

CHAPTER-I

INTRODUCTION

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INTRODUCTION

The liquid state of matter is an intermediate stage between solid and gases which is characterised by possessing neither the rigidity of solid nor the fluidity of gas, but characteristics of which are reminiscent of both. The main difficulty in understanding the liquids or solutions is inadequate knowledge of intermolecular forces on time scale. Usually these forces give rise to nonideality in solution properties which also depends upon pressure, temperature and concentration of the species in question. Generally six types of intermolecular forces have been recognized. The weak forces like Vanderwaals, dipole-dipole, ion dipole, (dispersive forces and the weak hydrogen bond electrostatic interactions give rise to structural characteristics involving the molecules in liquid state). These forces are weak as compared to ordinary chemical bond forces (ionic bond and covalent bond).

The nature of intermolecular forces can be studied using thermodynamic properties as well as spectroscopic properties of the liquids or solutions. In recent years, specially, in the field of organic chemistry, the structural characteristics of molecules are well elucidated by the vibrational models of the molecules i.e., IR spectroscopy,

while the other spectroscopic techniques like X-ray, Uv-visible, microwave as compared to IR are difficult to use with ease. In recent years the IR spectroscopy has also found its applications in liquid state or solution state chemistry.

The presence of hydrogen bond has been found to give abnormal properties to liquids like water, alcohols, and even the biological molecules like DNA and RNA etc. The hydrogen bond is nothing but an interaction involving two functional groups like -OH, -NH₂, -SH, -NH etc. in the same or different molecules. One of the groups must serve as proton donor and other as an electron donor. The energies involved in the hydrogen bond are in the range of 4 to 5 k.cal/mole.

For most purpose it is enough to describe hydrogen bond A-H---B as an electrostatic attraction between positive end of the bond dipole of AH and a centre of negative charge on B. The atom or group should be sufficiently electronegative to ensure the bond is strongly polar. The site of attraction on B is commonly identified as a lone pair of electrons. These requirements mean that both hydrogen bond donors AH, and hydrogen bond acceptors B, come chiefly from the elements nitrogen, oxygen and fluorine.

Strong and very strong hydrogen bonds are generally found with cations or anions. "Strong" and "Very strong" terms are generally defined with respect to the potential energy

well of hydrogen bond. Strong hydrogen bonds are especially prevalent between acids and their conjugate bases, $AH\text{-----}A^-$, and between bases and their conjugated acids, the protonated base $B^+\text{---}H\text{---}B$. The former may be adducts i.e., intra or intermolecularly hydrogen bonded, and the same distinction can be made for $B^+\text{-H---}B$ systems.

Ionization greatly affects hydrogen bonding. If the donor is positively charged, $(A-H)^+$, there will be an increased attraction for the electron density associated with the acceptor B, as well as a strengthening of a bond moment. By the same token, a positively charged acceptor will greatly weaken the hydrogen bonding. Conversely a negative charged AH will weaken the hydrogen bonding but a negatively charged acceptor will strengthen it. Proton addition, removal or transfer will likewise produce strong hydrogen bond donors, acceptors and adducts, respectively.

It has been found that marked changes occur to AH and B upon formation of hydrogen bond; molecular dimensions, energetics, vibrational frequencies and electron distribution are all affected. In addition there are changes which occur when the hydrogen bond is perturbed by the substitution by a deuteron for a proton, and also this has found useful to obtain deeper understanding of the nature and types of hydrogen bonding.

The properties of many polar compounds in nonpolar solvents like benzene or CCl_4 have been explained in terms of association through hydrogen bonding in solution. e.g., dimerization of benzoic acid in benzene or acetic acid in CCl_4 . Similarly the compounds like O-nitrophenol and p-nitrophenol are differentiated in terms of intra and intermolecular hydrogen bonding because of which they exhibit different properties. Many times the weak bond formation is also called as complexes (distinct from coordinative complexes).

The weak bonding involved profoundly gets affected by the change in the environment and by the variable substrate like pressure, temperature e.g., the changes in the properties of water, alcohols as function of temperature are explained in terms of breaking of hydrogen bonds by thermal energy.

G.C. Pimentel and A.L.Mc.Clellan [1] have given a very exhaustive account of H-bond in their book. From the advent of IR spectrometer in 1940 and 1950, it has been found that this branch of spectroscopy reveal the characteristic frequencies of molecular vibrations. Such frequencies are fixed by the masses of vibrating atoms, the molecular geometry, and the resulting forces holding the atoms in their equilibrium positions in the molecule. Since the restraining

forces (force constants) are simply related to bond orders, vibrational spectra have been a lucrative source of information concerning chemical bonding and molecular structure. Thus this spectroscopic tool has been widely used to study hydrogen bond.

In brief, the theory of IR spectroscopy is presented below :

Infrared spectrum provides a rich array of absorption bands. Either the wave length or wave number (cm^{-1}) is used to measure the position of a given infrared absorption. The "ordinary infrared" region extends from 4000 to 677 cm^{-1} ; the region from 667 to 50 cm^{-1} is called "far infrared" and the region from 12,500 to 4000 cm^{-1} is known as "near infrared". As is the case in ultraviolet spectroscopy, absorptions that occur at shorter wave lengths (higher frequency) are of higher energy. The wave number is directly proportional to the absorbed energy ($K=E/hc$), where as the wavelength is inversally proportional to the absorbed energy ($\lambda = hc/E$) i.e., ($\lambda = 1/k$)

1.1.1. MOLECULAR VIBRATION :

A molecule is not a rigid assemblage of atoms. A molecule can be said to resemble a system of balls of varying

masses, corresponding to the atoms of a molecule, and springs of varying strengths, corresponding to the chemical bonds of a molecule. There are two kinds of fundamental vibrations for molecules; "stretching" in which the distance between two atoms increases or decreases, but the atoms remain in the same bond axis, and "bending" (or "deformation") in which the position of the atom changes relative to the original bond axis. The various stretching and bending vibrations of a bond occur at certain quantised frequencies. When infrared light of that same frequency is incident on the molecule, energy is absorbed and amplitude of that vibration is increased. When the molecule reverts from the excited state to the original ground state, the absorbed energy is released as heat.

A nonlinear molecule that contains 'n' atoms has $(3n-6)$ possible fundamental vibrational modes that can be responsible for the absorption of infrared light. Thus such simple molecules as methane and benzene have theoretically, nine and thirty possible fundamental absorption bands respectively. In order for a particular vibration to result in the absorption of infrared energy, that vibration must cause a change in the dipole moment of the molecule. Thus, molecules that contain certain symmetry elements will display somewhat simplified spectra. The C=C stretching vibration of ethylene and the symmetrical C-H stretching of the four C-H bonds of methane do not result in an absorption band in

the infrared region. The predicted number of peaks will not be observed also if the absorption occurs outside the region ordinarily examined, if the vibrations result in absorptions that are so closed that they cannot be resolved, or if the absorption is of very weak intensity.

