

Atomic and Molecular Transitions

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Atomic and Molecular Transitions

- Not all radiative transition between different quantum state are allowed.
- This arises from the integral for R^2 .

$$R^2 = \left| \int \psi_i \vec{\mu} \psi_j dV \right|^2$$

- Both the value of the dipole moment and the overlap between the wave functions of the two states determine how strong the transition will be.



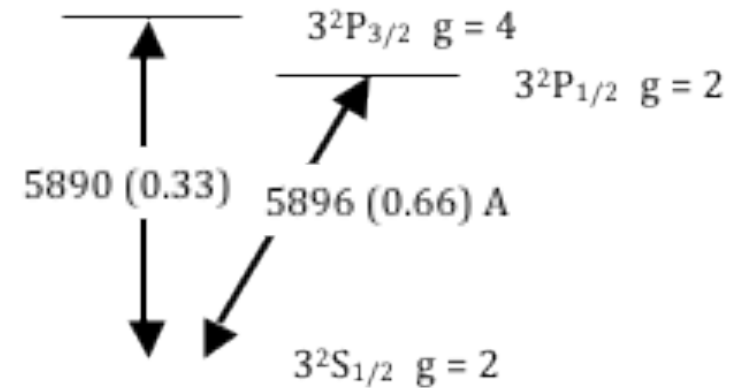
Selection Rules

- This leads to the concept of selection rules.
- If the Einstein coefficients are reasonably large, the transition is said to be “allowed”.
- Otherwise it is “forbidden.”



Atomic Transitions

- There is no restriction on the change in principle quantum number
- However $\Delta L = 0$ or ± 1
 $\Delta l = \pm 1$
 $\Delta J = 0$ or ± 1
- Furthermore transition between two states with $J = 0$ are forbidden.



Molecular Transitions

- Because of Born-Oppenheimer

$$\psi = \psi_e \psi_v \psi_r$$

- the transition probability can be written

$$R^2 = \left| \int \psi'_e \psi'_v \vec{\mu} \psi''_e \psi''_v dV \int \psi'_r \psi''_r dV \right|^2$$



Rotational Transitions

- When electronic and vibrational states don't change

$$R^2 = \left| \int R_e(r) \psi_v^2(r) dr \int \psi_r' \psi_r'' dV \right|^2$$

- A transition will be possible only if the permanent electric dipole moment is non-zero:

$$R_e = \int \psi_e' \mu_e \psi_e'' dV$$



Rotational Selection Rules

- The rules are determined by the rotational overlap integral

$$\int \psi_r' \psi_r'' dV$$

- This leads to the rule $\Delta J = \pm 1$ for the rigid rotator so that lines appear at

$$\sigma(J', J'') = B_e \{J'(J' + 1) - J''(J'' + 1)\}$$



Ro-Vibrational Transitions

- For ro-vibrational Transitions

$$R^2 = \left| \int \psi'_v R_e(r) \psi''_v(r) dr \int \psi'_r \psi''_r dV \right|^2$$

- Because the wave functions are orthogonal, the first integral disappears unless R_e is a function of r . If we expand R_e in a power series so that

$$R_e(r) \cong R_e(r_0) + \frac{\partial R}{\partial r}(r - r_0) + \dots$$



Ro-Vibrational Transitions

- Then

$$R^2 \cong \left| \frac{\partial R}{\partial r} \int \psi_v'(r - r_e) \psi_v'' dr \int \psi_r' \psi_r'' dV \right|^2$$

