ADDIS ABABA UNIVERSITY

COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES

DEPARTMENT OF CHEMISTRY

INVESTIGATION OF SOLVENT EFFECTS ON CARBONYL STRETCHING VIBRATIONAL FREQUENCY OF CAMPHOR

A MASTER THESIS

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A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY PRESENTED IN PARTIAL FULFILMENT OF REQUIREMENTS FOR DEGREE OF MASTER OF SCIENCE (PHYSICAL CHEMISTRY)

ADDIS ABABA, ETHIOPIA

AUGUST, 2021

ADDIS ABABA UNIVERSITY

COLLEGE OF NATURAL SCIENCES AND COMPITUTATIONAL SCIENCES

DEPARTMENT OF CHEMISTRY

This is certifying that the thesis prepared by Abiyot Fituma Kumsa entitled ”Investigation of solvent effects on carbonyl Stretching vibrational frequency of camphor” and submitted in partial fulfillment of the requirements of the Degree of Master of Science in Chemistry (Physical Chemistry) compiles with regulation of the University and meets the accepted standards with respect to originality and quality.

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Abstracts

Solvent effects on the carbonyl stretching vibrational frequency of Camphor were investigated. The solvents were chosen to cover wide polarity range and include carbon tetrachloride,2-propanol, methanol, and acetonitrile. For protonic and aprotonic solvents two distinct behaviors were observed. In non-protonic or aprotonic solvent there seems little or negligible polarity dependent shift was observed. The situation is different for protonic solvent where strong blue shift was obtained. These facts could be attributed to the low dipole moment of the chromophore (in aprotonic solvents) and hydrogen bonding with solvent molecules. The broadness in protonic solvents compared to that in aprotonic solvents support the suggestion made earlier and indicate the Band I is due to mainly hydrogen bonding. Similarly, the solvent dependence of Band II analyzed. Generally, a bathochromic shift was observed though the peak in acetonitrile appears at higher frequency than both protonic solvents. Additional shoulder peak of absorption was observed in methanol and propanol solvents. What is striking was that the shoulder is approximately same as that found in CCl_4 *solution. This may be due to complex (hydrogen bonding) between the carbon of carbonyl and oxygen of the alcohols.*

Key words: Camphor, Carbonyl carbon, Solvent, and hydrogen bonding

Acknowledgments

I would like to express my deepest gratitude to my research advisor, Dr. Mesfin Redi, for all their unreserved guidance, technical and moral support and encouragement during the entire project work and preparation of the thesis document. I am thankful to my co-workers Ato Tsige Desalegn, Ato Tadele Abebe and Ato Hailu Wolde for their friendly moral support and scientific discussion during the entire work. I would like to thank Ato Yisak Tsegazeb, Ato Hagos Yisak and W/o Mulu Hagos for their genuine guidance, advice and professional support in all aspects. Finally, I would like to express my deepest gratitude to my father Ato Fituma Kumsa and my wife W\o Genet Mengistu for their motivation, encouragement and moral support throughout my life.

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List of Abbreviations

FTIR	Fourier transforms infrared
ACN	Acetonitrile
ACT	Acetone
MeOH	Methanol
PrOH	Propanol
CCl_4	Carbon tetrachloride
k_B	Boltzmann constant
T	Absolute temperature
Eq	Equation
C=O	Carbonyl
IR	Infrared
Max	Maximum
υ	Fundamental vibration frequency,
c	Speed of light
k	Force constant
μ	Reduced mass
n	Molecule consisting of atoms
A	Absorbance
T	Transmittance
I^0	The intensity of incident radiation
I	The intensity of the transmitted radiation
ZnSe	ZincSelenide

1. INTRODUCTION

Radiation is a form of energy and we are constantly literature revision of its presence via our sense of sight and ability to feel radiant heat. It is types of absorption spectroscopy. Any technique that measures the amount of light absorbed a compound as the function of the wavelength of light. Infrared spectroscopy uses light from infrared region of electromagnetic spectrum. The absorption leads to absorption bands in the IR spectrum. The polarity of the bond has a significant impact on the intensity of an IR absorption band. The vibration that causes a significant change in the dipole moment of a chemical. It may be considered in terms of a wave motion where the wavelength, λ, is the distance between two successive peaks and the frequency, ν, is the number of peaks passing.

Infrared (FTIR) spectroscopy is a very powerful technique which uses electromagnetic radiation in the infrared region for the determination and identification of molecular structure as well as it uses for various quantitative analysis. It is important to note that atoms can absorb energy from electromagnetic radiation; this absorbed energy alters the state of the atoms within the molecule. These changes are usually manifest in alterations to the frequency and amplitude of molecular vibrations, which may be measured and plotted to produce an infrared spectrum [1-4].

Infrared spectrometers use optical devices for dispersing and focusing electromagnetic radiation of IR frequency which is passed through the sample and any changes in absorbance measured against a reference beam. There are three well defined IR regions (near, mid, and far).

The aim of this thesis work was therefore to investigate the effect of solvents on carbonyl vibration frequency of camphor. The observed vibration frequencies in different solvents are to be correlated with a polarity function. In addition, the effect of concentration on the band shape and position, especially in non-polar solvents, was examined.

2. THEORETICAL BACKGROUND

Camphor is organic compound that has a functional group of carbonyls (ketone), which was commonly used in creams, ointments, and lotions. It is a natural product deriving from the wood of camphor laurel (*Cinnamomum camphora L*).

It is a white, volatile crystalline substance with a strong odor and pungent taste, easily absorbed through the skin. Easily soluble in methanol, Propanol and acetonitrile but slight soluble in carbon tetrachloride. It has the potential for side effects, especially if you use it in high doses. Never take camphor internally or apply to broke skin, as it can be toxic. Camphor tree is native to China, India, Mongolia, Japan, Taiwan, and a variety of this fragrant every green tree in southern United State of America especially in Florida [5,6].

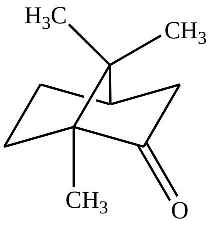

Figure 1: Structure of camphor ($C_{10}H_{15}O$).

2.1 Quantum Theory

Atoms and molecules exist in a number of defined energy states or levels and a change of level requires the absorption or emission of an integral number of a unit of energy called a quantum, or in our context, photon. The energy of a photon absorbed or emitted during a transition from one molecular energy level to another is given by the equation.

$$E=h\nu \qquad 1$$

Where h is known as Planck's constant and ν is the frequency of the photon. Since, $c=\nu\lambda$ Therefore$=h\,c/\lambda$, thus, the shorter the wavelength, the greater the energy of the photon and vice versa. A molecule of any substance has an internal energy which can be considered as the sum of the energy of its electrons, the energy of vibration between its constituent atoms and the energy associated with rotation of the molecule. The electronic energy levels of simple molecules are widely separated and usually only the absorption of a high energy photon, that is one of very short wavelength, can excite a molecule from one level to another.

The vibrational energy states of the various parts of a molecule are much closer together than the electronic energy levels and thus protons of lower energy (longer wavelength) are sufficient to bring about vibrational changes. Light absorption due to only to vibrational changes occurs in the infrared region.

2.2 Fundamental Concept of Spectroscopy

2.2.1 Spectroscopy

Spectroscopy is the interaction between matters with light. It is important to note that atoms can absorb energy from electromagnetic radiation; this absorbed energy alters the state of the atoms within the molecule. These changes are usually manifest in alterations to the frequency and amplitude of molecular vibrations, which may be measured and plotted to produce an infrared spectrum. Infrared spectrometers use optical devices for dispersing and focusing electromagnetic radiation of IR frequency which is passed through the sample and any changes in absorbance measured against a reference beam.

Infrared radiation of all wavelengths is transmitted from the source. Some of the wavelengths of IR radiation will be absorbed by the sample and some of them will pass through (they are transmitted). The IR radiation which is transmitted is measured by the detector resulting in a unique.IR spectrum for the sample of interest. This spectrum represents the IR absorption and transmission of that molecule.

No two unique molecules will produce the same IR spectrum, resulting in IR spectroscopy being a very useful tool for molecular characterization and quantification. Infrared refers to the part of the electromagnetic spectrum between the visible and microwave region. The energy of infrared light is no longer sufficient to induce transitions of valence electrons. Instead, infrared radiation excites vibrational and rotational motions in molecules. The average modern infrared instrument records spectra from an upper limit of around 4000cm^{-1} (by convention) down to 400 cm^{-1} as defined by the optics of the instrument (commonly based on potassium bromide) [7-9].

In the most basic terms, the infrared spectrum is formed as a consequence of the absorption of electromagnetic radiation at frequencies that correlate to the vibration of specific sets of chemical bonds from within a molecule. First, it is important to reflect on the distribution of energy possessed by a molecule at any given moment, defined as the sum of the contributing energy terms (equation 1).

