

# Week 12

PHY 402 Atomic and Molecular Physics

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## 4.7.3 Molecular electronic transitions

Finally, we move to the completely general transition

$$a = (s, \nu, K, m_K) \rightarrow b = (s', \nu', K', m'_K), \quad (4.41)$$

involving different electronic states with  $s \neq s'$ .

The matrix element is

$$D_{ba} = \langle \psi_b | \hat{\mathbf{D}} | \psi_a \rangle = \langle \nu' K' m'_K | \underbrace{\langle s' | \mathbf{D} | s \rangle}_{\equiv \hat{D}_{s's}(\mathbf{R})} | \nu' K' m'_K \rangle \quad (4.42)$$

Where we have used the

**electronic transition matrix element** for nuclear position  $\mathbf{R}$

$$\hat{D}_{s's}(\mathbf{R}) = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \dots \Phi_{s'}^*(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, \dots) \left( e \left( \sum_i Z_i \mathbf{R}_i - \sum_j \mathbf{r}_j \right) \right) \Phi_s(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, \dots) \quad (4.43)$$

Note that this is still an operator in the space of nuclear wave functions. As with permanent dipole moments before, we can expand the transition dipole moment around the nuclear equilibrium position

$$\hat{D}_{s's}(\mathbf{R}) = \hat{D}_{s's}(\mathbf{R}_0) + \left. \underline{\underline{\nabla D_{s's}}} \right|_{\mathbf{R}_0} (\mathbf{R} - \mathbf{R}_0) \quad (4.44)$$

For simplicity let us now take the first term only (even though this is often not quite accurate enough). We then define

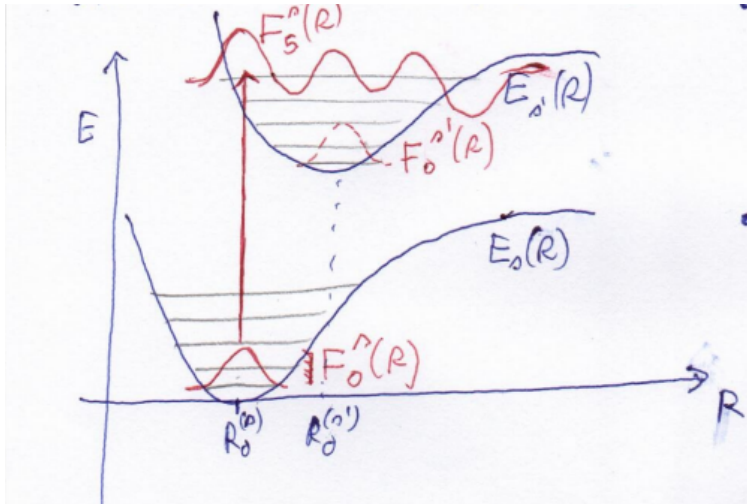
### Franck-Condon factors and molecular transition dipole matrix elements

$$D_{ba} = \underbrace{\left( \int_0^\infty F_{\nu'}^{*s'}(R) F_{\nu}^{*s}(R) \right)}_{\substack{= FC F_{\nu'\nu}^{s's} \\ \text{Franck-Condon factor}}} \underbrace{\left( \int \mathbf{H}_{K'm_{K'}}^*(\theta, \phi) \hat{D}_{s's}(\mathbf{R}_0) \mathbf{H}_{K'm_K}(\theta, \phi) d\Omega \right)}_{\substack{\text{electronic matrix-element} \\ \text{angular factor, angular momentum}}} \quad (4.45)$$

- We only could take out the Franck-Condon factor as a pre-factor because we had approximated  $\hat{D}_{s's}(\mathbf{R})$  in Eq. (4.43) as a constant in  $R$ .
- Electronic transitions are typically accompanied by vibrational and rotational transitions.
- Rotations obey the usual selection rules, discussed in section 4.7.1 and section 4.7.2, due to the second term.
- Vibrations are governed by the Franck-Condon factor. Note the FCF is non-zero since  $s \neq s'$ , and hence  $F_{r'}^{s'}$  and  $F_r^s$  are not (necessarily) orthogonal even if  $\nu' \neq \nu$ .
- $\hat{D}_{s's}(\mathbf{R}_0)$  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 described by the Franck-Condon factor, and best understood graphically:



left: Sketch illustrating FCF

- BO surfaces  $s, s'$  are in general shifted, with different equilibrium position  $R_0^{(s)}$  and  $R_0^{(s')}$ .
  - FCF measure overlap between initial and final vibrational states.
- electronic excitation is instantaneous  $\implies$  The nuclear wave-function  $F(\mathbf{R})$  remains unchanged during the transition (the nuclei are static) but later they can slowly start to vibrate.

