CHAPTER 2
Characterisation of liquids by Ultrasonic velocity, Refractive index and UV spectra

CHAPTER OVERVIEW

Section 2.1 gives an introduction to the physical properties of liquids. Section 2.2 presents a detailed review of ultrasonic waves. Section 2.3 discusses some important industrial, medical, and scientific applications of ultrasonic waves. Section 2.4 deals with the variation of ultrasonic velocity in liquids due to the variation of temperature and pressure. Section 2.5 gives some empirical equations framed by Rao relating the sound velocity to the parameters of the liquid medium. Section 2.6 introduces a derived acoustic parameter named specific acoustic impedance. Section 2.7 presents the adiabatic compressibility of a liquid which is the reciprocal of the adiabatic bulk modulus K: the only elastic modulus that can be defined for a liquid. Section 2.8 deals with the thermal variation of adiabatic compressibility of a liquid. Section 2.9 introduces the refractive index, a very important bulk property used for the characterization of substances. Section 2.10 presents the derived parameters connecting refractive index, density and ultrasonic velocity of a liquid. Section 2.11 deals with the theory of UV absorption spectra explaining molecular energy levels. Section 2.12 discusses how organic compounds are identified using UV absorption spectra. Section 2.13 describes the process of determining the concentration of a solution from UV absorption spectra.

2.1 INTRODUCTION

Liquid state occurs over a temperature range that separates the regions occupied by the solid and vapour states. At present there is no mathematically tractable model which gives an accurate
approximation to the liquid state. Such a model (in contrast to the crystal and gas models) needs to cover structural and thermal properties with equal emphasis. There are many conceptual models like dense fluid of hard spheres in thermal equilibrium with its container. If this or any other simple approximation is applied, it should be expected that liquid properties would show systematic trends and relationships. [Egelstaff, 1992]

The physical properties of liquids are of great interest in a number of fields in pure and applied sciences. In the present chapter a review is attempted on the various physical properties such as ultrasonic velocity, refractive index, adiabatic compressibility, characteristic absorption of UV radiation etc. that may come across in the present study. These macroscopic properties are not only characteristic of each liquid but also depend on the micro structure of the liquid. From the detailed analysis of these bulk properties we may be able to get an idea of the interactions that may occur in the molecular level.

2.2 ULTRASONIC WAVES

Ultrasonics or ultrasound, derived from the Latin words "ultra" meaning beyond and "sonic" meaning sound, is a term used to describe sound waves that vibrate more rapidly than the human ear can detect.

Sound waves travel as concentric hollow spheres. The surfaces of the spheres are compressed air molecules, and the spaces between the spheres are expansions of the air molecules through which the sound waves travel. Sound waves are thus a series of compressions and expansions in the medium surrounding them. Although we are thinking of sound waves as traveling through air, they also propagate through other media.
Most people can only detect frequencies of sound that fall between 16 and 16,000 Hz. Ultrasonics has come to describe sound waves with frequencies greater than 16 kHz. Some insects can produce ultrasound with frequencies as high as 40 kHz. Small animals such as cats and dogs hear frequencies of up to 30 kHz and bats are known to detect frequencies of up to 100 kHz.

The propagation velocity of a sound wave is obtained by multiplying the frequency of the sound wave by its wavelength. Thus, if the wavelength and frequency of the sound wave in a given medium are known, its velocity can also be calculated. As ultrasonic waves tend to have very high frequencies, it follows that they also have very short wavelengths. As a result, ultrasonic waves can be focused in narrow, straight beams. [Knight & David, 1980]

2.3 APPLICATIONS OF ULTRASONIC WAVES

The number of applications for ultrasound seems to be limited only by the human imagination. There are a number of ways that people have already found to make use of ultrasound. Some important applications are mentioned here. Ultrasonic waves can be used to break up fat globules in milk, so that the fat mixes with the milk. In addition, pasteurization, the removal of harmful bacteria and microorganisms, is sometimes done ultrasonically. [Kenneth, 1988]