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} + E_{translational} \qquad 2$$

The translational energy relates to the displacement of molecules in space as a function of the normal thermal motions of matter. Rotational energy, which gives rise to its own form of spectroscopy, is observed as the tumbling motion of a molecule, which is the result of the absorption of energy within the microwave region. The vibrational energy component is a higher energy term and corresponds to the absorption of energy by a molecule as the component atoms vibrate about the mean center of their chemical bonds. The electronic component is linked to the energy transitions of electrons as they are distributed throughout the molecule, either localized within specific bonds, or delocalized over structures, such as an aromatic ring.

Absorption of infrared light occurs principally based on a transition between energy levels of molecular vibration (equation 3). That is why an infrared absorption spectrum is a vibrational spectrum of a molecule.

The fundamental requirement for infrared activity, leading to absorption of infrared radiation, is that there must be a net change in dipole moment during the vibration for the molecule or the functional group under study. From Hooke's law, the fundamental vibrational frequency of a molecular ensemble can be expressed according to equation 3 [10-14].

$$\upsilon = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad 3$$

Where υ is fundamental vibration frequency, c is speed of light, k is force constant, and μ is reduced mass. The reduced mass can be calculated,

$\mu = m_1.m_2 / m_1 + m_2$. Where m_1 and m_2 are the component masses for the chemical bond under consideration. The force constant can be regarded as a measure of the strength of the spring in the ball and spring model for molecular vibration. That means as the force constant increases, the vibrational frequency also increases [12–14]. Thus, according to Hooke's law vibrational frequency of a given molecule is directly related to the strength of attraction force between two nuclei and inversely proportional to the effective mass. It is very easy to imagine that there are an infinite number of vibrations, which in reality would lead to a totally disorganized model for interpretation. Instead, we describe the model in terms of a minimum set of fundamental vibrations, based on a threefold set of coordinate axes, which are known as the normal modes of vibration.

There are three well defined IR regions (near, mid and far).

- **Near infrared** (12820-4000 cm^{-1} or 780-2500nm): poor in specific absorptions, consists of overtones and combination bands resulting from vibrations in the mid-infrared region of the spectrum.

- **Mid-infrared** (4000-400 cm^{-1} or 2500nm-25µ): provides structural information for most organic molecules.

- **Far-infrared** (400-33 cm^{-1} or 25µ-303µ) has been less investigated than the other two regions; however, it has been used with inorganic molecules. The low energies, typically encountered within the infrared region, are not sufficient to cause electronic transitions; however, they are large enough to cause changes in the frequency and amplitude of molecular vibrations.

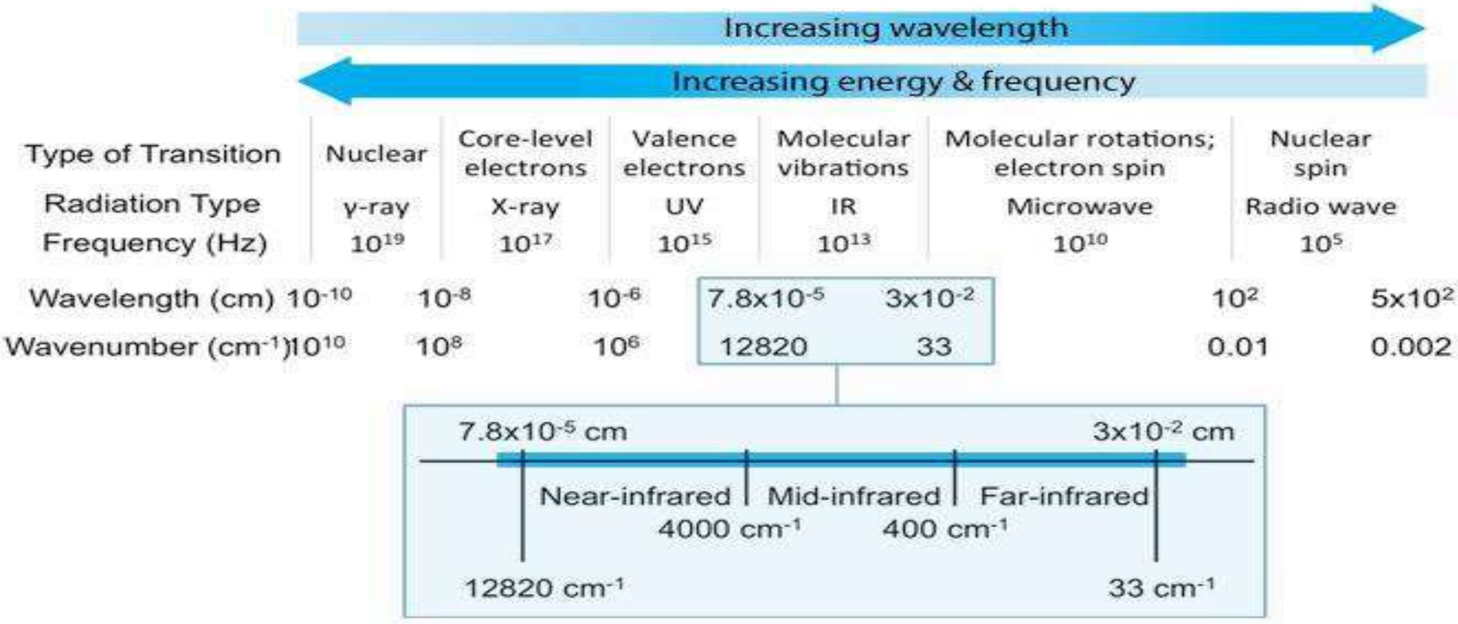

Figure 2: The electromagnetic spectrum and the infrared.

2.2.2Infrared Spectroscopy of Carbonyl Compounds

All carbonyl compounds absorb in the region 1760-1665 cm^{-1} due to the stretching vibration of the C=O bond. This distinctive carbonyl band is particularly useful for diagnostic purposes because it has a characteristic high intensity and few other functional groups absorb in this region. Different carbonyl compounds absorb in narrow ranges within the general carbonyl region. The exact wave number of the C=O stretch can give you clues as to whether the compound is a ketone, aldehyde, ester, or carboxylic acid; furthermore, it can tell you whether it is alpha beta carbonyl.

Table 1: List of wave number of carbonyl compound.

S/R	Frequency Range in cm^{-1}	Type of compound	Example
1	1750-1735	Saturated aliphatic ester	RCOOR
2	1740-1720	Saturated aliphatic aldehyde	RCOH
3	1730-1715	Unsaturated ester	RCH=COOR
4	1715-1710	Saturated aliphatic ketone	RCOR

Where R is any alkyl or aryl group, CO is C=O and OR /OH is O-R bond and O-H bond respectively.

2.2.3 Infrared Spectroscopy of Ketones

The carbonyl stretching vibration band carbonyl of saturated aliphatic Ketones appears at the frequency of 1715cm^{-1}. Conjugation of the carbonyl group with carbon-carbon double bonds or phenyl groups, as in alpha, beta-unsaturated aldehyde and benzaldehyde, shifts this band to lower wave numbers, 1685-1666 cm^{-1}.This is saturated ketones and the C=O band appears at1715cm^{-1}. Note the C–H stretches (around 2991 cm^{-1}) of alkyl groups. It is usually not necessary to mark any of the bands in the fingerprint region (less than 1500 cm^{-1}).

2.3 Vibrational Spectroscopy

The vibrational frequencies for any particular functional group are characteristic of that group. Most carbonyl stretches occur between 1650 and 1750 cm^{-l} and are used for the identification of materials and for the determination of structure in an unknown pure compound. A molecule composed of n-atoms has 3n degrees of freedom, six of which are translations and rotations of the molecule itself. This leaves 3n-6 degrees of vibrational for nonlinear, freedom (3n-5, if the molecule is linear). Furthermore, the number of observed absorptions may be decreased by molecular symmetry, spectrometer limitations, and spectroscopic selection rules. One selection rule that influences the intensity of infrared absorptions is that a change in dipole moment should occur for a vibration to absorb infrared energy. Absorption bands associated with C=O bond stretching are usually very strong because a large change in the dipole takes place in that mode.

2.4Absorption Law

The amount of infrared radiation absorbed by the sample, at any given wavelength, can be measured in different ways. The use of transmittance is common place in infrared spectroscopy [5,10, 11, and 15]. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting graph is presented as absorbance (A) versus wavelength. When the radiation passes through a solution, the amount of light absorbed or transmitted is an exponential function of the molecular concentration of the solute and also a function of length of the path of radiation through the sample [12].

$$A = \log \frac{I^0}{I} = -\log T \text{ And } \mathrm{A}=\mathrm{T}^{-1} \qquad 4$$

Where A=absorbance, T=transmittance, I^0=the intensity of incident radiation, I=the intensity of the transmitted radiation. This implies that the efficiency of light absorption at a given wavelength (λ) by an absorbing medium is characterized by an absorbance, A, which gives information about how much light, is absorbed at $\lambda_{\max}$.

