

4.7.3. Molecular electronic transitions

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Finally, we move to the completely general transition $a = \{s, v, k, m_k\} \rightarrow b = \{s', v', k', m_{k'}\}$ $s \neq s'$ involving different electronic states.

The matrix element

$$D_{ba} = \langle \psi_b | \vec{D} | \psi_a \rangle = \langle v' k' m_{k'} | \langle s' | \vec{D} | s \rangle | v k m_k \rangle \\ = \hat{D}_{s's}(\vec{R})$$

Where we have used the electronic transition matrix element for nuclear position \vec{R}

$$\hat{D}_{s's}(\vec{R}) = \int d\vec{r}_1 d\vec{r}_2 \dots \left(e \left(\sum_i Z_i \vec{R}_i - \sum_j \vec{r}_j \right) \right) \quad (4.30)$$

As with permanent dipoles before, we can expand this around the equilibrium position

$$\hat{D}_{s's}(\vec{R}) = \hat{D}_{s's}(\vec{R}_0) + \frac{\partial}{\partial \vec{R}} \hat{D}_{s's} \Big|_{\vec{R}_0} (\vec{R} - \vec{R}_0)$$

For simplicity take first term only (often not enough)
 \Rightarrow (similar to (4.27))

$$D_{ba} = \underbrace{\left(\int_0^\infty F_{v',v}^{*s'}(R) F_v^s(R) dR \right)}_{\text{FCF}_{v',v}^{s',s}} \underbrace{\left(\int \mathcal{Y}_{k'm_{k'}}^*(\theta, \varphi) \hat{D}_{s's}(\vec{R}_0) \mathcal{Y}_{k m_k}(\theta, \varphi) d\Omega \right)}_{\substack{\text{electronic} \\ \text{matrix-element}}} \quad (4.31)$$

angular factor, angular momentum

• Electronic transitions are accompanied by vibrational and rotational transitions

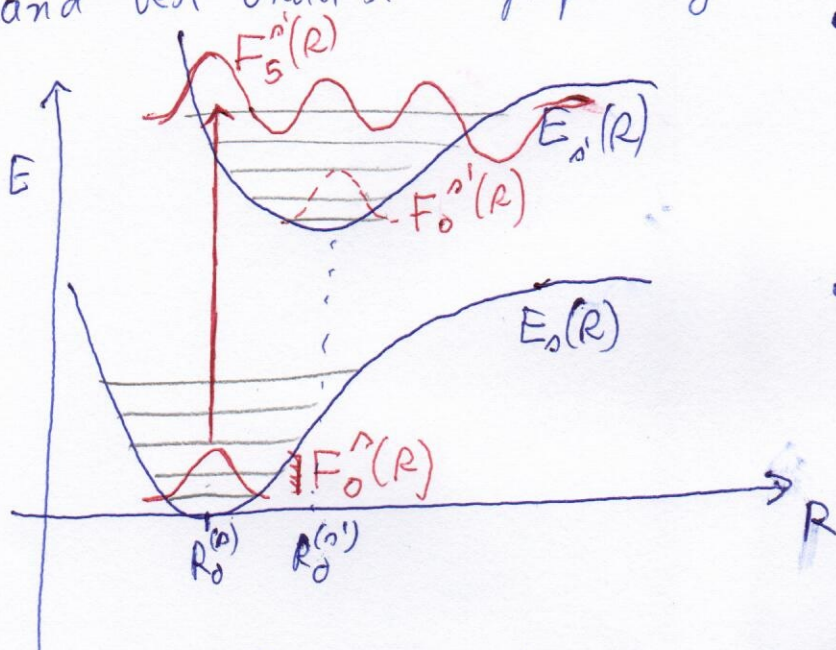
• these obey the usual selection rules (4.7.1) / (4.7.2) due to second term

• Note the FCF is non-zero since $s \neq s'$, so $F_{v',v}^{s',s} \leftrightarrow F_v^s$ are not (necessarily) orthogonal despite $v' \neq v$.

• $\hat{D}_{s's}(\vec{R}_0)$ gives rise to additional electronic selection rules in terms of $g/u, \Lambda, +/-$ etc. [see books]

Excitation of vibrations due to electronic excitation

These are ~~best~~ described by the Franck-Condon Factor, and best understood graphically:



- PO surfaces s, s' are in general shifted, with different equilibrium position $R_0^{(s)}$ and $R_0^{(s')}$

- FCF measures overlap between initial and final vibrational states

- electronic excitation instantaneous $\Rightarrow F_n(\vec{R})$ unchanged (nuclei static) but later they slowly start to vibrate.

