Chemistry 4631

Instrumental Analysis

Lecture 3

Atomic Spectroscopy

Quantum Transitions

The energy of a photon can also be transferred to an elementary particle by adsorption if the energy of the photon exactly matches the energy difference between the ground state and a higher energy state. This produces an excited state (*) in the elementary particle.

M + hv -----> M*

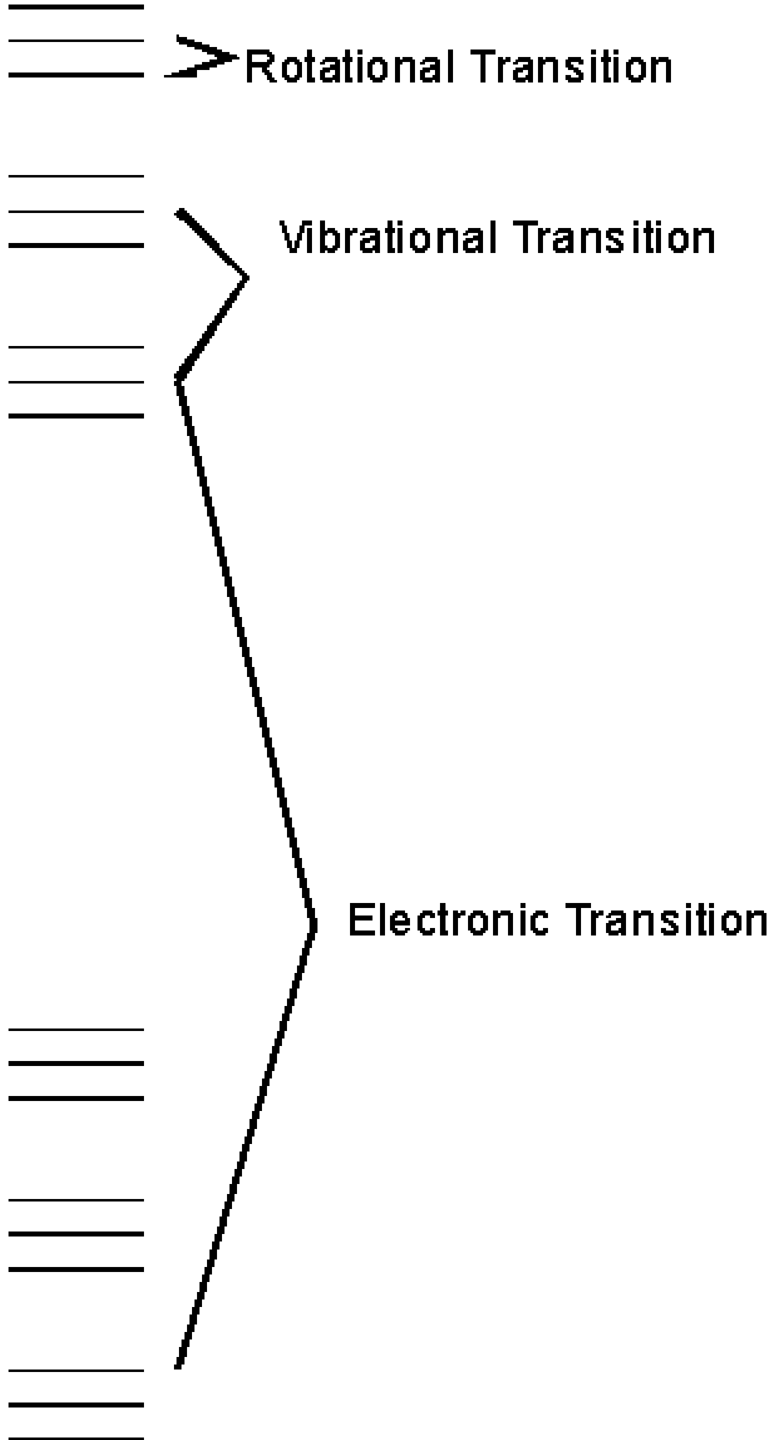
Atomic Spectroscopy

Quantum Transitions

Molecules also absorb incoming radiation and undergo some type of quantitized transition.

The transition can be:

- Electronic transition - transfer of an electron from one electronic orbital to another.
- Vibrational transition - associated with the bonds that hold molecules together.
- Rotational transitions