Additional (non fundamental) absorption bands may occur because of the presence of "Overtones" (or harmonics) that occur with greatly reduced intensity, at $1/2$, $1/3$ ---- of the wavelength (twice, thrice times --- the wave number) and difference bands. (the difference of two or more different wave numbers).

Some of the various stretching and bending vibrations that can exist within a molecule are shown schematically in fig.I. Bending vibrations generally require less energy and occur at longer wavelength (lower wave number) than stretching vibrations. Stretching vibrations are found to occur in the order of bond strengths. The triple bond (absorption at 2300-2000 cm^{-1}) is stronger than the double bond (absorption band at 1900-1500 cm^{-1}) which in turn is stronger than the single bond (C-C, C-N, and C-O absorption at 1300 to 800 cm^{-1}), when the single bond involves the very small proton (C-H, O-H or N-H), the O-H bond absorbs near 3570 cm^{-1} and the (O-D) bond absorbs near 2630 cm^{-1} , in this case the strength of the bonds are nearly the same but the mass of one atom is doubled.

The magnitude of the "molar extinction coefficient" in infrared spectroscopy varies from near zero to around 2,000. The value is proportional to the square of the change in the dipole moment of the molecule that the particular vibration causes. Absorption peaks caused by stretching vibrations are usually the most intense peaks in the spectrum.

1.1.2. O-H STRETCHING VIBRATIONS :

The free hydroxyl group produces a broad infrared band in the region $3650-3590\text{ cm}^{-1}$, and one can easily distinguish this band from the -NH stretching band which appears in the vicinity of 3500 cm^{-1} (2). The hydrogen bonded-OH occurs in the region ($3400\text{ to }3200\text{ cm}^{-1}$) lower than that of free hydroxyl frequency, whereas intramolecular H-bonded -OH shows pronounced shifts towards lower frequency and causes broadening and weakening of the band (3).

1.1.3. O-H BENDING VIBRATIONS :

In phenols -OH and -CO vibrations are coupled and these show bands at $1175-1340\text{ cm}^{-1}$ for -OH and -CO and at 1230, 1353 cm^{-1} for hydrogen bonded -OH.

1.1.4 -NH STRETCHING AND BENDING VIBRATIONS :

The most characteristic absorption of amines is that owing to -NH stretching vibration in the region $3570\text{ to }3333\text{ cm}^{-1}$

As with alcohols and amides, the complexity of the spectrum in this region depends on the degree of hydrogen bonding. In dilute solution in an inert solvent, the spectra of primary amines have two sharp bands in the region, owing to symmetric and asymmetric N-H stretching vibrations; the spectra of secondary amines have only one band in this region. Aliphatic amines tend to hydrogen bond much more effectively than aromatic amines, since they are stronger bases. N-H bending vibration band in primary amines appear in the region 1590 to 1650 cm^{-1} .

1.2 REVIEW OF THE EARLIER WORK IN LITERATURE

The most prominent effect of hydrogen bonding on the vibrational spectrum is the shift of the absorption of the A-H stretching mode (ν_s) and its harmonics ($2\nu_s$, $3\nu_s$ ----) to lower frequencies. This spectral change was first observed around 1930 for a number of compounds which form intramolecular H bonds : acetyl acetone (4), benzoyl acetone (5) salicylaldehyde and O-nitrophenol (Erreza and Mollet) (6,7). In 1932 R. Freymann noticed similar effects for alcohol solutions. (8). In addition, he found that the intensity and frequency of ν_s of an alcohol are dependent on concentration and temperature, and attributed the behaviour to molecular association. Simultaneously and independently, Hilbert, Wulf, Hendricks, and Liddel were conducting a systematic study of the IR spectra of many amines, alcohols

and phenols (9, 10) from it they generalised that the IR spectrum provides a criterion for detecting "chelation through hydrogen". (11, 12, 13). The importance of this generalization was quickly recognized (e.g. Pauling -14), and during the next few years a large volume of corroborative evidence appeared.

The process of hydrogen bond formation is known to be orientation (angle) dependent. The frequency shift ($\Delta\nu$) between free - OH vibration and those due to hydrogen bonds have been studied from the data for hydrogen bonds between phenol and various bases as acceptors, it has been indicated that $\Delta\nu \propto \Delta H$ and hence the interaction energy ΔH can be calculated. Similarly from the concentration dependence of $\Delta\nu$, one can calculate equilibrium constant and the association constant like dimerization constant.

Thus, as discussed above the IR spectroscopy gives useful information about hydrogen bonding. The author is fascinated by such interactions and hence thought that it is pertinent here to give a short account of the earlier reported work on IR spectroscopy with respect to hydrogen bond interactions.

Andre, Halleus (15) have reported that the equilibrium constant for the reaction $C_6H_5OH + B \rightleftharpoons C_6H_5OH \cdots B$ (Where 'B' is aniline or one of a series of pyridines) can be studied by IR spectroscopic measurement of intensity of the -OH stretching frequency.

Bellamy L.J. and Rogasch P.E. (16) have observed that proton transfer occurs in certain special types of H-bond and that as a direct result, the association energy is increased. It is probable that this effect is also responsible for at least a part of the broadening of the ν_{XH} absorption band. They have also reported infrared spectra (2000-3500 cm^{-1}) for 2-thiopyridone and 2-pyridone in CCl_4 and for mercaptobenzothiozole in Nujol Mulls.

Per M.Boll (17) after examination of the IR spectra in the solid state and in solution have shown that 2-nitrophenol form intermolecular H-bonds and 2-nitrosophenols exist as completely chelated systems. The spectrum of the compound considered to be 2-nitromorphin hydrochloride has strong bands at 1525 and 1530 cm^{-1} which correspond closely to the frequencies expected for a nitrocompound. The lack of fundamental band of -OH absorption for 1 nitroso-2naphthol and presence of only one band of -OH absorption for nitro resorcinol corresponding to intermolecular hydrogen bonding appears to be conclusive evidence that the phenolic group

adjacent to the 'NO' group is not free; the existence of resonance possibility with a quinone monoxime tends to stabilize the chelated system.

Nuttal R.H., Sharp D.W.A. and Waddington T.C. (18) have observed that the IR spectra of trimethyl ammonium salts give N-H stretching frequencies over 3100 cm^{-1} when H-bonding is not expected and approximately 2700 cm^{-1} in other cases; the -NH deformation frequency is near 1430 cm^{-1} in all cases. Three peaks due to -NH Vibration occurring above 3100 cm^{-1} appear in all the pyridinium salts investigated but one weak in salts expected to give H-bonding; strong bands below 3000 cm^{-1} suggest H-bonding. For triphenyl ammonium salts the -NH vibration frequencies are between 2850 cm^{-1} and 2440 cm^{-1} since the N-H bond is weak this does not necessarily imply hydrogen bonding.