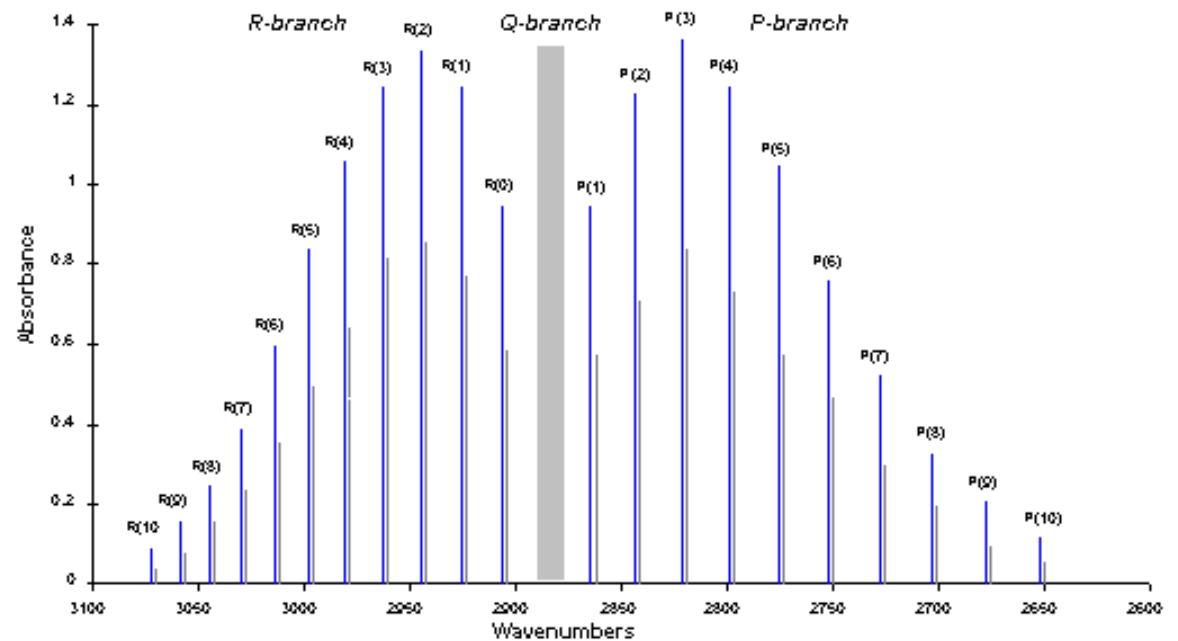
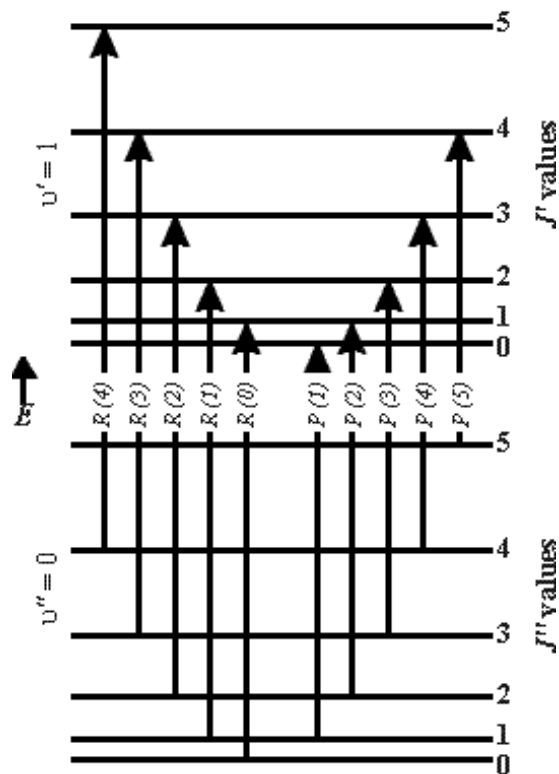
- For a harmonic oscillator the first term is zero except for $\Delta v = \pm 1$ so the transitions are at