The absorbance of a sample also follows Beer-Lambert Law which states that the fraction of incident radiation absorbed is proportional to the number of absorbing molecules in its path and is given by the equation [12–14].

$$\mathrm{A}= \varepsilon\ \mathrm{c}\ \mathrm{l} \qquad 5$$

Where Ɛ is molar absorption coefficient having the unit’s dm3/mol, c is the concentration in mol/cm^3, and l is path length in cm.

2.5 Factors Affecting Vibrational Frequency

There are various interrelated factors which shift the vibrational frequencies from their expected values. For this reason, the values of vibrational frequencies of the bonds calculated by the application of Hooke’s law are not exactly equal to their observed values from Hooke’s law; the fundamental vibrational frequency of a molecular ensemble can be expressed according to equation [7–9and16]. A molecule consisting of *n* atoms has a total of 3*n* degrees of freedom, corresponding to the Cartesian coordinates of each atom in the molecule. In a nonlinear molecule, 3 of these degrees are rotational and 3 are translational and the remaining corresponds to fundamental vibrations; in a linear molecule, 2 degrees are rotational and 3 are translational. The net number of fundamental vibrations for nonlinear and linear molecules is therefore [17, 18].

S/R	Molecule	Degree of Freedom
1	Linear	3n-5
2	Nonlinear	3n-6

Where n is the number of component atoms in the molecule.

The transition moment for a transition between lower and upper states with vibrational wave functions $\psi_\upsilon^{'}$ and $\psi_\upsilon^{''}$ respectively is given by:

$$R_\upsilon = \int \psi_\upsilon^{'} * \mu \psi_\upsilon^{''} dx \tag{6}$$

Where, x is $(r - r_e)$, the displacement of intermolecular distance from the equilibrium. The dipole moment, μ is zero for a homo nuclear diatomic molecule, resulting in $R_\upsilon = 0$ and all vibrational transitions being forbidden. For a hetero nuclear diatomic molecule, μ is non-zero and varies with x. This variation can be expressed as a Taylor series expansion [16]:

$$\mu = \mu_e + \left(\frac{d\mu}{dx}\right)_e x + \frac{1}{2!}\left(\frac{d^2\mu}{dx^2}\right)_e x^2 + \ldots \tag{7}$$

The subscript '*e*' refers to the equilibrium configuration. The transition moment of equation 8 now becomes:

$$R_\upsilon = \mu_e \int \psi_\upsilon^{'} * \mu \psi_\upsilon^{''} dx + \left(\frac{d\mu}{dx}\right)_e \int \psi_\upsilon^{''} * x \psi_\upsilon^{''} dx + \ldots \tag{8}$$

Since, $\psi_\upsilon^{'}$ and $\psi_\upsilon^{''}$ are Eigen functions of the same Hamiltonian and they are orthogonal, which means that, when $\upsilon^{'} \neq \upsilon^{''}$.

$$\int \psi_\upsilon^{'} * \psi_\upsilon^{''} dx = 0 \tag{9}$$

Thus, due to the orthogonality of the Eigen function, the first term of this equation 10, which denotes the magnitude of the permanent dipole of the molecule is 0 except when $\upsilon^{'} = \upsilon''$ holds. For the second term to have a value other than 0, both ($d\mu / dx \neq 0$) and $\int \psi_{\upsilon}^{'} * \psi_{\upsilon}^{''} dx \neq 0$ must be satisfied. These two conditions lead to the two selection rules. The nature of the Eigen function permits the integral to have a value other than 0 only when $\upsilon^{'} = \upsilon'' \pm 1$ holds.

Vibrational energies of molecules are quantized like all other molecular energies [9]. The allowed vibrational energies and the energy of a transition between two vibrational states respectively are given by the equations 9 and 10 below:

$$E_{\upsilon+1} - E_{\upsilon} = \left(\upsilon + 1 + \frac{1}{2}\right)h\upsilon - \left(\upsilon + \frac{1}{2}\right)h\upsilon = h\upsilon \qquad 10$$

2.5.1. Reaction Field and Solvatochromism

The influence of a molecule in solution (the solute) and its surrounding medium (the solvent) one can simple be described using the Onsager model. The basic assumption made in this model is that the solute is placed in a spherical cavity inside the solvent. The latter is described as a homogeneous, polarizable medium of constant dielectric constant. The solute dipole moment induces a dipole moment of opposite direction in the surrounding medium. Polarization of the medium in turn polarizes the charge distribution in the solvent. Thus, the field of the dipole moment in such a cavity polarizes the resulting in homogeneous polarization of the environment which will give to rise to a field at the dipole, which is called the reaction field(R).

The reaction field depends on the nature and arrangement of the surrounding solvent molecules. The useful approximation that has been developed is that, the solvent is regarded as a homogeneous isotropic dielectric continuum having a dielectric constant ε_r.

The dissolved molecules are assumed to be accommodated in this continuum in spherical cavities having a radius a. The dipole moment is represented by a point dipole located in the center of the spherical cavity. In this approximation the reaction field (R) of the dissolved molecule is given by [20]:

$$R = \frac{2(\varepsilon_r - 1)\mu}{(2\varepsilon_r + 1)a^3} \qquad 11$$

Where a is the Onsager cavity radius, ε_r is dielectric constant, μ is dipole the total dipole moment (permanent plus induced dipole moment) of the dissolved molecule.

The change in the position and intensity of the electronic band depend not only on the reaction field in the ground state but also on the reaction field in the excited electronic state. When the Franck–Condon principle for optical excitation process is taken into account, the fields in the excited state contain not only terms similar to that in the above equation but also other similar terms that depend on the refractive index, n of the solution. The effect of the field on the position and intensity of electronic bands is therefore determined by the dielectric constant and the refractive index of the solution in this approximation.

The effect of the reaction field is the main cause of strong Solvatochromism, which is observed in particular with molecules having large dipole moments, and hence strong reaction fields. The reaction field (on average) is always parallel to the dipole moment of the dissolved molecule.

A molecule having a permanent dipole moment μ_g in the electronic ground state and a moment μ_a parallel to it in the excited state, the solvent dependence of the wave number $\overline{\upsilon}_a^{sol}$ of the absorption maximum is given to a good approximation by the following equation [14]:

$$\overline{\upsilon}_a^{sol} = \upsilon_a^0 - \frac{(\mu_a - \mu_g)(F_{RM})}{hc} - \frac{2(n^2-1)}{a^3(2n^2+1)}.D \qquad 12$$

Where, υ_a^0 is the wave number of the absorption maximum in the free molecule (gas state). Equation 13corresponds to Equation 18 except that it also contains a term that depends on a quantity D. The term describes the solvent dependence of the position of the absorption band due to the position of the dispersion interactions between the dissolved molecules and the surrounding solvent molecules.

For the low electronic excitations, D>0, so that the dispersion interactions always cause a red shift with increasing refractive index of the solution [17]. The effective electronic field F_{RM} in equation 13 is the means of the reaction fields of the dissolved molecule in the ground state and in the Franck–Condon excited state.

The more simplified expressions for the determination of the spectral shift with solvent polarity variation have been formulated by Lippert and Mataga. Compounds in which a substantial change of the molecular dipole moment occurs up on electronic excitation usually reveal large spectral shifts with solvent polarity in absorption, in emission, or in both. Lippert–Mataga expression for the solvent induced changes in the absorption energy relative to their values in vacuum is: [5]:

$$hc\bar{\upsilon}_{abs} = hc\bar{\upsilon}^{0}_{abs} - \frac{\mu_g(\mu_e - \mu_g)}{a^3} . \left[\frac{\varepsilon_r - 1}{2\varepsilon_r + 1} - \frac{n^2 - 1}{2n^2 + 1} \right] \qquad 13$$

2.5.2. Electrochromism and Solvatochromism

The position and the intensity of electronic bands are influenced by an electric field. Pronounced changes in the position of bands are mainly due to the dipole moment of the molecule in the ground state and the change in the dipole moment in during the excitation process, and the pronounced changes in the intensity are due to the field dependence of transition moment which can be described by the transition polarizability [20].

2.5.2.1 Electrochromism

Changes in optical absorption due to the action of an external electric field are basically attributed to orientation effect, band shift effect and direct field dependence of the transition moment [17, 20].

Partial orientation of the molecule in solution can be achieved by means of an external electric field F_a. The direction of the transition moment, which is the measure of the intensity of the absorption band, can be found from the change in optical absorption due to this field.