Robert, Cardinaud (19) have reported the IR spectra of the isomeric nitrophenols and their deuteriated compounds in CCl_4 , and CCl_4 - dioxane mixtures and suggested that the ortho-isomer retains its internal chelation in all these solutions; the para isomer forms a cyclic dimer in CCl_4 and in dioxane complex in the CCl_4 -dioxane mixtures which contains two moles of the nitrophenol. The meta isomer forms a non cyclic dimer in CCl_4 .

Anne Marrie Dierck and Pierre Huyskenes (20) have reported that the displacements of the vibration frequencies of the -OH bond and the constant (K) which characterise the complexing of various substituted organic molecules were detected by IR spectroscopy. The systems studied at 27°C in CCl₄ were phenol + substituted anilines, phenol + substituted pyridines, aliphatic alcohols + pyridine.

Keith F. Purcell and Russell S. Drago (21) observed the approximation involved in using the observed -OH wave number shift of phenol upon H-bond formation a measure of the magnitude of the interaction. They have further reported that the equation $-\Delta H = 0.0116 \Delta \nu_{OH} + 0.63$ has been recast in terms of the change in the -OH bond energy of phenol on adduct formation, δE_{OH} , and the energy of formation of the new bond between the donor and hydrogen E_{HB} .

Boyarchuk (22) has compared and discussed the relative shifting of stretching vibration of H-acceptor and H-donor groups in H-bonds of the type Y:O---H-X (e.g. C:O---H-O) on the basis of literature data and it is shown that unlike the quantity $\Delta \nu / \nu$ (X-H), which is fully detected by the hydrogen bond energy. The quantity $\Delta \hat{\nu} / \nu$ (Y:O) depends also on the relative contribution of electrostatic and donor - acceptor interactions to the H-bond energy.

Hall A., Wood J.L. (23) observed that a sensitive indication of the strength of H-bonding association is the frequency of the intermolecular stretching vibration for a well characterised 1:1 complex (phenol + pyridine) frequency increases in a more polar environment. They have compared this behaviour with that of charge transfer complexes.

Whetsel, Kermit B Lady (24) have detected the thermodynamic constant for the self association of phenol in cyclohexane and CCl_4 . They measured the intensity of the first overtone -OH stretching band of phenol in 0-1 M solutions of 2.5 to 60°C. Selective measurements also were made in the fundamental -OH stretching region. Computer programs were developed for testing the fit of the first overtone data to a variety of self association models. They further reported that the formation constants in cyclohexane solution are more than twice as large as those in CCl_4 . The enthalpies of self association in the hydrocarbon solvent, however are only slightly larger than those in the chlorinated solvent. The effect of end group absorption of associated species on the calculated thermodynamic values was detected.

Ghersetti S. (25) has reported the standard change of the free energy $F^\circ_{298 \text{ K}^\circ}$ for the interactions between phenol and diphenyl sulphoxide, benzophenon and diphenyl

sulfon when evaluated in 14 different solvents by employing IR techniques, the results obtained show a strong sensitivity of this parameter to the nature of the solvent. On comparison with the results for the corresponding stretching frequency he pointed out that different effect of solvent on the spectroscopic features and thermodynamic parameters. He also noted that $-F^{298} \text{ } ^\circ\text{K}$ values (for the system examined) measured in the solvents investigated are linearly correlated.

Verma V.N., Rai D.K. (26) have recorded the IR absorption spectra of the isomeric aminophenols in the range $250\text{-}4000 \text{ cm}^{-1}$. The observed bands have been analysed in terms of fundamentals, combinations and overtones of a number of frequencies. These frequencies have been assigned to different modes of vibrations.

Prelygin I.S. Akhunov T.F. (27) studied and reported the vibrations of the -OH group in 15 mono and polysubstituted phenols. Dilute solutions (0.003 to 0.01 M) in CCl_4 , C_2Cl_4 and cyclohexane were examined. They measured and tabulated the structure, half width and integrated intensity of the -OH stretching bond for cis and trans forms.

Perelygin I.S. and Akhunov T.F. (28) have studied and reported H-bonding formed by PhOH and a series of its mono and polysubstituted chloroderivatives with MeCN in CCl_4

solutions. They have examined IR -OH stretching vibration bands ν_{OH} . The concentration of PhOH was 0.003M. through and that of MeCN was varied 0.025 to 1 M. They found that along with the bands of PhOH molecules alone some new broad bands appear in the spectrum, the frequency maximum of which is shifted towards the smaller wave numbers, and which grow in intensity with rising MeCN concentration. The bands are due to the -NH bonded PhOH molecules. They have given the position of the hydrogen bond ν_{OH} , frequency shift $\Delta\nu$, half width $\Delta\nu_{1/2}$, integrate absorptivity 'A', association constant K_{22} and the energy of H-bond formed for PhOH.

Korshunov A.V., Babushkina T.A. et.al (29) have reported that 19 complexes of $PhNH_2$ with 2,4,6 trichlorophenols by melting or simultaneous crystallization of the components from alcohol solution were prepared. IR spectra of the complexes (as KBr pallets or foils between NaCl pates) were obtained. The nuclear quadrupole resonance (NQR) spectra were measured at 77°K. They found that the complexes are formed owing to the pi-pi interaction between their components and owing to H- bonding of NH---O and OH---N types. Both phenomenons were observed in NQR frequencies of the O- and P- halogen atoms of triphenols bonded in complexes, in comparison with the frequencies of pure components. The complexes possessing a 1:2 stoichiometry in crystal state retain

this stoichiometry also in melt. The complexes with a 1:1 component ratio have a 1:2 stoichiometry in melt, the stoichiometry changes manifest themselves in shape of IR spectra.

Ragsdale and Ronald (30) have investigated the H-bonding interaction of PhOH with aromatic amine oxides by both colorimetric and spectroscopic measurements. The equilibrium constant for the H-bond formation were measured for 22 complexes using the first overtone of the -OH stretching frequency. They found an agreement between these constants and those measured colorimetrically by using different acid base ratio. Similar values were found for -OH vibration reaction for the PhOH adducts in both CH_2Cl_2 and CCl_4 . Only H-bonding interactions which resulted in enthalpies ranging from 5 - 9 K.cal/mole were calculated from the linear equation.

