CHAPTER 5

VIBRATIONAL OVERTONES OF ISOBUTANOL AND HIGH RESOLUTION SPECTROSCOPIC STUDY OF ITS HYDROXYL GROUP IN THE ΔV=3 REGION

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CHAPTER 5

VIBRATIONAL OVERTONES OF ISOBUTANOL AND HIGH-RESOLUTION SPECTROSCOPIC STUDY OF ITS HYDROXYL GROUP IN THE \( \Delta V=3 \) REGION

5.1 Introduction

Almost all lasers in one or another form have been applied in spectroscopic experiments since its development in the early 1960's. However many of the laser sources developed in the initial stage provide only a single lasing wavelength. Thus the true beginning of the era of modern laser spectroscopy is considered being aroused with the development of tunable coherent radiation source based on lasers. High-resolution spectroscopy has undergone a transformation during the last several years as a result of the considerable strides made over the experimental side and it has now become possible to do a line-by-line analysis of the spectra of polyatomic molecules. High resolution facilitates the determination of precise values of spectral line position and intensities, which makes the identification of molecular species more accurately. Tunable Diode Laser Absorption Spectroscopy (TDLAS) is one such technique that finds widespread use in obtaining high resolution spectra of gas species. As the name implies this technique utilizes a Tunable Diode Laser (TDL) source to access specific IR regions of the molecules. The use of TDL in conjunction with a long path length cell provides high sensitivity local measurements. This technique is commonly referred to as TDLAS.

The molecular rotational motion in solids and liquids are normally completely suppressed due to intermolecular interactions. At low pressures (\( \leq 20 \) torr) the molecules become essentially independent in gas phase with little or no effect due to the intermolecular interactions. Under these conditions, the interaction of the incident photon with the sample not only excites molecular vibrations but also molecular rotations. Then
each of the vibrational bands split into many fine lines. This means that vibrational bands in condensed phases are often sharper than they are in gas. It is often possible to distinguish possible structures or isomers by examining the patterns of vibrational spectrum or by counting the number of bands present.

The major application of TDL is high-resolution recording of vibrational-rotational spectra of molecules in the gas phase. Diode lasers have high spectral brightness and are coherent devices. These features allow the use of TDL for long path length measurements, with high degree of spatial resolution. The most important property of TDL is the probability of considerable emission frequency tuning with operating conditions changed. Since the gain curve position $v_5$ is determined by band gap energy $E_g$, all methods of changing $E_g$ can be used for coarse frequency tuning. $E_g$ can be tuned by varying the temperature $T$ of the semiconductor crystal by applying pressure or a magnetic field [1]. The fine frequency tuning, which is used for high-resolution spectroscopy is performed by shifting the frequency of effective cavity optical length mainly through change of index of refraction [1].

In measurements of trace gases by laser absorption spectroscopy, the absorption signal strength is proportional to the product of oscillator strength of the absorption transition and the number of molecules in the path of the laser beam. Hence at very low concentrations long path length is required for generating detectable absorption signals [2]. Use of multipass cell can increase the effective path length. The multipass optical system limits the beam divergence and provides large path length and facilitates operation at low pressure and thus broadening of spectral lines can be avoided.

The tunable diode laser based spectrometer used in the present work has a tunability range of 930-970nm. This range is ideal for the study the spectrum of the $–$OH group absorption frequencies of all OH containing molecules in the transition region $\Delta V=3$ by using a detector with a log output and hence use of chopper and lock-in amplifier can be avoided. In the present study, a near infrared tunable diode laser based high resolution spectrometer is used to investigate the highly resolved vibrational overtone band of the OH group in gas phase isobutanol in the $\Delta V=3$ region. A local mode analysis of the liquid phase overtone spectra of isobutanol is also carried out.
5.2 TDLAS— a brief review

The major application of TDLAS is high-resolution recording of vibrational-rotational spectra of molecules in the vapour phase [1]. Because of the versatility, selectivity and sensitivity of TDLAS numerous laboratory, ground based, aircraft and balloon-borne studies employ this technique.

