

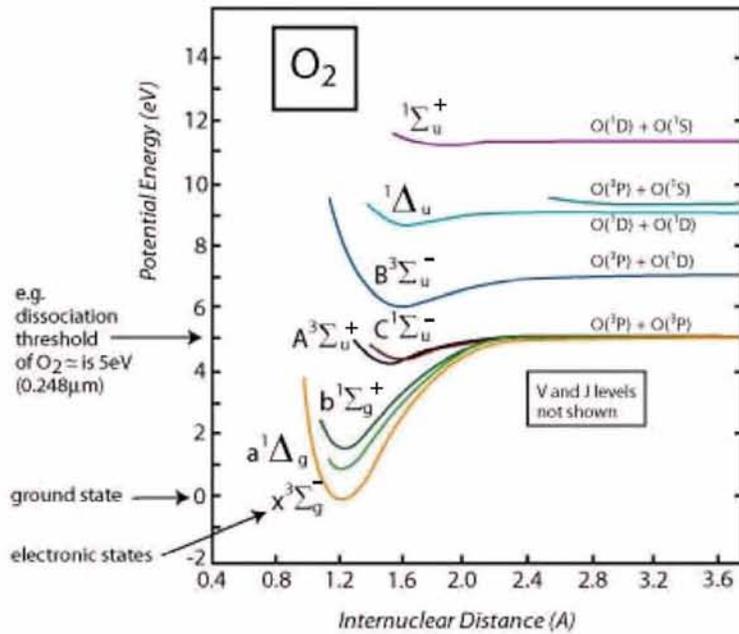
MIT OpenCourseWare  
<http://ocw.mit.edu>

12.815 Atmospheric Radiation  
Fall 2008

For information about citing these materials or our Terms of Use, visit: <http://ocw.mit.edu/terms>.

## Energy Levels in Molecules, contd.

e.g. energy level diagram for O<sub>2</sub>



Conversions: 1eV = 8067 cm<sup>-1</sup> = 1.24 μm (near infrared)  
 2eV = 16134 cm<sup>-1</sup> = 0.62 μm } (visible)  
 3eV = 24201 cm<sup>-1</sup> = 0.41 μm }  
 5eV = 40335 cm<sup>-1</sup> = 0.248 μm (ultraviolet)

Absorption and emission by gases

For transitions between two states, initial  $i$  and final  $f$ , the Einstein "b" coefficient is given by

$$b_{fi} = \frac{1}{4\pi} \times \frac{8\pi^3 \nu_{fi}}{3hc} \left| \int \Phi_f^* (\bar{\mu} \Phi_i) dV \right|^2 \left| \int \sum_f^* \sum_i d\sigma \right|^2$$

and we need this to be  $\gg 0$  for strong ("allowed") absorption or emission. This defines "selection rules".

$\Phi(r, \theta, \phi)$  = space-dependent part of the wavefunction describing state of molecule.

$\sum(\sigma)$  = spin-dependent part of wavefunction  
(total wavefunction =  $\Phi \cdot \sum$  )

$\bar{\mu}$  = dipole moment operator =  $e\bar{r}$

(a) Selection rules from  $\bar{\mu}$  (dipole)

For strong absorption/emission need  $\bar{\mu} \neq 0$

- (i) pure rotational transitions – permanent dipole required
- (ii) vibrational transitions where vibration does not produce a dipole moment – permanent dipole required
- (iii) vibrational transitions where vibration produces a (transient) dipole moment – permanent dipole not required.
- (iv) when vibrational transitions allowed then simultaneous vibrational + rotational transitions allowed
- (v) electronic transitions – permanent dipole not required (always a dipole between nuclei and electrons)

(b) Selection rules from  $\Phi_i$  and  $\Phi_f$  (symmetry)

Since  $\bar{\mu}$  (or  $\bar{r}$ ) is an odd function in space, and we require total integrated  $\Phi_f^* \bar{\mu} \Phi_i$  to be an even function to prevent significant cancellation between volume elements, then  $\Phi_f^*$  and  $\Phi_i$  must have opposite parity.

(La Porte's Rule). Formally this leads to:

i) for rotational energy transitions in a linear molecule

$$\Delta J = \pm 1$$

(special case is  $\Delta J = 0, \pm 1$  for a non-diatomic simultaneous rotational-vibrational transition where vibration is  $\perp$  to axis)

ii) for vibrational energy transitions in all molecules

$$\Delta v = \pm 1 \quad (\text{i.e. generally } v=0 \rightarrow v=1)$$

(i) (f)

(i.e. overtones and combinations are not allowed)

$$(nv) \quad (v_1 + v_2)$$

iii) for electronic transitions in linear molecules

The symbols provide the needed information on parity of wave function  $\left( \begin{matrix} 2S+1 \\ \Lambda^\pm \\ u, g \end{matrix} \right)$

i.e.  $\left. \begin{matrix} \text{(even)} & \text{(odd)} \\ g \leftrightarrow u \\ + \leftrightarrow - \end{matrix} \right\} \text{ allowed transitions}$