Collect and Czech (31) have measured the wave numbers of ν OH stretching bands in 29 ortho and P-substituted phenols in chloroform. They observed a linear correlation between $\nu(\text{OH})$ and Hammett's constants. The wavenumbers of OH-stretching in ortho substituted phenols and their deuterated analogs were measured in CCl_4 . They observed a strong intermolecular hydrogen bonding in all the ortho phenols substituted by the 2(4,5) aryleneazoly group.

Wolff H and Mathiaj D. (32) have analysed and reported the IR spectra of PhNH_2 and its adducts with proton acceptors like 2 fluoropyridine, pyridine, collidine, tetra-n-butyl ammonium bromide etc. considering fermi interaction of the symmetrical -NH_2 stretching vibration with the overtone of the -NH_2 deformation vibration.

Kivinen, Anti Murto et.al. (33) reported that hydrogen bonds formed between diphenyl amine(I) and several proton acceptors (e.g. Ph_2CO , Me_2NCOME , Me_2SO , $(\text{Me}_2\text{N})_3\text{P}$) were examined using IR spectroscopy. The equilibrium constants for the complexation of (I) with the proton acceptors were in accordance with priviously reported results (Sannigrahi,1963) The heat of hydrogen bonding for the $\text{I}-(\text{Me}_2\text{N})_3\text{P}$ complex obtained by them was 5.1K.cal/mole.

Davidoviss, Gisele, et.al(34) have reported that on the basis of IR (liquid, solution, vapour) and Raman (condensed phase) spectra, squelettal, -CH bending (in and out of plane) and bending modes of substitutents were assigned in 2,4,5 trimethyl thiozole; and in 14 disubstituted thiozole derivatives $\text{C}_3\text{NSHRR}'$ ($\text{R}=\text{R}'=\text{D,Cl,Br,Me}$) ($\text{R}=\text{NH}_2, \text{R}'=\text{D,Me}$) ($\text{R}=\text{Cl, R}'=\text{D,Br}$) in 2,4-, 2,5- and 4,5-positions.

Strait L.A. and Hrenoff M.K. (35) have observed the interaction of primary aliphatic amine- NH_2 groups with weak

proton donors e.g. CHCl_3 or Me_2CHOH and with π -electron donors e.g. C_6H_6 or $\text{C}_5\text{H}_5\text{N}$ by the change in combination in bands of $-\text{NH}_2$ group. They found that the ratio of the symmetric - asymmetric absorbances of the amines increased when association occurred irrespective of whether the $-\text{NH}_2$ group participated as a proton donor to a basic partner or as an electron donor to an acid partner.

Glazunov and Odinkov S.E. (36) have reported that from the IR (750 to 3550 cm^{-1}) spectra the evolution of the structure, frequency shifts; and observed intensities of the ν_{OH} IR bands, H-bonded complexes of *p*-nitrophenol (I) with 19 organic bases and hydrogen bonded complexes of *PhOH* with pyridine, Et_3N piperidine, and $\text{Et}_3\text{N-N-oxide}$ were studied. Some complexes of I were studied also by electronic (210-80 nm) spectra. They found that all complexes formed linear H-bonds without a proton transfer. CCl_4 , CH_2Cl_2 , and C_6H_6 were the solvents used to prepare 4×10^{-5} to 0.7M solutions.

Keiko V.V., Sinegovskaya L.M. et.al(37) have reported that IR frequency shifts on the $-\text{OH}$ group of phenol and its 4-Cl, 2,6 Me_2 and 2,4,6 - Cl_3 derivatives on complexation with acetone tetrahydropyran, *N*-methyl piperidin, and RSOR' ($\text{I,R,R}'=\text{Me,Me,Me,Vinyl,Vinyl,Vinyl}$) were detected and thermodynamic parameters for the complexation were obtained. An experimental criterion of the steric accessibility of an

electron donating atom in its interaction with ortho-substituted phenol was developed. The (O) atoms of I interact with phenols.

Reyntjens-Van-Damme D. and Zeegers-Huyskens T. (38) have reported the dipole moments in CCl_4 , IR absorption spectra under various conditions and UV spectra of a number of pentachlorophenol (PCP) complexes with N-base over a broad ΔPKa range. From the dipole moment measurements an inversion region of ΔPKa was found for which a 50% proton transfer can be expected. The complexes from this region exhibit certain anomalies in their IR spectra, in particular a broad continuous absorption, a strong temperature effect on the absorption in the far IR and particular sensitivity to changes in solvent polarity.

Ulashvich Y.V. and Tselinski I.V. (39) observed the spectral parameters of alkyl N-nitroamine complexes with different proton acceptors in CCl_4 solution. The νNH band structure of the complexes is due to the fermi resonance. The integral intensities and frequencies of the bands were measured. The intensity enhancement and frequency shift are closely integrated over the whole range studied. The general H-bonding intensity rule is valid.

Abrect, Gunnar et.al. (40) have studied and reported mixtures (1:1) of octylamine with chlorophenols. They observed 11 chlorophenols and of C_6Cl_5OH with 5 aromatic amines in CCl_4 solution by using IR spectroscopy. Data showed the absence of charged species and only the association constants (K_a) and the equilibrium constants (K_{PT}) of proton transfer had to be considered. Linear reactions exist between $\log K_a$ and ΔPK_a values for both sets of mixtures. $\log K_{PT}$ increases in both systems in proportion to the ΔPK_a values including that Huyskenes equation is valid. This increase is caused by decreasing enthalpy, which in turn is due to increasing acidity or basicity of the donor or acceptors respectively. The interaction of the hydrogen bond with their environmental causes a shift in the equilibrium. The intensity of the continuum and thus the proton polarizability is the greatest if proton limiting structures $OH---N$ and $O--H^+N$ have almost the same probability.

Segnin, Jean Paul, et.al(41) have studied and reported intramolecular H-bonding effects in O-substituted phenols by H-NMR and IR spectroscopy and CNDD/2 calculations. Full CNDO/2 geometry optimization indicates definite variations of the O-H bond length in intramolecular hydrogen bonded phenols, whereas these bond lengths are almost constant in P-or m-substituted derivatives. A good linear relation exists between the O-H bond length and the IR ν_{OH} frequency

shift, reflecting the intramolecular association. Strength comparison of O- and P-substituted phenols showed that intramolecular H-bond formation induces important σ -electron transfer from the substituent to the hydroxylic (O) via the bonded H-atom, whereas the electron population of this H-atom decreases. This transfer results in pi-electrons recognition of the $R-C_1-C_2-OH$ fragment increasing the electron releasing ability of the -OH group and the electron withdrawing power of R with this unusual electron recognition, the chemical shifts of the phenolic H in O-m- and P-substituted phenols are correlated simultaneously with the electron population only if both proton and its attached (O) are considered.