The total electronic dipole moment μ_g^F of a molecule in the electronic ground state in the electric field is [20]:

$$\mu_g^F = \mu_g + a_g F_e \qquad 14$$

Where μ_g is the permanent dipole moment, a_g is the polarizability tensor, F_e is the effective field strength at the position of the molecule. According to the above equation the dipole moment is influenced by the electric field. For $|\mu_g| >> |a_g F_e|$, the polarizability term in equation 13 may be disregarded. In this approximation the energy E_g^F of a dissolved molecule in the electronic ground state in the electric field is:

$$E_g^F = E_g^{sol} - \overrightarrow{\mu_g} F_e = E_g^{sol} - \mu_g F_e \cos\theta \qquad 15$$

Where E_g^{sol} is the energy of dissolved molecule in the ground state with no external field θ is the angle between the vector μ_g and F_e. According to equation 14 the energy E_g^F depends on the direction of the dipole moment μ_g in relation to the field F_e.

2.5.3. Band Shift in an External Electric Field

The electronic excitation of a molecule may be associated with a change in the dipole moment, $\mu_a - \mu_g$ where μ_a and μ_g are the dipole moments in the electronic excited state and ground state respectively. The energy of a molecule in the ground state in an electric field as it has been given in equation 16 is:

$$E_g^F = E_g^{sol} - \mu_g F_e \cos\theta \qquad 16$$

Similarly, the energy of the dissolved molecule in the excited state is:

$$E_a^F = E_a^{sol} - \overrightarrow{\mu_a} F_e = E_a^{sol} - \mu_a F_e \cos\theta \qquad 17$$

Where E_a^{sol} is the energy of the dissolved molecule in the excited state with no external field, F_e in the second part of the equation 17 and in the following equations, it is assumed for simplicity that the dipole moment μ_a in the excited state is parallel to the dipole moment μ_g in the ground state. For a given transition having absorption wave number $\overline{\upsilon}_a^{sol}$ in solution with no external field ($hc\overline{\upsilon}_a^{sol} = E_a^{sol} - E_g^{sol}$), the absorption wave number $\overline{\upsilon}_a^F$ in an electric field is given by [17].

$$\overline{\upsilon}_a^F = \frac{E_a^F - E_g^F}{hc} = \overline{\upsilon}_a^{sol} - \frac{(\mu_a - \mu_g) F_e \cos\theta}{hc} \qquad 18$$

2.5.4 Solvent Effects

The term solvent effects are used to describe the pronounced change in position and sometimes intensity of bands. It is well known that the frequencies of many vibrational normal modes not only depend on the molecular structure, but also are markedly affected by the environmental factors [1, 7, 16, and 20].

Solvent Effect on the Infrared Spectra

In dilute solution, the infrared frequency shifts from gas IR reflect the solvent–solute interactions [16, 20]. It is known that intramolecular frequency shifts are determined by the normal coordinate dependent parts of the attractive and repulsive interactions between solute and solvent molecules [2, 16]. The shift caused by each solvent is depending on the change in the dipole moment from the ground to excited state. When absorption spectra are measured in solvents of different polarity it is found that not only the position but also the intensity and shape of the absorption band can vary, depending on the nature of the solvent. Attempts made to express the polarity in terms of dielectric constant, dipole moment, or other properties of the solvent have not been very successful, largely due to the simplications used. The polarity of a solvent is determined by its solvation behavior, which in turn depends on the action of intermolecular forces (Coulomb, directional, inductive, dispersion, and charge transfer forces as well as hydrogen bonding forces) between the solvent and the solute. The macroscopic property, the dielectric constant, does not provide a direct measure of the interactions on the molecular scale, i.e., the solvating power of a solvent cannot be measured by a single parameter.

The vibrational spectrum of the molecule **A–B** depends not only on the strength of the bond between A and B, but also is markedly affected by environmental factors; such intermolecular interactions modify the spectra in the number of way**s**. The wave number of the normal vibrational modes of a molecule may be shifted to higher or lower values, the intensities can be altered i.e. with increasing solvent polarity there is a shift of absorption band to the higher or lower wave numbers. The measurement of such solvent induced infrared spectral change has been extensively used in the spectroscopic studies of solute–solvent interactions [23–25].

The wave number shift, Δῦ, is generally represented as the difference between the absorption in the vapor phase, ($\tilde{\upsilon}^{o}$), the solvent under consideration, ($\tilde{\upsilon}^{s}$). When measured in solution, the band maxima of all simple stretching vibrations are displaced to lower wave numbers whereas those of bending vibrations are shifted to higher wave numbers. The most solvent–sensitive infrared stretching vibrations are those of $X^{\delta+}=O^{\delta-}$ bonds (X=C, N, P, S), $X^{\delta-}$,$H^{\delta+}$ bonds (X=C, N, O, S, halogens) and $C^{\delta+}$-$X^{\delta-}$ bonds (X=halogens) [14].

The first theoretical treatment of infrared solute shifts was given in 1937 by Kirkwood, Bauser&Magat: Kirkwood-Bauer-Magat (KBM) relationship [20]:

$$\frac{\Delta\upsilon}{\upsilon^{0}}=\frac{\upsilon^{0}-\upsilon^{s}}{\upsilon^{0}}=C.\frac{\varepsilon_{r}-1}{2\varepsilon_{r}+1} \qquad 19$$

Where υ^{0} is the vibrational frequency in the gas phase, υ^{s} is the frequency in the solvent of relative permittivity, $\varepsilon_{r,}$ & C is the constant depending up on the molecular dimensions and electrical properties of the vibrating solute dipole. The electrostatic model leading to the above equation assumes that only the electronic contribution to the solvent polarization can follow the vibrational frequencies of the solute. Since molecular dipole relaxations are characterized by much lower frequencies ($10^{10}s^{-1}$ to $10^{12}s^{-1}$), dipole orientation cannot be involved in the vibrational interaction, and the above equation may be written in the following modified form:

$$\frac{\Delta\upsilon}{\upsilon^{0}}=\frac{\upsilon^{0}-\upsilon^{s}}{\upsilon^{0}}=C.\frac{n^{2}-1}{2n^{2}+1} \qquad 20$$

Where n is refractive index of the solvent. In polar solvents, the points of the KBM plot are usually shifted toward higher values of the deviation from the KBM equation have been attributed to hydrogen bonding and formation of molecular complexes and such interactions are not taken into account by the KBM equation. The relationships between Equation 21 and 22 have subsequently been modified and improved by a number of workers and review equations derived by Buckingham [5].

$$\frac{\Delta\upsilon}{\upsilon^{0}}=\frac{\upsilon^{0}-\upsilon^{s}}{\upsilon^{0}}=C_{1}+C_{2}.\frac{\varepsilon_{r}-1}{2\varepsilon_{r}+1}+C_{3}.\frac{n^{2}-1}{2n^{2}+1}\ \text{(Polar solvents)} \qquad 21$$

$$\frac{\Delta\upsilon}{\upsilon^{0}}=\frac{\upsilon^{0}-\upsilon^{s}}{\upsilon^{0}}=C_{1}+\frac{1}{2}\left(C_{2}+C_{3}\right).\frac{\varepsilon_{r}-1}{2\varepsilon_{r}+1},\text{(non–polar solvents)} \qquad 22$$

The Buckingham equation takes into account the fact that the influence of solvent dipolarity/characterized by $f(\varepsilon) = \varepsilon_r - 1/2\varepsilon_r + 1$ and solvent polarizability characterized by $f(n^2) = n^2 - 1/2n^2 + 1$ on the solute infrared vibrations are two independent effects. Based on the assumption that solute/solvent collision complexes are formed in solution, which should lead to a mutual correlation in dipolarity/polarizability changes, Bekarek et al. have added a third cross-term $f(\varepsilon_r).f(n^2)$ to the two terms of the equation 23.

$$\frac{\Delta\upsilon}{\upsilon^0} = C_1 + C_2 . f(\varepsilon_r) + C_3 . f(n^2) + C_4 . f(\varepsilon_r) . f(n^2) \qquad 23$$

The inductive effect solely depends upon the ‘Intrinsic’ tendency of a substituent to either release or with draw electrons by definition, its electro negativity acting through the molecular chain.

2.5.5 Origin of Solvatochromism:

State as compared to the ground state, stabilizing the ground state energy in polar solvents this is negative Solvatochromism, often seen for molecules with n–n* transitions Specific. Interactions. Specific interactions are the specific chemical interaction between the chromophore and the solvent, such as hydrogen bonding, complexation, acid-base chemistry, and charge transfer interactions. These interactions can lead to substantial changes in the electronic spectrum of the molecule. The electronic state energy is lowered by the electrostatic interaction of a positively polarized hydrogen atom of the solvent with a lone pair of electrons on a basic atom of the solute in the ground or the excited state. During the excitation process, if the electron density migrates away from the basic atom, formation of the hydrogen bond opposes this migration [25,26].

2.5.6 Intermolecular Force

Theoretical treatments of electronic spectra start by assuming the presence of isolated molecules. In experiments, spectra are recorded in a variety of environments and at reasonable solute concentrations. Thus, both solute-solute and solute-solvent interactions must be considered. The effect of the medium on the spectral properties of the solute molecules can be broadly divided into two categories i.e. general solvent-solute interactions and specific interactions [11, 27].