- The FCF can be thought of as re-expressing the (unchanged) initial vibrational state  $\nu$  for electronic state  $s$  in the new vibrational basis for electronic state  $s'$ .
- For electronic transitions we now no longer have  $\Delta\nu = 1$ . Instead the most likely  $\Delta\nu$  is the one that has the largest overlap between the initial and final vibrational wave functions. In the “Sketch illustrating FCF”, for an initial  $\nu = 0$ , the most likely final state would be  $\nu' = 5$ , because that places the large outer lobe of the  $\nu' = 5$  oscillator state on the upper surface into the same space like the ground state on the lower surface.
- This combination of electronic and vibrational state change is called vibronic transition.

### Electronic Spectra:

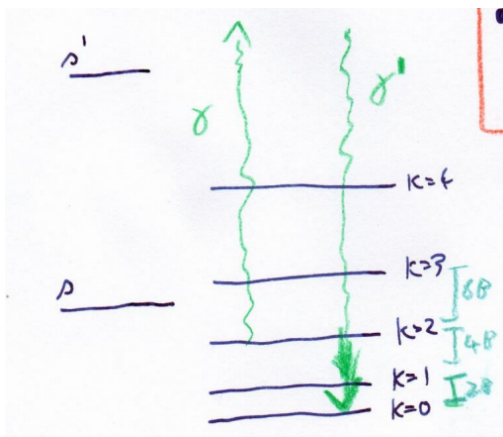
- Since  $E_{s'} - E_s \sim \mathcal{O}(eV)$  as in atoms, photon energies for molecular electronic transitions are in the visible/UV part of the electromagnetic spectrum.
- Photon frequencies are  $\nu = \frac{(E_{s'} + E_{\nu'} + E_{K'}) - (E_s + E_\nu + E_K)}{h}$ , from Eq. (4.27). hence
- $\nu = \underbrace{\nu_{s's}}_{large} + \underbrace{\nu_{\nu'\nu} + \nu_{K'K}}_{small}$  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 3.6 largely applies 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 in-elastic scattering process than in atoms:

$$\overset{\gamma}{\rightsquigarrow} \omega, \mathbf{k}, |a\rangle \rightarrow |b\rangle, \overset{\gamma'}{\rightsquigarrow} \omega', \mathbf{k}' \quad (4.46)$$

Molecules also naturally are already in rotationally excited states at room temperature, so that the final state can frequently even have a lower energy than the initial one.



left: Sketch illustrating a Raman transition, governed by

**Raman-selection rule**

$$\Delta K = \pm 2, 0. \quad (4.47)$$

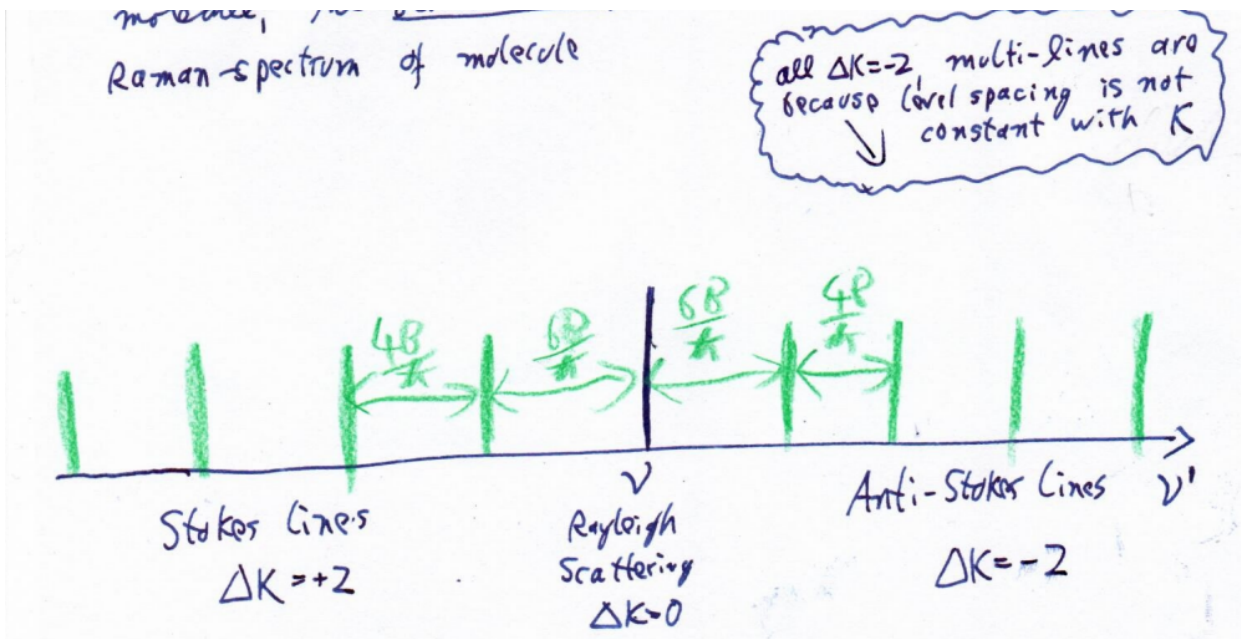
Since we have two subsequent transitions and the rule  $\Delta K = \pm 1$  for each of those, see Eq. (4.34).