- Here no longer $\Delta v = 1$

- this combination of electronic and vibrational state change is called vibronic transition,

Electronic spectra:

- Since $E_{s'} - E_s \sim \mathcal{O}(\text{eV})$ as in atoms, photon energies for molecular electronic transitions are in the visible/UV part of the elm spectrum

- Photon frequencies are

$$\nu = \frac{(E_{s'} + E_{v'} + E_{k'}) - (E_s + E_v + E_k)}{h}$$

(from Eq. (4.1))

hence

$$\nu = \underbrace{\nu_{s's}}_{\text{large}} + \underbrace{\nu_{v'v} + \nu_{k'k}}_{\text{small}}$$

with e.g. $\nu_{s's} = \frac{E_{s'} - E_s}{h}$ etc.

- Spectrum has appearance of bands and band systems (many bands) for each electronic transition, see next example

4.7.4 Raman scattering / Raman spectra

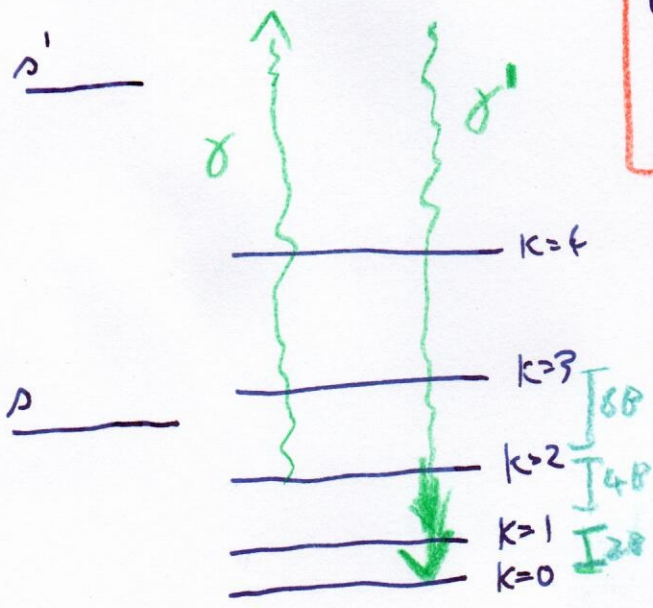
Our discussion of light scattering by atoms in section 3.4 applies largely to molecules as well.

Due to the large number and close energy spacing of rotational and vibrational energy levels in molecules, it is much more common to have an inelastic scattering process than in atoms.

$$\omega, \vec{k} \quad |a\rangle \longrightarrow |b\rangle \quad \omega', \vec{k}'$$

Molecules also naturally occur in rotationally excited states

• Raman-selection rule:
 $\Delta K = \pm 2, 0$ ($\Delta K = \pm 1$ each transition, see (4.24))
 (4.32)



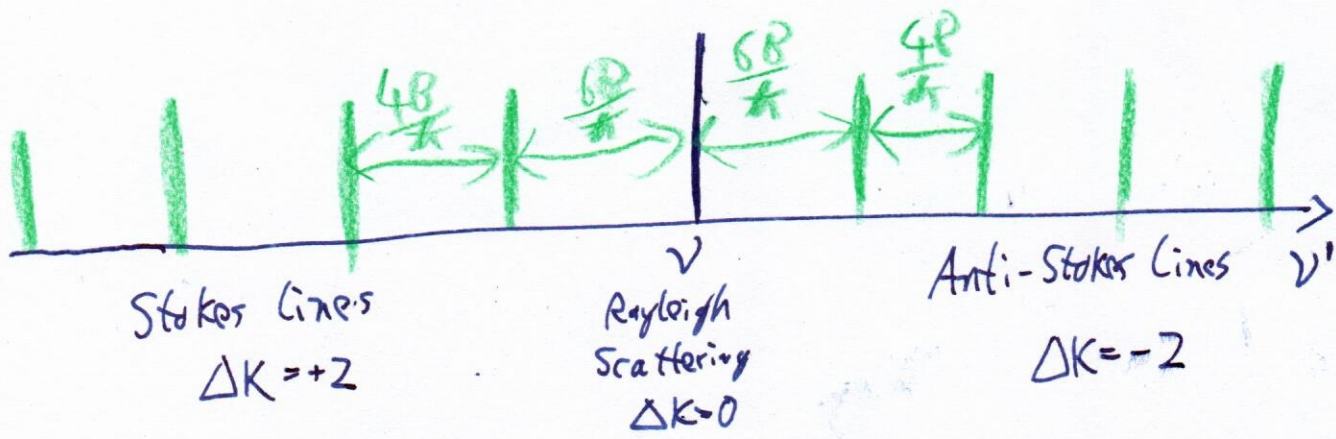
$$E_{rot} = \frac{h^2}{2I} K(K+1)$$

$\Delta K = -2$ in example
 $\Rightarrow \Delta E = 6B$

Let us assume we scatter light at frequency ν off a molecule, the scattered light has the following spectrum:

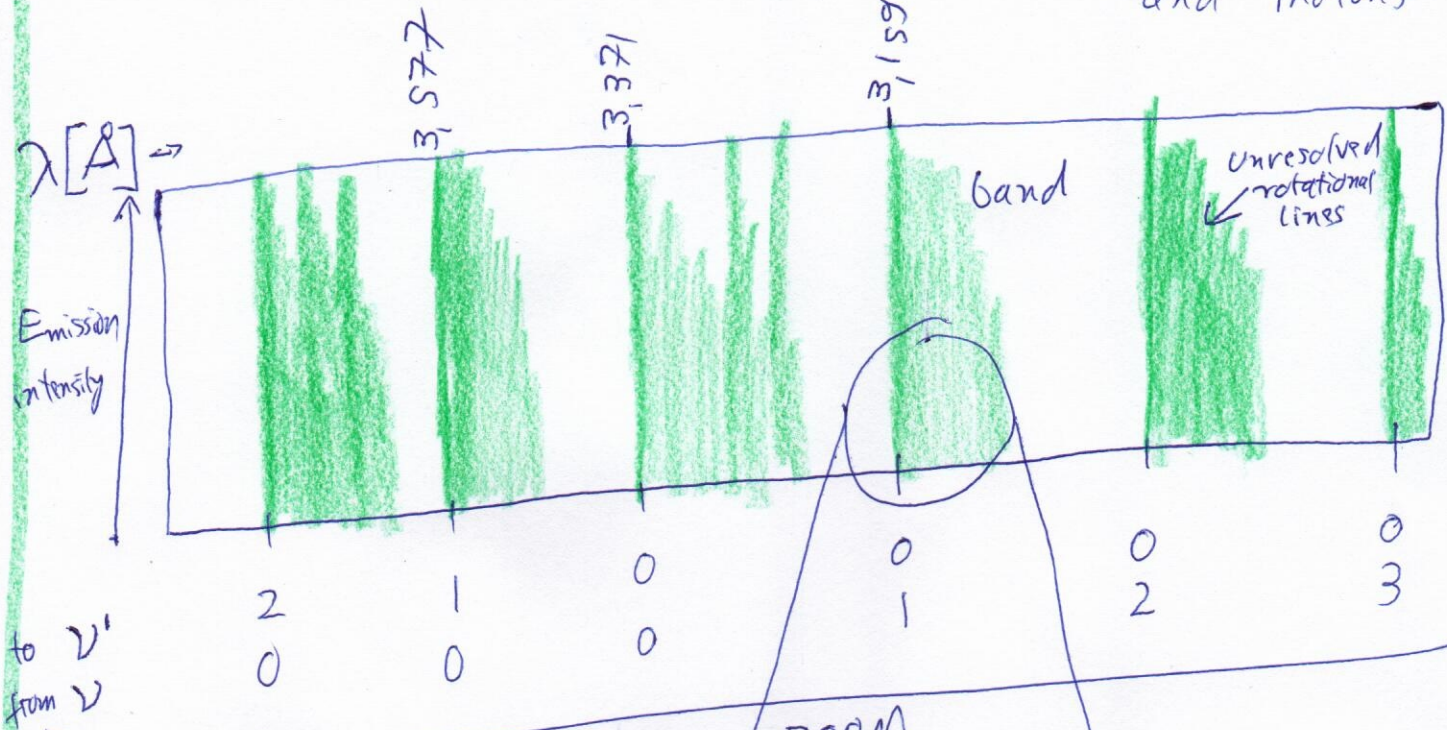
Raman spectrum of molecule

all $\Delta K = -2$ multi-lines are because level spacing is not constant with K



Example:

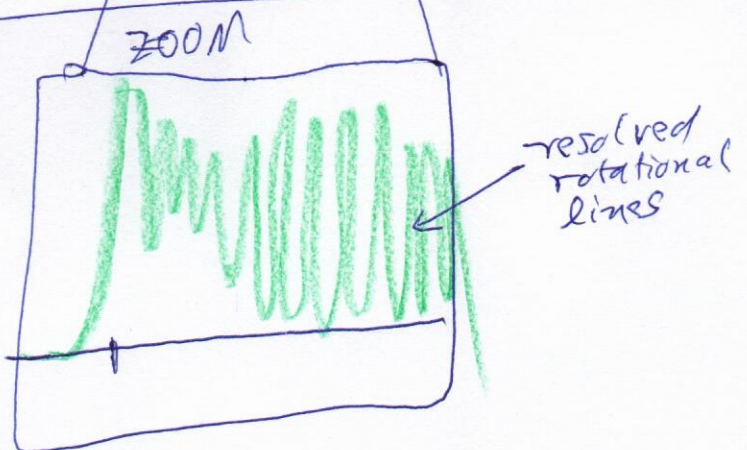
Molecular spectrum of N_2 , near $3\Pi_u \rightarrow 3\Pi_g$ transition. (taken from "Demtröder - Atoms, Molecules and Photons")



band-system

- asymmetric band spacing up vs. down Δv , due to n.n.ecc. equal f_{00} on s and s' .

- Rot lines not equally spaced (as expected from (4.25)) since I depends on K



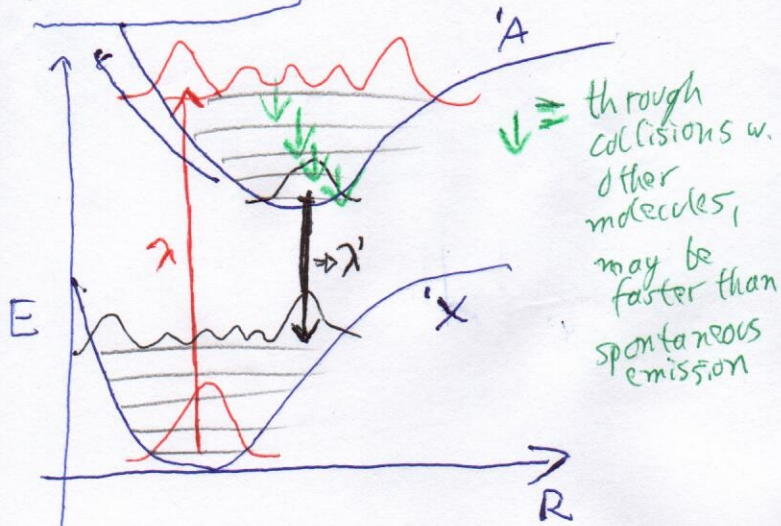
4.7.5 Fluorescence and Phosphorescence:

We can use the ~~phenomena~~ Franck-Condon principle illustrated on p. 80 to also understand the phenomena

Fluorescence: molecule absorbs at λ but emits at $\lambda' > \lambda$ (e.g. UV to visible, shirt glows when exposed to UV)

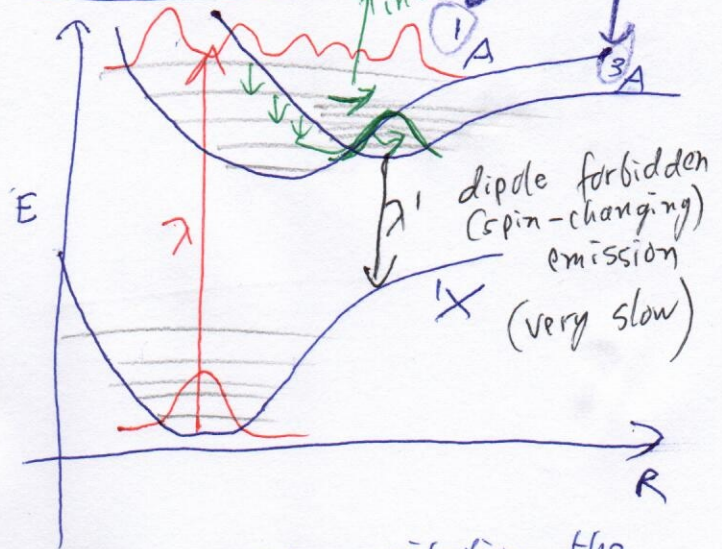
Phosphorescence: Same as fluorescence, but strongly delayed so that molecule continues to emit/glow long (seconds) after excitation (material) (light source is removed)

Fluorescence:



- Franck Condon principle results in excitation e.g. $v=0 \rightarrow v'=5$.
- Molecule then loses vibrations (cools) through collisions.
- Franck Condon principle requires de-excitation e.g. $v'=0 \rightarrow v=5$ at now larger wavelength / smaller energy

Phosphorescence:



- If after excitation the molecule makes a radiationless transition (e.g. via non-adiabatic couplings in Eq. 4.6) to a spin=1 state, the de-excitation can end up dipole forbidden
- this can lead to very long lifetime in the excited state.