Rotational Transition
Vibrational Transition
Electronic Transition

Atomic Spectroscopy

Quantum Transitions

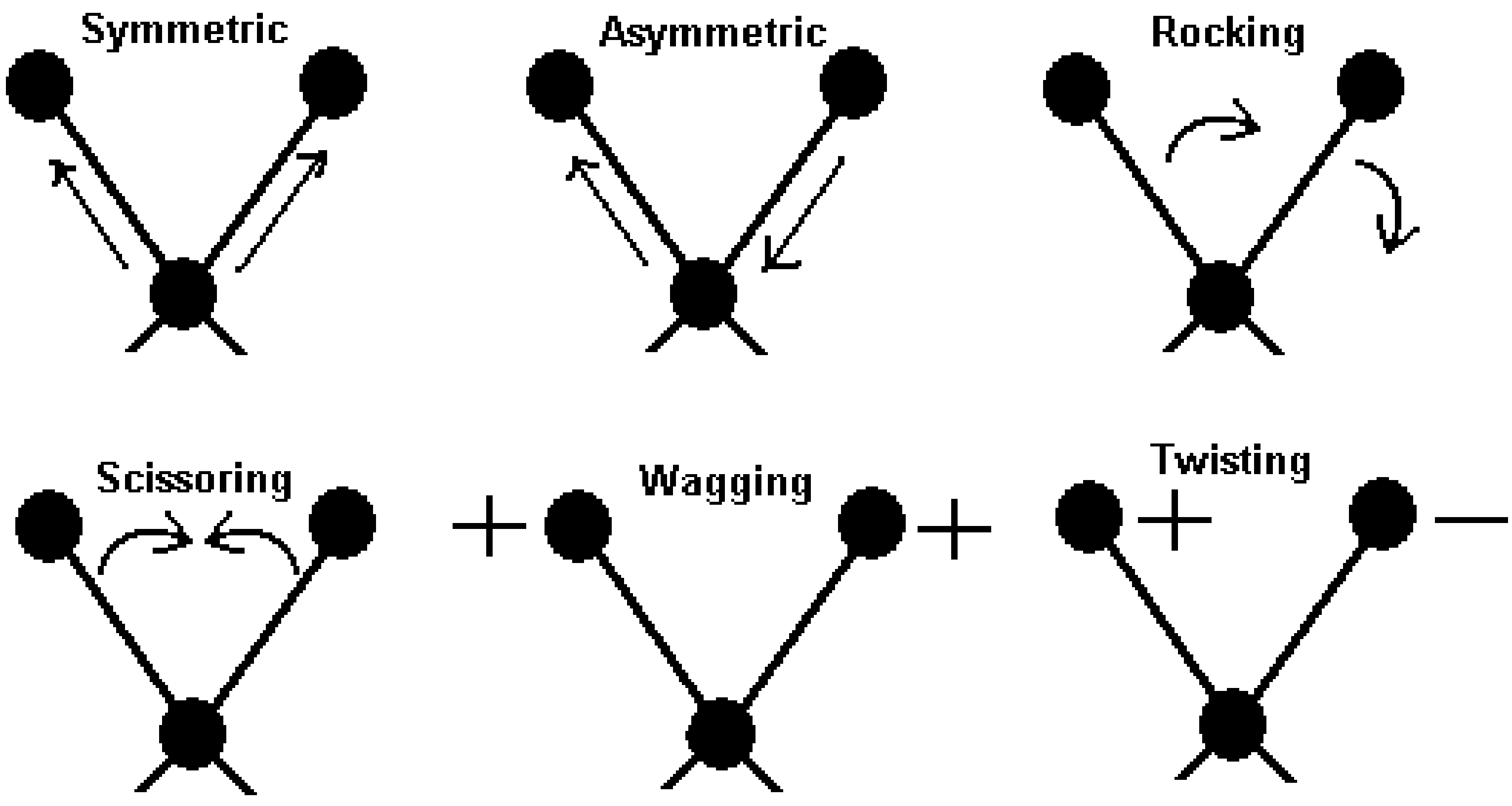
Overall energy of a molecule:

$$E = E_{electronic} + E_{vibrational} + E_{rotational}$$

$$\Delta E_{electronic} \sim 10\Delta E_{vibrational} \sim 10\Delta E_{rotational}$$

Molecular vibrations include:

- Symmetric stretching, asymmetric stretching, in-plane rocking, in-plane scissoring, out of plane wagging (bending), out of plane twisting.



- Infrared Absorption
  - IR radiation is not energetic enough to cause electronic transitions - so used to probe the vibrational and rotational states of the molecule.
- Ultraviolet Radiation
  - UV radiation is energetic enough to cause electronic transitions.

Atomic Spectroscopy

Quantum Theory

Postulates

– Atoms, ions, and molecules can exist only in certain discrete states, characterized by definite amounts of energy.
– Atoms, ions and molecules absorb or emit radiation in making transitions from one energy state to a second.

$E_1 - E_o = h\upsilon = hc/\lambda$

E_1 – energy of the higher state

E_o – energy of lower state

Atomic Spectroscopy

Emission of Radiation

Electromagnetic radiation is produced when excited particles (atoms, ions, or molecules) relax to lower energy levels.

Atomic Spectroscopy

Emission of Radiation

Excitation is caused by:

- Bombardment with electrons or other elementary particles (produces x-ray emission)
- Exposure to ac spark, heat, arc, or flame (produces UV, vis, IR)
- Irradiation with beam of electromagnetic radiation (produces fluorescence)
- Exothermic chemical reaction (produces chemiluminescence)

Atomic Spectroscopy

Emission of Radiation

Emission spectrum – plot of relative power of emitted radiation as a function of wavelength or frequency.