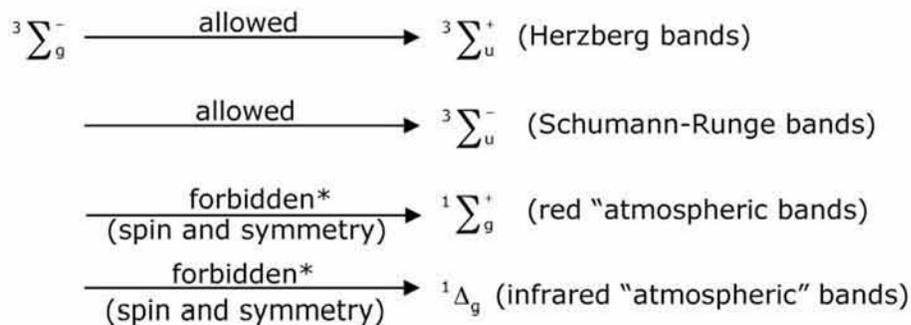
(c) selection rules from  $\sum$  (spin)

For  $b_n \neq 0$  need  $\int \sum_i^+ \sum_j^- d\sigma \neq 0$  but since  $\sum$ 's are orthogonal functions then need  $\sum_i = \sum_j$

Hence, transitions cannot involve a change of spin

This is important for electronic transitions. Note that spin is also given in the state symbol for electronic states.  $\left( \begin{matrix} 2S+1 \\ \Lambda^\pm \\ u, g \end{matrix} \right)$

e.g.  $O_2$  (see Energy Level diagram)



(\* observed as very weak "magnetic dipole" transitions)

## Shape of absorption and emission lines

(a) "natural" broadening due to (Heisenberg\*) uncertainty in energy of upper and lower levels.

$$\text{Integrated line strength} = S_{i0} = \int_0^\infty k_\nu \, d\nu$$

**\*NOTE**

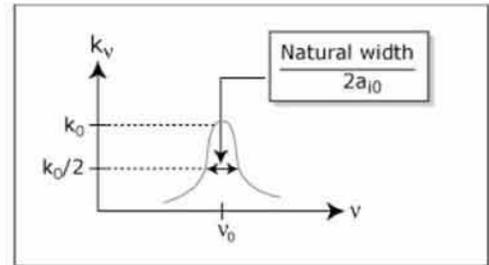
$$\Delta E \bullet \Delta t = \frac{h}{2\pi}$$

$$\Delta \nu \bullet \Delta t = \frac{1}{2\pi}$$

$$\Delta \nu \approx \frac{1}{2\pi \Delta t} = 2a_{i0}$$

$$= \int_0^\infty \frac{k_0}{1 + \left(\frac{\nu - \nu_0}{a_{i0}}\right)^2} \, d\nu$$

$$\left( k_0 = \frac{S_{i0}}{\pi a_{i0}} \right)$$

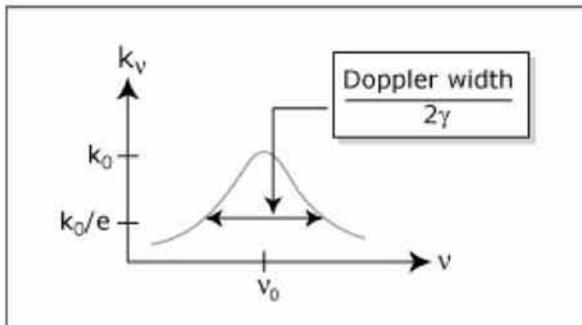


$$\left( \text{recall } a_{i0} = \frac{1}{4\pi\tau_{i0}} \right)$$

↑  
( $\Delta t$ )

(b) "doppler" broadening due to motion toward and away from observer (use Maxwellian distribution of velocities)

$$S_{i0} = \int_0^\infty k_\nu \, d\nu = \int_0^\infty \underbrace{\frac{S_{i0}}{\gamma\sqrt{\pi}}}_{k_0} \exp\left[-\left(\frac{\nu - \nu_0}{\gamma}\right)^2\right] \, d\nu$$



$$\left( \gamma = \frac{\nu_0}{c} \left( \frac{2KT}{m} \right)^{\frac{1}{2}} \right)$$

$$\left( \text{c.f. } v_{\text{molecule}} = \left( \frac{8KT}{\pi m} \right)^{\frac{1}{2}} \right)$$

(c) "pressure" broadening due to collisional and long distance interactions perturbing the energy levels

$$S_{i0} = \int k_\nu \, d\nu = \int_0^\infty \left[ \frac{k_0}{1 + \left(\frac{\nu - \nu_0}{\Gamma/4\pi}\right)^2} \right] \, d\nu$$

