Chemistry 3P51 – Fall 2013
Quantum Chemistry

Lecture No. 20
Oct 28th, 2013

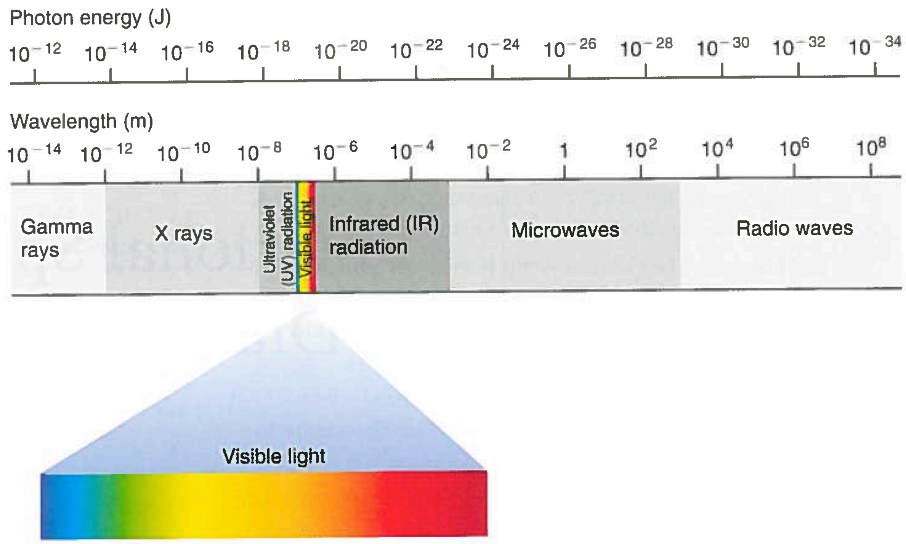
1

Objectives

- To motivate some ideas about vibrational and rotational spectroscopy.
- To present selection rules as the main tool in spectroscopy.
- To point out that vibrational and rotational transitions are related with dipoles absorbing energy in different portions of the light spectrum.

2

The electromagnetic spectrum



Important spectroscopies and their spectral range

Spectral Range	λ (nm)	$\nu/10^{14}$ (Hz)	$\tilde{\nu}(\mathrm{cm})^{-1}$	Energy (kJ/mol)	Spectroscopy
Radio	$\sim 1 \times 10^9$	$\sim 10^{-6}$	~0.01	$\sim 10^{-8}$	NMR
Microwave	~100,000	$\sim 10^{-2}$	~100	$\sim 10^{-2}$	Rotational
Infrared	~1000	~3.0	~10,000	$\sim 10^{3}$	Vibrational
Visible (red)	~700	~4	~14,000	$\sim 10^{5}$	Electronic
Visible (blue)	~450	~6	~22,000	$\sim 3 \times 10^{5}$	Electronic
Ultraviolet	<300	>10	>30,000	$>5 \times 10^{5}$	Electronic

Discrete energy levels are key in spectroscopy

- The fact that atoms and molecules posses discrete energy levels is a essential feature of all spectroscopies.

- If all molecules had a continuous energy spectrum, it would be very difficult to distinguish them based on their absorption spectra.

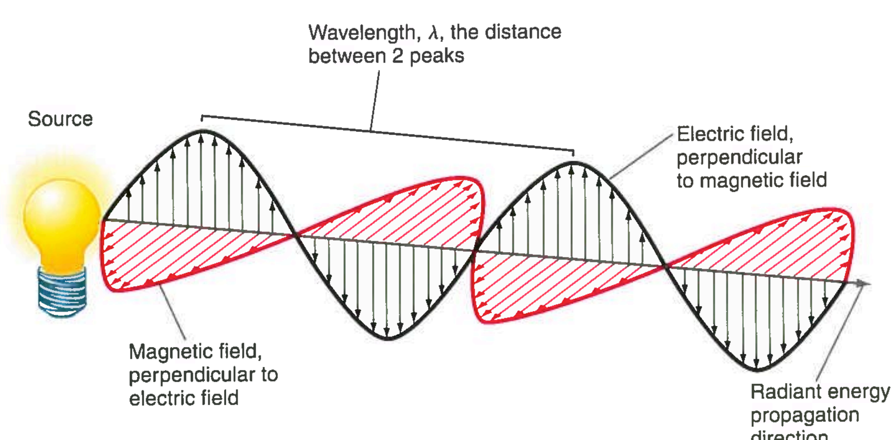
- Not all transitions occur. **Selection rules** tell us which transitions can be experimentally observed.

- In order to understand such transitions, we need to understand how electromagnetic radiation interacts with molecules.

5

The electric and magnetic fields associated with a traveling light wave

- Light is an electromagnetic traveling wave that has mutually perpendicular magnetic and electric components.



6

The electric field of a traveling light wave interacts with the dipole moment of a molecule

- When "shining light" on a molecule, the electric field associated with it, interacts with the **dipole moment** within the molecule.

- The **dipole moment** within a molecule can be of two types: **permanent** and **dynamic**.

- The **dynamic dipole** is what determines if a molecule will absorb energy in the **infrared** portion of the light spectrum. This is related with **vibrational transitions**.

- The **permanent dipole** is what determines if a molecule will absorb energy in the **microwave** portion of the light spectrum. This is related with **rotational transitions**.

7

Selection rules are related with integrals of transition dipole moment

- The transition probability from state *n* to state *m* is nonzero if the **transition dipole moment** satisfies

$$\mu_x^{mn} = \left|\langle \psi_m | \mu_x | \psi_n \rangle\right| \propto \left|\langle \psi_m | x | \psi_n \rangle\right| \neq 0$$
$$\mu_y^{mn} = \left|\langle \psi_m | \mu_y | \psi_n \rangle\right| \propto \left|\langle \psi_m | y | \psi_n \rangle\right| \neq 0$$
$$\mu_z^{mn} = \left|\langle \psi_m | \mu_z | \psi_n \rangle\right| \propto \left|\langle \psi_m | z | \psi_n \rangle\right| \neq 0$$

where *x, y, z* are the spatial variables and μ_x, μ_y, μ_z are the components of the dipole moment along the electric field in the corresponding direction.

8

Elements of vibrational and rotational spectroscopy

- We have modeled the **vibration** of a diatomic molecule by means of the **quantum harmonic oscillator**.

- For a quantum harmonic oscillator, transitions occur if

$$\Delta n = \pm 1$$

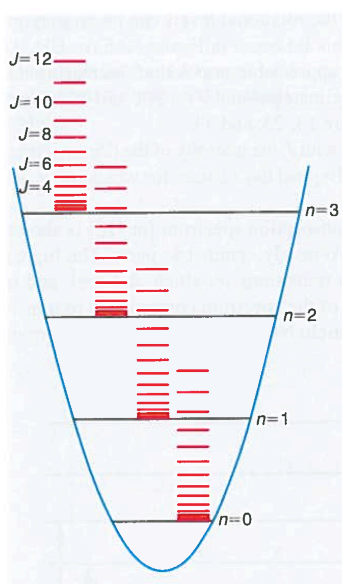
- We have modeled the **rotation** of a diatomic molecule by means of the **rigid rotor.**

- For the rigid rotor, transitions occur if

$$\Delta M = 0$$
$$\Delta J = \pm 1$$

9

Schematic representation of rotational and vibrational levels



10