Emission spectra are made up of line, bands, and a continuum.

Atomic Spectroscopy

Emission of Radiation

Lines – sharp well-defined peaks caused by excitation of an individual atom.

Bands – several groups of lines closely spaced and not resolved caused by small molecules or radicals.

Continuum – increasing background with lines and bands superimposed on top, caused by blackbody radiation.

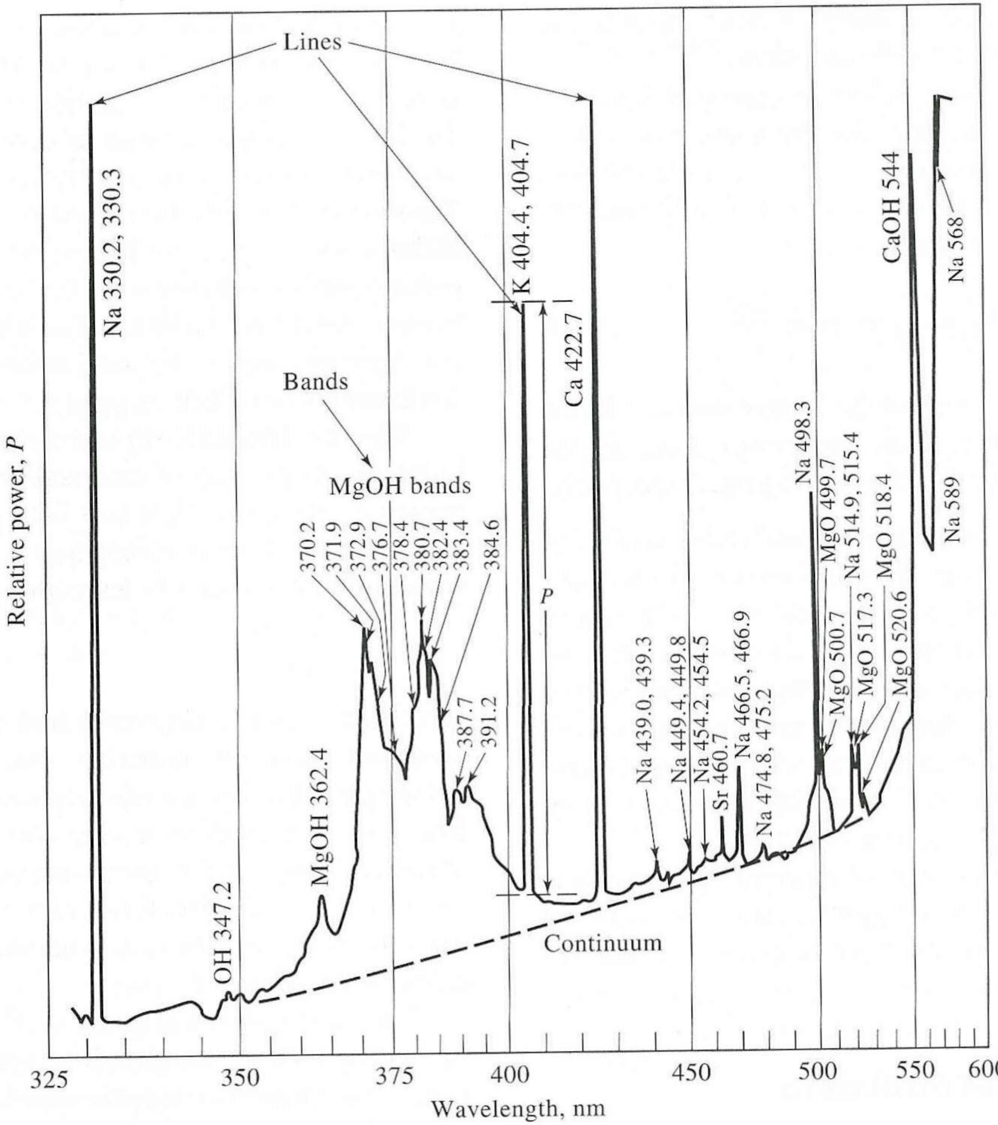


Figure 6-15 Emission spectrum of a brine obtained with an oxyhydrogen flame.
(F. Hermann and C. T. J. Alkemade, Chemical Analysis by Flame Photometry, *2nd ed., p. 484. New York: Interscience, 1963. With permission.)*