A. Dipole-Dipole Forces

It is the forces of attraction which depends on the electrostatic interaction between molecules possessing a permanent dipole moment μ due to their unsymmetrical charge distribution. When two dipolar molecules are optimally oriented with respect to one another at a distance r, then the force of attraction is proportional to $1/r^3$. An alternative arrangement is the anti-parallel arrangement of two dipoles as shown below [3]:

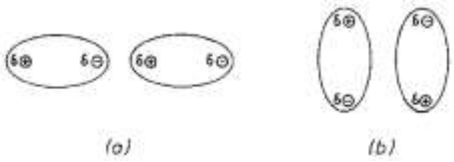

Figure 3: (a) shows "head-to tail" arrangement of two dipole molecules: (b) shows anti parallel arrangement of the two dipole molecules.

The fact that dipole orientations leading to attraction are statistically favored leads to a net attraction, which is strongly temperature dependent, according to the equation (k_B=Boltzmann constant; T=absolute temperature.

$$U_{dipole-dipole} = \frac{-1}{(4\pi\varepsilon^0)^2} \cdot \frac{2\mu_1^2\mu_2^2}{3K_B.T.r^6} \qquad 24$$

B. Dipole-Induced Dipole Forces

The electric dipole of a molecule possessing a permanent dipole moment μ can induce a dipole moment in a neighboring molecule. This induced moment always lies in the direction of the inducing dipole. Thus, attraction always exists between the two partners, which is independent of temperature. The induced dipole moment will be bigger the larger the electronic polarizability α of the polar molecule experiencing the induction of the permanent dipole. The net dipole/induced dipole energy of interaction for two different molecules, each possessing a permanent dipole moment μ_1 and μ_2 and polarizability α_1 and α_2, often referred to as the induction or Debye interaction [5].

$$U_{dipole-induced.dipole} = \frac{-1}{(4\pi\varepsilon^0)^2} \cdot \frac{\alpha_1.\mu_2^2 + \alpha_2.\mu_1^2}{r^6} \qquad 25$$

C. Instantaneous Dipole-Induced Dipole Forces

Even in atoms and molecules possessing no permanent dipole moment, continuous electronic movement results at any instant in a small dipole moment, μ which can fluctuating polarize the electron system of the neighboring atoms or molecules. This coupling causes the electronic movements to be synchronized in such a way that a mutual attraction results. The energy of such type is so-called dispersion or London interactions [11].

$$U_{dispersion} = \frac{-1}{\left(4\pi\varepsilon^0\right)^2} \cdot \frac{3\alpha_1.\alpha_2}{2r^6} \cdot \left(\frac{I_1.I_2}{I_1 + I_2}\right) \qquad 26$$

Dispersion forces are universal for all atoms and molecules; they alone are responsible for the aggregation of molecules which possess neither free charges nor electric dipole moments. Due to the greater polarizability of π-electrons, especially strong dispersion forces exist between molecules with conjugated π-electron systems (e.g. aromatic hydrocarbons). For many other dipole molecules with high polarizability as well, the major part of the cohesion is due to dispersion forces.

2.5.7 Conjugation Effect

Conjugation of a carbonyl with and C=C bond is thought to lead to an increase in resonance interaction. Again, the resonance forms lead to charge separation which clearly de-emphasizes their importance.

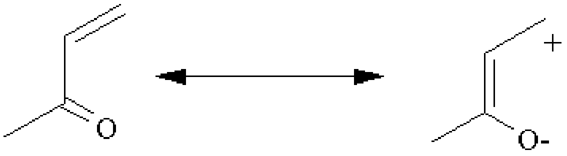

Figure 4: Conjugate of carbonyl compound.

However, this conjugative interaction is useful in interpreting several features of the spectrum. First it predicts the small but consistent shift of approximately 10 cm^{-1} to lower frequency, observed when carbonyls are conjugated to double bonds or aromatic rings [28]. Next the dipolar resonance form suggests a more polar C=C than that predicted for an un conjugated C=C. In terms of the change in dipole moment, contributions from this structure suggests that the intensity of infrared absorption of a C=C double bond would increase relative to an un conjugated system. Conjugation is associated with an increase in intensity of the C=C stretching frequency. Finally, examination of figures above reveals an intricacy not previously observed with simple non-conjugated carbonyls. Resolution of this additional complicating feature can be achieved if we consider that conjugation requires a fixed conformation. For most conjugated carbonyls, two or more conformations are possible [29].

2.5.8 Mesomeric Effect

Mesomeric effect is due to the delocalization of electrons. A group that can donate electrons in to a neighboring bond has a positive mesomeric effect, +M and is called electron donor by Mesomeric effect, one that attracts electrons out of the bond has a negative mesomeric effect,– M and is an electron acceptor [10]. This causes the weaken in a carbonyl bond leading to lowering of absorption frequency due to conjugations shown in case of Camphor [10, 14].

The resonance reduces the double bond tendency of the C=O of camphor, so its absorption band is displaced towards a rather smaller wave number. All camphor has an IR absorption frequency lower than 1720 cm^{-1}.

2.5.9 Concentration Effect

The absorption of spectroscopic measurement of solutions is done under dilute solutions. Since, in concentrated solutions there are solute-solute interactions other than solute-solvent interactions. And these solute-solute interactions may cause changes regarding the intensity and frequency of bands. These intermolecular interactions are strong if hydrogen bond exists [27].

2.5.10 Hydrogen Bonding

Molecules possessing hydroxyl groups or other groups with a hydrogen atom bound to an electronegative atom X are strongly associated and have abnormal boiling points. These observations led to the contention that particular intermolecular forces apply here. These are designated as hydrogen bridges, or hydrogen bonds, characterized by a coordinative divalency of a hydrogen atom involved. A general definition of the hydrogen bond is: when a covalently bound hydrogen atom forms a second bond to another atom, this condition bond is referred to as a hydrogen bond [19].

2.6.11 Isosbestic point

If two or more species are in equilibrium in solution and if the absorption spectra of the two species overlap, then there will be a point known as the Isosbestic point at which irrespective of the concentration of the two species, the absorption of the solution will remain a constant. At the Isosbestic point, the total absorbance does not change with time. However, the absorbance on either side of the Isosbestic point changes as the reaction proceeds. At the Isosbestic, the molar absorptivity of the reactant and the product are equal. If the absorption spectra of the reactants and products do not cross, there will be no Isosbestic [30].

3. OBJECTIVES

3.1. General Objective

To investigate the origin of the absorption FT-IR spectral range between 1600 cm^{-1} and 1800 cm^{-1} of Camphor sample in different solvents and concentration of camphor.

3.2. Specific Objectives

The specific objectives of this study include:

- Study solvent effects on the vibrational frequency of carbonyl stretching of camphor
- Study concentration effects on the vibrational frequency of carbonyl stretching of camphor
- Compare the direction and magnitude of spectral shift in protonic and aprotonic solvents.

4. MATERIALS AND METHODS

4.1 Materials and Chemicals

The chemicals; Camphor (Analytical grade, Sigma-Aldrich, Germany 96%) and were used for the investigation of Solvatochromism shift in this work and all were used without further purification. Solvents; Water (distilled), acetonitrile (99.8% Carlo-Erba reagent HPLC grade), Methanol (99.9% Carlo-Erba reagent HPLC grade), 2-propanol (99.9% Carlo-Erba reagent HPLC isocratic), carbon tetrachloride (99% Riedel-De Haen Germany), and acetone (Analytical grade, Scharlau, Spain, Germany) was used for cleaning action of different equipment.

4.2. Methods and Procedures

IR (FTIR) spectra of the solutions were measured by using PerkinElmer spectrum 65 FT-IR spectrophotometer and the spectral range is 1600-1900cm^{-1}. The spectra were measured with a cell known as ZnSe surface through reflectance. The solutions were slightly heated in the case of non-polar solvents carbon tetrachloride.

4.3. Analysis of FT-IR

The obtained data of FT-IR measurements was analyzed and fitted to straight line using origin 8.0software.

5. RESULTS AND DISCUSSION

5.1 Infrared (FT-IR) Absorption Spectra of Camphor in Different Solvents

The infrared spectra of camphor were recorded with solvents of varying polarity which cover a wide Spectral range 1600cm^{-1} – 1800cm^{-1}. The solvents used were acetonitrile, methanol, 2-propanol and carbon tetra chloride and the spectra were presented below in Figure 5.

