



# 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.



# Atomic Spectroscopy

## Quantum Transitions

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

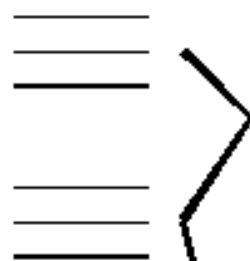
The transition can be:

- 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

The diagram shows a set of four horizontal lines representing energy levels. A bracket on the right side of these lines is labeled "Rotational Transition".



Vibrational Transition

The diagram shows two sets of four horizontal lines, one above the other. A bracket on the right side spans both sets and is labeled "Vibrational Transition".



Electronic Transition

The diagram shows two sets of four horizontal lines, one above the other, with a significant energy gap between them. A large bracket on the right side spans both sets and is labeled "Electronic Transition".

# Atomic Spectroscopy

## Quantum Transitions

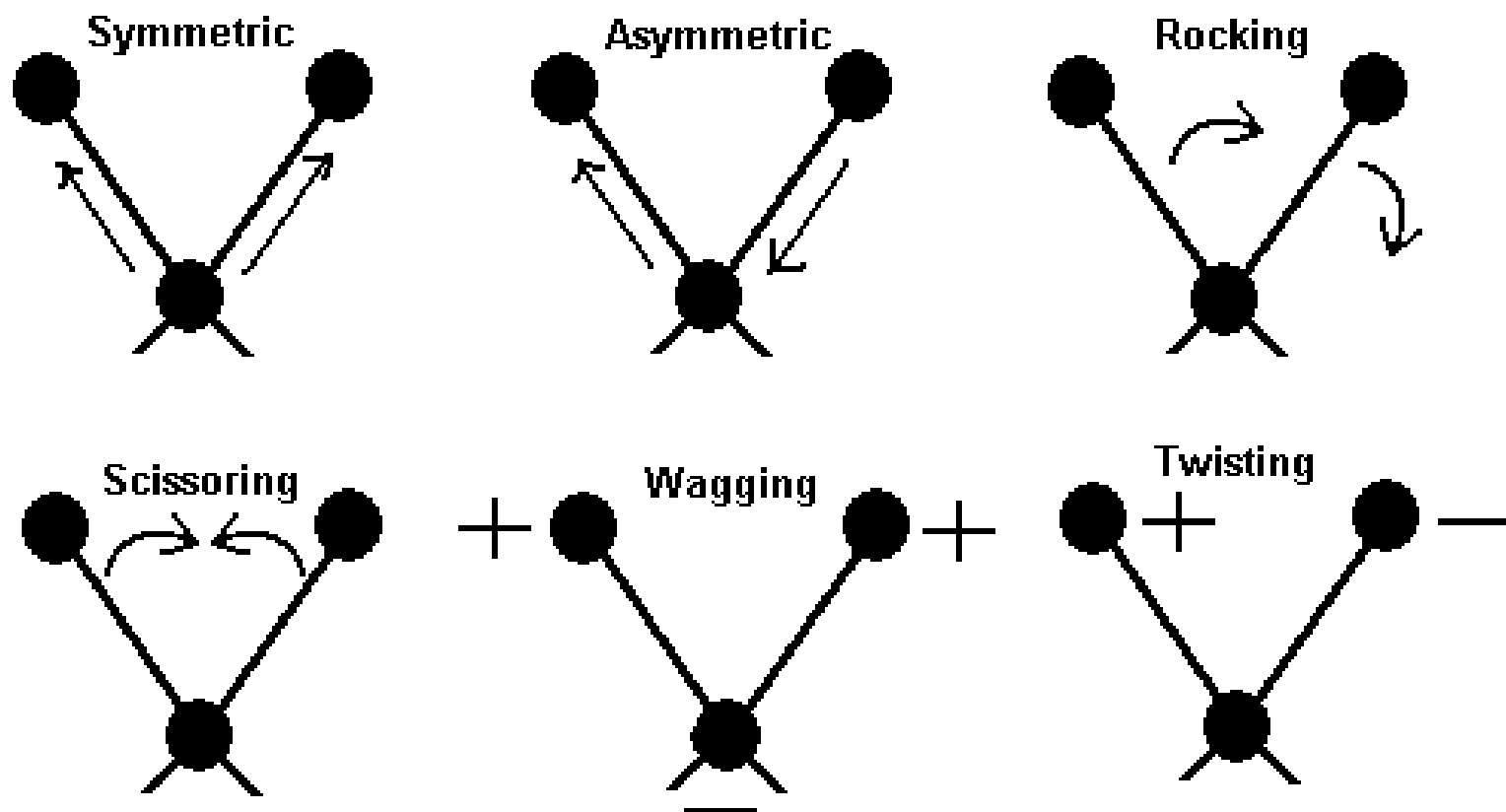
Overall energy of a molecule:

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

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

## 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.

$$E_1 - E_0 = h\nu = hc/\lambda$$

$E_1$  – energy of the higher state

$E_0$  – 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.**

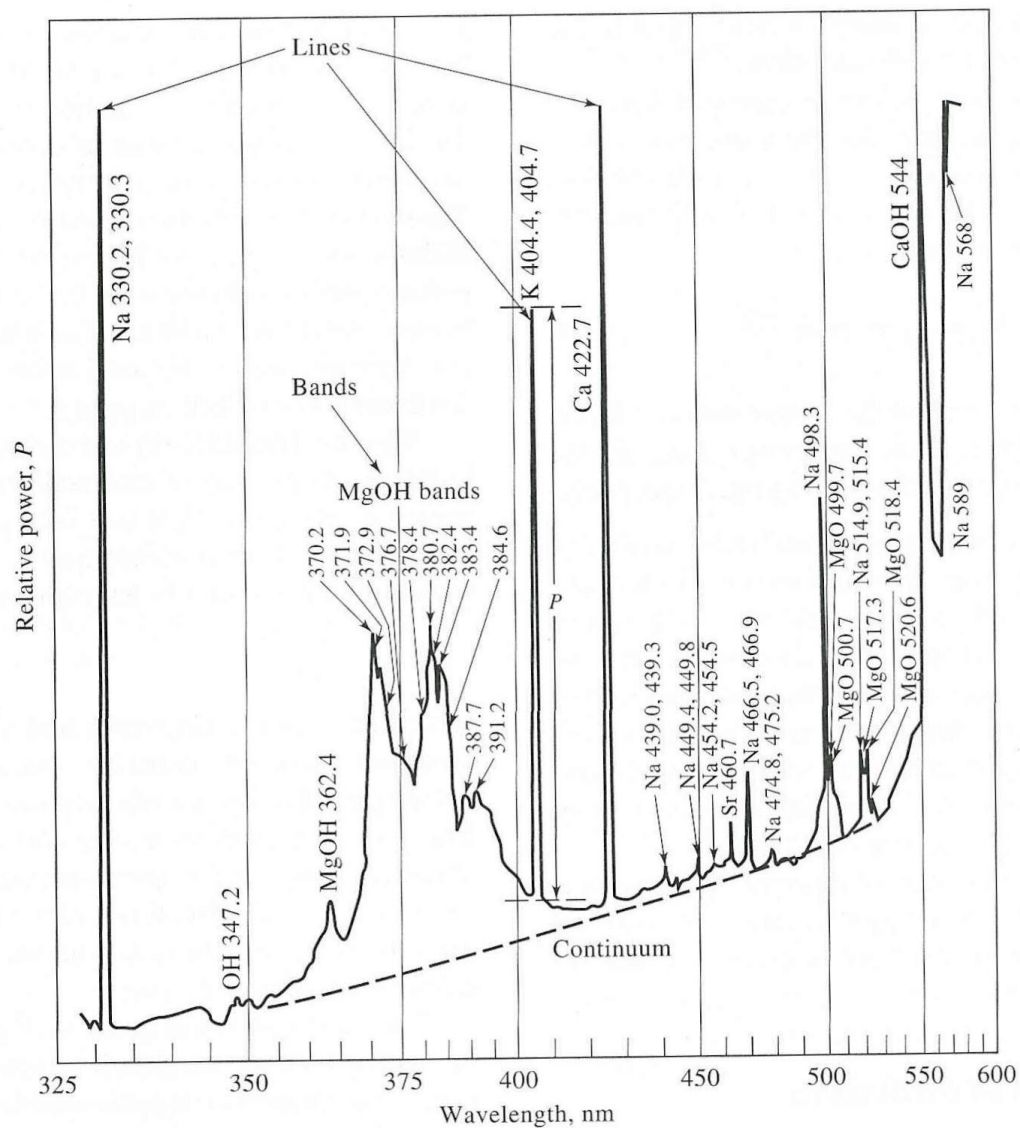
