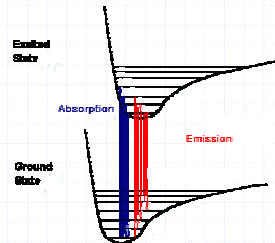


Physical Chemistry

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



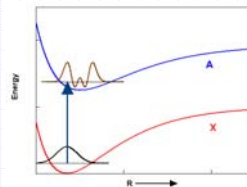
Electronic selection rules

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

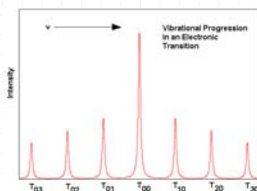
$$\Delta E = \Delta E_{elect} + \Delta E_{vib} + \Delta E_{rot}$$



Electronic transition energies

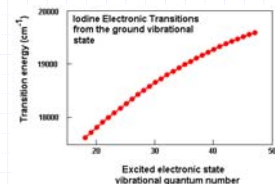
- Use model formulas
- Often neglect rotational transitions
- Vibrational parameters not identical
- Gives a series of transitions for different vibrational changes

$$\begin{aligned} \Delta E &= T_e + \frac{h}{2}(v'_0 - v_0) + h(n'v'_0 - nv_0) \\ &= T_{00} + h(n'v'_0 - nv_0) \end{aligned}$$



Electronic spectroscopy of diatomic molecules

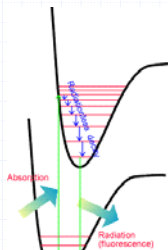
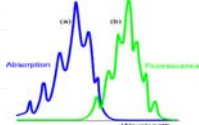
- I_2 has many vibrational progressions
- Example: transitions to the ground vibrational state with $n' = 0$
- Spacing determined by the vibrational parameters of the excited state
- For a harmonic oscillator, the plot is linear
- Curvature indicates need for correction for anharmonicity



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

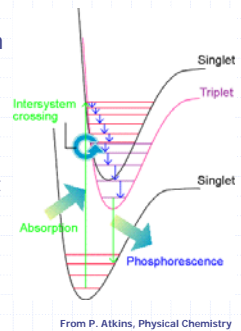
Fluorescence

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



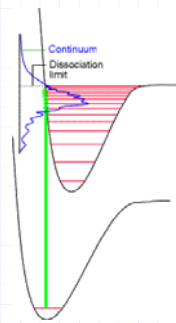
Phosphorescence

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



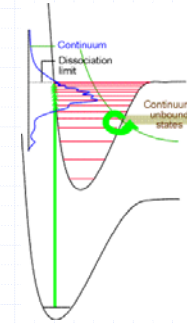
Effect of continuum states

- ◆ 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



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**



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 homonuclear)
 - $g \leftrightarrow u$
 - $u \leftrightarrow g$
 - Rules are often violated to some degree
 - ◆ Fluorescence versus phosphorescence
 - Fluorescence is fast because it is not forbidden.
 - Phosphorescence is slow because it involves forbidden transitions.
 - Requires intersystem crossing
 - ◆ Dissociation may occur after some absorption