In ultrasonic soldering, high frequency vibrations are used to produce microscopic bubbles in molten solder. This process removes the metal oxides from the joint or surface to be soldered and eliminates the need for flux [Knight & David, 1980]. Ultrasonic method is used extensively to locate and track submarines and explosive mines below the surface of water. An important industrial application is the ultrasonic flow meter in which the rate of flow of liquid through a pipe can be determined by analyzing the Doppler shift of ultrasonic waves. This technique (Doppler Scan) has been applied to estimate the rate of blood flow in arteries [Dale, 2000].
It can also be used for the treatment of joint pains and for the elimination of kidney and bladder stones. Cavitation of the liquid by ultrasound creates turbulence in the liquid and result in the cleaning action. Ultrasonic cleaning is very popular for jewelry, surgical instruments, camera lenses etc. [Basil Brown, 1965]

2.3.1 APPLICATIONS IN RESEARCH

Study of cavitation in liquids is one of the important areas of research. When a liquid is heated the cavitation process increases. Since ultrasonic sound can control cavitation, it is a powerful tool in the investigation of the process. A contemporary subject of research involves emission of light as the cavity produced by a high intensity ultrasonic wave collapses. This effect is called sonoluminescence.

The velocity of ultrasonic wave is strongly dependent on the density, adiabatic compressibility, temperature, chemical structure etc.

The relation connecting ultrasonic velocity $U$, density $\rho$ and adiabatic compressibility $\beta_s$ of a liquid [Stefan & zdenko, 1981] is given by,

$$U^2 = \frac{1}{\rho \times \beta_s} \quad (2.1)$$

The relation connecting ultrasonic velocity, density and Rao's specific sound velocity $r$ of a liquid [Robert & Stephen, 1969] is given by,

$$U = (r \times \rho)^{\frac{1}{3}} \quad (2.2)$$

or

$$r = \frac{U^{1/3}}{\rho} \quad (2.3)$$

22
The relation connecting ultrasonic velocity, density and Specific acoustic impedance $Z_A$ of a liquid [Philip & Uno Ingrad, 1968] is given by,

$$U = \frac{Z_A}{\rho}$$ (2.4)

At present ultrasonics is a thrust area of research. Literature survey shows that a lot of works are in progress in the field of ultrasonics.

2.4 VARIATION OF ULTRASONIC VELOCITY IN LIQUIDS

The velocities of ultrasonic waves $U$ in liquids vary from about 700 to 2500 m/s. It varies with temperature and pressure also.

2.4.1 VARIATION WITH TEMPERATURE

![Graph showing the variation of ultrasonic velocity with temperature](image)

Fig.2.1 Temperature dependence of ultrasonic velocity in water
For most pure liquids, at temperatures far from critical values, the ultrasonic velocity decreases with increase in temperature. For water, ultrasonic velocity increases by about 2 m/s for each Kelvin rise of temperature up to 346 K and thereafter it decreases. This is shown in fig. 2.1. In short, all pure liquids except water have a negative temperature coefficient of sound velocity at ordinary temperature.

2.4.2 Variation with Pressure

For almost all liquids, the pressure coefficient of ultrasonic velocity is a positive constant. This is due to the increase in bulk modulus of a liquid during the application of pressure. In the case of water the ultrasonic velocity increases nearly at the rate of 0.2 m/s for an increase of pressure of one atmosphere.

2.5 Theory of Sound Velocity - Rao's Rule

There has been considerable attention in ultrasonics to the development of empirical rules relating the sound velocity to the parameters of the medium. The most famous of these is Rao's rule, first presented by Rao.M.R in 1940. In its simplified form, it states that

\[ U^{1/3} V = R_1 \]  \hspace{1cm} (2.5)

Where \( V \) is the molar volume and \( R_1 \) is a constant for a given liquid, sometimes called the Rao constant or Rao number. While great deal of effort has been expended in endeavoring to connect this constant to the molecular structure of organic materials, it served mainly as a rough guideline to the behavior of sound velocity. A variant of Rao's rule was later developed by Wada.Y. [David & Cheeke, 2002]
Rao's rule can also be written as
\[ \frac{1}{\beta_S} \left( \frac{\partial \beta_S}{\partial T} \right)_p = 7 \alpha \]  \hspace{1cm} (2.6)

Where \( \beta_S \) is the adiabatic compressibility and \( \alpha \) is the expansion coefficient of a liquid.