Trace gas detection is of great interest in industrial process control and pollution monitoring. Nowadays the requirements for accurate and precise monitoring of trace gas constituents in the atmosphere has become increasingly important as a direct result of concerns over the cause and effects of atmospheric pollution. TDLAS has now established itself as one of the highly selective and versatile techniques for atmospheric analysis of trace gas constituents. The aim of diode laser trace gas monitoring is to establish absolute concentrations. TDLAS has been used for atmospheric concentration measurement of CH₄ [3], CO [4], HCl [5], H₂O [6], HNO₃ [7], NO [6,7], NO₂ [7], N₂O [8], SO₂ [7] etc. The applications of lead-salt and GaAs based tunable diode lasers for atmospheric trace gas monitoring are reviewed recently [9]. The necessity for reliable tools for trace gas monitoring is obvious but the type of technique depends very much on the particular application being addressed and the specific trace gas species of interest.

High sensitivity laser spectroscopic techniques are needed to detect the very low mixing ratios or concentrations of trace species ranging from several parts per million to sub parts per trillion levels for carbon monoxide, hydroxyl radical etc. Operating at infrared wavelengths, most trace gases except nitrogen and oxygen to be monitored via their characteristic vibrational spectra and the high spectral resolution reduces the possibility of interferences from other species.

Sandstrom and Malmberg [10] demonstrated the potential of the TDLS technique for simultaneous contact free monitoring and measurement of the oxygen concentration as well as gas temperature in a reheating furnace during production. Werle et al [11] discussed the currently available semiconductors for spectroscopy in the near- and mid-infrared region based on direct band to-band transitions as gallium-arsenide, indium-phosphide, antimonides and lead-salt containing compounds together with the main features of different tunable diode laser absorption spectrometers for trace gas analysis.
In a recent paper Vicet et al [12] presented antimonide quantum well diode lasers emitting near 2.0-2.4 μm at room temperature and experimental TDLAS setup for open path gas detection using these devices.

Kormann et al [13] described the application of a three-laser tunable diode laser absorption spectrometer for atmospheric trace gas measurements. Gas monitors for industrial applications must have high reliability and require little maintenance. Monitors for in-situ measurements using TDLAS in the near infrared can meet these requirements.

Linnerud et al [14] demonstrated that in-situ open path measurements in the near infrared using TDLAS can be done with the accuracy and reliability required for industry in a number of different applications. Nelson et al [15] developed a tunable diode laser system to measure air-pollutant emission from on-road motor vehicles. The high resolution TDL spectroscopy of the van der Waals complex Ar-CH₄ in the 7μm region was analyzed and compared with a spectrum predicted from ab initio calculations [16].

5.3 High Resolution Overtone Spectroscopy – some reported works

High-resolution laser spectroscopy has been a powerful tool for investigating the structure of molecules, ions and free radicals. The potential importance of high-resolution spectroscopy in air pollution and other meteorological studies is evident from the number of publications in this field. High-resolution spectra of C-H, O-H, and N-H stretching vibrational overtone transitions that occur at higher frequencies have been studied earlier. It is difficult to record the high-resolution spectrum of higher vibrational states due to the very small value of transition dipole moment connecting the two states. Moreover, the spectrum must be recorded at low pressure to avoid the pressure broadening [17].

Recently, intensive experimental work has been focused to study the high-resolution spectra of stretching overtones, using various highly sensitive techniques like Fourier transform spectroscopy, intracavity laser absorption spectroscopy, laser photo acoustic spectroscopy, tunable diode laser spectroscopy etc. Taking advantage of high resolution Fourier transform spectroscopy, Zhu and co-workers recorded high-resolution spectra of GeH₄ [18] in the ΔV =2-5 and SiH₄ [19] in the ΔV =3-5 stretching overtone
regions. The above group also recorded the high-resolution spectra of the same molecules in the $\Delta V = 6-7$ overtone regions using intracavity laser absorption spectroscopic technique. The high resolution Fourier transform spectrum of arsine ($\text{AsH}_3$) was recorded in the region 3989-4274 cm$^{-1}$ at a resolution of 0.008 cm$^{-1}$ by the same group [20].

