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Vibrational Overtone Study of T-Butyl Alcohol and N-Butyl Alcohol

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Abstract:

Raman and FT-IR absorption spectra of *t*-butyl alcohol and *n*-butyl alcohol pure components have been recorded in the liquid state in the region of 400-4000 cm^{-1} . The data obtained have been used to propose complete vibrational assignments for each of the liquid component and the structural features are discussed. The variations in frequency shifts, intensities and line widths are discussed with a view to understanding the origin of such variations.

Keywords: Infrared spectra, *t*-Butyl alcohol, *n*-Butyl alcohol

1. Introduction

Spectroscopy is essentially the study of the interaction between electromagnetic radiation and matter. The spectrum of a molecule is the response of the molecule subjected to radiation of various wavelengths and it provides the most important physical properties of a molecule — its structure. Spectroscopy, therefore, is a powerful tool for structure determination of compounds. Many other interactions in the molecule can also be studied by spectroscopic techniques. Some of them are, rotation interactions, anharmonicity rotation — vibration interactions, centrifugal distortion, magnetic interactions, dipole moments, inter—and intra-molecular interactions etc. A molecule can have many types of motions. The molecule as a whole rotates, the molecule undergoes vibrations due to the periodic displacement of its atoms from their equilibrium positions, the electrons associated with each atom or bond moves etc. Each of their kinds of motion is quantized. A molecule can exist only in distinct states that correspond to a discrete amount of energy. Thus absorption occurs only when radiation containing exactly the right "packet" of energy incident on the molecule under study. Transitions can take place between the levels E_1 and E_2 provided the appropriate amount of energy $E_2 - E_1$ is absorbed by the system. Emission is the reverse process of absorption. The absorbed or emitted energy can take the form of electromagnetic radiation and the frequency of the radiation has the simple form

$$\nu = (E_2 - E_1) / h$$

Where 'h' is Planck's constant. The absorbed quantum of energy brings about different kinds of excitations in a molecule and each require its own distinctive energy (E). That is each type of excitations corresponds to the absorption of light in different regions of the electromagnetic spectrum. The position of an absorption band is usually discussed in wave number (cm^{-1}) and is measured in cm^{-1} . Radio frequency light (10^2 cm^{-1}) brings about the reversal of spin of a nucleus or electron. Microwave radiation (in the range from 1 to 100 cm^{-1}) causes bodily rotation of the molecule about the center of gravity. Infrared radiations causes vibrational excitation of molecules and the range is 100 to 10^4 cm^{-1} . Ultraviolet and visible light brings about the movement of valence shell electrons, typically from a filled bonding molecular orbital to an unfilled antibonding orbital. In the present studies, vibrational spectroscopy in the infrared (IR) region and vibrational overtone spectroscopy in the near infrared (NIR) region have been employed as a technique to investigate structural aspects of a sample organic molecule. In recent years considerable interest has been focused to the study of the different aspects of higher excited vibrational levels of the ground electronic state of polyatomic molecules containing X-H bonds. The major reasons are, it is recognized in the study of non-radiative electronic relaxation process that higher excited vibrational — levels of the ground electronic state play a key role in accepting the excited electronic energy, second, the normal mode model, which is found successful in describing the fundamental vibrations of molecules; fails to provide a satisfactory explanation of the observed higher overtones. Third, an understanding about the nature of higher excited vibrational levels (vibrational overtones) is essential in the development of the theory of multi photon photochemistry and bond selective chemistry. Finally overtone spectroscopic studies provide an important link between spectral properties and chemical reactivity by measuring the behaviour of the molecule as it moves along a coordinate associated with bond breaking.