Atomic Spectroscopy

Emission of Radiation

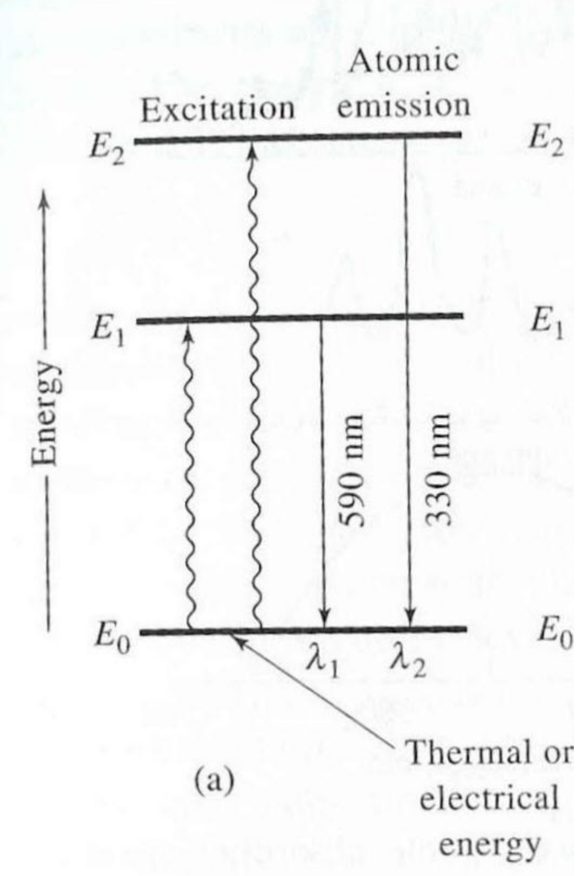
Line Spectra

Produced when radiating species of individual atomic particles are well separated in a gas phase.

Line widths are ~ 10^{-4} Å

Atomic Spectroscopy

Emission of Radiation



Atomic Spectroscopy

Emission of Radiation

Line Spectra

E_o – lowest or ground state energy of the atom.

E_1 and E_2 – higher energy electronic levels.

i.e. for Na, E_o is located in the 3s orbital

E_1 – 3p E_2 – 4p

Atomic Spectroscopy

Emission of Radiation

If the electron decays from E_1 to E_0, the emitting photon has a frequency and wavelength of

$$\upsilon_1 = (E_1 - E_0)/h$$

$$\lambda_1 = hc/(E_1 - E_0)$$

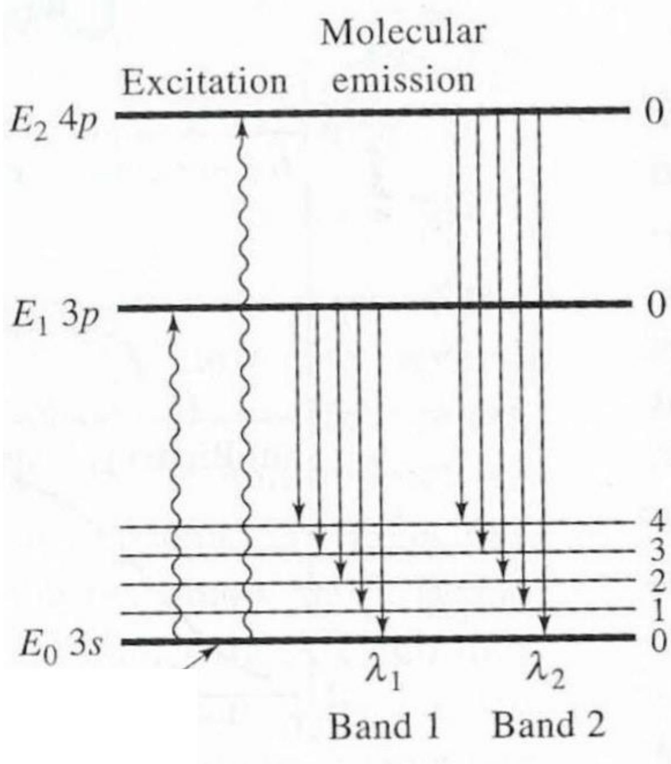
Atomic Spectroscopy

Emission of Radiation

Band spectra occur with gaseous radicals or small molecules.

Bands arise from numerous quantized vibrational levels that are superimposed on the ground-state electronic energy level of a molecule.

Atomic Spectroscopy



(b)

Atomic Spectroscopy

Emission of Radiation

Continuum Spectrum

Produced when solids are heated to incandescence.

The thermal radiation produced is called blackbody radiation.

This radiation is characteristic of the temperature of the emitting surface.