Chou and coworkers [21] recorded the high resolution absorption line shapes of the R (7) and P (2) transitions in the first overtone band of HBr at room temperature using a pair of distributed feedback diode lasers operating near 2 $\mu$m. Lummla et al [22] recorded the first and second CH overtone vibration–rotation absorption spectra of monoiodoacetylene (HCCI) using FTIR spectrometer with a resolution of about 0.005 cm$^{-1}$ and third overtone spectrum using a ring laser spectrometer with a spectral resolution of about 0.02 cm$^{-1}$.

Douketis et al [23] used photoacoustic technique to record the high-resolution vibrational overtone spectrum of $\text{H}_2\text{O}_2$ vapour. Held et al [24] studied the high resolution FTIR spectroscopy the first overtone of N-H stretch and the fundamental of C-H stretch in gas phase pyrrole. The first overtone N-H stretch is rotationally analyzed using an asymmetric top model and was found to exhibit two separate perturbations. Luckhaus [25] reported the rovibrational spectrum of hydroxylamine (NH$_2$OH) recorded by interferometric Fourier Transform Spectroscopy with a resolution up to 0.004 cm$^{-1}$ close to the Doppler limit at room temperature, in the spectral range of 800 cm$^{-1}$ up to the visible region. They also carried out detailed rotational analyses of all the fundamentals and overtones up to 10500 cm$^{-1}$.

The measured intensities of several OH vibrational overtone bands of vapor phase methanol, ethanol and isopropanol were used to model the trends in the intensities as a function of excitation level [26]. Two empirical approaches were used for yielding intensity predictions for the higher overtone transitions up to sixth OH overtone level. These methods are applied to recent HNO$_3$ overtone measurements resulting in new intensity predictions for higher photochemically active overtone bands [25].

Murtz et al [27] demonstrated the use an offset-locked CO overtone laser sideband spectrometer as suitable for very high-resolution molecular spectroscopy in the 2.6–4.1 $\mu$m spectral region. Hu et al [28] utilized high resolution Fourier–transform intra-
cavity laser absorption spectroscopy to record the $\Delta V_{OD} = 5$ stretching overtone of HOD at a resolution of 0.05 cm$^{-1}$ in the region 12550-12900 cm$^{-1}$.

High-resolution infrared emission spectrum of sodium monofluoride was recorded by Muntianu and coworkers [29] using a Fourier transform spectrometer and assigned a total of 1131 vibration-rotation transitions from the $V=1 \rightarrow 0$ to $V=9 \rightarrow 8$ vibrational bands. Vaittinen et al [30] reported local mode effects on the high-resolution overtone spectra of H$_2$S recorded by intracavity laser absorption spectroscopy in the region 12270-12670 cm$^{-1}$. The rovibrational analysis provided upper state rotational parameters for the three interacting vibrational states.

5.4.1 The TDLAS Experimental setup

The basic experimental arrangement used for the present work consists of a tunable diode laser, a sample cell, beam splitter, detection system and vacuum system. The block diagram of the experimental set up used is shown in the Figure 5.1. A brief description of the arrangement is given below.

**Source:** A tunable diode laser (Model No.6321, New Focus Inc.) having tuning range 935-975 nm is a stable, narrow line-width laser source. Its tunability, temperature stability, single mode operation etc makes it an ideal source for high-resolution spectrometer. The maximum output of the source is 15 mW. The laser is operated at a temperature of 20°C. Output power can be varied by changing the current. The grating spectral filter used in the laser head is narrow enough to force the laser to operate in a single longitudinal mode. The laser can be operated manually from the front panel of the controller or remotely using computer control.