Guozhen L. (42) have measured the -OH frequency shift $\Delta\nu_{OH}$ for a series of tert-butyl phenols in reaction with several nitrogen and oxygen Lewis bases using FTIR. The accuracy and reliability of $\Delta\nu_{OH}$ were good. According to the relationship between $\Delta\nu_{OH}$ and the heat of adduct formation ΔH , the latter was predicted. The calculated ΔH values were shown to agree with experimental data.

Shreiber V.M. (43) have reported that the IR spectrum of O-nitrophenol is observed and the assignment of low frequency bands corresponding to vibrations which involve

stretching and bending of the H-bond is proposed and the cis-trans equilibrium constant is established. The parameters of the ν OH band in gas phase, solutions and solid state have been studied at 15 - 600 °K. The interpretation of temperature transformations of the band profile is given in terms of anharmonic coupling of ν OH with low frequency vibrations. Solvent effects on the OH band are analysed.

Arenas J.F., Gonzalez-Davila M. et.al(44) studied and reported the ν (OH), ν (C:O) bands of thiozole -2-carboxylic acid in solid state and DMSO solutions in inert and proton donor solvents for 2-aminothiozole. The IR spectra of acid show bands in the ν (OH) region which arise from OH-N_c strong intermolecular association, where N_c is the thiozolinic nitrogen atom, and well resolved doublets in ν (C:O) region which arise presumably from rotational isomer solutions of 2-aminothiozole show -NH₂ stretching bands corresponding to the free and associated molecules which arise from N-H-N_c intermolecular associations.

Pillay M, Krishna umamaheshwari A (45) have analysed the sensitivity of the hydroxylic stretching frequency of a particular substance in different solvent in the presence of proton acceptors, viz. organic bases

to understand the nature of the interaction between the two entities and the extent of complex formation. The type(S) complexes formed by 4 - nitrophenol, 2,4 dinitrophenol and picric acid with nitrogenous bases including the tertiary amine, viz. triethyl amine, 1,4 diazobicyclo (2,2,2) otane(DABCO), 1,5-diazabicyclo (5,4,0) undec-5 ene (DBU) and 4 - (N,N-dimethyl amino) pyridine (4-DMAP) in non hydroxylic solvents, such as chloroform, dichloromethane, acetone, acetonitrile and THF.

Majerz, Irena, Sobczyk, Lucjan (46) have studied and reported the dipole moments and IR spectra in the range of protonic stretching vibrations of the complexes; phenol-aliphatic amines in various solvents. The (crit) values of ΔPKa at which the proton transfer degree reaches 50% were established. The correlation curve ΔPKa (crit) Vs the onsager parameter ($\epsilon - 1$) ($2\epsilon + 1$) shows a hyperbolic form.

Zundel, Georg, et.al. (47) have reported that hydrogen bonds with double min. proton potential show so called polarizabilities which are about two order of magnitude larger than usual polarizabilities of electron systems. Such H-bonds are indicated by continua in the IR spectra. It is shown experimentally as well as theoretically that symmetric or symmetric hydrogen bonded

chains show particularly large proton polarizabilities due to collective proton motion, protons can be conducted within psec. along these chains the proton transfer processes in the active centres of the bacteriorhodopsin molecule as well as the proton conduction process from the active centre to the outside of the purple membrane are discussed on the basis of these results.

Frohlich H (48) has studied the intermolecular hydrogen bonding by IR spectroscopy for benzyl alcohol and PhOH .

Wang, jinben, Zhang, et.al. (49) have reported IR spectra of binary mixtures of aniline or N-methyl amine with n-heptane, CCl_4 , C_6H_6 or toluene. The solvent effect on the -NH group stretching vibration frequencies were discussed. IR spectra of several mixtures containing a nitrogenous Lewis base (e.g. pyridine) in CCl_4 were also studied and the involved cross-association constants were calculated. The results indicated that aniline is the stronger proton donor than N-methyl aniline when it is associated with pyridine in CCl_4 and the proton accepting ability of several bases increase in the order aniline

~ N-me-thyle aniline < tributyl amine < pyridine
triethyl-amine when they associate with ethanol in CCl_4 .

Moreover IR spectra of ternary mixtures (ethanol + pyridine + CHCl_3) were briefly analysed in terms of interaction between unlike molecules.

After this short review of the literature survey we can summarise the important findings and conclusive points about the use of IR spectroscopy in understanding the structural characteristics of chemical compounds.

1.3 STUDY OF PURE MATERIALS :

Very little information is available on H-bonding in gases. For IR study of a substance in the gas phase, its vapour pressure must be above a few millimeters Hg at an accessible temperature.

For the experimental point of view, the liquid state is most desirable for study by IR and many investigations of H-bonding of pure liquids have been reported. Unfortunately, there are counteracting difficulties in interpretation. Most of the hydrogen bonding liquids contain a series of polymeric units with different characteristic frequencies and absorption coefficients. In the region of ν_{OH} the band widths of many H-bonded species meld into a single broad band whose frequency is determined by average over many species, each species with

its own (unknown) band shape and absorption coefficient.

Finch and Lippincott have made careful measurements of frequencies and band intensities of ν_s for several alcohols over the temperature range of 232 to 298 °K (50,51). These authors interpreted the systematic temperature dependancies in terms of changes of force constants and absorption coefficients. Even though their contention is probably correct, that "the (spectral) shifts ---- can not be explained solely on the basis of a shift in the monomer-dimer-polymer equilibrium", such an equilibrium shift must occur and undoubtedly contributes to the observed frequency and intensity changes.

There are also many difficulties in the study of pure solids. Frequency shifts, intensity changes, and band splitting caused by crystal interactions complicate the interpretation of the vibrational spectrum of a crystal. These effects can sometimes be recognized, provided the crystal structure is well known. Even then the situation is not clear if there are two or more non equivalent H-bonds in the structure. As a partial solution to these problems Hrostowski and Pimentel proposed a powerful tool for identifying crystal interactions - the use of dilute mixed crystal of its deuterated counterpart (52). In this

technique any band splittings caused by intermolecular interactions are lost in the dilute crystal, whereas splitting caused by non H-bonds and band structure associated with intermolecular combination modes are retained. This method was first applied to a H-bonded crystals by Hiebert and Hornig (53), who showed that the doublet observed in the IR spectrum of the HCl crystal is caused by crystal interactions.

