

## **Chapter 13: Calculating Spectra: Prediction of Vibrational Frequencies (Infrared) and Electronic Transitions (Ultraviolet-Visible)**

### **Key Notes:**

#### Fundamental Aspects:

The absorption of infrared (IR) light by a molecule will cause excitation of the vibrational motions of the atoms present. Different types of bonds in the molecule will absorb light of different wavelengths, thus allowing *qualitative* identification of certain bond types in the sample. The total number of degrees of internal motion for a nonlinear molecule with  $N$  atoms is given by  $3N - 6$ . A linear molecule will have  $3N - 5$  total degrees of internal motion. Most of these internal degrees of motion are experimentally observable vibrational modes. IR spectroscopy is a widely used type of qualitative analysis for sample identification.

The absorption of ultraviolet or visible (UV-Vis) light by a molecule can excite electrons from lower energy, filled molecular orbitals to higher energy, empty molecular orbitals. This process is called an electronic transition. The specific wavelengths of light absorbed depend on the types of functional groups present in the molecule, and this information can help with qualitative identification of these functional groups. Ultraviolet-Visible spectroscopy is more commonly used for *quantitative* analysis, where the identity of the absorbing species is known, and its solution concentration is sought. The Beer-Lambert Law is used to relate the amount of light absorbed by the sample to its solution concentration.

#### Applications of Infrared Spectroscopy:

Infrared data is used to help determine molecular structure. Correlation tables are available that match certain organic functional groups with absorbed wavelengths of light. A detailed comparison between a sample spectrum and reference spectra of pure compounds allows the identity of a substance to be determined. Infrared spectroscopy is often used in conjunction with other spectroscopic techniques to identify organic compounds.

#### Calculating Infrared Spectra:

Any of the methods discussed in Chapters 6 – 9 can be used to calculate vibrational frequencies. In order for the calculated and experimental results to be directly comparable, the *structure must first be optimized* before a frequency calculation is performed. Frequency calculations should be computed with the same method and level of theory used to optimize the geometry. Density functional theory gives the best overall agreement with experimental data. With larger molecules, the computational expense of DFT can become prohibitive. While other less expensive methods may have poorer accuracy, the results can still be useful for comparison with experimental data. The calculated results with many software packages allow animation of each molecular vibration and can help students better comprehend what is happening at the molecular level.

### Applications of Ultraviolet-Visible Spectroscopy:

Since certain functional groups present in organic molecules absorb light at characteristic wavelength in the UV-Vis region, the technique can be used to qualitatively identify the presence of these groups. Correlation tables are available for this purpose. For systems that contain conjugated double bonds, there are sets of rules that allow prediction of the wavelength of maximum absorbance ( $\lambda_{\text{max}}$ ). The most common use of UV-Vis spectroscopy is quantitative analysis, where the concentration of the dissolved analyte is calculated from the Beer-Lambert Law, which states that the amount of light absorbed by a sample is directly proportional to its concentration. Standard solutions of the analyte are used to produce a working curve of light absorbed versus concentration. Solutions of unknown concentration are then analyzed.

### Calculating Ultraviolet-Visible Spectra:

The ability to calculate the UV-Vis spectrum of a molecule can help in interpretation of an experimental spectrum, will show the orbitals involved in a given electronic transition, and can shed light on the electronic structure of the molecule. The *geometry must first be optimized*, the ground state wavefunction is calculated, and then a calculation is performed that mixes some of the higher energy, empty (virtual) molecular orbitals into the ground state wavefunction. This is the basis of what is called the configuration interaction method. From these calculations an approximation to the energy of the excited electronic states can be calculated. The energy difference between the ground state and various excited states is then found to give the frequency of each transition.