**Beam splitter:** A beam splitter with variable split ratio splits the laser beam into two reference beam and signal beam. The reference beam falls directly on the reference photodiode of the photodetector. The signal beam is fed into the multipass cell that contains the sample, and the output from the multipass cell falls on the signal photodiode of the detector.
Sample cell: For enhancing sensitivity of weak absorptions the contributions of several factors are to be considered. One simple way of achieving this by increasing the effective absorption path length as the radiation propagates back and forth within the cavity. Multipass advantage can be utilized for the purpose. A multipass cell (Model 5611, New Focus Inc.) is the absorption cell used in the present study and can be operated up to 760torr. Light enters and exits the cell through the front window assembly and makes 182 passes between the mirrors and provides an optical path length of 36m in the 0.3litre cell. The input and output beam height is 2.5 inches. Both input and output beams are in horizontal plane and cross at the center of the coupling mirror. The input and output beams enter and exit the cell at an angle from the centerline of the cell.

The detector system: Nirvana auto-balanced photoreceiver (Model 2017, New Focus Inc.) consists of two photodiodes labeled as signal and reference. There are three outputs—linear, log and signal monitor. This detector enables traditional balanced detection. In the balance mode the linear output provides a voltage proportional to the difference between the photocurrents of the signal and reference diodes. It also provides auto balance detection with zero DC voltage and noise suppressed AC signal proportional to received signal optical power. In this state the detection automatically balances the photocurrent from signal and reference diodes. The signal monitor output enables constant monitoring of the signal. The log output at auto-balanced state provides a convenient measurement of absorption present in the signal path. The output voltage is given as

\[ \text{Log (output)} = -\ln \left( \frac{P_{\text{ref}}}{P_{\text{sig}}} - 1 \right) \]

The log output is bandwidth limited up to the selected gain compensation cut-off frequency. Common mode noise within this bandwidth is cancelled in the log output. The split ratio of the detector is fixed to 2:1 by using the log output the chopper and lock-in-amplifier can be avoided.

The log output from the photodetector is directly interfaced with a PC using lab VIEW 6.0 software. The software is programmed to obtain the spectrum as wavelength against absorption, as the absorption in the cell is proportional to the output voltage.
Sample container: A sample container with fine needle valve is used for the regulated flow of the sample to the multipass cell. High purity spectroscopic grade liquid sample is taken in the sample container connected to the inlet of the multipass cell and when the pressure in the multipass cell reached the required value the sample is allowed to flow into the multipass cell using the needle valve that regulates the flow.

Vacuum system: A rotary pump is used to evacuate the multipass cell and for the sample gas feeding. The multipass cell is evacuated continuously while recording the spectra.

The calibration of the spectrophotometer is done using Hitran Database 1996. The setup provides a resolution of 0.01nm.

5.4.2 High-resolution overtone spectrum of isobutanol - Experimental

High purity isobutanol (extra pure AR, 99.5%) obtained from M/s SISCO Research Laboratories Pvt. Ltd., Mumbai, India is used for recording the spectrum. The sample was used without further purification. The overtone absorption spectrum of isobutanol in the gas phase was measured with a high-resolution tunable diode laser. The details of the arrangement are discussed and the experimental parameters are given below. The sample in the liquid phase is taken in the sample reservoir. When the required pressure is reached the valve connecting multipass cell and sample reservoir is opened.

5.4.3 Experimental parameters

The experimental conditions used for recording the spectrum of isobutanol vapour is given below.

Laser power = 2.8mW
Scan speed = 0.02nm
Temperature = 20°C
Pressure = 1.2mbar
Path length = 36m
Tuning range = 949-959nm
Figure 5.1 Schematic representation of the high-resolution experimental setup: a-Tunable diode laser, b-photodetector, c-computer, d-multipass cell (sample holder), e-sample container, f-vacuum system
5.4.4 Results and discussion

In the present work we describe the high-resolution O-H stretching overtone spectra of gas phase isobutanol in the $\Delta v=3$ region measured using TDLS. The molecular structure of isobutanol is given in Figure 5.2.