There are several ways to obtain the IR spectrum of a solid, each with its peculiar problems. If single crystal studies are attempted, the preparation of sufficiently thin samples of known crystal orientation can be a major difficulty. If a solid is prepared by freezing quickly either a liquid or gas, the sample must be annealed. Significant spectral changes usually occur during the annealing process, particularly in the region of ν_s as has been observed for hydroxyl amine (54) hydrazoic acid (55), and ammonium azide (56). The equivalent of a power spectrum can be obtained by mull technique, but the C-H interference of a Nujol medium obscures a portion of the ν_s region. The pressed disc technique avoids this interference, but is susceptible to a more sinister fault. Farmer (57) observed that the KCl pressed disc spectra of six carboxylic acids, eight phenols, and two alcohols can be altered radically by

changing the grinding technique for example he presents one spectrum (650-1600 cm^{-1}) of benzoic acid ground and pressed in KBr, and another of benzoic acid in KCl, prepared by a different grinding and preheating treatment. These spectra are so dissimilar that they could not be accepted.

1.4 STUDY OF SOLUTIONS :

The great value of solutions for spectroscopic studies of H-bonding lies in the possibility of controlling and determining the species present. At extreme dilution, intermolecular associations are eliminated or restricted to solvent-solute associations. At higher concentrations, intermolecular interactions become important but remain under control through the variables of temperature and concentration.

If the solvent interacts either as a hydrogen donor or as base, the situation is complicated by the disturbance of polymeric equilibria and the presence of associated species involving the solvent. For example neither chloroform nor benzene is an inert solvent for hydrogen bonding compounds. The amide polymeric equilibria are distinctly altered in these solvents, as compared to CCl_4 solutions and the IR spectra clearly indicate solvent-solute interaction. A third major source of difficulty is in the solubility of water.

Often solution experiments require solute concentrations below 10^{-2} M at which traces of water can interfere. Many solvents can absorb enough water from the atmosphere to be detected in the IR spectrum and to hinder solution studies at extremely high dilution.

1.5 MATRIX ISOLATION TECHNIQUE :

Pimentel and collaborators developed a novel approach to the IR investigation of H-bonding. In this method, the matrix isolation technique, a gaseous mixture of H-bonding substance in a large amount of inert gas (e.g. N_2) is quickly frozen at a temperature at which no diffusion can occur. The solid nitrogen forms a rigid matrix that isolates whatever species are present during the deposition. The absorptions of H-bonded species are narrowed and this is the unique advantage of the method. The usual problem of overlapping bands is thus eliminated. During spectral examination careful temperature control is required.

1.6 PRACTICAL RULES FOR IR STUDIES OF HYDROGEN BONDING:

In general, the following rules have been framed for the studies of hydrogen bonding using IR spectral data.

- 1) Select solvent with attention to its H-bonding properties.

- 2) Vary the concentration and determine the sensitivity of the spectrum to this variable. If possible use a concentration sufficiently low to permit control of the intermolecular association.
- 3) Measure and control the cell temperature.
- 4) In publications, while reporting specify the solvent, the temperature, and the concentration.
- 5) Raise the cell temperature 20 - 30°C to detect and identify the bonded species.
- 6) Use deuterium substitution to verify assignments.
- 7) Dry the solvent for studies at high dilution.
- 8) Remove alcohol (added as an antioxidant) from chloroform solvent.
- 9) Anneal solid samples, particularly if condensed from a gas.
- 10) For IR pressed disc spectra, check against mull spectra, vary grinding procedure.

1.7 THE A-H STRETCHING MODE : [ν_s]

Whenever there is formation of H-bond there is unusual effect on the IR spectrum. The most prominent of the spectral change occur in the region of near 3500 cm^{-1} . These changes have properly assumed the importance of qualitative criteria for H-bond formation and quantitative indices of the H-bond energy and of other physical properties. Hence it is necessary to establish the relationship between IR and H-bond.

physical properties. Hence, it is necessary to examine the behaviour of in detail.

1.7.1 EFFECT OF TEMPERATURE:

There is a reduction in the IR intensity of the association band by a temperature rise of 10-2-°c. The IR spectra of benzyl alcohol in CCl_4 presented by Congeshall and Saier (58) offer a striking and typical example as shown in fig. I Ia. This extreme sensitivity of to temperature changes reflects the following characteristics :

- a) H-bonding systems involve monomeric and usually several polymeric species in rapid equilibrium;
- b) each polymer has a characteristic and the higher the polymer, the lower is ;
- c) each polymer has a characteristics absorption coefficient 'A' at and the higher the polymer, higer is 'A'.
- d) Since 'A' may increase by as much as an order of magnitude on bond formation, a small shift of equilibrium produces a magnified spectral chage.

Of much greater importance is the spectral measurement of equilibrium constants at several temperatures. Such data permit calcultions of the

thermodynamic properties of H-bond formation.

It is generally accepted that the temperature effect reveals, the shift of equilibria involving a variety of polymeric species, each with a characteristic and 'A'. There is no question that this is a dominant factor in the behaviour. Recently, it has been suggested that there is another effect of temperature that both the frequency and the absorption coefficient of each particular hydrogen bonded species may change with temperature..

Liddel and Becker examined the peak intensity and frequency of for monomeric methanol in CCl_4 . They discovered that the intensity decreases by almost 36 percent if a dilute solution in CCl_4 (0.005M) is warmed from 263°K to 323°K and the frequency increases about 6 cm^{-1} (+0.2 percent). No such changes were observed in the C-H stretching modes. Since little dimeric or polymeric material was present, the change of absorption coefficient implied that the -OH group interacts with CCl_4 in a fashion that influences the intensity of the stretching mode and which is temperature sensitive.

1.7.2 EFFECT OF CONCENTRATION :

The drastic spectral changes also can be caused by variation of concentration of a H-bonding substance in an inert solvent. Fig.IIb (59) represents a spectra of benzyl alcohol at several concentraions. The narrow band at (3610 cm^{-1}), due to - OH groups not participating in hydrogen bonds, dominates the lower frequency absorption in most dilute solution. At high concentration the broad bandf centered near 3330 cm^{-1} , due to H-bonded polymers, is by for the more intense feature.

1.7.3 EFFECT OF SOLVENT :

There is extreme influence of various solvents on IR of H-bonding substances. Fig.III shows the effect of solvent on the spectrum of the changes indicate enviromental influence on the distribution of monomeric and polymeric species. The solvent disturbances persist however, even at such low concentrations that no polymeric species are present. This is evident in the spectra of Fig. IV which shows the IR region near 3600 cm^{-1} for H_2o at low concentration in a variety of solvents. The superposition of the CCl_4 spectrum (dotted curves) shows that every spectral characteristic of the band is sensitive to the solvent; the structure and its spacing, the frequency, the band width, and the integrated intensity

(i.e. the absorption coefficient) (60, 61).

It is clear that many solvents interact and produce new H-bonding equilibria involving the solvent. These additional equilibria furnish an extraneous and interfering factor in a reference spectrum. On the other hand a dilute solution of a proton donor in a basic solvent involves well defined species and avoids the usual complications of polymeric equilibria. Consequently, the spectral examination of such systems furnishes some of the most definitive information available on H-bonding.