It was pointed out by Rao that \( R_1 \) undergoes regular increments among the members of a homologous series of liquids so that
\[ R_1 = pM + c_1 \]  \hspace{1cm} (2.7)

Where \( M \) is the molecular weight. \( p \) and \( c_1 \) are constants and \( p \) characterizes the series (the \( CH_2 \) group in the homologous series).

One of a few relations between ultrasonic velocity and liquid structure was provided by the early study of Shaaffs. He assumed that although the realistic equation of state for the liquid was too complicated, some properties of organic liquids such as the sound velocity could be deduced from the Van der Waals equation
\[ (p + \frac{a}{V^2})(V - b) = RT \]  \hspace{1cm} (2.8)

Where \( R \) is the universal gas constant, \( a \) and \( b \) are constants called Van der Walls constants.

Shaaffs obtained for organic liquids
\[ U = \gamma RT \left[ \frac{M}{3(M - \rho b)^2} - \frac{2}{(M - \rho b)} \right]^{1/2} \]  \hspace{1cm} (2.9)

If \( B \) is the effective volume occupied by the molecules of one mole of a liquid, it is related to Van der Walls constant \( b \) by the equation,
\[ b = 4B \]  \hspace{1cm} (2.10)
The space filling factor, ie, the fraction of total molar volume actually occupied by the molecules, according to Shaaffs is given by

\[ r_1 = \frac{B}{V} \]  \hspace{1cm} (2.11)

Where \( V \) is the molar volume.

According to Debye the quantity \( B \) is equal to the molecular polarization known as the molecular refraction \( R_m \). From the law of Clausius – Mossotti,

\[ R_m = \left( \frac{n^2 - 1}{n^2 + 1} \right) \frac{M}{\rho} \]  \hspace{1cm} (2.12)

Where \( n \) is the index of refraction.

Shaaffs pointed out that the product \( UV \) was a simple function of \( R_m \) (or \( B \)) at least for substances formed from \( H, N, O \) and \( C \). therefore

\[ U = W \left( \frac{B}{V} \right) = W r_1 \]  \hspace{1cm} (2.13)

Where \( W \) is a constant approximately equal to 5000 m/s. physically, \( W \) represents the sound velocity, when the entire volume of space is filled with molecules. [Robert & Stephen, 1969]

2.6 **Specific Acoustic Impedance**

Using the electro mechanical analogy specific acoustic impedance \( Z_A \) of an acoustic wave is given by, [David & Cheeke, 2002]

\[ Z_A = \frac{P}{v} \]  \hspace{1cm} (2.14)

Where \( v \) is the particle velocity and \( P \) is the acoustic pressure
The above equation is an acoustical analogy of Ohm's law in electrical engineering. The acoustic pressure \( P \) corresponds to an electric voltage and the acoustic impedance \( Z_A \) to the electric impedance. The difference between acoustic impedance and electric impedance is that the electrical impedance exists between two points in a current carrying circuit whereas the latter is a point property. The product \( P v \) represents the instantaneous acoustic power similar to the electrical instantaneous power \( EI \). The former represents the energy flow per unit area per unit time while the latter is the total power delivered to the circuit across which the potential difference is maintained.

In general the acoustic impedance is a complex quantity. For a travelling wave in finite medium acoustic impedance has a real value and is called the wave resistance \( \rho U \). In short \( Z_A \) can be defined as the product of velocity of sound \( U \) and the density \( \rho \) of that medium. [Philip & Uno Ingrad, 1968]

\[
Z_A = U\rho \tag{2.15}
\]

In the case of travelling plane waves pressure and particle velocity are related as shown below.