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH} \rule{1cm}{1mm} \text{CH}_2\text{OH} \\
\text{CH}_3
\end{array}
\]

Figure 5.2 Molecular structure of Isobutanol

Many groups have gathered data for O-H stretching overtones in different alcohols. Absorption spectra of gas phase methanol and methanol-d were reported by Fang and co-workers [31] using intracavity dye laser photo acoustic spectroscopy. The OH overtone spectra of these samples were described in terms of a nearly symmetric top structure with nearly free internal rotation about the top axis. The study also reveals the presence two types of conformationally non-equivalent C-H bands due to the presence of lone pair electrons on the oxygen atom. The solvent effects in O-H and O-D stretching overtone spectra of methanol have been measured in different solvents and found that the anharmonicity constants are almost identical but the mechanical frequencies change as a function of the solvent used [32]. An internal coordinate Hamiltonian model has been constructed to model the torsional motion in the O-H stretching vibrational overtone region of methanol [33].

Overtone absorption spectra of gas phase ethanol in $\Delta v=3-6$ region of O-H were studied by Fang and Swofford [34] by intracavity photo acoustic spectroscopy. Each O-H
overtone levels shows two side bands, which are assigned as the transitions of two conformers of the O-H bond in the trans and gauche position with respect to the methyl group. The torsional of the O-H group about the C-O axis give rise to two distinct conformers- one trans conformer and two equivalent gauche conformers.

Fang and Compton [35] reported overtone absorption spectra of gas phase 1-propanol, 2-propanol and tert-butyl alcohol measured with intracavity photoacoustic and FT-IR spectroscopy. The OH overtones in these molecules are considerably narrow and show both rotational and conformational structure. This implies a more isolated nature of O-H stretching vibration. The relatively broad C-H overtones also show evidence of conformational non-equivalent sites for methyl groups in an anisotropic environment.

Weibel et al [36] reported the OH fourth overtone absorption spectra of ethanol, ethanol (1,1-d₂) and ethanol (2,2,2-d₃), recorded using intracavity dye laser photoacoustic technique. The distinct absorption bands are assigned as due to the trans and gauche conformational isomers. Comparison of the spectra revealed a coupling between the O-H and methylene C-H vibrations in only the gauche conformer of ethanol, an effect that had not been observed in the fundamental spectrum. Ab initio electronic structure and vibrational frequency calculations are used to clarify and support the analysis of the ethanol O-H vibrational spectrum and to evaluate the relative energies of the conformers.

Since the energy differences between different conformers are very small, it is usually difficult to resolve this difference by standard procedures like nuclear magnetic technique, fundamental IR and Raman spectroscopy. But the vibrational overtones are very sensitive to the local environment; a difference of only 10 cm⁻¹ in fundamental frequencies can be resolved in the high vibrational overtone level, since the separation is amplified n times in the V=n overtone level. Overtone spectra are thus used to deduce the conformational details of several molecules, as demonstrated by Fang and Swofford [34] who studied the molecular conformation of gas phase ethanol using overtone spectroscopy. Wong and Moore [37] also studied the molecular conformation of alkanes and alkenes using vibrational overtone spectroscopy.

Several recent studies combine ab initio calculations and OH overtone spectra in order to correlate structural and spectral features. Fedorov and Snavely [38] measured the O-H overtone spectrum of gas phase isobutanol in the ΔV=4 region using an
intracavity laser photoacoustic spectrometer. The geometry optimizations and total
energies of five different conformations were calculated by both the ab initio 3-21G* and
6-31G** levels and demonstrate that a linear correlation exist between calculated OH
bond lengths and the observed OH overtone transition energies. Xu et al [39] measured
the O-H stretching vibrational overtone spectra in the ΔV= 3, 4, and 5 regions of gaseous
2-butanol by using cavity ring-down spectroscopy (CRDS) and calculated electronic
energies using density functional theory (DFT) at the B3LYP/6-31+G(d,p) and B3LYP/6­
311+G(d,p) levels. Because of the complexity of 2-butanol nine stable conformers are
found and no clear pattern of assignments emerged. Two bands are observed for each
overtone level corresponding to these conformers. In a subsequent study Xu et al [40]
reported the OH overtone spectra of isobutanol in the ΔV=3- 5 regions using CRDS.
They observed three bands corresponding to each overtone level. These three bands are
assigned to the O-H stretching vibrational absorption of the five stable conformations of
the molecule. This was further confirmed by DFT calculations using highly accurate
B3LYP/6-31+G(d,p) and B3LYP/ 6-311+G(d,p) levels. The band intensities of each band
are also obtained. The molecular vibrational abundance and O-H stretching frequencies
of different vibrations of the calculated molecular conformations are in agreement with
the experimental results. The range of calculated electronic energies among conformers is
less than 0.7 kcal/mol.

