

Lecture 11: Fundamentals of Molecular Spectroscopy, Microwave spectroscopy

Molecular spectroscopy refers to the field of looking at molecules using electromagnetic radiation. This technique is used both to detect and to manipulate and understand molecules. The information obtained from molecular spectroscopy relates to the energy levels and the shapes and charge densities of molecules. There are a few generic concepts and principles for all spectroscopy that we list below:

1. The energy of a molecule can be thought of as composed of different parts: Rotational Energy, Vibrational Energy and Electronic Energy. The energy spacing between rotational levels is smaller than that between vibrational levels which is smaller than that between Electronic levels.
2. The Electromagnetic spectrum can be thought of as divided into different regions based on the wavelength/frequency/energy of the light source used. The table below lists these energies and the transitions that are probed by these energies.

Name of light	frequency(Hz)	motions probed
Microwave	10^9 - 10^{13}	Rotations
Infrared	10^{13} - 10^{14}	Vibrations
Visible and Ultraviolet(UV-Vis)	$10^{14} - 10^{16}$	Electronic Transitions

3. When light of a certain wavelength falls on a molecule, then the molecule will absorb light and go to an excited state such that the difference in energy between the ground state and the excited state is hc/λ , where

λ is the wavelength of the light used. Alternatively, the molecule may emit light of a particular wavelength by going from the higher energy state to the lower energy state. You may wonder why something like this is true. In fact, you may ask why light with a smaller wavelength (and therefore larger energy) cannot cause the same transition. However, this is in fact the case and you can understand that it by imagining that light and the two states are all wavefunctions with different frequency and we need to match the frequencies appropriately in order to make transitions. This condition is used to predict the wavelength of absorption of light.

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

Where ν and $\bar{\nu}$ are frequency and wavenumber respectively.

4. In addition to the energy and frequency criterion, there are some other conditions that are necessary in order for light to be absorbed. These refer to the symmetry of the molecule and the wavefunctions involved. They are referred to as selection rules. There are two kinds of selection rules - gross selection rules and specific selection rules for each type of transition. These rules can be developed using quantum mechanics supplemented with the quantum mechanical theory of interaction of radiation with matter. We will not derive them in this course, but simply use them as rules.
5. The absorption spectrum refers to the absorption of light of different energies/wavelengths/frequencies/wavenumbers. Alternatively, there is also a possibility of stimulated emission, wherein light of a certain energy stimulates a transition of the same energy. We can think of a tunable light source which impinges on the sample and the transmitted/scattered light is collected by a detector. The output is described as spectral lines. Typically, the X-axis consists either of frequency, wavelength or wavenumber of the light and Y-axis either plots the intensity of absorbed/transmitted/scattered light. Based on this graph, we can identify specific wavelengths at which light is absorbed. This gives information about the energy spacings and can be used to characterize the molecule. The other properties of the spectrum like the line-width and the line intensity can give useful information but they will not be discussed in this course.

1 Rotational/Microwave Spectroscopy

We will restrict the discussion in this course to diatomic molecules. The rotational motion of the diatomic molecule can be modeled as a rigid rotor with energy levels given by

$$E_J = \frac{\hbar^2}{2I} J(J+1) \quad \text{where } J = 0, 1, 2, \dots$$

The letter J is used for molecules whereas l was used for atoms. Similarly, the quantum number M_J is used to denote the quantization of the Z-component of angular momentum. The moment of inertia of a diatomic molecule about its center of mass is given as $I = \mu r^2$ where μ is the reduced mass and r is the bond length of the molecule. We write the energy expression as

$$E_J = hcBJ(J+1) \quad \text{where } B = \frac{\hbar}{4\pi cI}$$

The quantity B is referred to as the rotational constant of the molecule. It has units of inverse length and is typically expressed in cm^{-1} . When we have a transition from one state to another, the wavenumber of the light absorbed is proportional to B .

The gross selection rule for a molecule to show a rotational spectrum (i.e. absorb light leading to a rotational transition) is that it should have a permanent dipole moment. A permanent dipole moment will lead to an oscillating electric field as the molecule rotates and this can interfere with the electric field due to the light. This can be thought of as the handle by which light sees the molecule. Thus, amongst diatomic molecules, only the heteronuclear molecules will show a rotational spectrum.

The specific selection rules for rotational transitions are given below

$$\Delta J = \pm 1 \quad \Delta M_J = 0, \pm 1$$

The plus sign in ΔJ corresponds to absorption and the minus sign to emission of light.

Typically, a rotational absorption spectrum consists of a number of lines at different wavenumbers corresponding to different transitions. The transitions from J to $J+1$ are characterized by an energy difference given by

$$E_{J+1} - E_J = 2hcBJ$$

and the corresponding wavenumber is $2BJ$. Thus the lines are observed at $2B, 4B, 6B, \dots$. Typical values of B are from 0.1 - 10 cm^{-1} .