# Atomic Spectroscopy

## 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

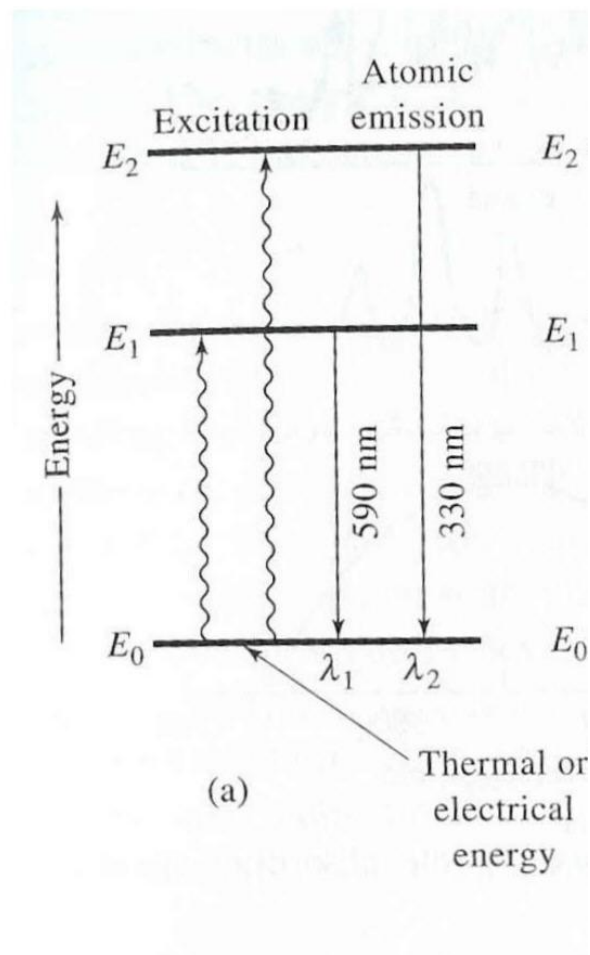
### Line Spectra

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

Line widths are  $\sim 10^{-4}$  Å

# Atomic Spectroscopy

## Emission of Radiation



# Atomic Spectroscopy

## Emission of Radiation

### Line Spectra

$E_0$  – lowest or ground state energy of the atom.

$E_1$  and  $E_2$  – higher energy electronic levels.