2. Experimental

High_purity (>99%) n- Butyl Alcohol and t- Butyl Alcohol supplied by SISCO Research Laboratory Ltd, Bombay (SRL) is used for the present studies. The sample is used without further purification. The spectrum recorded from CARY 5000 spectrophotometer at the Sophisticated Test and Instrumentation Centre (STIC), Cochin University of Science and Technology (CUSAT)

2.1. Details about n- Butyl Alcohol

Molecular Weight	:	74.12 g/ mol
Chemical Formula	:	CH ₃ -(C H ₂) ₂ - CH ₂ -OH
Appearance	:	Clear, Colorless Solution
Stability	:	Stable under ordinary conditions of use and storage

2.2. Details about t- Butyl Alcohol

Molecular Weight	:	74.1246 g/mol
Chemical Formula	:	CH ₃ — C(CH ₃) ₂ — OH
Appearance	:	Clear , Colorless Solution
Stability	:	Stable under ordinary conditions of use and storage

3. Result and Discussion

This section contains a presentation of the results of an experimental study of the near infrared overtone spectrum of liquid phase n-butyl alcohol and a comparison of these results with the corresponding results obtained for liquid phase t-butyl alcohol. In contrast to the studies in the fundamental region, the localized nature of the X-H stretching overtones ensures that, changes relative to a parent molecule reflect primarily the electric nature of the substituent. It has long been known that the positions of the overtone band maxima for substituted benzenes are shifted relative to benzene. Mizugai and Katayama studied the frequency shifts of more than 30 kinds of liquid phase monosubstituted benzenes and a number of disubstituted benzenes at the fifth overtone level the by thermal lens technique. They observed that a frequency shift of the overtones from that of benzene are proportional to a_1 values, the inductive part of the Hammett σ . Overtone frequencies are quite sensitive to inductive effects of adjacent substituents. The influence of lone pair electrons on overtone spectra is also well documented. In nitrogen atom the electronic configuration leads trivalency and to the presence of a lone pair electron occupying hybridized orbitals in nitrogen containing compounds. These orbitals' spatial orientation allows interaction between the electron pair and suitably oriented bonds on neighboring atoms. In the present study we have examined the substituent effect in the selected aliphatic molecules with —OH as substituent group, in terms of the change in the local mode parameters of X-H oscillators in these molecules. This has led us to draw specific conclusions on the differing effects of the —OH group in the two compounds.

3.1. XRD Analysis of n-butyl alcohol

	AV=2	AV=3	AV=4	LIV=5	A	B	V
Meth)I CH	5710	8380	10930	-	2975.6	- 60.7	-0.99995
Methylene CH	5660	8300	-	13180	2960.2	-65.7	-0.99996
OH	7087	10405	13605	-	-365	-71.1	-1

Table 1: Observed overtone transition frequencies (cm^{-1}) with least square correlation coefficients (V) are listed below.

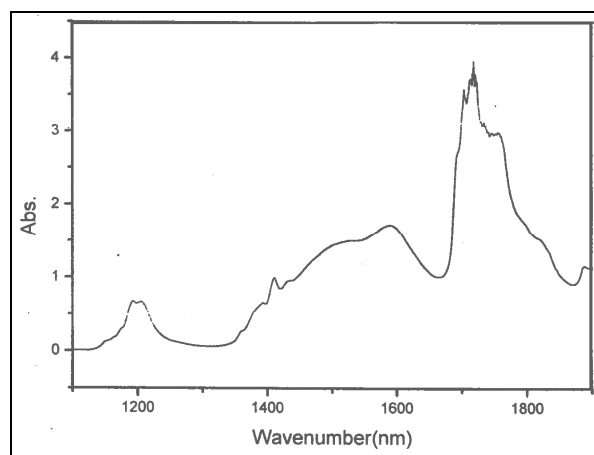


Figure 1

FIG 1: Methyl CH overtones peaks in the V=2 region (a) & V=3 region (b), methylene CH overtone peaks in the V=2 region (c) & V=3 region (d), and OH overtone peaks in the V=2 region (e) in n-butyl alcohol