For forward travelling wave,

\[
P = Z_A U \tag{2.16}
\]

For backward travelling wave,

\[
P = -Z_A U \tag{2.17}
\]

Where, \( Z_A = U\rho \) is the specific acoustic impedance of the medium. The pressure and particle velocity for a forward travelling wave are in phase but for a backward travelling wave they are out of phase. [David, 2000]
2.7 **Compressibility of Liquids**

The only elastic modulus that can be defined for a liquid is the bulk modulus $K$. The compressibility of a liquid is usually small and numerically comparable with that of solid. If $V$ is the original volume of a liquid, $\Delta V$ the change in volume and $\Delta P$ the pressure applied then bulk modulus is given by,

$$K = -V \frac{\Delta P}{\Delta V}$$  \hspace{1cm} (2.18)

The value of the bulk modulus depends on the rate at which the pressure changes are carried out. If the pressure is applied slowly, the liquid may remain at a constant temperature and the resulting bulk modulus is called the isothermal bulk modulus $K_T$. If the pressure changes are rapid the adiabatic conditions are satisfied and the elastic constant is Adiabatic bulk modulus $K_S$. Compressibility is the reciprocal of bulk modulus. Isothermal compressibility $\beta_T$ is the reciprocal of isothermal bulk modulus $K_T$ and Adiabatic compressibility $\beta_S$ is the reciprocal of adiabatic bulk modulus $K_S$.

A less direct method of measuring the adiabatic compressibility of a liquid is from measurements of ultrasonic velocity $U$ and density $\rho$ using the equation,

$$\beta_s = \frac{1}{U^2 \rho}$$  \hspace{1cm} (2.19)

The structural change of the molecules in the mixture takes place due to the existence of electrostatic field between the interacting molecules. Thus the structural arrangement of molecules results in considerable change in adiabatic compressibility $\beta_S$. [Baldev et al., 2002]
2.8 VARIATION OF COMPRESSIBILITY WITH TEMPERATURE

According to Rao, the effect of temperature on the adiabatic compressibility $\beta_s$ as

$$\left(\frac{V^{1/3}}{M\beta_s}\right)^{1/7} = k(T_c - T) \quad (2.20)$$

Where $V$ is the molar volume, $M$ is the molecular weight, $T_c$ is the critical temperature and $k$ is a constant for each liquid.

Another relation connecting adiabatic compressibility and density is, [Partington, 1962]

$$\beta_s^{1/7} \rho = a \text{ constant.} \quad (2.21)$$

2.9 REFRACTIVE INDEX

The refractive index is the ratio of the wave velocity of light in vacuum to the wave velocity in the medium. The refractive index is a physical property of the medium that depends on the wavelength of the light, and the temperature. The wavelength used is that of the yellow sodium D line (a doublet 589.0-589.6 nm), and the index of refraction is given the symbol $n_D$. The temperature needs to be specified, and is usually 20 or 25°C. The refractive index decreases with increasing temperature, and for most organic compounds one can correct for the temperature using $dn/dt = -0.0004/\degree C$.

2.9.1 THE TEMPERATURE COEFFICIENT OF THE REFRACTIVE INDEX OF WATER

Refractive index is a characteristic property of a substance. Thermal coefficient of refractive index is also a characteristic property. Hawkes.J.B and Astheimer.R.W determined the refractive index of water for sodium light ($\lambda = 589.3$AU) from -5°C to +25°C using a Jamin interferometer. Measurements of the rate of change of refractive index with temperature, $(dn/dT)$, have been made on water.
The refractive index as well as the temperature coefficient of refractive index was plotted against temperature in fig.2.2 and fig.2.3 respectively. It is a mathematical observation that irregularities in the relationship between two variables have a more marked effect on the derivatives than on the function itself. For this reason anomalies in the index of refraction will more easily be found in the thermal coefficient of the index than in the index-temperature relation. [Hawkes & Astheimer, 1948]