### Fundamental Aspects

Spectroscopy is the interaction of light with matter. In this context “light” refers to the entire electromagnetic spectrum. Light can be treated as a wave where the speed of light ( $c$ ) is equal to the wavelength ( $\lambda$ ) in meters multiplied by the frequency ( $\nu$ ) in hertz (cycles per second, or  $\text{s}^{-1}$ ):

$$c = \lambda \nu \approx 3.00 \times 10^8 \text{ m}\cdot\text{s}^{-1}$$

Light can also be treated as a particle (photon) whose energy is equal to Planck’s constant ( $h$ ) multiplied by the frequency:

$$E = h\nu = hc/\lambda \quad h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$$

The electromagnetic spectrum shown below summarizes the various wavelengths, frequencies, and regions.

Different types of spectroscopy utilize different regions of the electromagnetic spectrum. Light at longer wavelengths, beyond the red end of the visible spectrum, lies in the infrared region (*ca.* 25,000 – 2500 nm). Typical units used to report IR data are reciprocal centimeters ( $\text{cm}^{-1}$ ), and the most common IR spectrophotometers cover the mid-IR region, 4000 to  $400 \text{ cm}^{-1}$ . Infrared light can be absorbed by a molecule and will excite the vibrational modes. For a nonlinear polyatomic molecule with  $N$  atoms, there are  $3N - 6$  degrees of internal motion. Linear molecules will have  $3N - 5$  degrees of internal motion. Bond stretching typically occurs at higher energies. Vibrational modes that involve changes in bond angles usually have lower energies. Some of these motions are shown below:

In order for the infrared light to be absorbed, there must be a change in the dipole moment of the molecule as it vibrates. This condition may not be met by *all* the possible modes of internal motion, so some modes are not observable using IR spectroscopy and are *IR inactive*. Another less common technique used to explore molecular vibrations is Raman spectroscopy. In this technique, only those vibrations which result in a change in the polarizability of a molecule are observed. In some cases, vibrations that are IR inactive will be *Raman active*, so both techniques can be used. When the vibrational modes of a molecule are calculated and are compared with experimental results, it is important to remember that some modes may be IR inactive. Some modes will only be observable using Raman spectroscopy. In depth analyses of molecular symmetry using group theory can distinguish between IR and Raman active modes, but these details will not be covered here.

A detailed analysis of a Infrared (IR) spectroscopy is typically used in *qualitative analysis*, meaning that the technique can provide information about the chemical *identity* of a sample under study. Samples can be solutions, pure liquids, solids, and (more commonly) pastes or mulls made from a solid and mineral oil (Nujol®). Different types of chemical bonds present in a sample absorb characteristic wavelengths of infrared light. With practice, a scientist can interpret the infrared spectrum of a sample and learn what types of chemical bonds, or functional groups, are present. In conjunction with additional information about the sample, a scientist may be able to identify exactly what molecule is present. The ability to calculate the infrared spectrum of a given molecule can greatly assist in the interpretation of an experimental spectrum. The area of an IR spectrum between *ca.* 1300 – 900  $\text{cm}^{-1}$  is called the fingerprint region, and often contains many peaks that are difficult to assign to particular vibrational modes. The calculated frequencies can be animated to show the corresponding molecular motions, and more peaks in the spectrum can be identified.

At shorter wavelengths than the IR region is the visible region, 700 to 400 nm. Beyond the violet end of the visible region lies the ultraviolet, 400 – 200 nm. Light in the ultraviolet-visible region of the electromagnetic spectrum can be absorbed by a molecule and will excite electrons from lower energy, filled molecular orbitals to higher energy, empty molecular orbitals. This is called an electronic transition. The wavelength at which the maximum absorption of light occurs ( $\lambda_{\text{max}}$ ) is characteristic of the electronic structure of the molecule. The electronic structure, in turn, depends on the functional groups present in an organic molecule, or on the metal ion (and its oxidation state) for a transition metal containing inorganic molecule or ion. Thus, UV-Vis spectroscopy can be used in *qualitative analysis* to help identify the molecular structure of the sample under study. More commonly, UV-Vis spectroscopy is used in *quantitative analysis*, where the solution concentration of a known substance is found. The Beer-Lambert Law states that the amount of light absorbed by a sample is proportional to the solution concentration of the sample. The ability to calculate the UV-Vis spectrum of a given molecule can help in the interpretation of an experimental spectrum and can show which molecular orbitals are involved in each electronic transition. These calculations can also help to understand the electronic structure of a molecule.