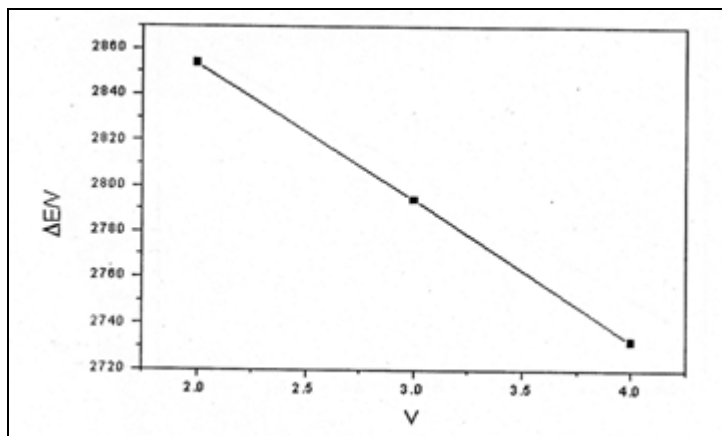


Figure 2: B-S plot for methyl CH overtones in n-butyl alcohol

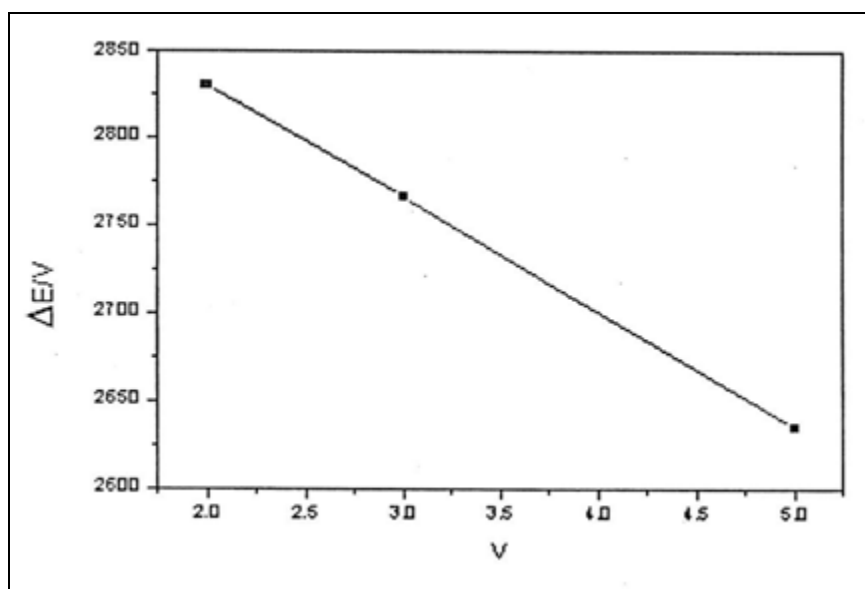


Figure 3: B-S plot for methylene CH overtones in n-butyl alcohol

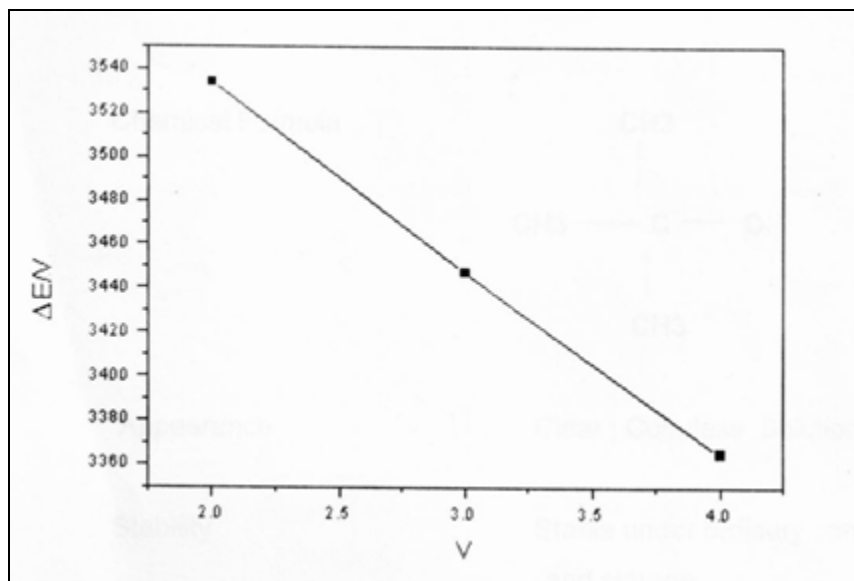


Figure 4: B-S plot for OH overtones in n-butyl alcohol

3.2. XRD Analysis of *t*-butyl alcohol

	V=2	V=3	V=4	V=5	A	B	ν
CH	5760	8440	10990	-	3015.9	- 67.3	-0.9999
OH	7070	10340	13460	-	3701.7	- 84.4	-0.9999