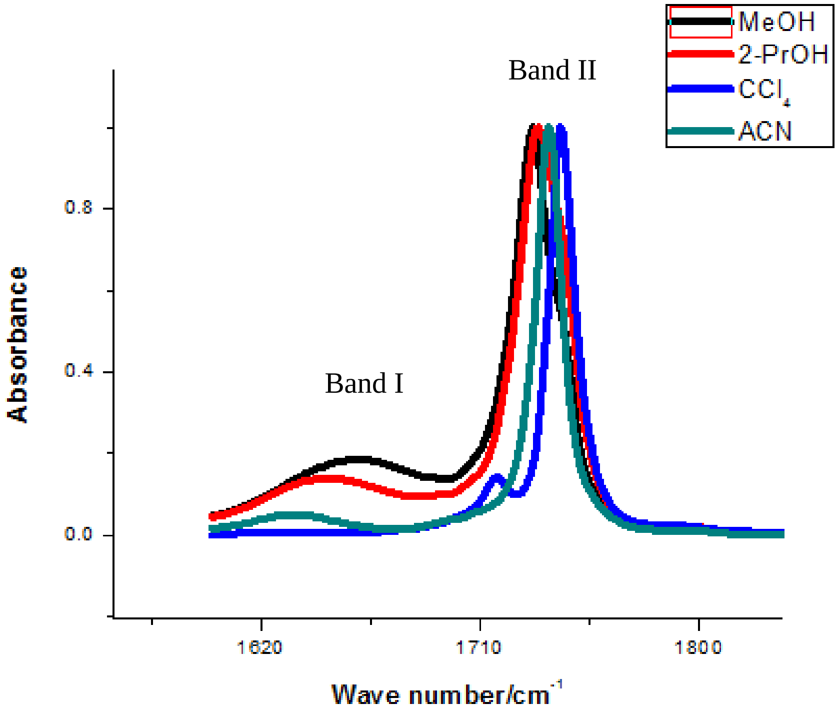

Figure 5: IR spectra of camphor in different solvent.

Two distinct absorption spectral ranges were observed. For convenience the absorption bands around 1650cm^{-1}and 1750cm^{-1}were designated band I and II respectively. In the frequency of peak absorption were at 1630cm^{-1}, 1650cm^{-1}, 1640cm^{-1} and 1710cm^{-1}respectivelyfor acetonitrile, methanol, 2-propanol and carbon tetrachloride. The general trend observed was red shift which is attributed weakening of the carbonyl bond due to increasing dipolar interaction. The carbonyl(C=O) double bond absorption 1750cm^{-1} may be due to specific interaction.

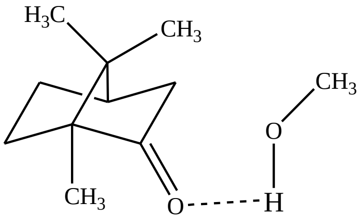

Figure 6: Hydrogen Bonding

Which may assume to the hydrogen bonding interaction (which is a specific type interaction)? The strong shift lower frequency and very wide broadening of band support the above assumed cause of lowering the energy. Observed were two bands in the common absorption spectral region of double bonds and –OH bonding which was between 1600cm^{-1}–1800cm^{-1}. From the structure of camphor absorption chromophore is carbonyl which is due to higher band constant resulted in the electro negativity differences between C and O atoms is expected to absorb1700cm^{-1}.

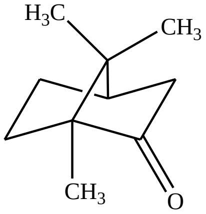

Figure 7: Camphor

From the structure of camphor absorption chromophore is carbonyl which is due to higher band constant resulted in the electro negativity differences between C and O atoms is expected to absorb 1700cm^{-1}.IR spectra of camphor in different solvent of varying polarity revealed that there is a shift of the absorption bands to shorter frequency i.e., to lower energy with increasing solvent polarity two bands were observed for all the solvents. For the single purpose of simplification, the bands observed at lower and higher energies are denoted as band I and band II respectively.

Table 2: Absorption maxima, ν max (cm^{-1}), of Camphor in different solvents. Dielectric constant, $\boldsymbol{\varepsilon_r}$ and refractive index, n of solvents was taken from Ref. [22].

S/R	**Solvents**	$\boldsymbol{\varepsilon_r}$	*N*	$\frac{\varepsilon_r - 1}{2\varepsilon_r + 1}$	$\frac{n^2 - 1}{2n^2 + 1}$	$\frac{\varepsilon_r - 1}{2\varepsilon_r + 1} - \frac{n^2 - 1}{2n^2 + 1}$	**Frequency of band II (cm^{-1})**	**Frequency of band I (cm^{-1})**
1	CH_3OH	32.60	1.3284	0.3940	0.2101	0.22080	1732	1660
2	$CH_3CH(OH)CH_3$	18.30	1.3772	0.3670	0.2033	0.21714	1734	1654
3	CAN	37.50	1.4601	0.4802	0.1748	0.21627	1738	1638
4	CCl_4	2.24	1.3441	0.2262	0.2150	0.01650	1743	1717

Table 3: Absorption maxima of camphor observed in different solvents. Dielectric constant and refractive index solvents where taken from Ref 22.

S/N	**Solvents**	**Band II**	**Band I**	**Ɛr**	**n, D**	**f(Ɛr,n²)**
1	CH_3OH	1732	1660	32.60	1.3284	0.393
2	$CH_3CH(OH)CH_3$	1734	1654	18.30	1.3772	0.367
3	ACN	1738	1638	37.50	1.4601	0.373
4	CCl_4	1743	1717	2.24	1.3441	0.139

The absorption frequency of a chromophore is determined mainly by the magnitudes of the effective mass μ and the force constant k. Thus, if a specific chromophore is considered then the shift induced through the interaction with the solvent is related to the change in the force constant. Therefore, the bathochromic shift observed as function of an increase in solvent polarity may be explained by the increase in interaction between C=O (carbonyl) solvent molecules and the observed shift is consistent with the theory.

Dipolar interaction between a solute and solvent molecule increases with an increase with the polarity of the solvent. In-polar solvents, the solute molecules are comparatively more solvated, to the extent of complete solvation, and therefore the solute molecules likely exist as monomers. In contrast, in non-polar solvents association of solute molecule may occur, especially at higher concentrations.

The spectral shift observed in these different solvents depends on the difference in permanent dipole moments of the excited and ground state and the strength of interaction between solvents and solute. The wave numbers of peak absorption ν_{max} the two bands in different solvents are plotted as a function of polarity function f, and the graph is presented in Figures 5.

This two bands around1620-1640cm^{-1}, 1670-1740 cm^{-1} are conjugated carbon-carbon double(C=C) and carbonyl(C=O) bond.

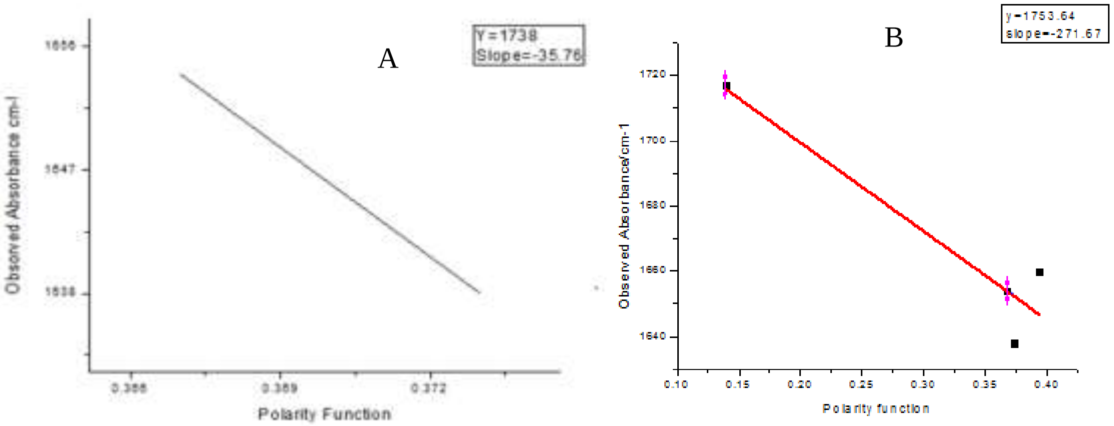

Figure 8: Plot of ν(C-O) band I (A) and band II (B) versus polarity function (f) for Camphor in different solvents.

The linear fit of the data points shows a negative slope. In fitting the data points, the values for methanol,2-propanol, Acetonitrile and carbon tetrachloride solvents were excluded. It resulted with correlation coefficient of R^2=0.6684 and 0.8406 and slopes values of -35.7607 and-271.6745 were observed for the Band I and Band II, respectively.

The correlation coefficient obtained in the case of using the data obtained was poor (0.67and0.84 for Band I and Band II, respectively), which may indicate poor correlation linearity. Figures to show graphs of infrared electronic wave number maxima versus Lippert–Mataga polarity function Δ*f*. A linear progression was done and the data was fit to straight line. Figures and represents the Lippert–Mataga plot of wave number maxima versus polarity function Δ*f* of band I and band II for camphor in different solvents. The obtained result indicates unsatisfactory correlation coefficient R^2 = 0.668 for band I and R^2=0.84 for band II.

For a single vibrational transition, based on Solvatochromism theory a single slope is expected, and an observation of more than one slope is an indication of the existence of two or more chromophores resulting from isomeric structures. Accordingly, the two different slopes observed for the Band I and Band II with-35.76and-271.67 values respectively are considered.

