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Spectroscopic studies of some aliphatic alcohols

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Abstract : Spectra of a number of aliphatic alcohols (pure as well as diluted with hexane and CCl_4) have been studied in the 500-14000 cm^{-1} region. In addition to the fundamental and overtone bands of CH and OH stretch vibrations, a large number of combination bands involving different frequencies have been observed. Vibrational constants for the CH and for free as well as associated OH stretch vibrations have been determined. It is found that where as the peaks due to CH stretch remain almost unchanged in magnitude on dilution, the peaks due to OH vibration show a blue shift The blue shift decreases in the higher overtones in the case of CCl_4 diluted sample but remains nearly constant in the case of hexane diluted sample. This has been explained as due to the formation of OH....Cl bond. The combination bands were explained in terms of local-normal and normal-normal combinations.

Keywords : Associated and free OH peak, blue shift, intermolecular hydrogen bonding, local-normal and normal-normal combinations.

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1. Introduction

The overtone spectra of aliphatic alcohols (methanol, ethanol, n-propanol and isopropanol) have been a subject of study for more than five decades [1-18].Thus, infrared (IR) and near infrared (NIR) spectra of methanol and its deuterated compounds were measured in pure and in solution with CCl_4 (at a particular dilution) in the 3850-16600 cm^{-1} region by Morita and Nagakura [1]. In addition to fundamental and overtone bands, a number of combination bands of CH and OH stretching vibrations were observed in this study. The fundamental and the first overtone band due to OH stretch in ethanol, isopropanol and methanol were recorded by Asselin *et al* [2] and the vibrational frequencies and the anharmonicity constants were determined. Swofford *et al* [12] measured the higher overtone bands of CH and OH stretch vibrations of methanol and its isotopic substituents in pure as well as in mixed form

in the 15800-17400 cm^{-1} region using thermal lensing technique. As is well known, the alcohol molecules form strong hydrogen bonds so that monomer, dimer, trimer or even higher oligomers coexist. Since absorption frequencies of these differ slightly, these peaks superpose and give a broad absorption band. This is referred as associated OH peak [13]. Only at high dilutions *i.e.* with small concentration of alcohol it is possible to observe the peak due to free OH vibration. This peak is very sharp and is shifted appreciably from the corresponding peak in neat alcohol. Swofford *et al* [12] have concluded that the hydrogen bonding causes a change in the vibrational frequency of the OH bond but the anharmonicity constant remains unchanged. Sandorfy and coworkers [5,15] on the other hand, reported that the hydrogen bonding affects the anharmonicity also.

In this paper, we have made a more systematic study

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of the fundamental and overtone bands of CH and OH stretch vibrations in methanol, ethanol, n-propanol and isopropanol in neat as well as in diluted form (using both CCl_4 and hexane as solvents). In our earlier studies on butanol [17,18] it has been noted that a separate sharp peak due to free OH is often seen on dilution with CCl_4. This new peak shows an increasing blue shift as the dilution is increased. The magnitude of the blue shift is seen to decrease as we go to higher harmonics (*i.e.* from v to $v + 1$, $v + 2$, $v + 3$...). In the case of n-butanol, the shift of the monomer peak becomes negligibly small for $\Delta v = 3$. For $\Delta v > 3$, a red shift is seen. This has been explained due to OH...Cl bond formation. If this is true, then this shift should not show a decrease of shift for higher Δv when diluted with a solvent for which such bond is not expected. To test this observation, we studied the overtone spectra of different alcohols in pure and in diluted form with CCl_4 as well as with hexane and the results obtained are reported here. We have also observed the combination bands of local-normal and normal-normal modes and have also calculated the off-diagonal local-normal coupling coefficient for (u_{CH} + CH_3 rocking) and (u_{CH} + CH_3 deformation) in these molecules.

2. Measurements

We have used samples of different alcohols with high purity (from BDH) in our measurements without any further purification. The IR spectra were recorded using a double beam Perkin Elmer model 883 spectrophotometer. For each measurement, the spectra, were recorded repeatedly. Every time the cuvette was cleaned, dried and rinsed several times with desired sample before filling it finally for recording the spectra. For NIR spectra we have used a Lambda-19 UV/VIS/NIR spectrophotometer. All the measurements were made at room temperature (25°C) and sample path length 1.0 cm. The spectra were recorded between 500–14000 cm⁻¹.