$$E_{rot} = \frac{\hbar^2}{2I} K(K+1) \quad (4.48)$$

$= B$

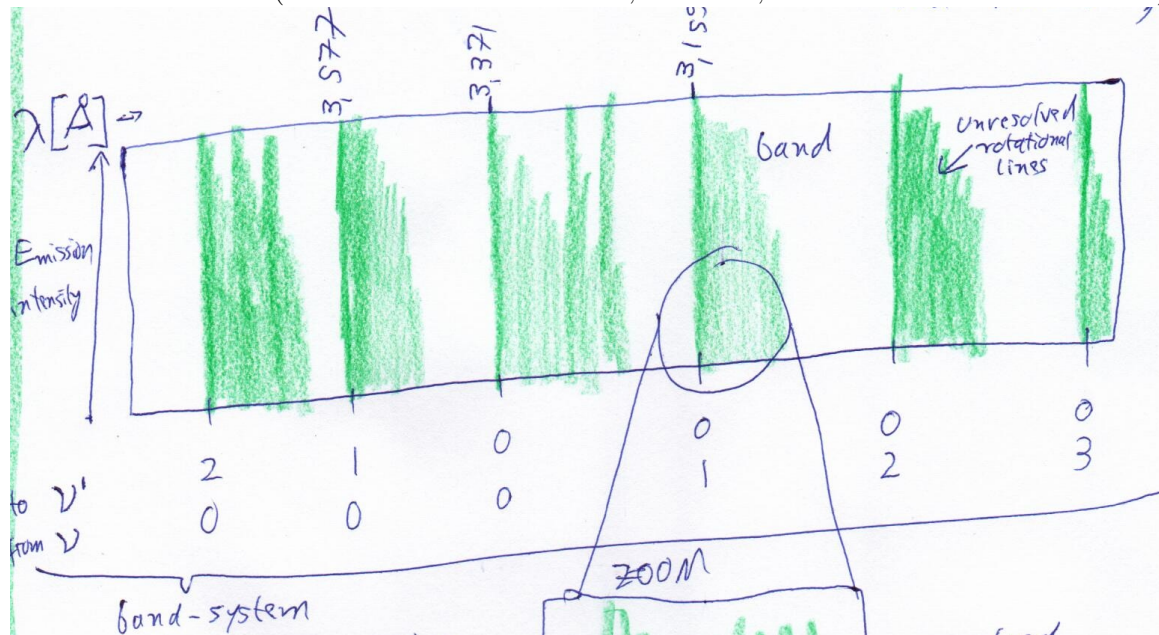
$\Delta K = -2$  in the example, hence  $\Delta E = 6B$ .

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

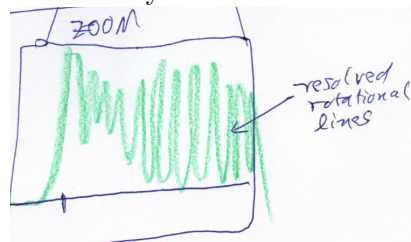


Clarification of inset: All lines besides the central one correspond to a fixed change of angular momentum by  $|\Delta K| = 2$ . However we still get multiple lines, since the rotational level spacing grows roughly quadratic in  $K$ .

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



We can zoom into the band system shown above, to see the details of a single band with individually resolved rotational lines, seen below

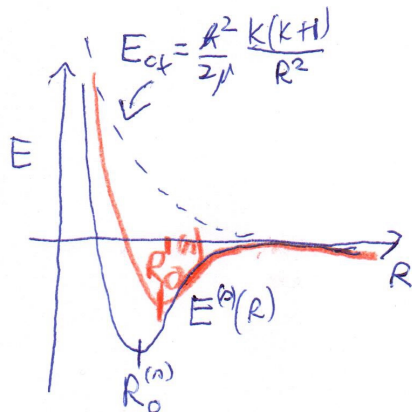


left:

- asymmetric band spacing up vs. down  $\Delta\nu$ , due to the not necessarily equal  $\hbar\omega_0$  on  $s$  and  $s'$ .
- rotational lines are not equally spaced, as expected from Eq. (4.35), since  $I$  does actually depend on  $K$ .

