Spectroscopy

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Molecular Energy

The energy of a molecule is divided into several parts:

Type	*D E* ***(eV)***	***Type of Radiation***
Translation	10^{-18}	
Rotation	5×10^{-4}	**Microwaves**
Vibration	**0.3**	**Infrared**
Electronic	**5**	**Visible/UV**

Since kT at 300°K = 0.03 eV it is evident that there are many excited translational and rotational states at room temperature. Some excited vibrational states will be present but many molecules will still be in the vibrational ground state. Almost all molecules will be in the electronic ground state. [Note: 1 eV = 23 kcal/mole = 96 kJ/mole]

Rotational Spectra

The energies of the rotational transitions are about 5 x 10^{-4} eV. Thus the transitions are in the microwave region of the E-M spectrum

A. Moment of Inertia (I)

Rotational properties can be expressed in terms of the moments of inertia of molecules about 3 perpendicular axes. Rotational spectra can be classified according to the 3 classes of moments of inertia that molecules have.

B. 3 Classes

- **Spherical (CH_4, SiH_4, SF_6) All moments equal**
- **Symmetric (NH_3, CH_3Cl Þ prolate [cigar shaped], C_6H_6 Þ oblate [pancake shaped] Two moments equal**
- **Linear (CO_2, HCl, HCºCH) One moment equal to zero.**

- **Asymmetric (H_2O, CH_2O, CH_3OH) All moments unequal**

C. Energies for Spherical and Linear Rotors

Energy $E = 1/2\ I\ w^2$ **for a classical rotor**

Angular momentum $J = Iw$ **for a classical rotor**

Angular momentum is quantized for quantum mechanical rotor $[J(J+1)]^{1/2}\ h/2p$

Energy for the quantum mechanical rotor

$J(J+1)\ (h/2p)^2/2I$ **J = 0,1,2. . .**

From these equations we see that:

- **As J increases energy levels get farther apart**
- **Large molecules have large I and have closely spaced energy levels**
- **Spectra gives info about bond lengths and bond angles**
- **Spectra consists of equally spaced lines**

D. Symmetric rotors

Another quantum number needed (K) in addition to J

E. Asymmetric rotors

Quantum numbers J, K and M needed

F. Selection Rules

The molecule must be polar (have a permanent dipole). The rotating molecule looks like an oscillating dipole that stirs the electromagnetic field into oscillation. Thus homonuclear diatomic molecules and symmetrical linear molecules such as carbon dioxide are inactive. Spherical rotors usually do not have rotational spectra.

For linear rotors: $\Delta J = \pm 1$

Examples:

- **Which of the following molecules have rotational spectra? nitrogen, carbon dioxide, water, acetylene, benzene, hydrogen, nitric oxide, nitrous oxide, methane**
- **Calculate the moment of inertia of water around the axis which bisects the HOH angle.**

Vibrational Spectra

Ballpark figures

- **The force constant “k” for a typical bond (C-H stretch) is about 500 N/m.**
- **Since the mass of a proton is 1.7 x 10^{-27} kg, then ω ~ 5 x 10^{14} rad/s.**
- **The separation of the levels is :**

  $\Delta E = (h/2\pi)\ \omega = 6 \times 10^{-20}$ J or about 30 kJ/mole.
- **The separation of the levels equals the energy of transition from 1 level to another and equals 6 x 10^{-20} J.**
- **If this energy transition is caused by a photon then**

  $\lambda = c/\nu = hc/\Delta E \sim 3{,}000$ nm and $1/\lambda \sim 3{,}000\ cm^{-1}$
- **Thus these transitions require IR radiation.**

<u>Other results</u>

E=0 is not allowed.

- **The math reason is that allowing the quantum number ν to be -1/2 (to give E=0) would make the wavefunction ill-behaved.**
- **The physical reason is the particle is confined and the positions of the nuclei are not completely uncertain. The momentum (and thus KE) cannot be zero.**

Oscillation depends on the reduced or effective mass "μ". This means that for a molecule with a bond between a heavy atom and a light atom, "μ" ~ mass of the light atom.

Selection rules for molecules

If a molecule is to be able to interact with the electromagnetic field and absorb or create a photon of frequency n**, it must possess, at least transiently, a dipole oscillating at that frequency. The transient dipole moment is called the transition moment.**

This means that the electric dipole moment must change during the vibration. As a result:

N_2, H_2, I_2 are not IR active

CO_2, H_2O are IR active

From a quantum number point of view Dn = ± 1.

Polyatomic Molecules

To determine the number of possible vibrational changes we need to consider the total number of coordinates needed to specify the motion of the molecule. Each atom may change by changing one of its coordinates, so the total # of coordinate changes (often called "degrees of freedom") would be 3N.

Three of these coordinates are needed to specify the center of mass movement - translational motion. The remaining 3N-3 are internal, either rotations or vibrations.

Two coordinates are necessary to specify rotational changes for a linear molecule. This leaves 3N-5 possible vibrational changes.

Three coordinates are necessary for a non-linear molecule so there are 3N-6 possible vibrational changes. Each change is called a "mode".

H_2O 9-6 = 3 vibrational modes

CO_2 9-5 = 4 vibrational modes

- **1 asymmetric stretch (active)**
- **2 bending modes that are degenerate**
- **1 symmetric stretch (inactive)**

Normal modes are independent, synchronous motions of atoms or groups that may be excited without affecting other groups.

Electronic Spectra

The energies of the electronic transitions are around 1 to 10 eV. This makes the transitions in the visible portion of the spectrum.

The nuclei in a molecule see different forces after an electron transition has occurred. This can result in vibrations as well. In a liquid these vibrational lines merge and the result is very broad bands. In addition rotational transitions take place.

A. The Franck-Condon Principle

This principle says that the electron transitions take place faster than the nuclei can respond. This leads to an electronic transition from a vibrational ground state in the lower electronic state to an excited vibrational state in the excited electronic state.

(see diagram) These types of diagrams are called Jablonski diagrams.

B. Electronically Excited States

There are 3 major ways to dissipate energy:

- **Radiative – Fluorescence and Phosphorescence**
- **Nonradiative – Vibrational, rotational, and translational energy given to surrounding molecules by collisions. This is called thermal degradation.**
- **Chemical Reactions**

C. Fluorescence

- **UV and visible photons excite electrons to higher states. (Absorption spectra shows vibrational structure of upper state).**
- **Excited molecules are subjected to collisions and give up energy down to lower vibrational levels. If it survives long enough it may undergo spontaneous emission and emit remaining energy as radiation in going to the lower electronic state. The spectra has the vibrational spectra of the lower state.**
- **Fluorescence occurs at a lower frequency than the incident radiation because the radiation is emitted after some vibrational energy has been discarded.**
- **The emitted radiation stops when incident radiation stops.**

D. Phosphorescence

- **The system absorbs energy to a higher singlet electronic state as in fluorescence.**
- **Collisions allow energy to lower the vibrational energy. For phosphorescence there must be a triplet state as well as the singlet state that have some common energy. This allows for intersystem crossing (which does break the selection rule) and the molecule crosses into a triplet state.**
- **The molecule continues to deposit energy and step down the vibrational ladder. The molecule becomes trapped in this state and is not able to quickly shed the energy because of selection rules. By weakly emitting radiation (breaking the selection rule for spin) the molecule can slowly change from the excited triplet state to the ground singlet state.**