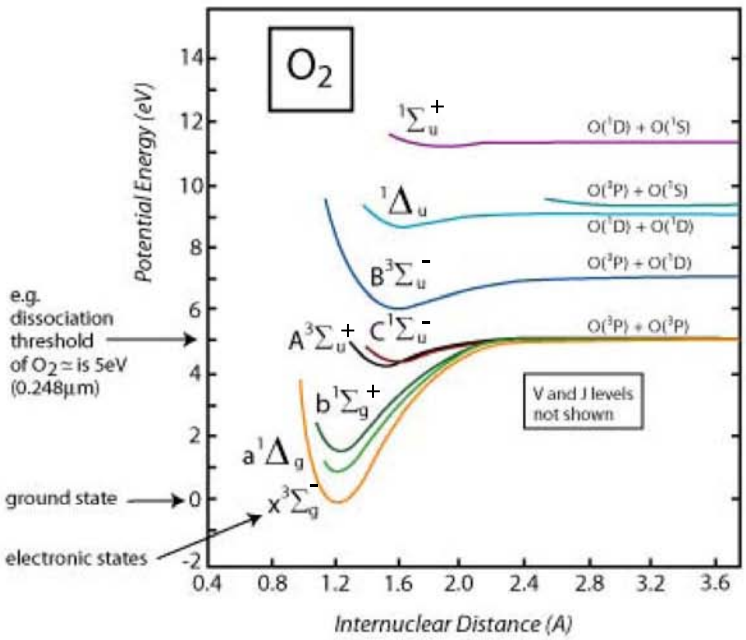
Energy Levels in Molecules, contd.

e.g. energy level diagram for O_2



Conversions: $1ev = 8067\ cm^{-1} = 1.24\ \mu m$ (near infrared)

$2ev = 16134\ cm^{-1} = 0.62\ \mu m$ } (visible)

$3ev = 24201\ cm^{-1} = 0.41\ \mu m$ } (visible)

$5ev = 40335\ cm^{-1} = 0.248\ \mu m$ (ultraviolet)

Absorption and emission by gases

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

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

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 = $\Phi \cdot \sum$)

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

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

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

- (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 Φ_i and Φ_f (symmetry)

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

$\Delta v = \pm 1$ (i.e. generally $v=0 \rightarrow v=1$)
(i) (f)

(i.e. overtones ($n\nu$) and combinations ($\nu_1 + \nu_2$) are not allowed)

iii) for electronic transitions in linear molecules
The symbols provide the needed information on parity of wave function $\left({}^{2S+1}\Lambda^{\pm}_{u,g} \right)$

i.e. (even) $g \leftrightarrow u$ (odd), $+ \leftrightarrow -$ } allowed transitions

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

For $b_{fi} \neq 0$ need $\int \sum_i^* \sum_j d\sigma \neq 0$ but since $\sum$'s are orthogonal functions then need $\sum_i \equiv \sum_j$

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. $\left({}^{2S+1}\Lambda^{\pm}_{u,g} \right)$

e.g. O_2 (see Energy Level diagram)

${}^3\Sigma_g^-$ —allowed→ ${}^3\Sigma_u^+$ (Herzberg bands)

—allowed→ ${}^3\Sigma_u^-$ (Schumann-Runge bands)

—forbidden* (spin and symmetry)→ ${}^1\Sigma_g^+$ (red "atmospheric bands)

—forbidden* (spin and symmetry)→ ${}^1\Delta_g$ (infrared "atmospheric" bands)

(* 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.

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

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

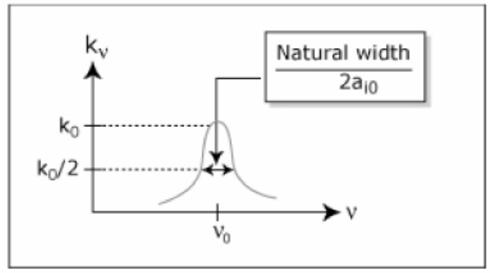
$$\left(k_0 = \frac{S_{i0}}{\pi a_{i0}}\right)$$

*NOTE

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

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

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

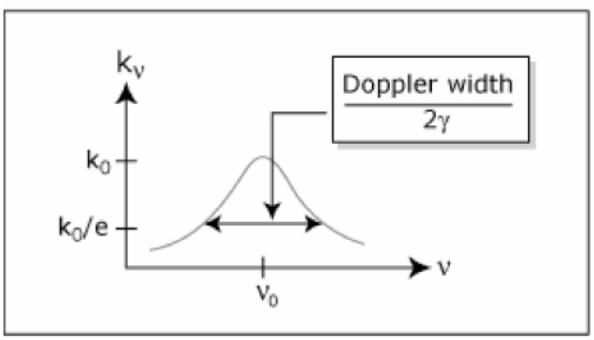


(recall $a_{i0} = \frac{1}{4\pi\tau_{i0}}$)