Fig.2.2 Variation of refractive index of water with temperature
Fig. 2.3 Thermal coefficient of the index of refraction of water for 
\( \lambda = 5893 \text{AU} \)

### 2.10 PARAMETERS CONNECTING REFRACTIVE INDEX, DENSITY AND ULTRASONIC VELOCITY OF LIQUIDS.

Novel empirical relations connecting refractive index \( n \), ultrasonic velocity \( U \) and density \( \rho \) of liquids derived by Mohanan et al. are given below. A detailed discussion is given in sections 3.3 and 3.4 of the next chapter. [Mohanan et al., 1997]

1. Specific optic impedance,

\[
Z_0 = \frac{120\pi \rho}{n}
\]  

(2.22)
2. Specific optical volume,
\[ n = \frac{n}{\rho^{0.45}} \]  
(2.23)

3. Specific opto-acoustic velocity,
\[ \eta = \frac{U^{0.15}}{n} \]  
(2.24)

2.11 UV-VISIBLE ABSORPTION SPECTRA

The relative energies of the various sorts of orbitals present in organic compounds and the possible electron jumps that might cause are shown in fig.2.4. When light passes through the compound, energy from the light is used to promote an electron from a bonding or non-bonding orbital into one of the empty anti-bonding orbitals. In each possible case, an electron is excited from a full orbital into an empty anti-bonding orbital. Each jump takes energy from the light, and a big jump obviously needs more energy than a small one. Each wavelength of light has a particular energy associated with it. If that particular amount of energy is just right for making one of these energy jumps, then that wavelength will be absorbed - its energy will have been used in promoting an electron. For a bigger energy jump, the absorbed light is having a higher frequency or a lower wavelength.

An absorption spectrometer works in a range from about 200nm (in the near ultra-violet) to about 800 nm (in the very near infra-red). Only a limited number of the possible electron jumps absorb light in that region. The important jumps are shown in black, and a less important one in grey. The grey dotted arrows show jumps which absorb light of wavelength less than 200 nm, which is outside the region of the spectrum we are working in.
Fig. 2.4 Representation of $\pi \rightarrow \pi^*$, $\eta \rightarrow \pi^*$ and $\eta \rightarrow \sigma^*$ transitions

1. From $\pi$ bonding orbitals to $\pi$ anti-bonding orbitals ($\pi \rightarrow \pi^*$)
2. From non-bonding orbitals to $\pi$ anti-bonding orbitals ($\eta \rightarrow \pi^*$) and
3. From non-bonding orbitals to sigma anti-bonding orbitals ($\eta \rightarrow \sigma^*$).

In order to absorb light in the region from 200 - 800 nm, the molecule must contain either $\pi$ bonds or atoms with non-bonding orbitals. A non-bonding orbital is a lone pair on oxygen, nitrogen or a halogen. Groups in a molecule which absorb light are known as chromophores. [Jacques Kagan, 1993]

Fig. 2.5 shows a simple UV-visible absorption spectrum for buta-1,3-diene. Absorbance (on the vertical axis) is just a measure of the amount of light absorbed. The higher the value, the more of a particular wavelength is being absorbed. It is seen that absorption peak is at a value of 217 nm. This is in the ultra-violet and so there would be no visible sign of any light being absorbed. Therefore buta-1,3-diene is colourless. In buta-1,3-diene, CH$_2$=CH-CH=CH$_2$, there are no non-bonding electrons. This means that the only electron
jumps taking place (within the range that the spectrometer can measure) are from pi bonding to pi anti-bonding orbitals ($\pi \rightarrow \pi^*$).

