odd rotational level has parity $-$
 Each even rotational level has parity $+$

So $J' = 0 \rightarrow J'' = 0$ then $+ \rightarrow +$

Diagram for diatomic molecule



Selection rules are really

$$\Delta J = 0, \pm 1$$

parity $+\leftrightarrow-$

$$\Delta v = \pm 1, \pm 2, \dots$$

But if $\Delta J = 0$, parity is $+\leftrightarrow+$ so these transitions are forbidden.

Energy levels of the spectrum are

$$\begin{aligned} hc\bar{\nu} &= E_v n + 2E_0 [J+1, -J] \\ &= hc\omega n + 2hcB [J+1, -J] \end{aligned}$$

Where

$J+1$ corresponds to $\Delta J = +1$

$-J$ corresponds to $\Delta J = -1$

For the fundamental vibration-rotation band of a molecule ($n=1$), the lines are at

$$\begin{aligned} hc\bar{\nu} &= E_v + 2E_0 [J+1, -J] \\ &= hc\omega + 2hcB [J+1, -J] \end{aligned}$$

except

that the $J=0$ state cannot have a $\Delta J = -1$ transition.