$$\sigma = \sigma_0 + B' J'(J' + 1) - B'' J''(J'' + 1)$$

$$\sigma_0 = G(v') - G(v'')$$

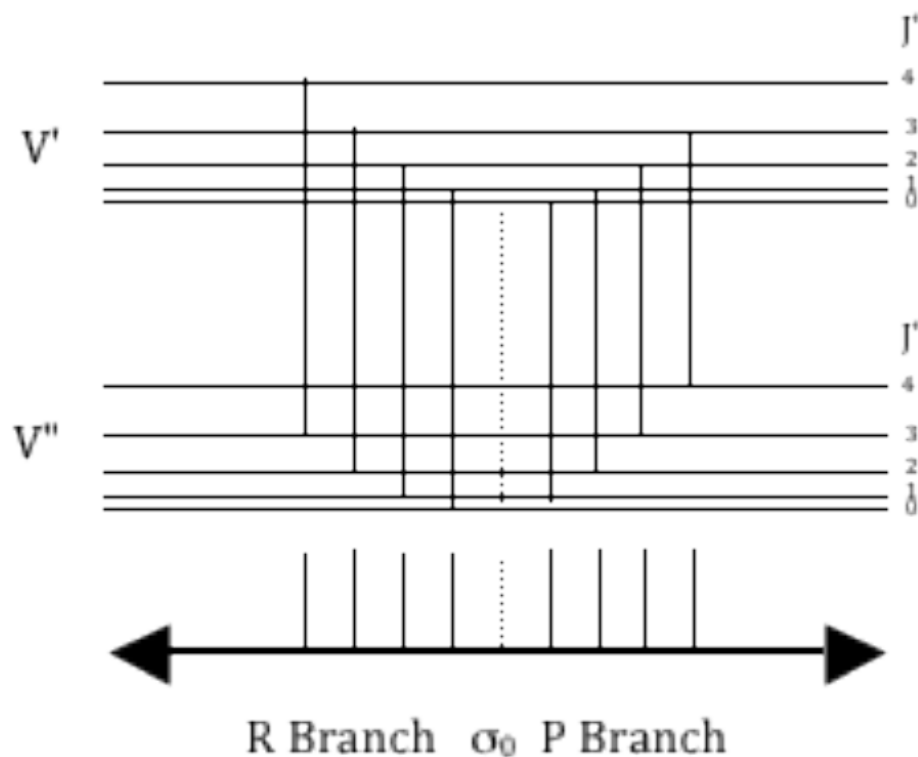
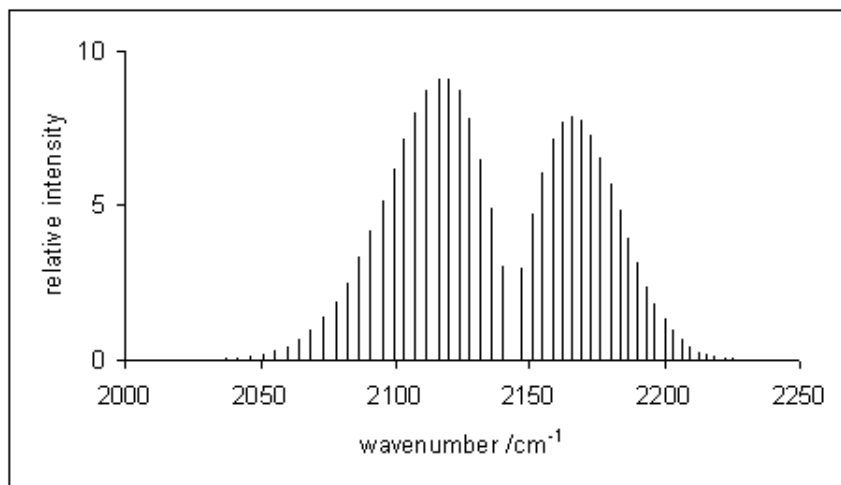


Typical Ro-vibrational Spectra



Ro-Vibrational Transitions

- The rotational overlap integral allows for $\Delta J = \pm 1$
- The two possibilities for change in J are called the
 - R branch: $J' = J'' + 1$
 - P branch: $J' = J'' - 1$