![Absorption Spectrum of Buta-1,3-diene](image.png)

**Fig.2.5 UV absorption spectrum of buta-1,3-diene**

A chromophore such as the carbon-oxygen double bond in ethanal, for example, obviously has pi electrons as a part of the double bond, but also has lone pairs on the oxygen atom. This means that both of the important absorptions from the last energy diagram are possible. An electron may be excited from a pi bonding to a pi anti-bonding orbital ($\pi \rightarrow \pi^*$), or from an oxygen lone pair (a non-bonding orbital) into a pi anti-bonding orbital ($n \rightarrow \pi^*$). The non-bonding orbital has a higher energy than a pi bonding orbital. This means that the jump from an oxygen lone pair into a pi anti-bonding orbital needs less energy. This means it absorbs light of a lower frequency and therefore a higher wavelength. Ethanal can therefore absorb light of two different wavelengths. [Rohatgi Mugherjee, 1986]

1. The pi bonding to pi anti-bonding ($\pi \rightarrow \pi^*$) absorption peaks at 180 nm.
2. The non-bonding to pi anti-bonding ($n \rightarrow \pi^*$) absorption peaks at 290 nm.

Both of these absorptions are in the ultra-violet, but most spectrometers won't pick up the one at 180 nm because they work in the range from 200 - 800 nm.

2.11.1 Conjugation, delocalisation and absorption wavelengths

Consider these three molecules:

\[
\begin{align*}
CH_2 &= CH_2 & CH_2 &= CH - CH = CH_2 & CH_2 &= CH - CH = CH - CH = CH_2 \\
(\text{Ethene}) & & (\text{buta-1,3-diene}) & & (\text{hexa-1,3,5-triene})
\end{align*}
\]

Ethene contains a simple isolated carbon-carbon double bond, but the other two have conjugated double bonds. In these cases, there is delocalisation of the pi bonding orbitals over the whole molecule. All of the above molecules give similar UV-visible absorption spectra. For ethene, $\lambda_{\text{max}} = 171$ nm, for buta-1,3-diene, $\lambda_{\text{max}} = 217$ nm and for hexa-1,3,5-triene, $\lambda_{\text{max}} = 258$ nm. The only difference being that the absorptions move to longer and longer wavelengths as the amount of delocalisation in the molecule increases.

The maximum absorption is moving to longer wavelengths (shorter frequencies or lesser energies) as the amount of delocalisation increases. Therefore there must be less energy gap between the bonding and anti-bonding orbitals as the amount of delocalisation increases.

In fig.2.6, ethene is compared with buta-1,3-diene and hexa-1,3,5-triene. In ethene, there is one pi bonding orbital and one pi
anti-bonding orbital. In buta-1,3-diene, there are two pi bonding orbitals and two pi anti-bonding orbitals. In hexa-1,3,5-triene, there are three pi bonding orbitals and three pi anti-bonding orbitals. The highest occupied molecular orbital is often referred to as the HOMO - in these cases, it is a pi bonding orbital. The lowest unoccupied molecular orbital (the LUMO) is a pi anti-bonding orbital. It is to be noted that the gap between these has fallen. It takes less energy to excite an electron in the buta-1,3-diene case than with ethene. In the case of hexa-1,3,5-triene, the excitation energy is still less. If this is extended to compounds with really massive delocalisation, the wavelength absorbed will eventually be high enough to be in the visible region of the spectrum, and the compound will be seen as coloured. [Rohatgi Mugherjee, 1986]

**Fig.2.6 Comparative study of excitation energies in ethane, buta-1,3-diene and hexa-1,3,5-triene.**

A good example of this is the orange plant pigment, beta-carotene present in carrots.
2.11.2 CANONICAL FORMS

There are two possible Kekulé structures for benzene as shown in fig.2.7 (a). The real structure is somewhere between the two. All the bonds are identical and somewhere between single and double in character. Molecular orbital energy levels of benzene are shown in fig.2.7 (b). It is found that the characteristic absorption wavelength for the transition from HOMO to LUMO is 255nm.

![Energy levels of benzene](image)

**Fig.2.7 (a) Kekulé structures and (b) molecular orbital energy levels of benzene**

METHYL ORANGE

We know that methyl orange is yellow in alkaline solutions and red in acidic ones. The structure in alkaline solution is given in fig.2.8.