The overtone spectrum of gas phase isobutanol obtained using the high-resolution
spectrophotometer setup is shown in Figure 5.3. The experimental results obtained using
high-resolution spectrophotometer and the reported values are given in Table 5.2. The
reported values of O-H mechanical frequency and anharmonicity for different alcohols
obtained from their overtones are given in the Table 5.1
Table 5.1 The O-H stretching mechanical frequencies and anharmonicities in different alcohols

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Mechanical frequency (cm$^{-1}$)</th>
<th>Anharmonicity (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol [31]</td>
<td>3855</td>
<td>86</td>
</tr>
<tr>
<td>Ethanol [35]</td>
<td>3832-3846</td>
<td>85-86</td>
</tr>
<tr>
<td>1-propanol [35]</td>
<td>3831-3852</td>
<td>86</td>
</tr>
<tr>
<td>2-propanol [39]</td>
<td>3791-3831</td>
<td>83-86</td>
</tr>
<tr>
<td>2-butanol [39]</td>
<td>3798-3826</td>
<td>85</td>
</tr>
<tr>
<td>t-butyl alcohol [35]</td>
<td>3814</td>
<td>86</td>
</tr>
<tr>
<td>Isobutanol [40]</td>
<td>3826-3850</td>
<td>85-86</td>
</tr>
</tbody>
</table>

The mechanical frequency and anharmonicity of isobutanol are close to that of ethanol and 1-propanol. Isobutanol possesses a stereo structure similar to those of ethanol and propanol [41]. However, it is noticed that the band profiles of the overtones of this molecule are different from other alcohols [40].

Isobutanol molecule exhibits different conformations because the hydroxyl group staggars between two CH bonds and -H(CH$_3$)$_2$ groups rotate around C-C single bond. The conformations of isobutanol is named according to different dihedral angles of $H_5O|C_2C_3$ and $O_iC_3C_3H_9$, where trans (t) is nearly 180°, gauche (g) is near 60° and gauge' (g') is near -60°. All the possible conformations are: Tt, Tg, Tg', Gg, G'g', Gt, G’t, Gg' and G'g. It is confirmed by density function theory (DFT) calculations that all these conformations are stable. However among the total nine conformers possible, four of them viz, Tg, Gg, Gt, and Gg' are the mirror images of Tg', G'g', G't and G'g respectively. The distributions of these conformers and its mirror images are equal. Therefore there are only five different stable conformers for isobutanol. All the possible conformations of isobutanol are given in the Figure 5.4.

The O-H trans conformations of form a and b are close to each other, O-H gauche conformations of form c and d, whose hydroxyl axis parallel to the methyl axis, are close
to each other. In gauche form e the hydroxyl axis is parallel to the carbonyl axis. Thus, in general, there are three kinds of conformations in isobutanol and corresponding to it three bands are observed in each overtone region. Therefore one band is due to the OH stretching overtone absorption of forms a and b, the second band is due to the OH stretching overtone absorption of forms c and d, and the third band is due to the OH stretching overtone absorption of form e. The assignments of this molecule is done in agreement with the previous experimental assignment for ethanol where the higher energy band is assigned to the conformation with the O-H bond trans to the alkyl group and the lower energy band is assigned to the two equivalent conformations with the O-H group gauche to the alkyl group. But in isobutanol the gauche conformations are not equivalent. The assignments of gauche conformations were done by ab initio calculations together with thermodynamical considerations [40]. The lowest energy peak of the observed triplet belongs to the most energetically favourable conformer that has the longest O-H bond. The relative percentage of the abundance of the molecular conformation follows the Boltzmann formula

\[
\frac{N_i}{N_j} = \exp \left[ \frac{-(E_i - E_j)}{kT} \right]
\]

