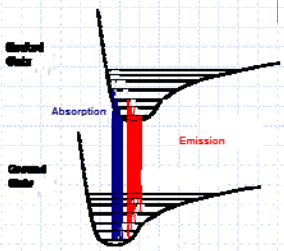
Physical Chemistry

Lecture 26

Electronic Spectroscopy of Diatomic Molecules

Electronic spectroscopy of diatomic molecules

- Two types of spectroscopy
  - Absorption
  - Emission
- Absorption usually occurs only from the ground vibrational state of the ground electronic state
  - Only state populated at usual conditions
- Emission often occurs from many different rovibrational states because of the way the excited state is created
  - Emission spectra often more complex than absorption spectra



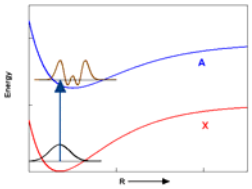
Electronic selection rules

- $\Delta\Lambda = 0, \pm 1$
- $\Delta S = 0$
- Inversion symmetry must change
  - $g \leftrightarrow u$
  - $u \leftrightarrow g$
- Transitions between Σ^+ and Σ^- are forbidden
- Rules are often violated!

Electronic spectroscopy of diatomic molecules

- Energy change in a transition is a sum of changes
  - Electronic
  - Vibrational
  - Rotational
- Franck-Condon principle
  - During an electronic transition, the nuclear centers remain fixed.
  - Estimate intensities by overlap of wave functions

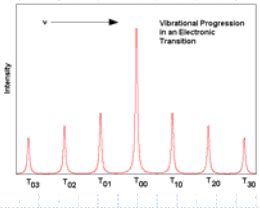
$$\Delta E = \Delta E_{elect} + \Delta E_{vib} + \Delta E_{rot}$$



Electronic transition energies

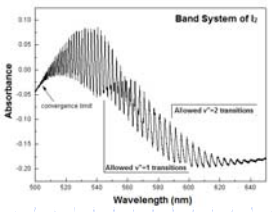
- Use model formulas
- Often neglect rotational transitions
- Vibrational parameters not identical
- Gives a series of transitions for different vibrational changes

$$\Delta E = T_e + \frac{h}{2}(\tilde{\nu}_0'' - \tilde{\nu}_0') + h(n''\tilde{\nu}_0'' - n'\tilde{\nu}_0')$$
$$= T_{00} + h(n''\tilde{\nu}_0'' - n'\tilde{\nu}_0')$$



Electronic spectroscopy of diatomic molecules

- I_2 has many vibrational progressions
- Example: transitions to the ground vibrational state with n' = 0
- Spacing determined by the vibrational parameters of the excited state
- For a harmonic oscillator, the plot is linear
- Curvature indicates need for correction for anharmonicity



$$\frac{\Delta E}{hc} = T_{00} + An + Bn^2$$

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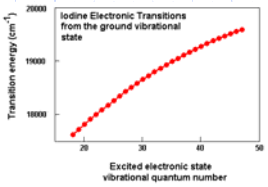
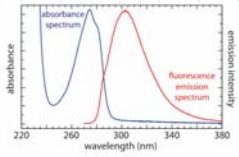
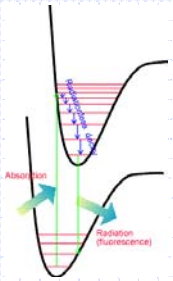


$$\frac{\Delta E}{hc} = T_{00} + An + Bn^2$$

Fluorescence

- Direct return to ground state after excitation
- "Fast" process
- Often involves frequency change due to radiationless decay through the upper manifold of states
- Example: Tyrosine





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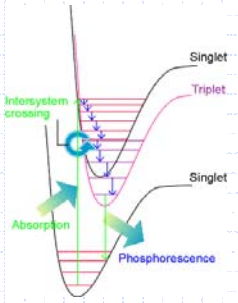
Phosphorescence

- Emission after absorption
  - Intersystem crossing
  - Often singlet-to-triplet change of state
  - Must have low-lying triplet state
    - Example: aromatic molecules
- Persists much longer than fluorescence



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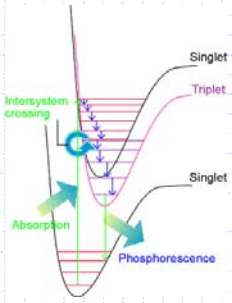
Phosphorescence



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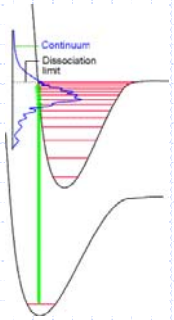
Effect of continuum states

- The spectrum is discrete only if the energy structure is discrete
- Above a certain energy, transitions are into the continuum states
  - Gives a continuous energy absorption as a function of frequency



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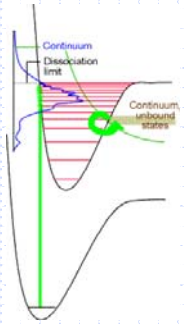
Dissociation and Predissociation

- Unbound states have an effect on spectroscopy
- Absorption that puts the molecule in an unbound state results in dissociation
- Sometimes coupling of an unbound state to a bound state causes the appearance of continuum absorption -- predissociation



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Summary

- Electronic spectroscopy of diatomic molecules is complex
  - Selection rules
    - Spin does not change in a transition, $\Delta S = 0$
    - Angular momentum changes: $\Delta\Lambda = 0$ or ± 1
    - Inversion symmetry must change (for homoatomics)
      - $g \leftrightarrow u$
      - $u \leftrightarrow g$
    - Rules are often violated to some degree
- Fluorescence versus phosphorescence
  - Fluorescence is fast because it is not forbidden.
  - Phophorescence is slow because it involves forbidden transitions.
    - Requires intersystem crossing
- Dissociation may occur after some absorption