i.e. for Na,  $E_0$  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

$$\nu_1 = (E_1 - E_0)/h$$

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

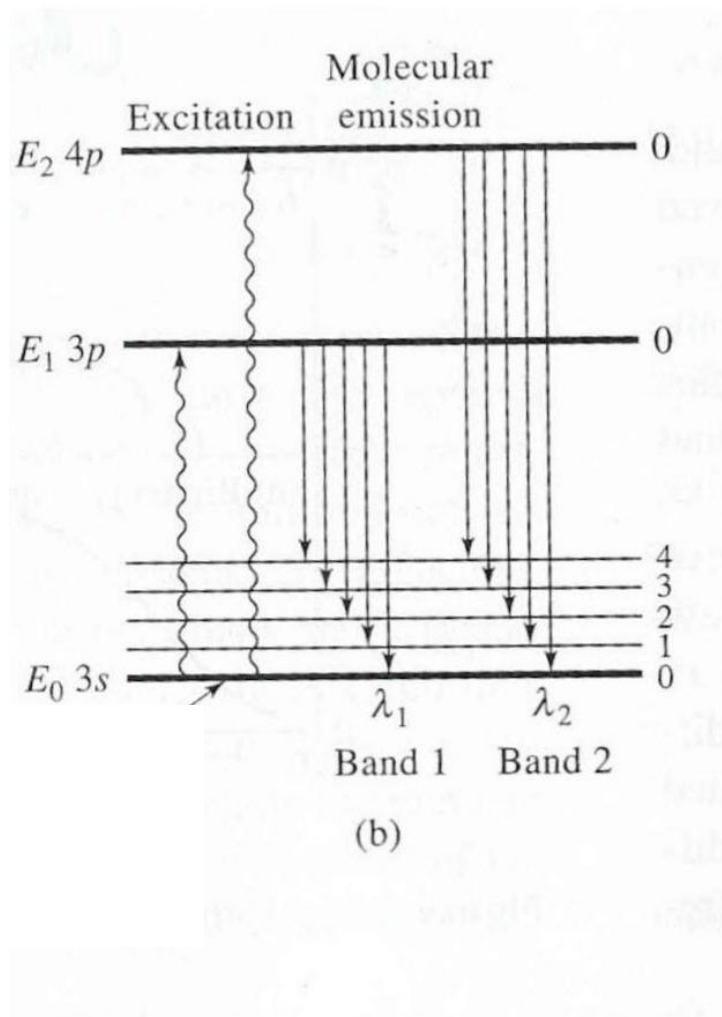
# Atomic Spectroscopy

## 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



# Atomic Spectroscopy

## Emission of Radiation

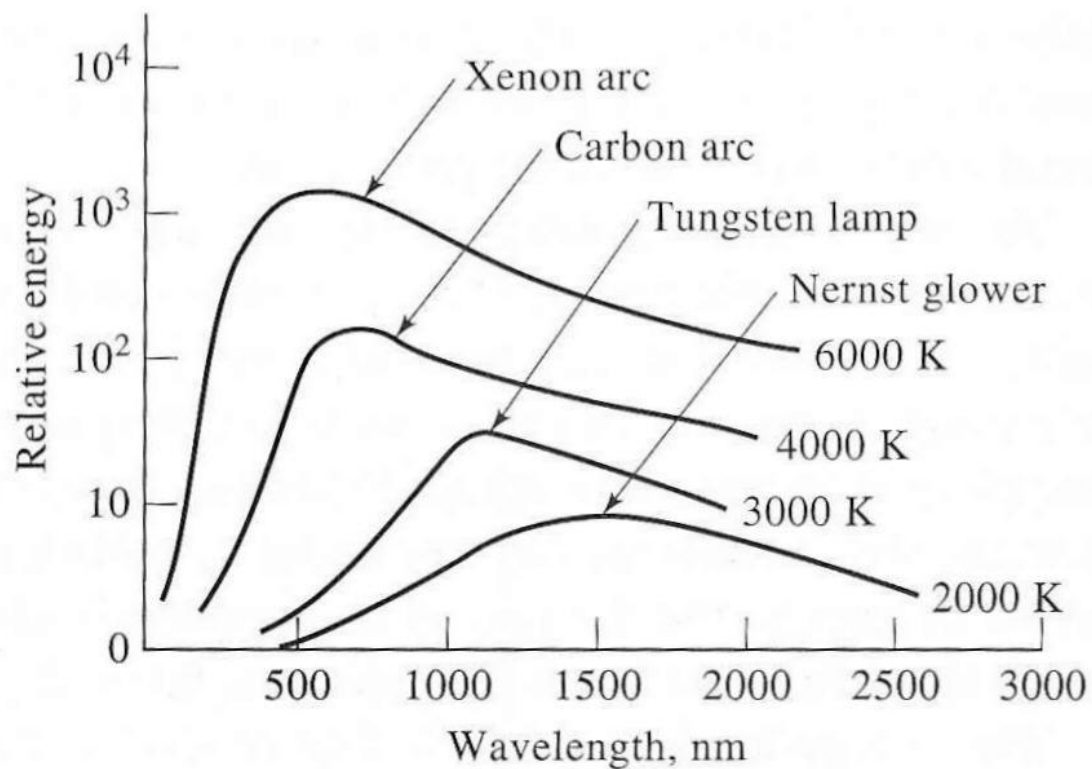
### Continuum Spectrum

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

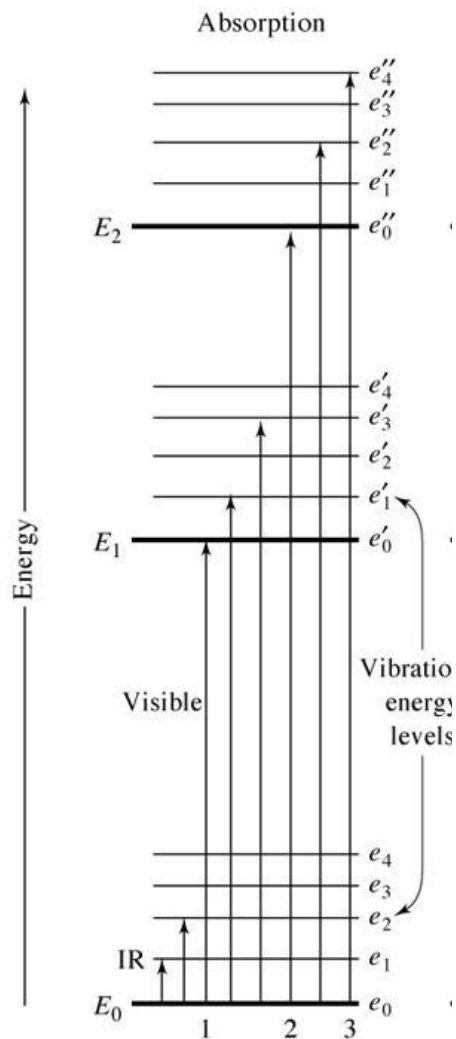


**Figure 6-18** Blackbody radiation curves.

# Atomic Spectroscopy

## Absorption

Figure 6.24



(a)