Here \(N_i/N_j\) is the population ratio of the two conformers, \(E_i\) and \(E_j\) are the total energies of the two conformers, and \(T\) is the temperature. From the calculated results the percentage for form a, b, c, d, and e isobutanol is 6%, 33%, 22%, 9% and 27% respectively [40].
Figure 5.3: High-resolution TDLS spectrum of OH stretching in the \( \Delta V=3 \) overtone region of isobutanol.

Table 5.2: Comparison of TDLS results of isobutanol with the reported theoretical and experimental (cavity ring-down spectroscopy) values.

<table>
<thead>
<tr>
<th>Conformation</th>
<th>TDLS</th>
<th>ab initio [40]</th>
<th>CRDS [40]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Form a</td>
<td>10539</td>
<td>10542</td>
<td></td>
</tr>
<tr>
<td>Form b</td>
<td>10527</td>
<td>10525</td>
<td></td>
</tr>
<tr>
<td>Form c</td>
<td>10499</td>
<td>10490</td>
<td></td>
</tr>
<tr>
<td>Form d</td>
<td>10485</td>
<td>10485</td>
<td>10486</td>
</tr>
<tr>
<td>Form e</td>
<td>10451</td>
<td>10449</td>
<td>10448</td>
</tr>
</tbody>
</table>
Figure 5.4: Stable conformations of isobutyl alcohol.
At a higher vibrational energy, the overtone spectrum is relatively simple for small molecules. The interpretation and assignment become more complex as the number of oscillators increases. This is especially true for molecules having several conformers where the vibrational overtone transitions have contributions from all the conformers. The rotational structures of the OH overtone in isobutanol are not yet analyzed, as they are so complicated owing to the above reason, and also due to the strong interaction with adjacent states causing loss of regularity in the spectral pattern.

5.4.5 Conclusions

The highly resolved overtone spectrum of the –OH group in isobutanol for the Δν=3 transition is recorded in a linear high-resolution spectrometer using tunable diode laser and a long path length cell. The resolved bands are assigned as the O-H stretching absorption of the three kinds of conformations of the hydroxyl group. The observed OH overtone peak positions corresponding to the different conformers agree with ab initio theoretical predictions and the reported CRDS results.

5.4 Overtone Spectroscopic Analysis of Liquid Phase

Isobutanol

5.5.1 Introduction

The local mode model of molecular vibrations has been used extensively for the description of CH and OH stretching overtone spectra of polyatomic molecules [39,40,42]. The NIR spectra of CH stretching up to sixth overtone region and OH stretching up to fifth overtone region in normal, secondary, and tertiary butanol were studied by Rai and Srivastava [42] using thermal lens technique. Earlier works on these samples in the third and fourth harmonic regions were reported by Mizugai et al [43] and by Swofford et al [44]. Rai and Srivastava [42] also reported the IR spectra of the three
butyl alcohols and observed that the fundamental vibrational frequency for both the C-H and O-H bonds increases as one go from normal to tertiary butanol. Rai and coworkers [45] observed a considerable blue shift for OH stretching fundamental absorption peak of n-butanol on dilution with carbon tetrachloride. The magnitude of blue shift decreases for the 2←0 transition and there is no shift for the 3←0 transition. This observation is interpreted on the basis of formation of O-H...Cl hydrogen bond.

5.5.2 Experimental

High purity (>99%) isobutanol supplied by M/s SISCO Research Laboratories Pvt. Ltd., Mumbai, India is used for the present studies. The near infrared absorption spectra in the region 2000-700nm are recorded from pure liquid on a Hitachi Model 3410 UV-VIS-NIR spectrophotometer. The spectra are recorded using a path length of 1cm with air as reference at room temperature (26±1)°C.