Atomic Spectroscopy

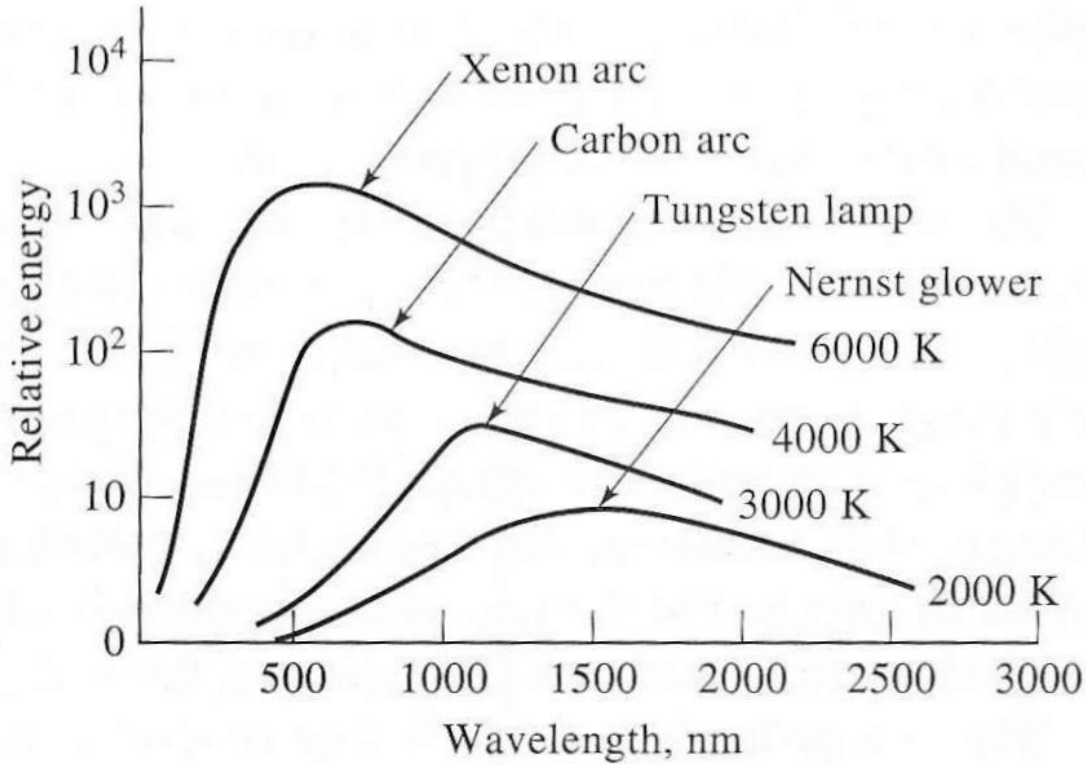
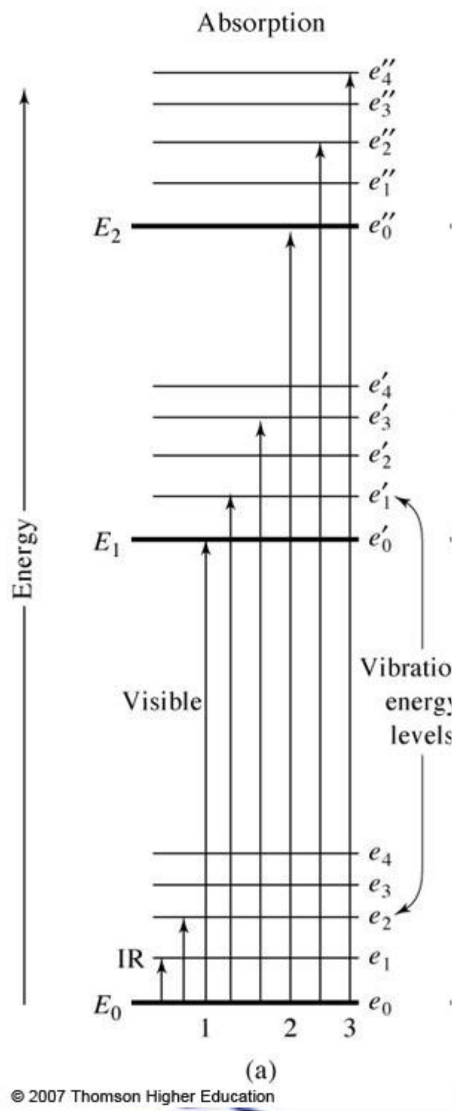


Figure 6-18 Blackbody radiation curves.

Atomic Spectroscopy

Absorption

Figure 6.24



Atomic Spectroscopy

Absorption of Radiation

When radiation passes through a solid, liquid or gas, certain frequencies may be selectively removed.

Absorption – process in which electromagnetic energy is transferred to the atoms, ion, or molecules of the sample. Absorption promotes these particles from ground state to one or more higher excited states.

Atomic Spectroscopy

Absorption of Radiation

Since atoms, ions, or molecules have only limited number of discrete energy levels, the energy of the photon must exactly match the energy difference between the ground and excited states for absorption to occur.

Atomic Spectroscopy

Absorption of Radiation

Absorption spectrum – plot of absorbance as a function of wavelength or frequency.