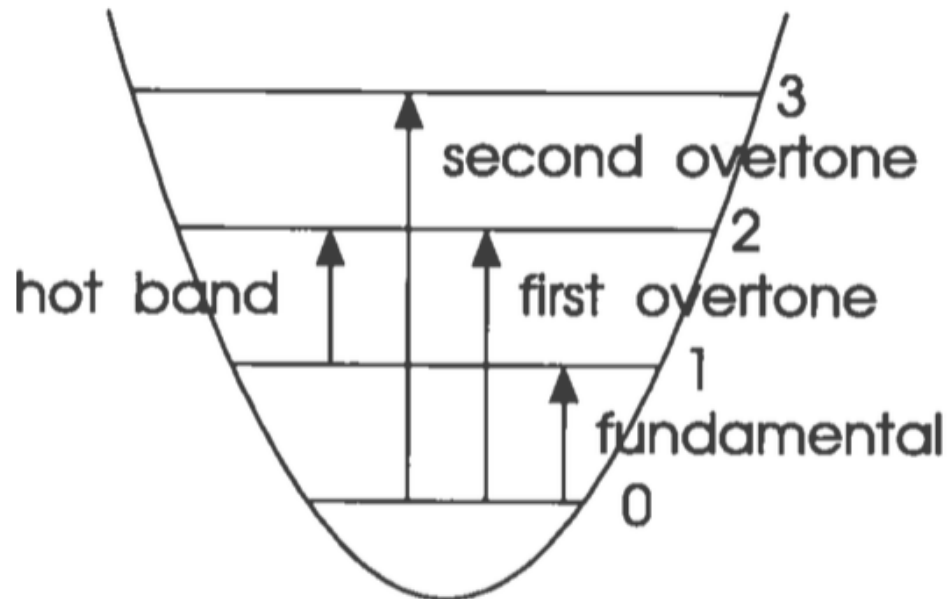
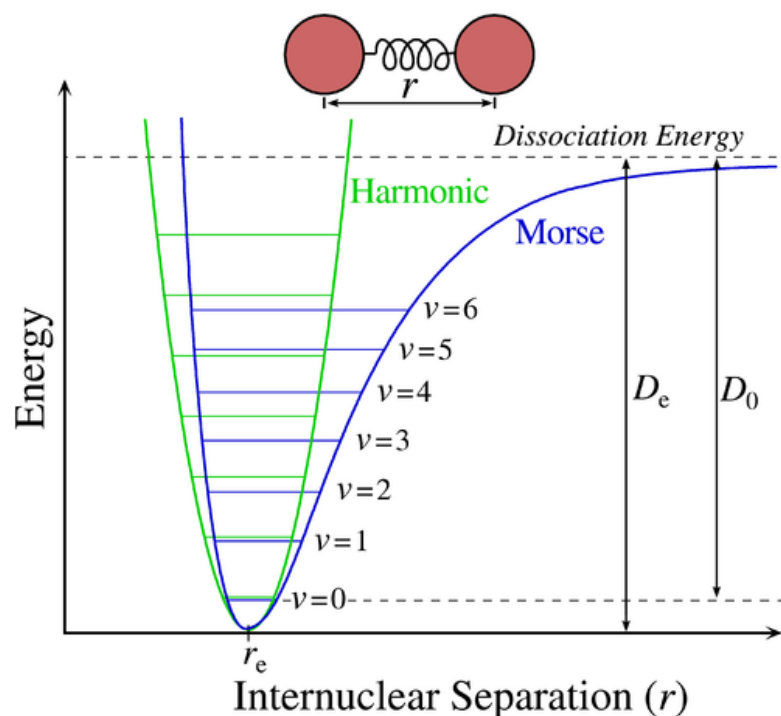