It is also clear that the solvent characteristics of chloroform derive in part from its proton donor potentiality, permitting H-bond formation. In proportion to the amount of H-bonded complex, the spectrum of chloroform itself is drastically altered, the C-H stretching mode being many fold more intense (62,63). Similarly the proposal of using a CCl_4 triethyl amine mixture as an IR transmitting solvent for organic acids has the same disadvantage (64). As found by Ard and Fountaine (61) the spectrum obtained in mixed solvent is not of the H-bonded complex between amine and acid in equilibrium with the monomeric acid. The enhanced solubility of the acid in the mixture is a direct result of hydrogen bonding. Thus while CHCl_3 or mixed solvent may be useful in

achieving concentrations sufficient for spectral study.

The type of hydrogen bonding also depends upon the dielectric constant of the solvent. Different solvents have different dielectric constants e.g. chloroform is a solvent with low dielectric constant, acetone is a solvent with medium dielectric constant, and water has a very high dielectric constant.

1.8 PRESENT WORK :

The work of systematic investigation of the nature of hydrogen bond between various phenols and amines and their (1:1) adducts in solution phase is presented in this work. The effect of such bonding has been investigated using the IR spectral data in fundamental region. The systems studied are:

- a) Pure solvents - chloroform, acetonitrile and acetone,
- b) Pure solids - P-nitrophenol, P-toluidine, P-anisidine, (by KBr pellets technique.)
- c) P-nitrophenol, aniline, P-toluidine and P-anisidine in solution phase at different concentrations in above mentioned three solvents.
- d) [P-nitrophenol + aniline] (1:1) adduct at different concentrations in three solvents.
- e) [P-nitrophenol + P-toluidine] (1:1) adduct at different concentrations in three solvents.

f) [P - nitrophenol + P - anisidine] (1:1) adduct at different concentrations in three solvents.

In order to study the differences in intramolecular and intermolecular hydrogen bond, the O-nitrophenol and P-nitrophenol were selected. The spectra were obtained in solution phase with solvents like chloroform, acetonitrile and acetone. These solvents chosen as these have different dielectric constant. The acetone solvent can also form hydrogen bond with the solute while acetonitrile is an aprotic one. Thus, the effect of these solvents on the free -OH or free -NH or bonded -OH or bonded -NH can also be studied. The effect due to concentration to affect the monomer dimer equilibria in case of binary solution have been investigated by doing the measurements at different concentrations. Similarly the acid base type or hydrogen bonding between -OH and -NH₂ have been studied in case of ternary mixture also at different total concentration. The methodology adopted and the results obtained with the discussion of possible interpretation are presented in following pages.

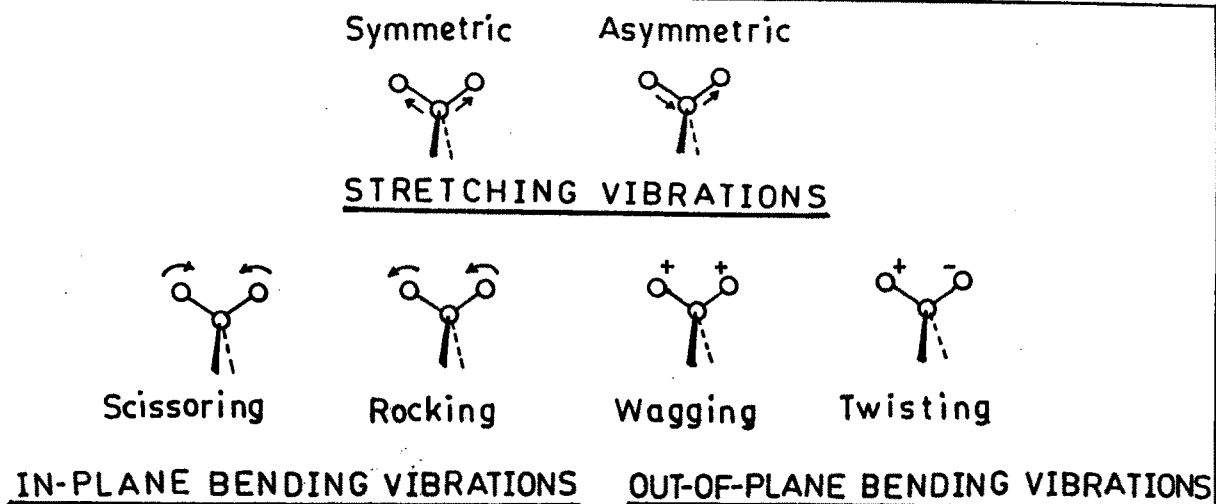


Fig. I - Vibrations of a group of atoms (+ and - slightly vibrations perpendicular to the plane of the paper).

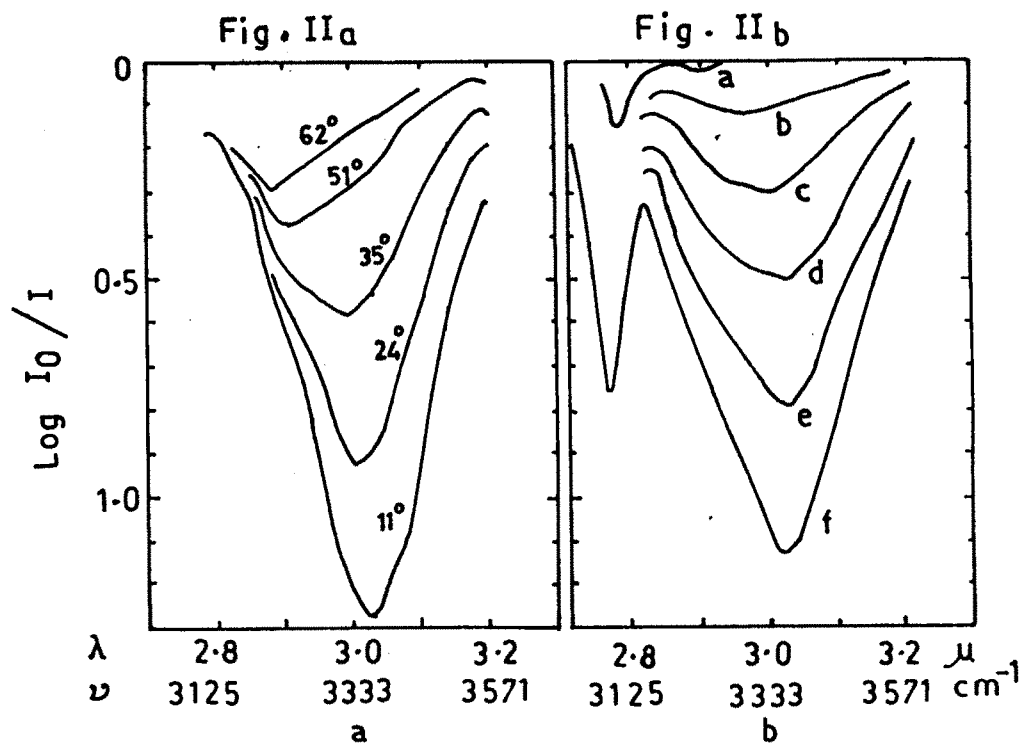


Fig. II - IR spectra of benzyl alcohol in CCl_4 , (a) At various temperatures (11-62°C, 0.24 M), (b) At various concentrations : a. 0.0486 M ; b. 0.0972 M ; c. 0.155 M ; d. 0.194 M ; e. 0.243 M ; f. 0.278 M .