$\Gamma \propto$  collisional frequency ←

**NOTE**

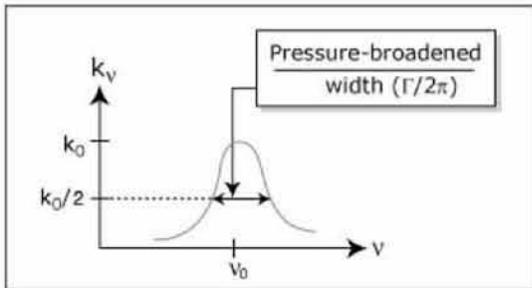
Collision freq. ( $\text{sec}^{-1}$ ) in a 2-component gas ( $m_1, r_1, n_1$  and  $m_2, r_2, n_2$ ) is:

$$(n_1 + n_2)(r_1 + r_2)^2 \left( 8\pi K T \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \right)^{\frac{1}{2}}$$

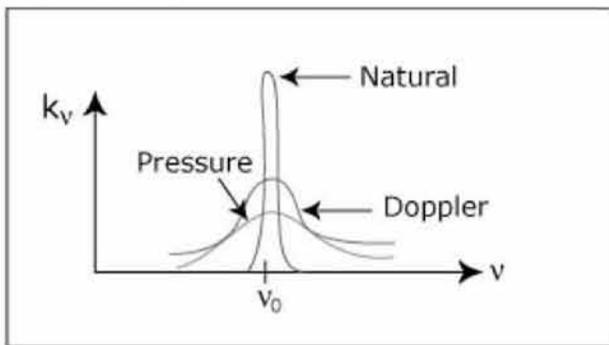
i.e.  $\Gamma = \Gamma_0 (1 \text{ atm}, 273\text{K}) P^{\bar{\alpha}} T^{-\bar{\beta}} \quad \left( \bar{\alpha} \approx 1, \bar{\beta} \approx \frac{1}{2} \right) \quad (P = nKT)$

( $\Gamma_0, \bar{\alpha}, \bar{\beta}$  from laboratory measurements)

( $k_0 = 4S_{10}/\Gamma$ )



(d) Summary



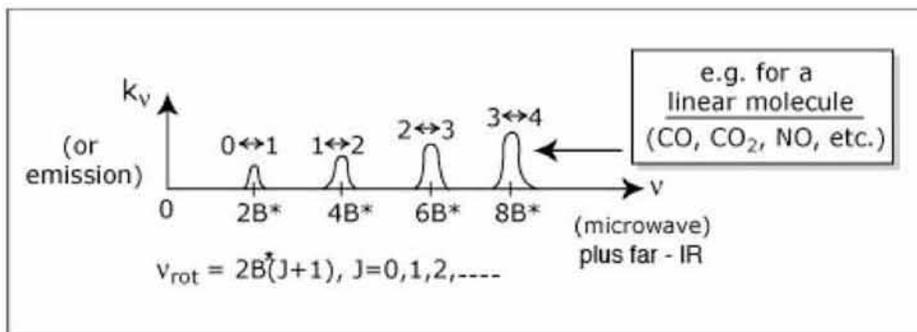
If increase T: Natural  $\rightarrow$  Doppler

If increase P: Doppler  $\rightarrow$  Pressure

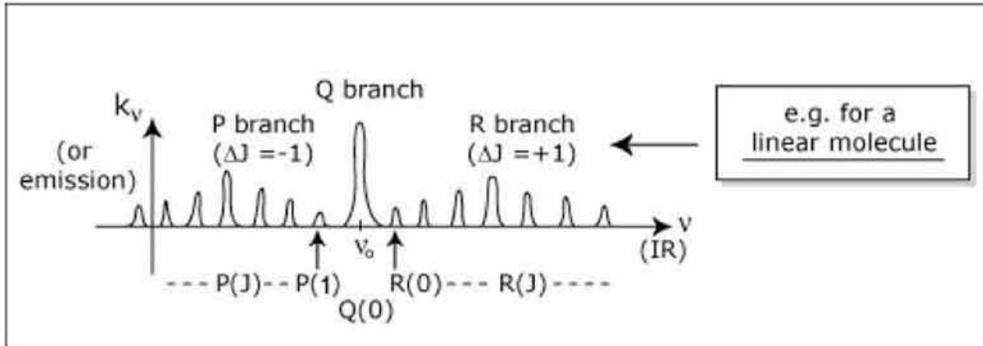
Absorption bands

Can get rotational, vibrational, and electronic transitions together:

(a) rotational bands (e.g. H<sub>2</sub>O) – due to  $\Delta J = \pm 1$



(b) vibrational-rotation bands – due to  $\Delta J = 0, \pm 1$  and  $\Delta v = \pm 1$



$$\nu_{\text{vib-rot}} = \nu_0 \begin{cases} +2B^*(J+1) & J = 0, 1, 2, \dots \text{(R)} \\ +0 & J = 0, 1, 2, \dots \text{(Q)} \\ -2B^*(J) & J = 1, 2, 3, \dots \text{(P)} \end{cases}$$

← rotn. rise + vibn. rise  
 ← rotn. fall + vibn. rise

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

(c) electronic – vibration – rotation bands