Ro-Vibrational Transitions

- For an anharmonic oscillator, the vibrational overlap integral allows

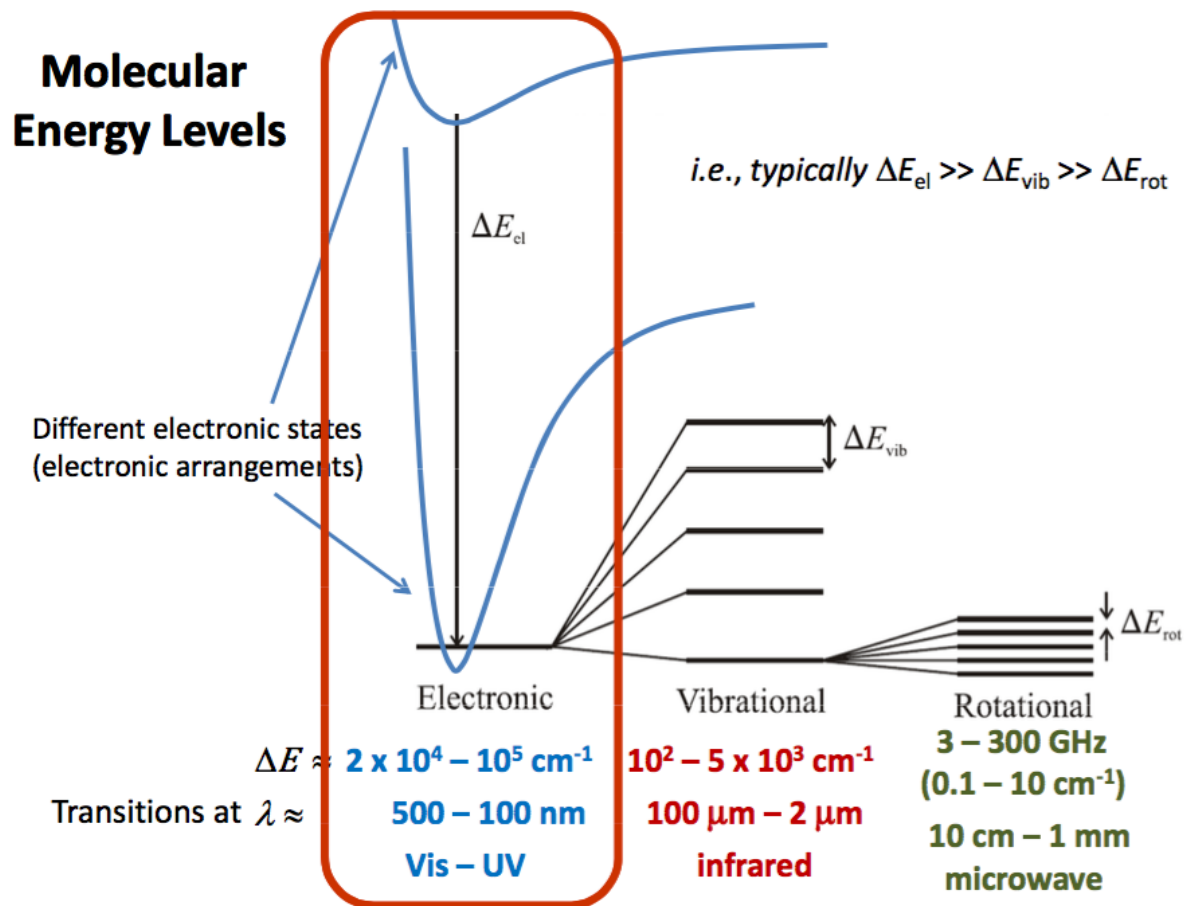
$$\Delta v = \pm 1, \pm 2, \pm 3, \dots$$

- This leads to additional series of branches



Electronic Transitions

- Electronic state changes too.
- Transition rules are relaxed, leading to additional possibilities.