Table-2 .Observed overtone transition frequencies (cm^{-1}) with least square correlation coefficients (V) are listed below.

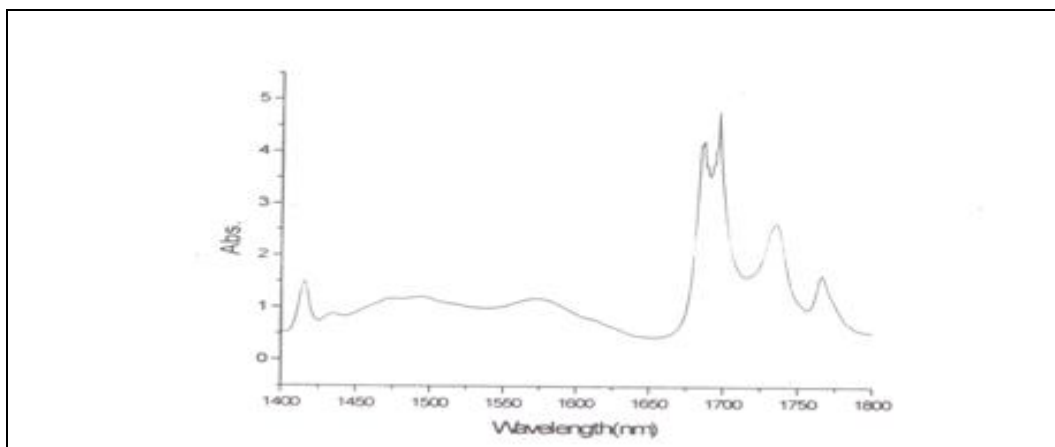


Figure 5: CH (a) and OH (b) overtone peaks of *t*-butyl amine in the $\Delta V = 2$ region

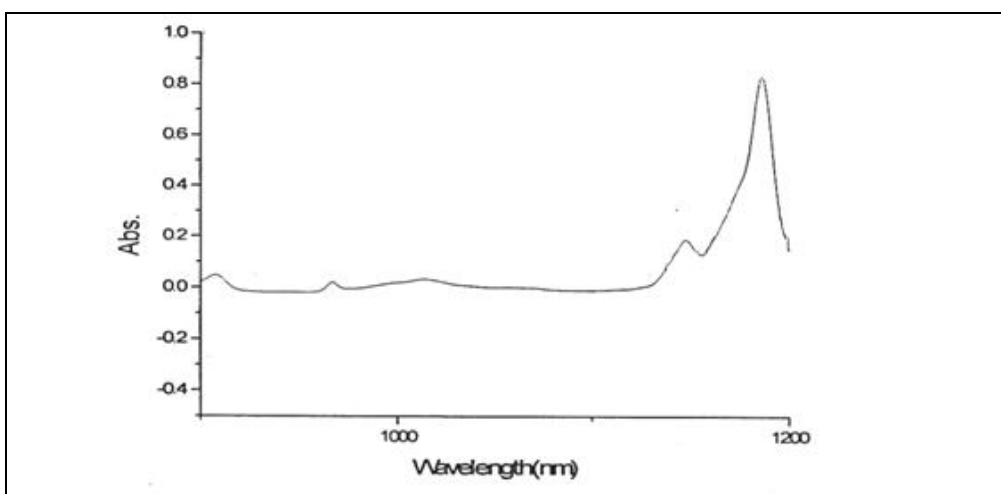


Figure 6: CH overtone peaks in the $\Delta V = 3$ region (a) & $\Delta V = 4$ region (b) and OH overtone peak (c) in the $\Delta V = 3$ region of *t*- butyl alcohol