![Methyl orange](image)

**Fig.2.8 yellow form of methyl orange**

In acid solution, a hydrogen ion is (perhaps unexpectedly) picked up on one of the nitrogens in the nitrogen-nitrogen double bond.
The positive charge on the nitrogen is delocalised (spread around over the structure) especially out towards the right-hand end of the molecule as we have written it. The normally drawn structure for the red form of methyl orange is shown in fig. 2.9 b. These two forms (fig. 2.9 a and b) can be thought of as the result of electron movements in the structure, and curly arrows are often used to show how one structure can lead to the other as shown in fig. 2.10.
In reality, the electrons haven't shifted fully either one way or the other. Just as in the benzene case, the actual structure lies somewhere in between these.

The yellow form has an absorption peak at about 440 nm. That's in the blue region of the spectrum, and the complementary colour of blue is yellow. That's exactly what you would expect. The red form has an absorption peak at about 520 nm. That's at the edge of the cyan region of the spectrum, and the complementary colour of cyan is red. Again, there's nothing unexpected here. The change from the yellow form to the red form has produced an increase in the wavelength absorbed. An increase in wavelength suggests an increase in delocalization which means that there must be more delocalisation in the red form than in the yellow one. [Herzberg, 1950]

2.12 Identification of Organic Compounds using UV Spectra

It is well known that the wavelength of maximum absorption (\(\lambda\)-max) depends on the presence of particular chromophores (light-absorbing groups) in a molecule.

For example, a simple carbon-carbon double bond (ethene) has a maximum absorption at 171 nm. The two conjugated double bonds in buta-1,3-diene have a maximum absorption at a longer wavelength of 217 nm. There are two peaks in the spectrum of ethanal (containing a simple carbon-oxygen double bond) at 180 and 290 nm. If the peaks on a given UV-visible absorption spectrum are compared with a list of known peaks, it would be fairly easy to pick out some structural features of an unknown molecule. Lists of known peaks often include molar absorptivity values also as shown in table 2.1. That might help one to be even surer.
<table>
<thead>
<tr>
<th>Electron jump</th>
<th>wavelength of maximum absorption (nm)</th>
<th>molar absorptivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>lone pair to pi anti-bonding orbital</td>
<td>290</td>
<td>15</td>
</tr>
<tr>
<td>pi bonding to pi anti-bonding orbital</td>
<td>180</td>
<td>10000</td>
</tr>
</tbody>
</table>

Table 2.1 List of UV absorption peaks due to electronic transitions in ethanal.

2.13 Use of UV-absorption spectra to find concentrations

Beer-Lambert Law is

$$\log_{10} \frac{I_0}{I} = \varepsilon lc$$ \hspace{1cm} (2.25)

Where $l$ is the length of the solution through which the light passes and $c$ is the concentration of solution, $\varepsilon$ is the molar absorptivity of the solution, $I_0$ is the intensity of the incident light and $I$ is the intensity of the transmitted light.

The expression on the left of the equation is known as the absorbance of the solution and is measured by a spectrometer. The equation is sometimes written in terms of that absorbance.

$$A = \varepsilon lc$$ \hspace{1cm} (2.26)

(Detailed explanation is given in section 5.5 of chapter 5)
2.13.1 FINDING CONCENTRATION BY PLOTTING A CALIBRATION CURVE

Make up a number of solutions of the compound under investigation - each of accurately known concentration. For each solution, the absorbance at the wavelength of strongest absorption is measured using the same container. Then a graph of that absorbance against concentration is plotted. This is a calibration curve. According to the Beer-Lambert Law, absorbance is proportional to concentration, and so we would expect a straight line. That is true as long as the solutions are dilute, but the Law breaks down for solutions of higher concentration, and so we get a curve under these circumstances. Having drawn a best fit line, the calibration curve will probably look something like fig.2.11. If the Beer-Lambert Law worked perfectly, it would pass through the origin. If the absorbance is known, we can just read the corresponding concentration from the graph as below.

![Calibration Curve](image)

Fig.2.11 Determination of concentration of solution from calibration curve.