↑ (Δt)

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

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



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

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

(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

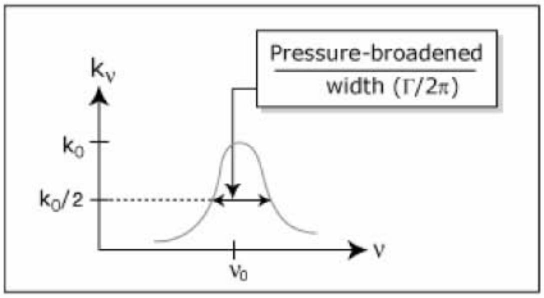
Collision freq.(sec^{-1}) in a 2-component gas (m_1, r_1, n_1 and m_2, r_2, n_2) is:

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

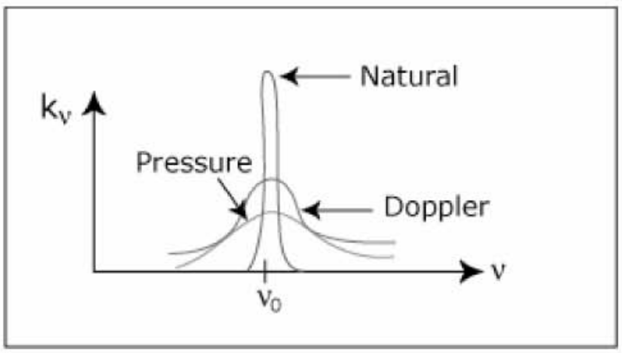
i.e. $\Gamma = \Gamma_0$ (1 atm, 273K) $P^{\bar{\alpha}}\, T^{-\bar{\beta}}$ $\left(\bar{\alpha} \simeq 1,\ \bar{\beta} \simeq \frac{1}{2}\right)$ $(P = nKT)$

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

$\left(k_0 = 4S_{i0}/\Gamma\right)$



(d) Summary



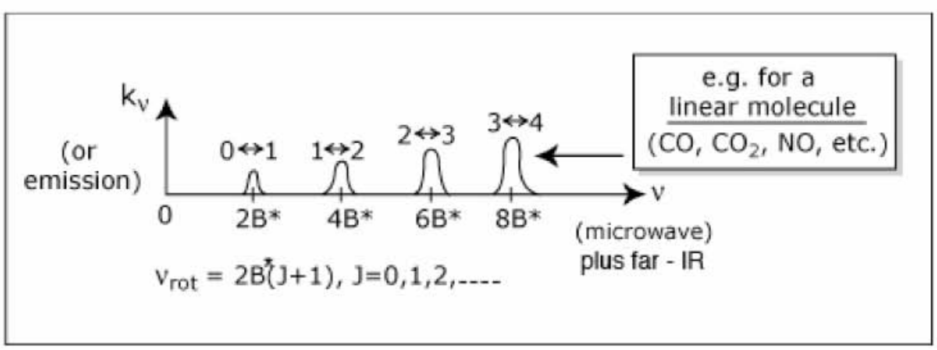
If $_{\text{increase}}$T: Natural → Doppler

If $_{\text{increase}}$P: Doppler → Pressure

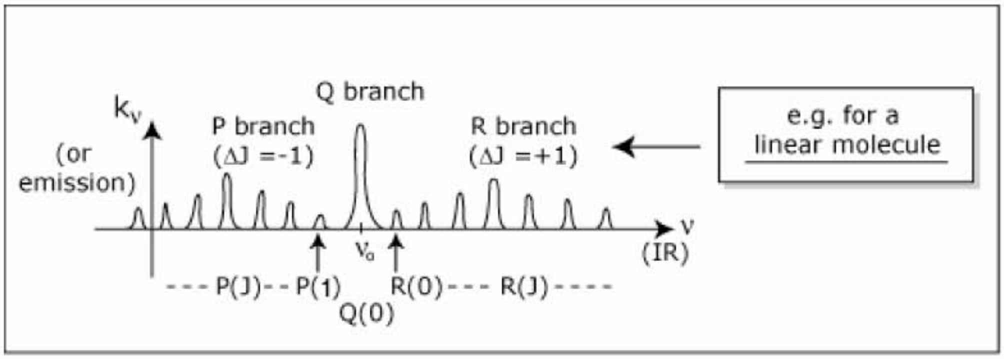
Absorption bands

Can get rotational, vibrational, and electronic transitions together:

(a) <u>rotational bands</u> (e.g. H_2O) – due to $\Delta J = \pm 1$



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



rotn. rise + vibn. rise

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

rotn. fall + vibn. rise

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

(c) electronic – vibration – rotation bands