Electronic Transitions

- The transition probability can be written

$$R^2 = \left| \int \psi'_v R_e(r) \psi''_v(r) dr \int \psi'_r \psi''_r dV \right|^2$$

- where $R_e(r) = \int \psi_e' \mu \psi_e'' dV$



Electronic Transitions

- R_e does not vary strongly with r , so one can often approximate the transition probability as

$$R^2 = R_e^2(\bar{r}_{v'v''})q_{v'v''}S_{J'J''}$$

- The Franck-Condon Factor

$$q_{v'v''} = \left| \int \psi_{v'}' \psi_{v''}'' dV \right|^2$$

- Line Strength Factor

$$S_{J'J''} = \left| \int \psi_r' \psi_r'' dV \right|^2$$



Electronic Transitions

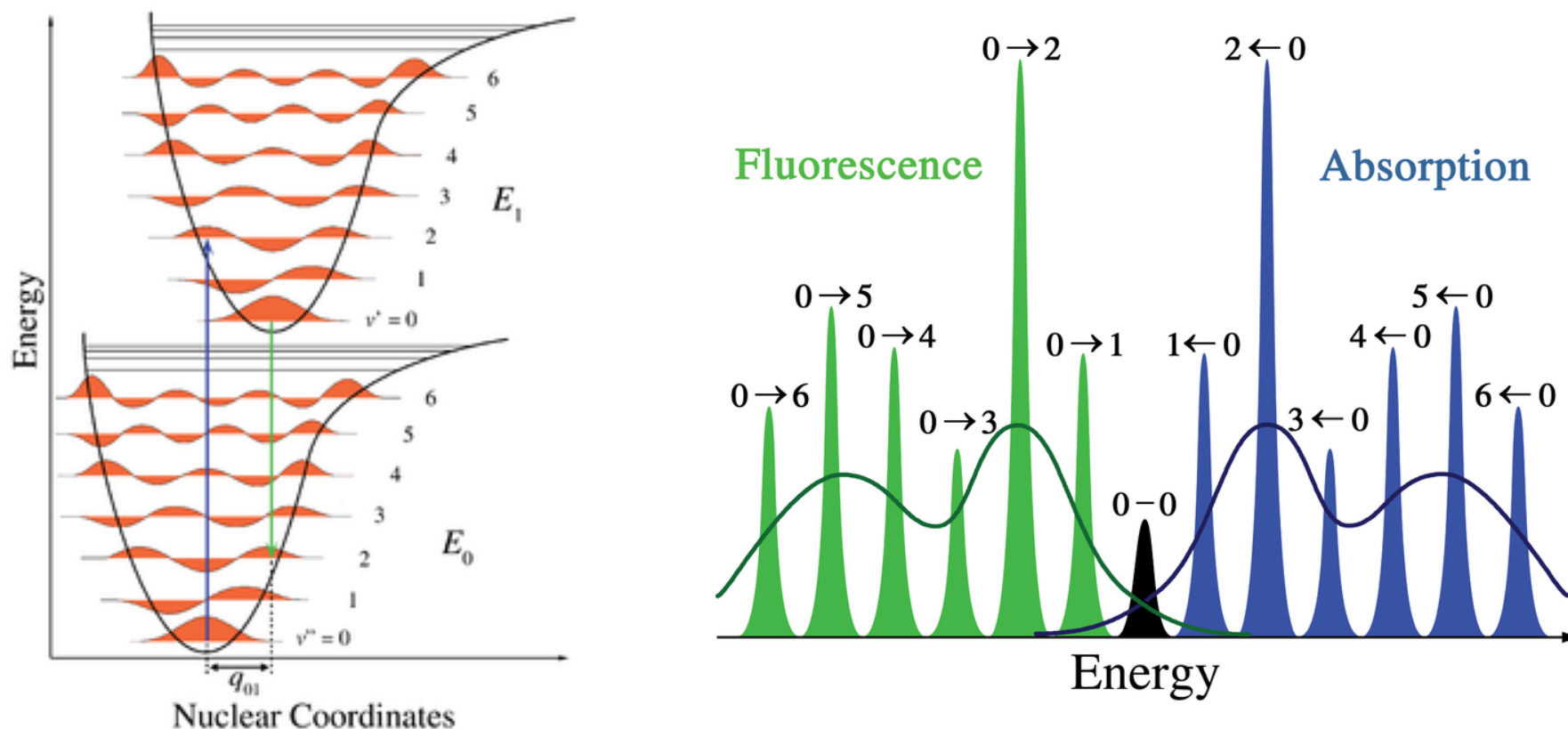
- The electronic selection rules depend on the integrals