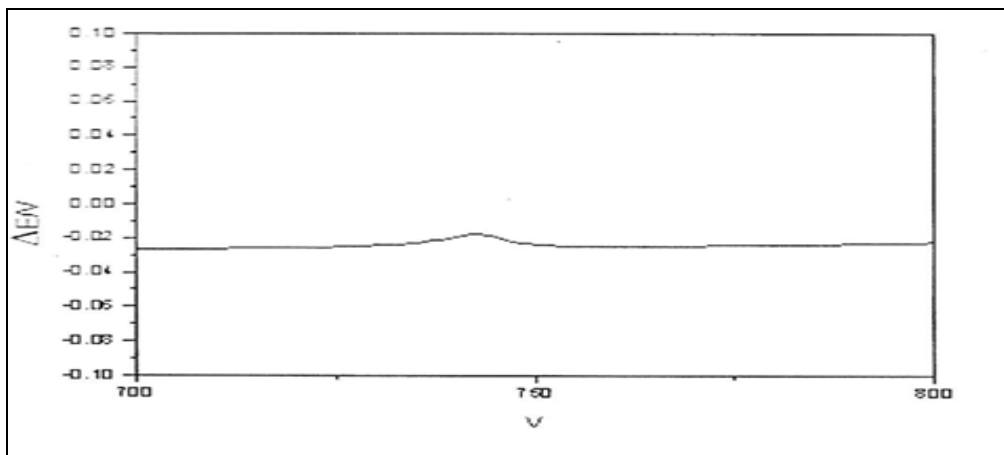


Figure 7: OH overtone peak of *t*-butyl alcohol in the $\Delta V = 4$ region

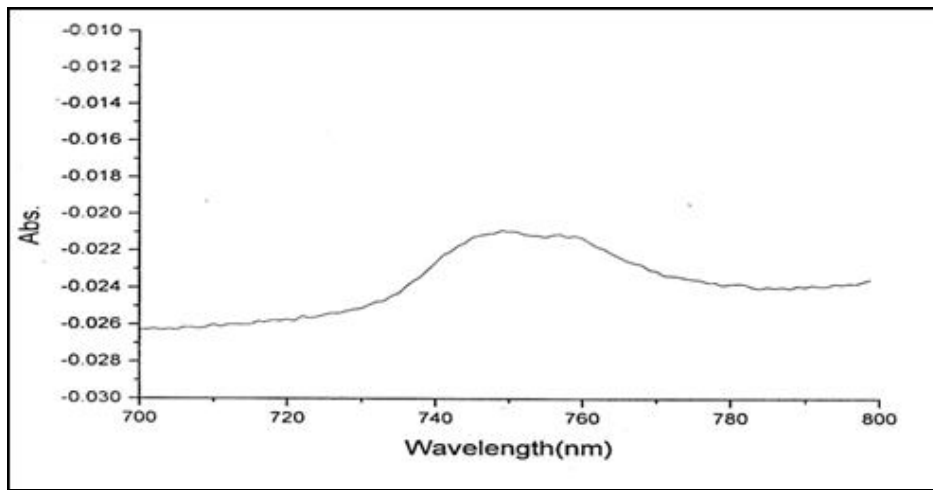


Figure 8: OH overtone peak of t-butyl amine in the $\Delta V = 4$ region

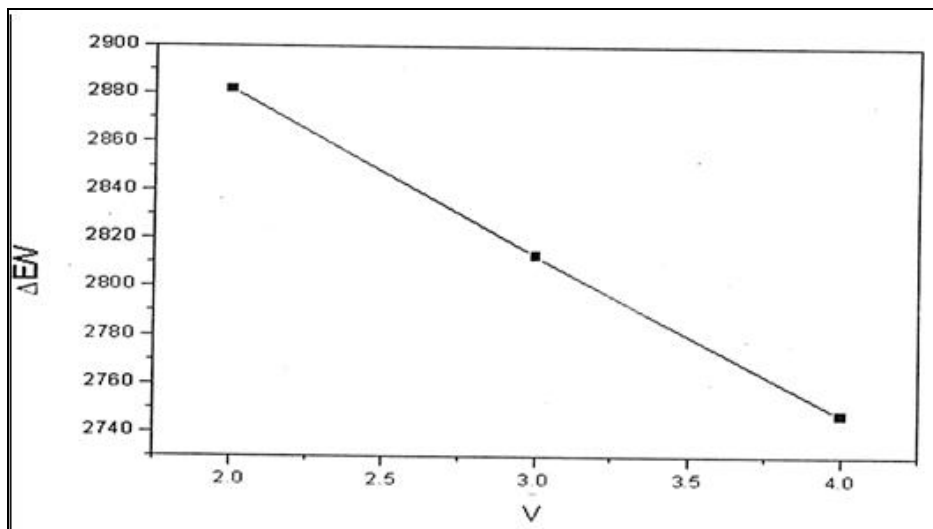


Figure 9: B-S plot for CH overtones in t-butyl alcohol

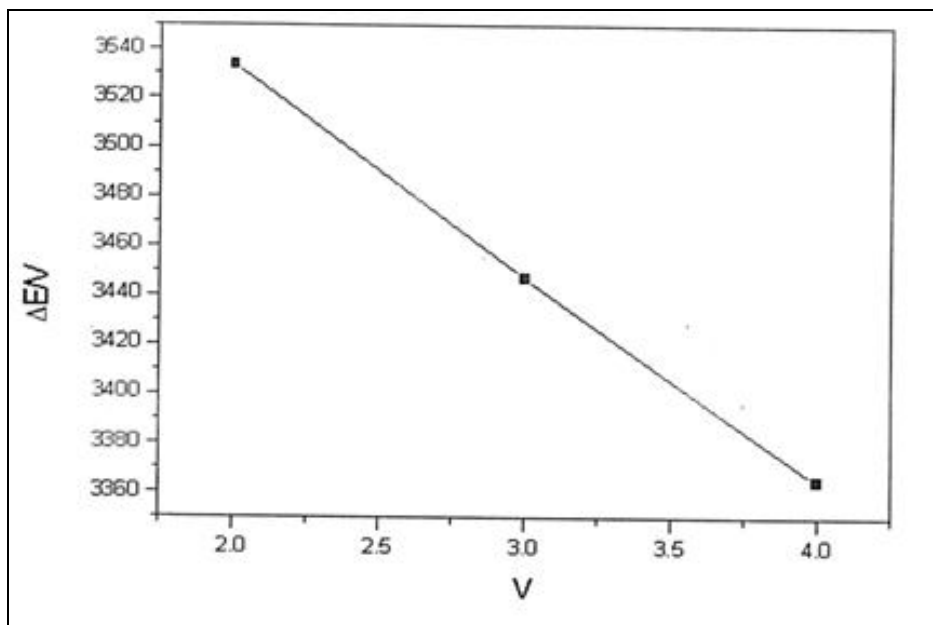


Figure 10: B-S plot for OH overtones in t-butyl alcohol

4. Conclusions

The near infrared vibrational overtone spectra of liquid phase n-butyl alcohol and t-butyl alcohol are spectrophotometrically recorded and analyzed using the local mode model. It is demonstrated how the influence of the environment on the C-H oscillator can be observed in the energies of the overtone peaks of the molecules studied. The observation is that the lone pair trans-effect of -OH group plays dominant role in n-butyl alcohol and the inductive effect of -OH group plays dominant role in t-butyl alcohol in determining the C-H bond strength. The difference in the value of mechanical frequency in t-butyl alcohol and n-butyl alcohol is the manifestation of the substituent effect in these molecules. The well-known fact that secondary C-H bonds are more reactive than primary C-H is reflected significantly lower dissociation energy values for the secondary C-H.

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