### 4.7.5 Coupling between rotations and vibrations

See book “Demtröder, Atoms, Molecules and Photons” for (too many) more details.



left: Sketch for rotation-vibration coupling:

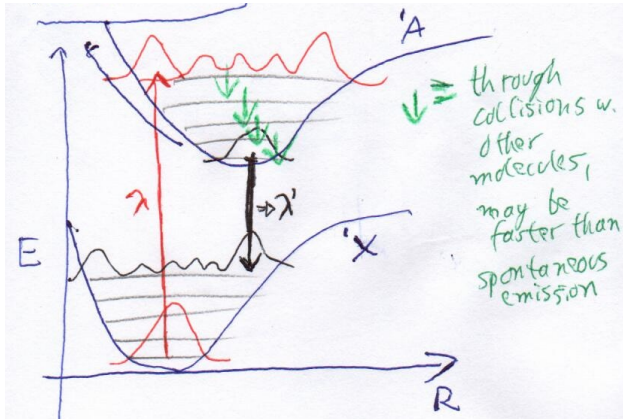
- For large rotations  $K$ , we need to fully include the centrifugal potential  $E_{cf} = \hbar^2 K(K+1)/(2\mu R^2)$  in Eq. (4.24).
  - This causes an effective outwards shift of the basic BO surface (blue) towards larger separations (red), with then a larger equilibrium separation  $R_0'^{(s)} > R_0^{(s)}$ .
  - This is called centrifugal distortion.
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- The discussion so far in week 12 and week 11 allowed a completely independent treatment of electronic energies, vibrations and rotations. This crucially hinges on the replacement  $R \rightarrow R_0$  above Eq. (4.25) and the harmonic approximation used for Eq. (4.26).
  - In reality an increase of angular momentum (rotation) causes a shift of the equilibrium position  $R_0^{(s)} \rightarrow R_0'^{(s)}$ , see figure. This is due to the centrifugal force pulling the nuclei apart. This has the following effects:
    - (i) For large  $K$  rotational energies deviate from Eq. (4.25) since the moment of inertia changes due to the stretch.
    - (ii) A sudden increase in rotation  $K$  may in turn excite vibrations, since the equilibrium position is shifted.
    - (iii) A sudden increase in vibration  $\nu$  towards the anharmonic part may in turn change the rotation state, since the mean separation of nuclei and hence moment of inertia is changed.

### 4.7.6 Fluorescence and Phosphorescence

We can use the Franck-Condon principle illustrated earlier to also understand the phenomena:

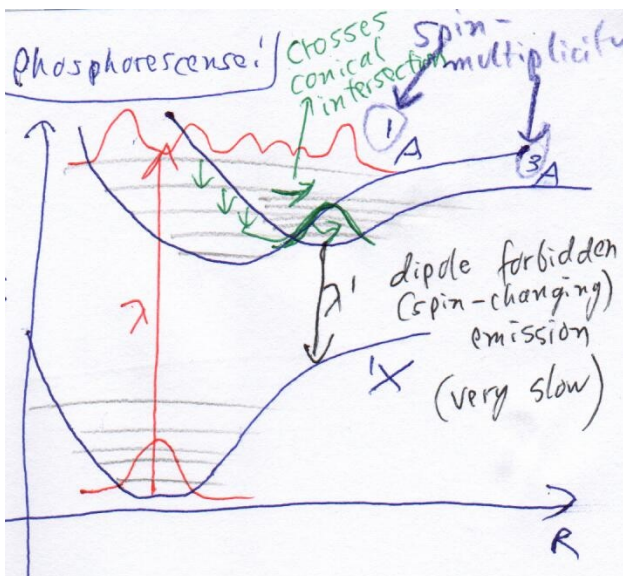
**Fluorescence:** Molecule absorbs at  $\lambda$  but emits at  $\lambda' > \lambda$  (e.g. UV to visible, shirt glows when exposed to UV).

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



left: Fluorescence:

- Franck-Condon principle results in excitation to higher vibrational state, e.g.  $\nu = 0 \rightarrow \nu' = 5$ .
- Molecules then relaxes to lower vibrational states (cools down) through collisions with other molecules (green arrows).
- Franck-Condon principle final requires de-excitation at a position with a much reduced electronic energy gap as shown by the black arrow and hence much larger wave length. (In the example shown  $\nu' = 0 \rightarrow \nu = 5$ )



left: Phosphorescence:

- If after excitation the molecule makes a radiationless transition (e.g. via non-adiabatic couplings in Eq. (4.6)) to another spin state, the de-excitation can end up being dipole forbidden (since elm radiation does not change the spin).
- This can lead to very long lifetime in the excited state and hence much delayed spontaneous emission of the photon.