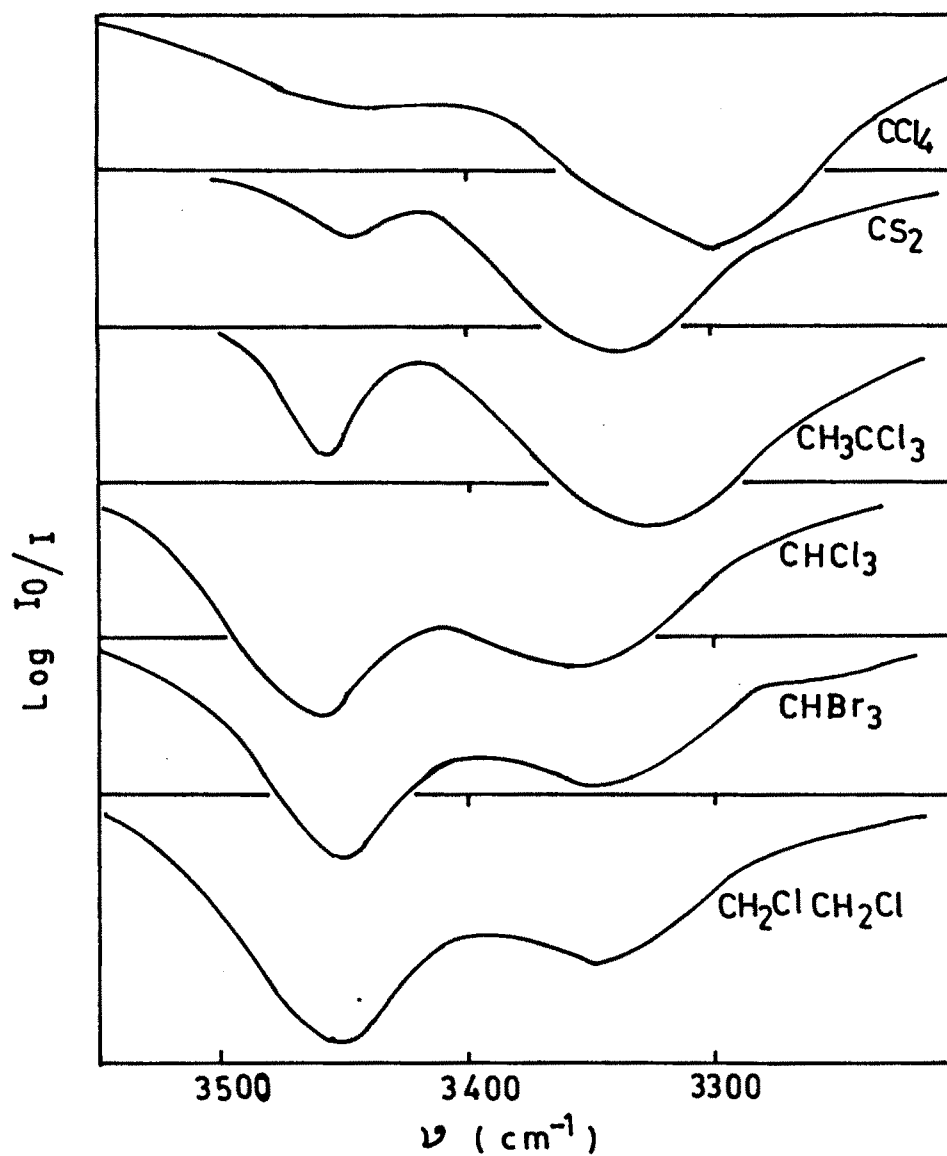


Fig. III — IR spectrum of N-methylacetamide in various solvents in the N-H stretching region : 0.4 M at 30° C .

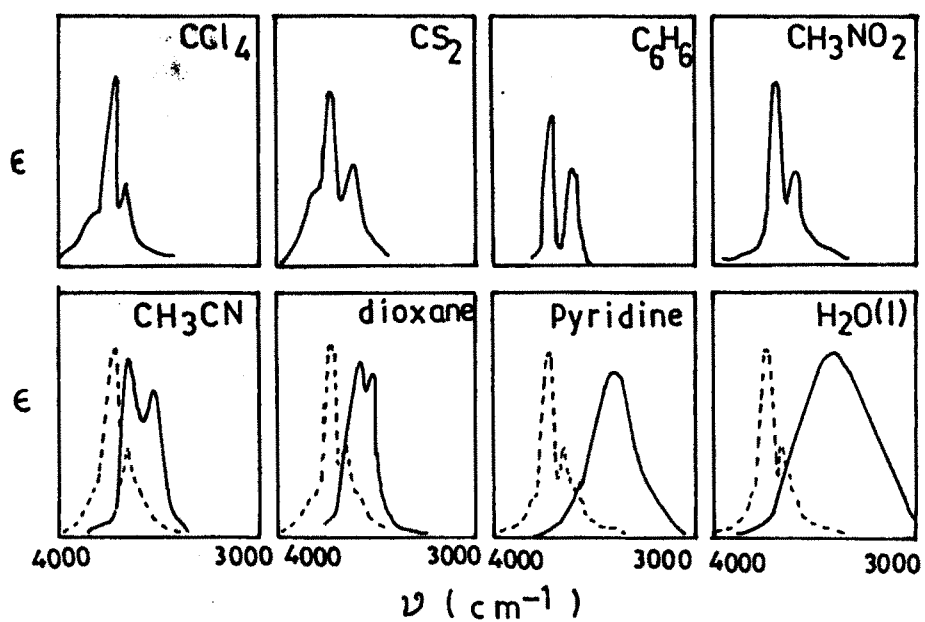


Fig. IV — IR absorption of water in various solvents. Broken lines, H_2O in CCl_4 .

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