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# 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:**

$$A = -\log T = \log P_0/P$$

## 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

$$A = \epsilon bc$$

$\epsilon$  - 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

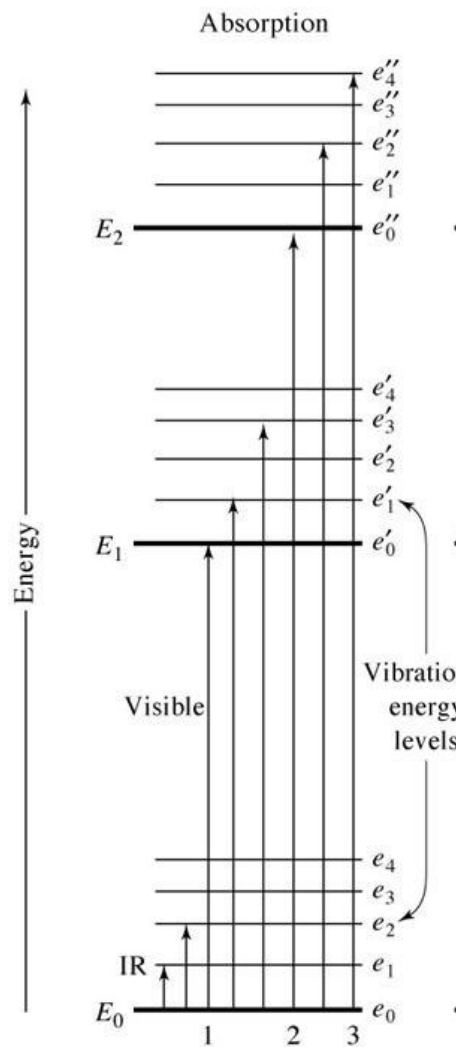
Absorption spectra for molecules are more complex, since the number of energy states in a molecule are much greater.

Overall energy of a molecule:

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

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

# Atomic Spectroscopy



(a)

