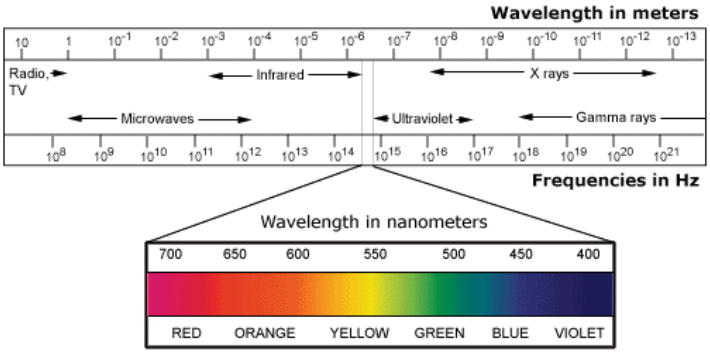
Atmos. Chem. Lecture 4, 9/16/13
Light and Spectroscopy

Why/how do molecules absorb light?

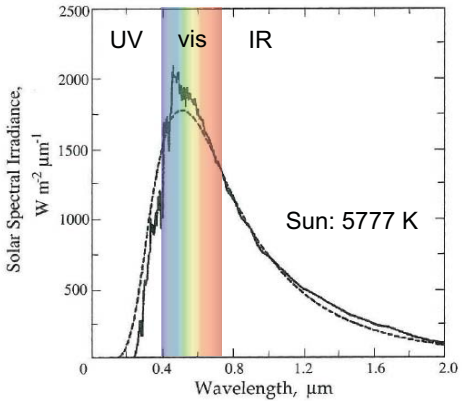
- Light: fundamentals
- Vibrational, rotational, electronic transitions

PSet 1 – due in class 9/25

Electromagnetic spectrum



Blackbody radiation



$$F_B(\lambda) = \frac{2\pi c^2 h \lambda^{-5}}{e^{ch/k_B \lambda T} - 1}$$

$$F_B = \sigma T^4$$

$\sigma = 2/15\ \pi^5\ k^4\ c^{-2}\ h^{-3}$
$= 5.671 \times 10^{-8}\ W\ m^{-2}\ K^{-4}$

S&P

Light and energy

$$E = h\nu = \frac{hc}{\lambda}$$

Average Bond Energies (kJ/mol)

Single Bonds						Multiple Bonds	
H—H	432	N—H	391	I—I	149	C=C	614
H—F	565	N—N	160	I—Cl	208	C≡C	839
H—Cl	427	N—F	272	I—Br	175	O=O	495
H—Br	363	N—Cl	200			C=O*	745
H—I	295	N—Br	243	S—H	347	C≡O	1072
		N—O	201	S—F	327	N=O	607
C—H	413	O—H	467	S—Cl	253	N=N	418
C—C	347	O—O	146	S—Br	218	N≡N	941
C—N	305	O—F	190	S—S	266	C≡N	891
C—O	358	O—Cl	203			C=N	615
C—F	485	O—I	234	Si—Si	340		
C—Cl	339			Si—H	393		
C—Br	276	F—F	154	Si—C	360		
C—I	240	F—Cl	253	Si—O	452		
C—S	259	F—Br	237				
		Cl—Cl	239				
		Cl—Br	218				
		Br—Br	193				

*C=O(CO_2) = 799

Zumdahl, *Chemistry*, 8th ed.

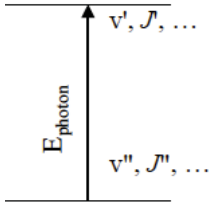
Photochemistry: Absorption of light

$A + h\nu \rightarrow A^*$

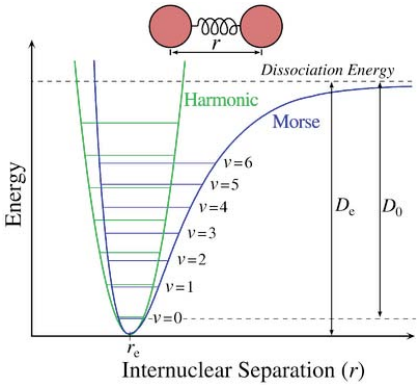
Excited state: vibrational, rotational, electronic

Molecule can absorb radiation efficiently if:

1) The photon energy matches the energy spacing between molecule's quantum levels
2) Optical transition between these quantum levels is allowed by "selection rules" ("forbidden" transitions are weaker)
3) Electronic: overlap between wavefunctions is high



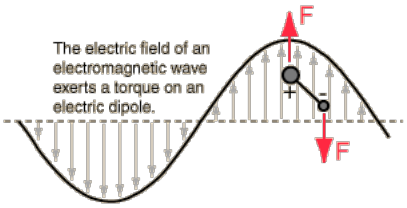
Vibrational excitation



http://wiki.verkata.com/en/wiki/Morse_potential

[*Note: Additional material is discussed here during lecture.*]