The poor correlation obtained here is due to the use of literature dielectric constant. The situation improves when microscopic dielectric constants calculated above were used (R^2 = 0.66 for band I and R^2 = 0.84 for band II), as shown in Figure 7A and 7B. This confirms that the calculated microscopic dielectric constant is more appropriate in describing the solvation property than the literature once.

5.2 Infrared absorption spectra of camphor in different concentration

The infrared (FTIR) absorption spectrum of camphor shows two bands in the spectral range between 1600–1900 cm^{-1}. Additional band was obtained in non-polar solvents and concentrated solutions between Band I and Band II. This band attributed to hydrogen-bond dimmer. In order to verify this argument, series of IR spectra of camphor were collected at different concentrations of by qualitative determination in all types of solvents. The spectra corresponding to different concentrations in CCl_4, MeOH, PrOH and ACN solvents are presented in Figures 9, 10, 11, and 12, respectively. Where CCl_4 is carbon tetra chloride, ACN is acetonitrile, MeOH is methanol and PrOH is 2- Propanol.

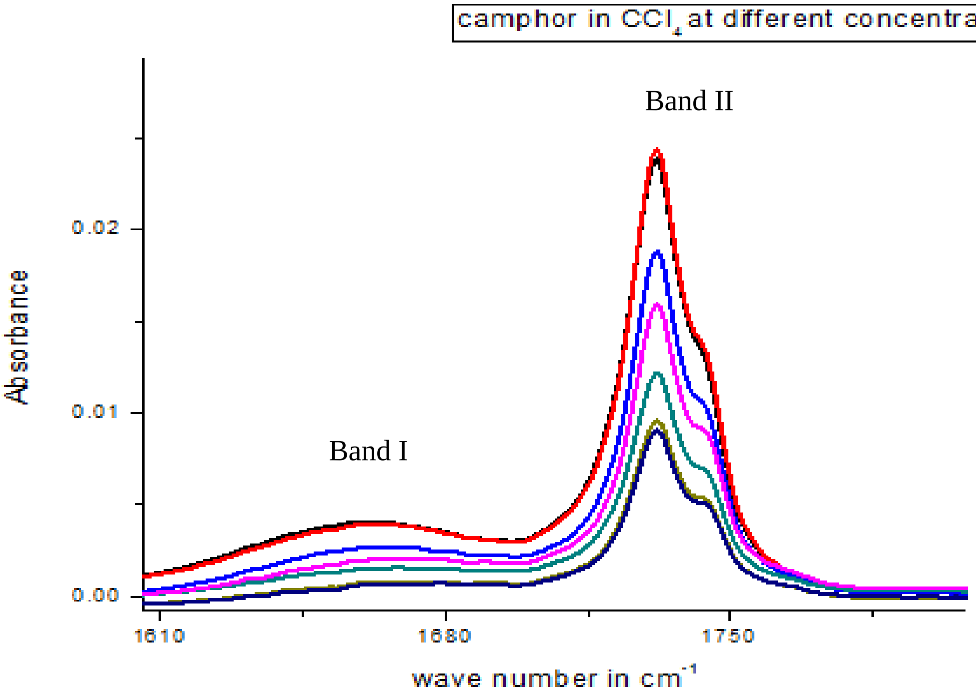

Figure 9: Normalized IR spectra camphor in CCl_4 at different concentration.

From Figure, it was observed that with increasing the sample concentration, the intensity of the monomer band diminishes at the same time a new broad band located at lower frequencies band II appeared at 1743 cm^{-1} CCl_4. Around 1717 cm^{-1} there was new band exist, which was because of self-association or oxygen of camphor makes hydrogen bond with any hydrogen of camphor. In order to verify the origin, the concentration dependent new band the spectra were plotted as a function of molar decadic absorption coefficient vs. wave number. A distinct Isosbestic point obtained at 1780 cm^{-1}. The existence of Isosbestic point is an indication of the formation of associations, and only a single Isosbestic point indicates the existence of only two species, monomer and dimmer. There was an overlap between monomer and dimmer spectra, and they were obtained iteratively using nonlinear regression analysis (Eq22).

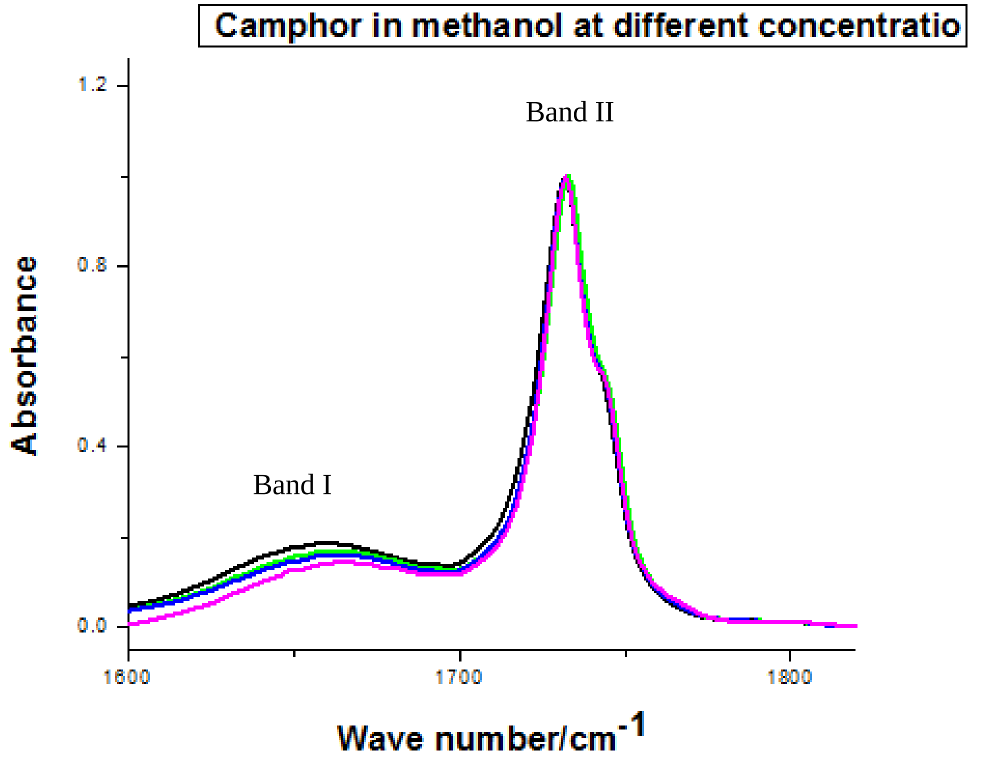

Figure 10: Normalized IR spectra camphor in methanol at different concentration.

From Figure 10 above it was observed that with increasing the sample concentration, the intensity of the monomer band diminishes at the same time a new broad band located at lower frequencies band II appeared at 1732 cm^{-1} MeOH. The formation of bands at 1732cm^{-1} for methanol advocates the formation of Camphor or carbonyl C=O vibrations compound. In order to verify the origin, the concentration dependent new band the spectra were plotted as a function of molar decadic absorption coefficient vs. wave number. It is in the range of the hydroxyl stretching vibration, these spectra strongly influenced by H-bonding. The OH band of camphor molecules in associated species absorbs at lower wave numbers as hydrogen bonding leads to a weakening of the OH band. In highly diluted solutions, the monomer form of frequency 1730 cm^{-1} of camphor is predominant. Higher carbonyl concentrations additional bands of frequency band I 1660 cm^{-1} are observed which are due to H-bonded camphor molecules. The increase of the camphor concentration the oligomer band becomes predominant and intensity of the free–OH band increase. No frequency shift is observed this indicate there is no solute–solvent interaction. A distinct Isosbestic point obtained at 1743cm^{-1}. The existence of Isosbestic point is an indication of the formation of associations, and only a single Isosbestic point indicates the existence of only two species, monomer and dimmer. There was an overlap between monomer and dimmer spectra, and they were obtained iteratively using nonlinear regression analysis (Eq 22).