Absorbance is defined as:

$$A = -\log T = \log P_o/P$$

Beer's Law

Absorbance is proportional to the path length, b, through the medium and the concentration, c, of the absorbing species.

$$A = abc$$

a - absorptivity, proportionality constant in L/g cm

b - units - cm c - units - g/ L

$$A = \varepsilon bc$$

ε - molar absorptivity in L/mol cm

b - cm c - mol/L

(Deviations in Beer's law occurs at higher concentrations (> 0.1M) due to molecule interactions)

Atomic Spectroscopy

Absorption of Radiation

Atomic Absorption

A medium containing monoatomic particles, i.e gaseous Hg or Na, will show absorption at well-defined frequencies when UV or vis radiation is passed through the medium.

Atomic Spectroscopy

Absorption of Radiation

Atomic Absorption

The UV or vis radiation energy causes transitions of the outermost or bonding electrons only.

X-ray radiation energy causes transitions of the innermost electrons.

Atomic Spectroscopy

Molecular Absorption

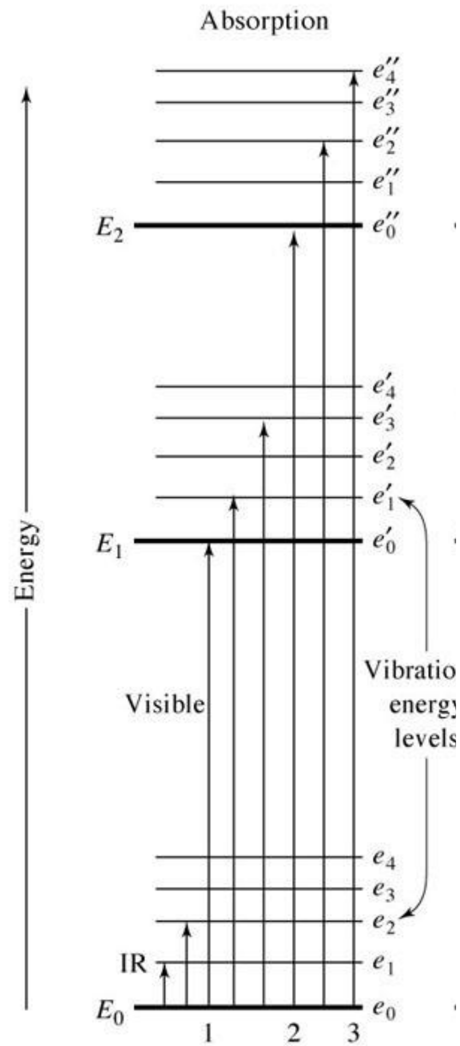
Absorption spectra for molecules are more complex, since the number of energy states in a molecule are much greater.

Overall energy of a molecule:

$$E = E_{electronic} + E_{vibrational} + E_{rotational}$$

$$\Delta E_{electronic} > 10\Delta E_{vibrational} > 10\Delta E_{rotational}$$

Atomic Spectroscopy



(a)

Atomic Spectroscopy

Molecular Absorption

For transition of an electron from E_0 to E_1,

$\upsilon = 1/h(E_1 + e_i - E_0)$

$i = 1, 2, 3, \ldots n.$

Atomic Spectroscopy

Molecular Absorption

For less energetic near and mid IR, the transitions are only in the k vibrational levels of the ground state.

$$\upsilon_i = 1/h(e_i - e_o)$$

$$i = 1, 2, 3, \ldots k.$$

Atomic Spectroscopy

Molecular Absorption

The rotational energy levels are associated with electronic vibrational level.

The energy difference is small and transitions occur in the 0.01 to 1 cm range, this is in the microwave to longer IR range.

Atomic Spectroscopy

Molecular Absorption

Since electronic transitions for molecules also have accompanying vibrational and rotational transitions, the spectrum will consist of a series of closely spaced absorption lines called absorption bands.

Pure vibrational absorption is in the IR region with no electronic transitions, so the IR spectrum has narrow closely spaced absorption peaks.

Atomic Spectroscopy

Molecular Absorption

Absorption in a Magnetic Field

If the electrons of the nuclei are subject to a strong magnetic field, additional quantized energy levels occur.

These transitions are studied by nuclear magnetic resonance (NMR) and electron spin resonance (ESR)