Rotational excitation



http://hyperphysics.phy-astr.gsu.edu/hbase/molecule/rotrig.html

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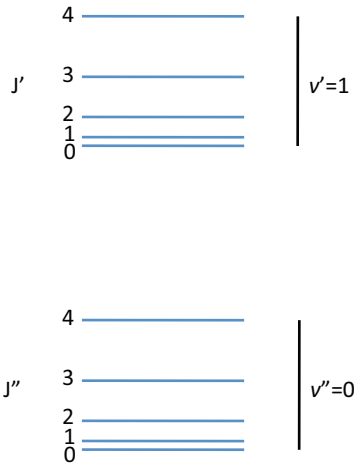
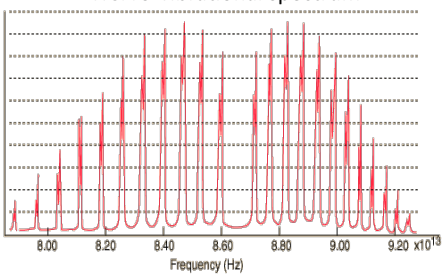
Ro-vibrational transitions



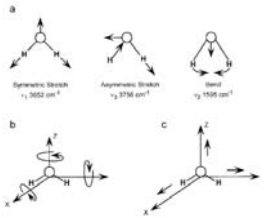
HCl ro-vibrational spectrum



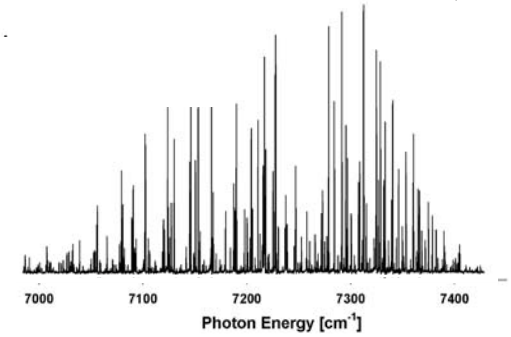
http://hyperphysics.phy-astr.gsu.edu/hbase/molecule/vibrot.html

Polyatomic molecules

- Rotations (3)
- More vibrations (3N-6)
- Combination bands, overtone bands more common



Finlayson-Pitts and Pitts



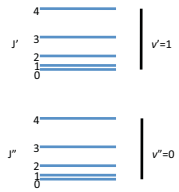
v_1+v_3 band of H_2O

(from S. Nizkorodov, UCI)

Courtesy of Sergey Nizkorodov. Used with permission.

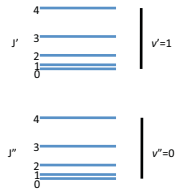
Electronic transitions

Quantum numbers: Λ, S, Ω



Excited (upper) electronic state

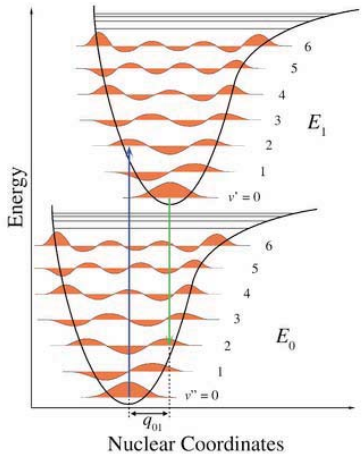
For more detail see F-P&P, pp. 46-47; or Herzberg, *Molecular spectra and molecular structure*, Van Nostrand 1950



Ground (lower) electronic state

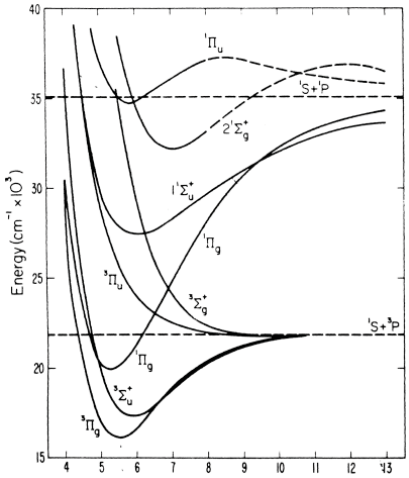
[*Note: Additional material is discussed here during lecture.*]

Franck-Condon Principle



http://en.wikipedia.org/wiki/Franck%E2%80%93Condon_principle

In reality…



http://physics.nist.gov/PhysRefData/PES/RefData/Mg_pot/Exc.html

1.84J / 10.817J / 12.807J Atmospheric Chemistry
Fall 2013