$$\Delta\Lambda = 0, \pm 1 \quad \Delta S = 0$$

- Depending on spin-orbit coupling other rules may apply.



Franck-Condon Principle

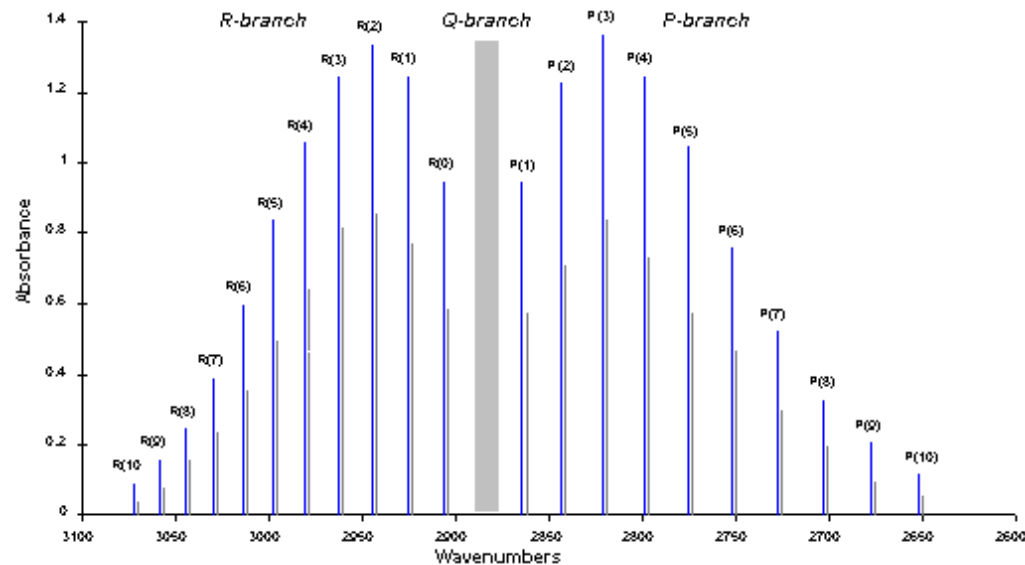


The Franck-Condon factor will be a maximum for those cases where maximums in the two wave functions overlap each other.



Electronic Transitions

- For rotation $\Delta J = \pm 1$ holds.
- However, if the orbital angular momentum of either electronic state is non-zero, then $\Delta J = 0$ is allowed which allows for a Q branch.