Atomic Spectroscopy

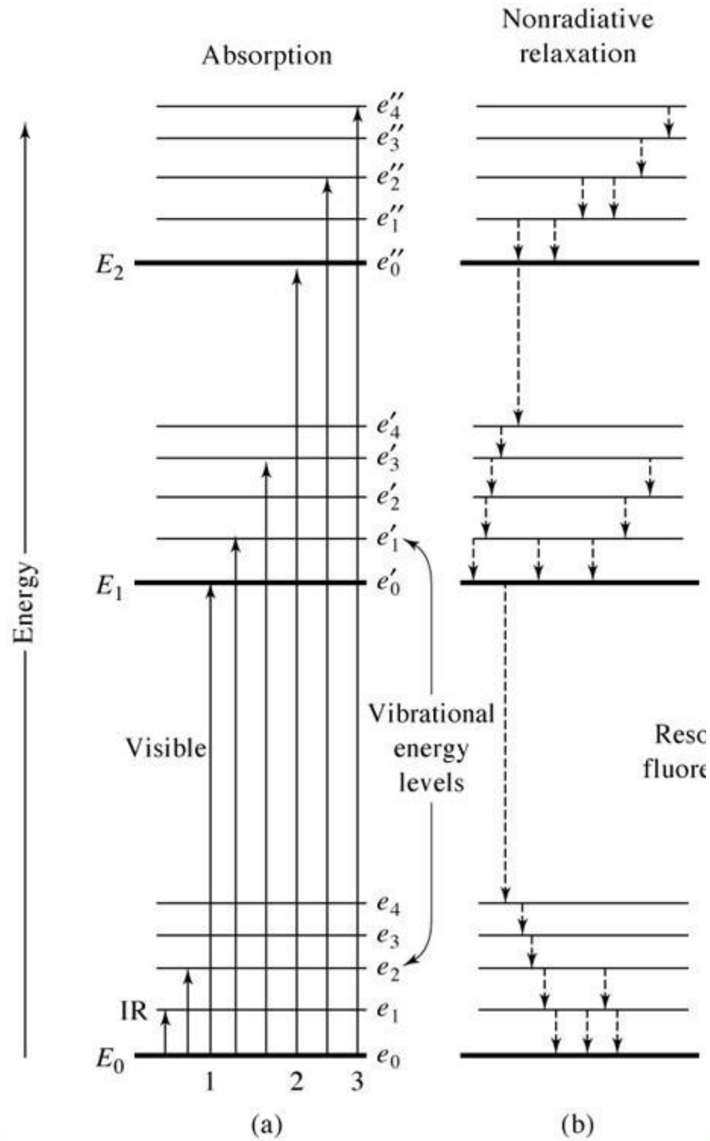
Molecular Absorption

Relaxation Process

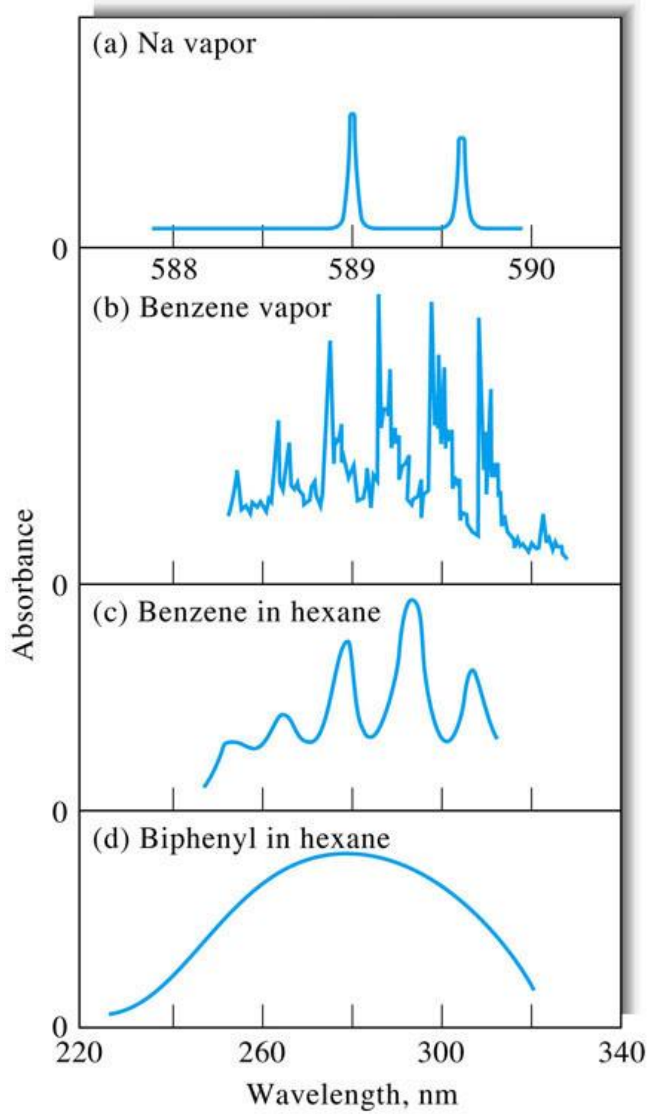
Nonradiative Relaxation

Involves the loss of energy in a series of small steps, the excitation energy is converted to kinetic energy by collisions with other molecules.

Atomic Spectroscopy



Atomic Spectroscopy



Atomic Spectroscopy

Molecular Absorption

Fluorescence and Phosphorescence

Relaxation

Radiant emission that occurs when the excited species returns to ground state.