### **Applications of Infrared Spectroscopy**

Infrared data is used to help determine molecular structure. The ability to compare experimental and computed spectra can aid in the correlation of specific vibrational motions of the molecule

with observed spectral peaks. Correlation tables are available that match certain organic functional groups to absorbed wavelengths. There exist reference IR spectra of pure compounds. The fingerprint region (*ca.* 1300 – 900 cm<sup>-1</sup>) of the reference spectra can be compared with an experimental spectrum to identify a particular molecule. Computed IR data can also help in identifying transition state structures (Chapter 14). Other purposes for performing these calculations include computation of force constants for geometry optimization (Chapter 11) and determination of zero point vibration and thermal energy corrections to the total energies, as well as other thermodynamic quantities of interest (Chapter 15).

### Calculating Infrared Spectra

Any of the methods discussed previously (molecular mechanics, *ab initio*, semiempirical, or density functional theory) can be used to calculate IR spectra. The geometry of the molecule *must be optimized* before the frequency calculation is done so that the calculated results and experimental results are done on molecules with the most similar geometry possible. Molecular mechanics can give usable results if the molecule being studied is similar in structure to those used to create the force field. Since many molecules will not have adequate parameters in the standard force fields available, molecular mechanics is not the best method for these calculations. Both semiempirical and *ab initio* methods have known, systematic errors that can be compensated for. Once the calculation is complete, the wavelengths obtained are multiplied by a scaling factor in order to bring them into better agreement with experimental data. The best method for calculating vibrational frequencies is density functional theory. Although calculated results using DFT give the best overall agreement with experimental values, the computational costs associated with DFT can be prohibitive.

### Applications of Ultraviolet-Visible Spectroscopy

Since certain functional groups present in organic molecules absorb light at characteristic wavelengths in the UV-Vis region, the technique can be used to qualitatively identify the presence of these groups. Tables of absorption data for various functional groups are available. If the molecule of interest contains a conjugated system of double bonds, a set of simple rules, called the Woodward-Fieser Rules, can be used to predict the wavelength of maximum absorption ( $\lambda_{\text{max}}$ ). Many transition metal ion containing complexes absorb light in the visible region of the spectrum. The light absorbed causes electronic transitions of the d-electrons. Different groups attached to the metal will change the electronic energy levels, thus changing the color (value of  $\lambda_{\text{max}}$ ). Quantitative analysis of the electronic structure of inorganic molecules can be performed in this manner. The more common application of UV-Vis spectroscopy is in quantitative determination of the concentration of a dissolved analyte, found through application of the Beer-Lambert law:

$$A = \epsilon bc$$

where  $A$  = amount of light absorbed,  
 $\epsilon$  = molar absorptivity or extinction coefficient (L·mol<sup>-1</sup>·cm<sup>-1</sup>)  
 $b$  = pathlength of light through the sample (cm)  
 $c$  = concentration in units of molarity (mol·L<sup>-1</sup>)

### Calculating Ultraviolet-Visible Spectra

The ability to calculate the UV-Vis spectrum of a molecule can help in the interpretation of an experimental spectrum, will show the orbitals involved in a given electronic transition, and can also shed light on the electronic structure of the molecule. The first step in the calculation is to perform a geometry optimization. Any of the four methods (molecular mechanics, *ab initio*, semiempirical, or density functional theory) could be used for this. Next, the ground state wavefunction is calculated. This generates occupied (filled with two electrons each) and unoccupied (virtual) molecular orbitals. Molecular mechanics cannot be used for this step, since no electrons or orbitals are used in this method. Any of the other techniques could be used. Next, a calculation is performed that mixes some of the virtual orbitals into the ground state wavefunction while the geometry is held constant. This process provides an approximation to the energy of the excited electronic states at the fixed geometry of the ground state. The transition frequency is calculated by finding the difference between the excited state and ground state energies.