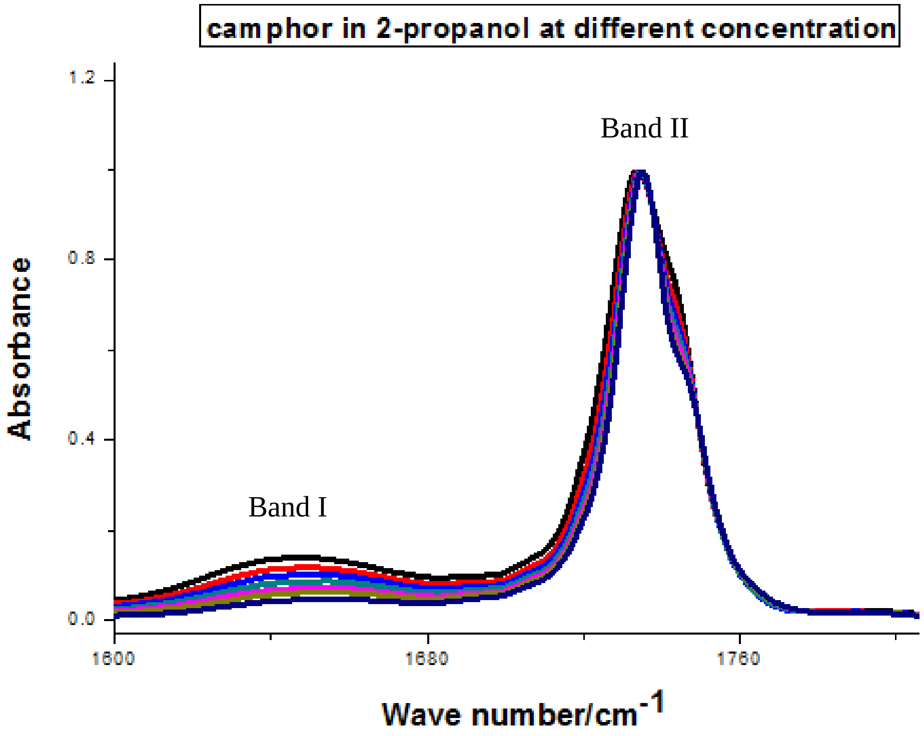

Figure 11: Normalized IR spectra of camphor in 2-propanol at different concentration.

From Figure 11 above it was observed that with increasing the sample concentration, the intensity of the monomer band diminishes at the same time a new broad band II located at lower frequencies appeared at 1734 cm^{-1} 2-propanol. The formation of bands at 1734 cm^{-1} for 2-propanol advocates the formation of Carbonyl C=O vibrations compound. Especially in the case of 2–

propanol, bands a rise at higher frequencies and the theoretical values listed in Table 3 suggest that these might also originate from larger camphor compounds.

It is in the range of the hydroxyl stretching vibration, these spectra strongly influenced by H-bonding. The OH band of camphor molecules in associated species absorbs at lower wave numbers as hydrogen bonding leads to a weakening of the OH band. In highly diluted solutions, the monomer form of frequency band I 1654 cm^{-1} of camphor is predominant. At higher carbonyl concentrations additional bands of frequency1732 cm^{-1} are observed which are due to H-bonded camphor molecules. The increase of the camphor concentration the oligomer band becomes predominant and intensity of the free–OH band increase. No frequency shift is observed this indicate there is no solute–solvent interaction. In order to verify the origin, the concentration dependent new band the spectra were plotted as a function of molar decadic absorption coefficient vs. wave number. A distinct Isosbestic point obtained at 1742 and 1745cm^{-1} respectively. The existence of Isosbestic point is an indication of the formation of associations, and double Isosbestic point indicates the existence of only two species, monomer and dimmer. There was an overlap between monomer and dimmer spectra, and they were obtained iteratively using nonlinear regression analysis (Eq22).

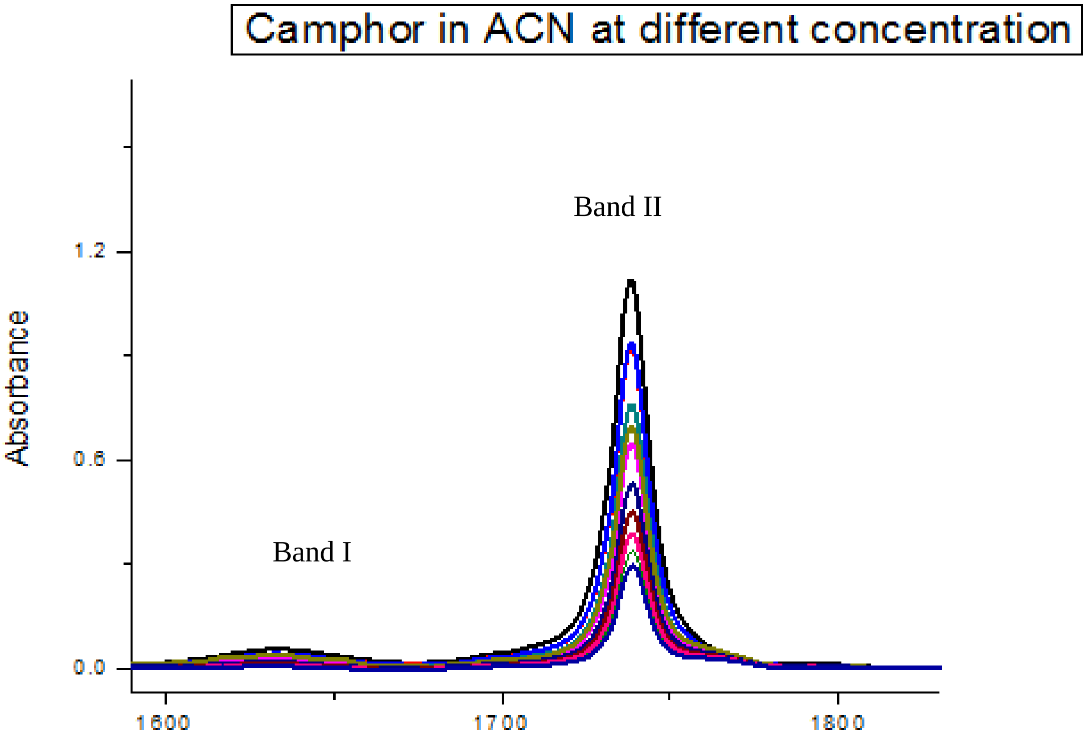

Figure 12: Camphor in acetonitrile at different concentration.

It is in the range of the carbonyl vibration stretching, these spectra strongly influenced by dipole interaction and hydrogen bonding of camphor or by self-association. That means the integrated intensity and change in dipole moment of the C=O bond increase due to the bond formation or because of acetonitrile is extremely polar.

In highly diluted solutions, the monomer form of frequency band II 1738 cm^{-1} of camphor is predominant. At higher carbonyl concentrations additional bands of frequency band-I 1639 cm^{-1} are observed which are due to highly polar acetonitrile with camphor molecules. The increase of the camphor concentration the oligomer band becomes predominant. In the absence of camphor characteristic carbonyl band has been observed at 1741 cm^{-1}. As more and more camphor is added, the intensity of the original band decreases, while the half width slightly increases and new band II appear at the frequency of 1738cm^{-1}. The concentration of camphor involved in the complex formation was obtained from the peak intensities of the free C=O and in various concentrations of camphor in carbon tetrachloride. Two bands appear which increased due to higher concentration, and bands get altered. The integrated intensity and change in dipole moment of the C=O bond increase due to the bond formation. New band I appear at the frequency of 1711 cm^{-1}, the concentration of camphor involved in the complex formation was obtained from the peak intensities of the free C=O and in various concentrations of camphor in ACN. Two bands appear which increased due to higher concentration, and bands get altered. Such a result may be attributed to the accumulated effects such as steric factors, resonance, and stabilization etc. which determine the electron density around proton accepting atom.

6. CONCLUSION

In this thesis the investigation of Solvatochromism in Camphor was performed in different solvents of varying polarity. The FT-IR spectra were recorded for the camphor with carbon tetrachloride, acetonitrile, methanol and 2-propanol in camphor. From these measurements, identify the nature of interactions. The increasing concentration of camphor the dipole moment derivative also increases. Two distinct or band I and band II, properties in vibrational absorption spectra camphor compounds have been observed. That means from non-polar carbon tetrachloride to polar solvent likes acetonitrile, methanol and 2-propanol generally hypsochromic (blue shift) and from methanol and 2-propanol to highly polar solvent, acetonitrile bathochromic (red shift) with increase in polarity of the employed solvents have been observed. Thus, this opposite shift in polar and non-polar solvents reveals the existence of the solute molecule in different structural forms that favors in these two different polarities.

The value of correlation coefficient that obtained from Lippert–Mataga plot in the presence of all the employed solvents was unsatisfactory. From Lippert–Mataga plot, the microscopic (solvation) dielectric constants of Carbon tetrachloride, methanol, 2-propanol and acetonitrile derivatives were determined. These shows Solvatochromism can not only be explained in terms of solvent polarity parameters, dielectric constant and refractive index. Thus, to overcome such problem there should be one global equation in which solvent effects and specific interactions are considered.

Band I existed in protonic solvents such as methanol and 2-propanol due to intermolecular attraction, i.e., hydrogen bonding between solute and solvents. Band I also existed in aprotic solvents, even if there was a dipole-dipole interaction between camphor and the solvent, but as the concentration decreased, Band I appeared due to self-association. i.e., hydrogen bonding between camphor molecules. Finally, the band also exists in non-polar solvent; this is also due to self-association of camphor molecules.

To conclude that Hydrogen bonding was exists in all conditions as camphor interact with protonic solvents and as self-association between camphor in non-polar solvents as well as in less concentrated aprotic solvents.

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