Atomic Spectroscopy

Molecular Absorption

Resonance fluorescence

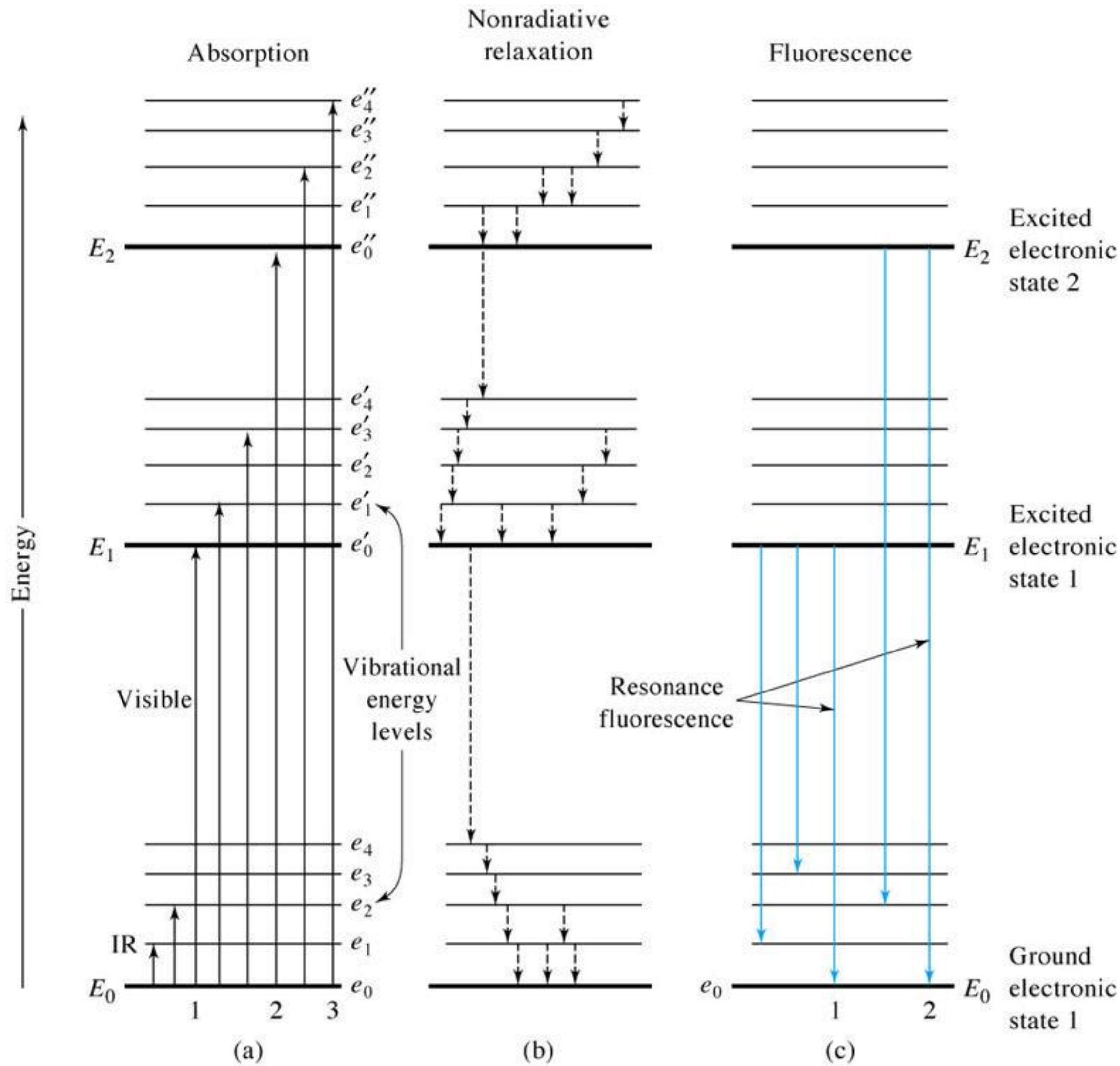
Process where the emitted radiation is identical to excitation radiation.

$(E_1 – E_0)$ **$(E_2 – E_0)$**

Most common for atoms in gaseous state, with no vibrational energy superimposed on the electronic energy.

Atomic Spectroscopy

Figure 6.24



Atomic Spectroscopy

Molecular Absorption

Nonresonance Fluorescence

Occurs for molecules in solution or in the gaseous state.

Typically vibrational relaxation occurs before electronic relaxation, so the emitted energy is smaller than the absorbed energy.

The emitted radiation has a lower frequency or longer wavelength than excitation radiation.

This shift (or difference) in frequency or wavelength is called the Stokes shift.

Assignment

- Read Chapter 1
- Read Appendix 1
- Go over Lab Lecture 1
- Homework 1: Ch. 1: 11 and

  Appendix 1: 1, 2, 10, and 12

  (extra credit) – Due Jan 24th
- Read Chapter 6
- HW2: Ch. 6: 2-12, 14, 15, 18, 19 (extra credit) (Due 1-29)