5.5.3 Results and discussion

The overtone spectra of liquid phase isobutanol recorded by using a conventional spectrophotometer in the spectral region ΔV_{CH}= 2-6 and ΔV_{OH} =2-5 are given in Figures 5.3- 5.9. The peak assignments of the spectra is given in the Table 5.3. The transition energies of the OH and CH stretching overtones are fitted to the one dimensional Birge – Sponer equation for an anharmonic oscillator. Calculated mechanical frequencies, anharmonicities and dissociation energies of the O-H and C-H stretching vibrations evaluated from the above spectra are given in the Table 5.3.

The C-H overtone The transition frequencies of CH oscillators in alkanes and alkenes have been found from gas phase spectra and found that the progression occur in the order \( \nu_{CH_4} > \nu_{CH_3} > \nu_{CH_2} > \nu_{CH} \) [37,46]. Based on the work of Greenlay and Henry [46] and that of Rai and Srivastava [42] it is easy to identify the absorption peaks due to the distinctive types of C-H oscillators and O-H oscillator in the molecule of the present study.
The mechanical frequency and anharmonicity of O-H oscillator in isobutanol are 3834 cm\(^{-1}\) and -91 cm\(^{-1}\) respectively. The mechanical frequency value is found to be close to that of isobutanol in the gas phase (Table 5.1). The observed values of methyl C-H mechanical frequency and anharmonicity in isobutanol are ~3043 cm\(^{-1}\) and ~-60 cm\(^{-1}\) respectively. These values are remarkably closer to the corresponding values in most of the normal and branched alkanes [47].

Table 5.3 Observed overtone transition energies (cm\(^{-1}\)), mechanical frequencies \(X_1\) (cm\(^{-1}\)) and anharmonicities \(X_2\) (cm\(^{-1}\)) of OH and CH of isobutanol. The least square correlation coefficients (\(\gamma\)) are also given.

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>(\Delta V=2)</th>
<th>(\Delta V=3)</th>
<th>(\Delta V=4)</th>
<th>(\Delta V=5)</th>
<th>(\Delta V=6)</th>
<th>(X_1)</th>
<th>(X_2)</th>
<th>(\gamma)</th>
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<td>8319</td>
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<td>13261</td>
<td>15542</td>
<td>2995.5</td>
<td>-57.7</td>
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Figure 5.5 Methyl (‘b’), methylene (‘c’) and methyne (‘d’) CH overtone peaks of isobutanol in the $\Delta V= 2$ region

Figure 5.6 The OH overtone peak of isobutanol in the $\Delta V= 2$ region
**Figure 5.7** Methyl ('b'), methylene ('c') and methyne ('d') CH overtone peaks of isobutanol in the $\Delta V = 3$ region

**Figure 5.8** The OH overtone peak ('a') in the $\Delta V = 3$ region and the CH overtone in the $\Delta V = 4$ region of isobutanol. Peaks marked as b, c and d represent methylene and methyne CH overtone peaks, respectively.
5.9 The OH overtone peak (‘a’) in the $\Delta V = 4$ region and the CH overtone peaks $\Delta V = 5$ region of isobutanol. Peaks marked as b, c and d represent methyl, methylene and methyne CH overtone peaks, respectively.

5.10 The OH overtone peak (‘a’) in the $\Delta V = 5$ region and the CH overtone peaks $\Delta V = 6$ region of isobutanol. Peaks marked as b, c and d represent methyl, methylene and methyne CH overtone peaks, respectively.
5.5.4 Conclusion

The overtone spectra of the C-H and O-H stretching vibrations of liquid phase isobutyl alcohol are measured using conventional absorption spectrophotometer. Resolvable peaks are observed for methyl, methylenic and methynic C-H bonds and O-H bonds. The peaks are assigned using the local mode model. The O-H overtone band in the $\Delta V=5$ region shows three distinct peaks as observed in the gas phase spectrum, indicating the presence of different conformers.

References