# Atomic Spectroscopy

## Molecular Absorption

For transition of an electron from  $E_0$  to  $E_1$ ,

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

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

# Atomic Spectroscopy

## Molecular Absorption

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

$$\nu_i = 1/h(e_i - e_0)$$

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

# 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

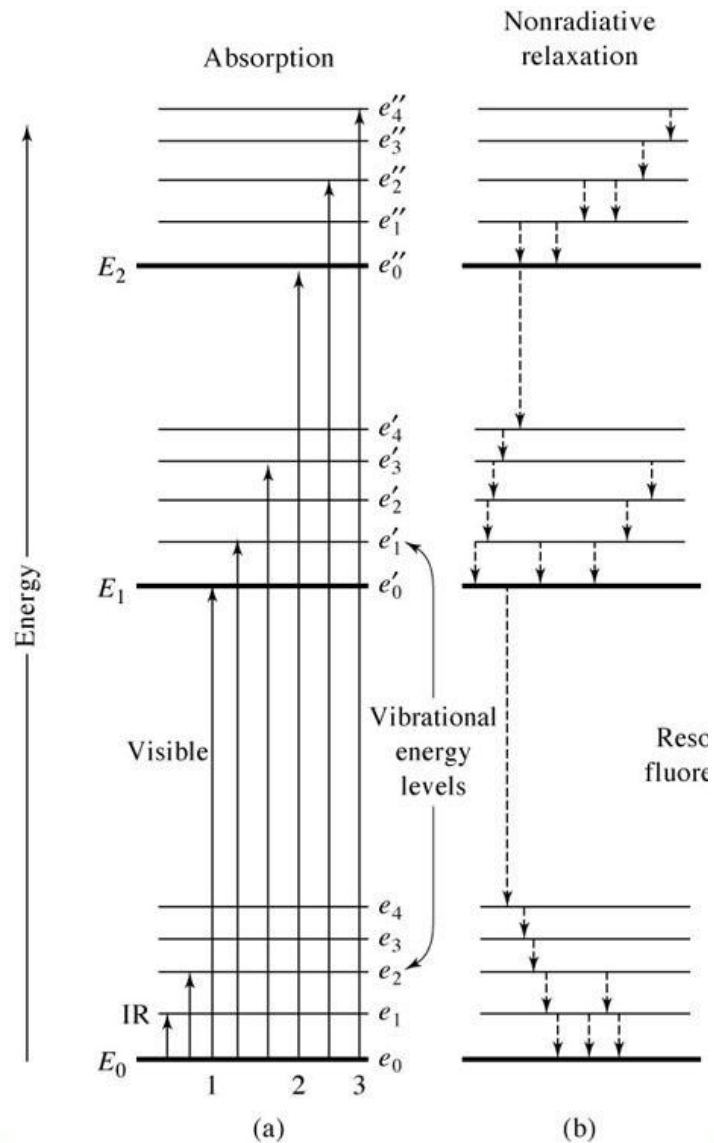
## Molecular Absorption

### Relaxation Process

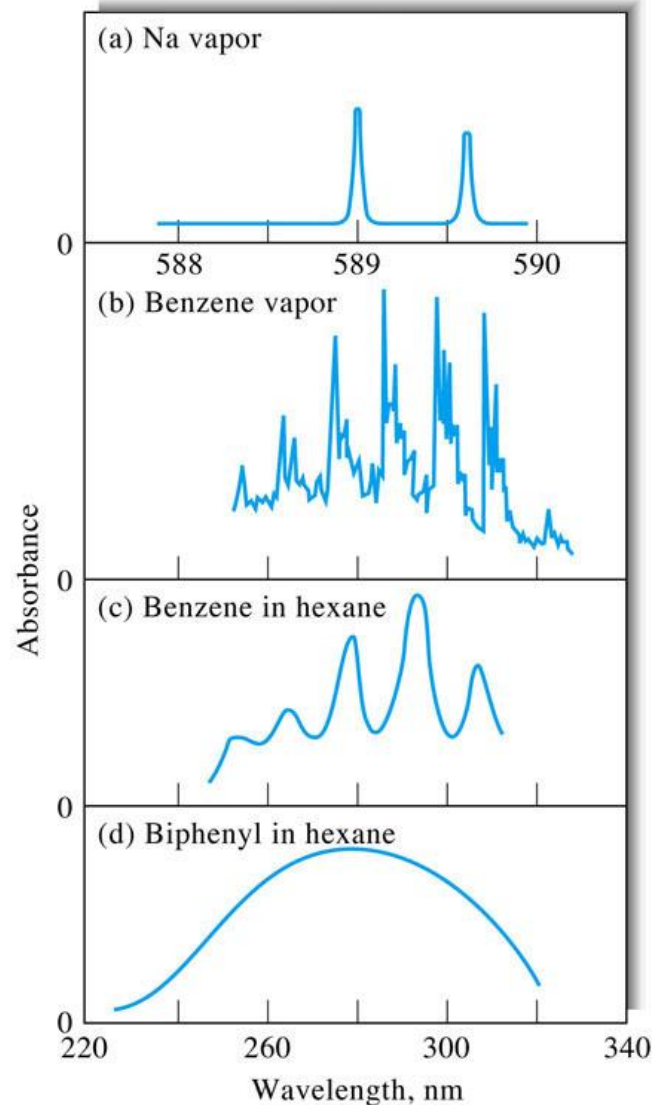
### Nonradiative Relaxation

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



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# 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