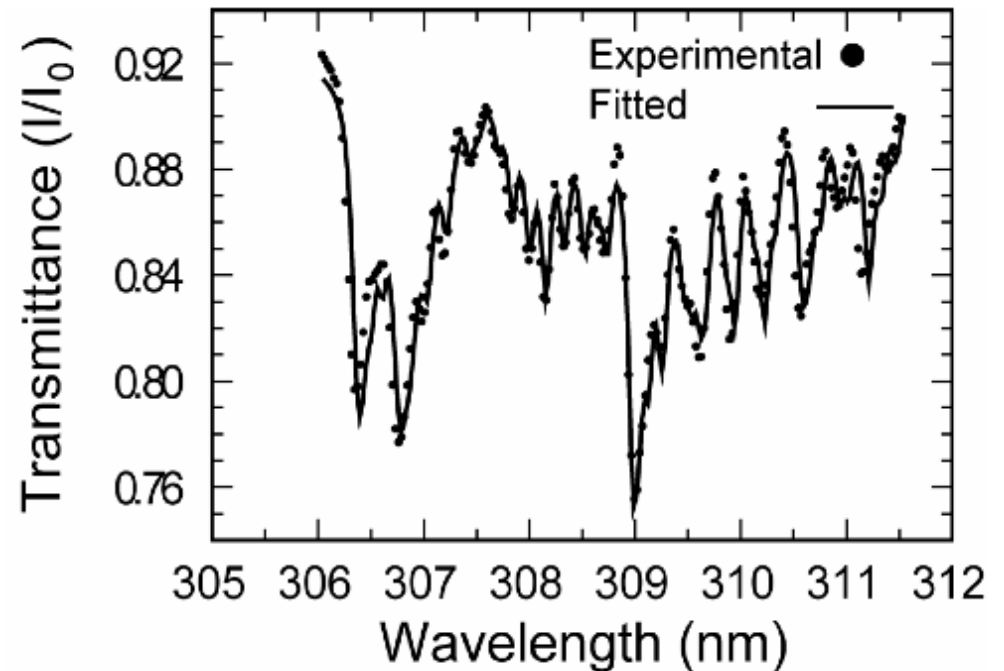
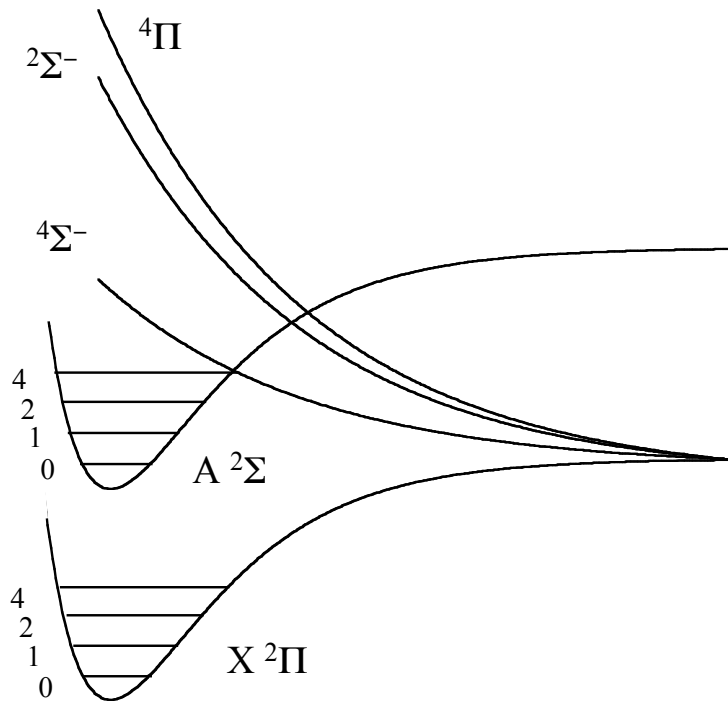
Electronic Transitions

Title	Label	Transition	$S_{J', J''}$ (Emission)
R - Branch	$R(J'')$	$J' = J'' + 1$	$\frac{(J' + \Lambda)(J' - \Lambda)}{J'}$
Q - Branch	$Q(J'')$	$J' = J''$	$\frac{\Lambda^2(2J' + 1)}{J'(J' + 1)}$
P - Branch	$P(J'')$	$J' = J'' - 1$	$\frac{(J' + \Lambda + 1)(J' - \Lambda) + 1}{J' + 1}$



OH Absorption Spectrum

X-A Transitions



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Example includes R1, R2 and Q2 bands.

Additional Branches

- Our simple look is not quite right. Because of non-ideal behavior, other transitions are often allowed.
- Branch labeling for Delta J
 - -3, -2, -1, 0, 1, 2, 3
 - N, O, P, Q, R, S, T