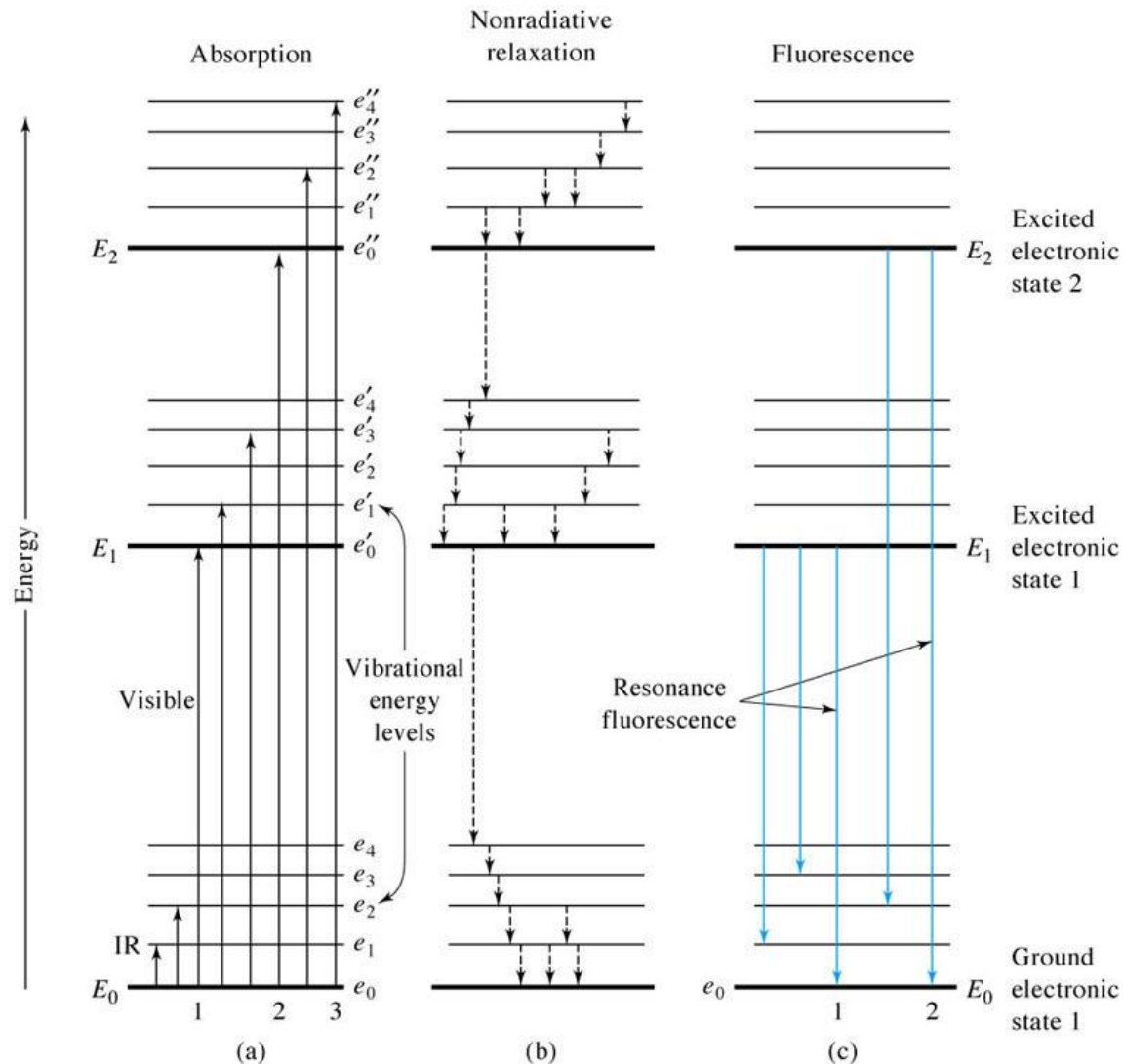


Figure 6.24

# 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 today
- Read Chapter 6
- HW2: Ch. 6: 2-12, 14, 15, 18, 19 (extra credit)  
(Due 1-23)

500 nm  $\sim 2.47$  eV

250 nm  $\sim 4.95$  eV

Co(III)(6H<sub>2</sub>O) d-d transition

538nm ( $\sim 2.30$  eV)

CH<sub>3</sub>I n- $\sigma^*$  transition

258 nm ( $\sim 4.80$  eV)

C-C bond  $\sigma$ - $\sigma^*$  transition

135 nm ( $\sim 9.18$  eV)

(one electron can only be promoted by 1 photon)(absorption)

## ELECTROMAGNETIC SPECTRUM