3. Results and discussion

The absorption spectra of these alcohols in the region 500–14000 cm⁻¹ show a number of bands, some of which are very broad. The broad bands are often due to fundamental and overtone of the OH stretching vibration or its combination with other vibrations. Along with these broad bands, there also appear some sharp bands in the spectra. Some of these bands are due to fundamental and overtone

Table 1. Transition frequencies and widths (both in cm⁻¹) for CH stretch vibration for methanol, ethanol, n-propanol and isopropanol.

Sample	1 ← 0	2 ← 0	3 ← 0	4 ← 0	5 ← 0
Methanol	2835.0	5795.5	8407.9	10977.1	13330.0
	2935.0	110*	160*	218*	298*
	2944.0				
Ethanol	2890.0	5781.5	8462.4	11071.4	13437.2
	2928.0	120*	168*	225	315*
	2974.0				
n-Propanol	2884.0	5793.4	8424.1	10987.2	13362.3
	2925.0	150*	190*	240*	330*
	2969.0				
Isopropanol	2882.0	5728.5	8458.6	11046.9	13509.8
	2932.0	100*	145*	245*	325*
	2975.3				

*Represents FWHM for different vibrational transitions.

frequencies of the CH stretch vibration. As expected several peaks are seen corresponding to fundamental band of the CH stretch however, there appears only one peak to its overtone [see Table 1]. The band involving $\Delta v = 2$ (for the CH stretching mode) is broad due to overlap of the peaks but the peaks with $\Delta v = 3$ and 4 are relatively sharp. The intensities of the peaks decrease as we go to the higher harmonics or when the concentration of the alcohol is reduced.

The larger width of the OH peak as compared to CH is due to the presence of several oligomers of the alcohol molecules with slightly different OH frequencies. The fundamental band for the associated OH stretch vibration is seen near 3350 cm⁻¹. However, for higher harmonics, a small shift towards higher frequency is noted as we go from methanol to isopropanol. When we dilute the alcohol by adding a solvent, the spectrum shows an additional sharp peak near 3635 cm⁻¹. This peak is ascribed to free OH stretching vibration. The intensity of this sharp peak increases with dilution. In fact, the peak position also shows a small blue shift whose magnitude decreases as dilution increases. As mentioned earlier, the sample of alcohol contains monomers, dimers, trimers *etc.* due to hydrogen bonding. On dilution, the possibility of hydrogen bond formation is reduced and the number of monomers would increase. This causes the appearance of a new sharp and distinct peak due to the free OH (monomer alcohol) in the spectrum of the molecule. The increase in

the intensity of this peak on dilution is due to the increase in the number of monomers. The peak due to $2 \leftarrow 0$ transition of the monomer lies near 7120 cm^{-1} while that due to $3 \leftarrow 0$ peak is near 10460 cm^{-1}. It is interesting to note that the intensity of the CH or the associated OH peak decreases as we go from fundamental to overtone bands, while that for free OH it increases or remains nearly the same on dilution. It is perhaps due to Franck-Condon factor.

As mentioned earlier, we used hexane as well as carbon tetrachloride for diluting the alcohol. The peak due to free OH appears in both cases with nearly the same intensity. However, the frequency of this peak in hexane diluted alcohol is always greater than the corresponding peak in carbon tetra chloride diluted samples. For both solvents, the frequency increases with the increase of dilution and approaches a limiting value. However, when we go from

one overtone to another, in the case of CCl$_4$ diluted samples, the blue shift in the position of the band decreases and shows a tendency to become a red shift for the higher overtones. On the other hand, in the hexane diluted samples no such change is seen. This observation is in accordance with our observations in n-butanol [17,18] and is due to OH...Cl bond formation in CCl$_4$ diluted samples, which will be absent in the case of hexane. The shift of the OH peak in isopropanol at different dilutions for the different overtones is shown in Figures 1(a), (b) and (c), while the peak positions and the bandwidths for the different OH bands are given in Table 2. The peaks due to free OH in isopropanol at different dilutions in CCl$_4$ as well as in hexane are given in Table 3. Similar results are found for methanol, ethanol and n-propanol also.

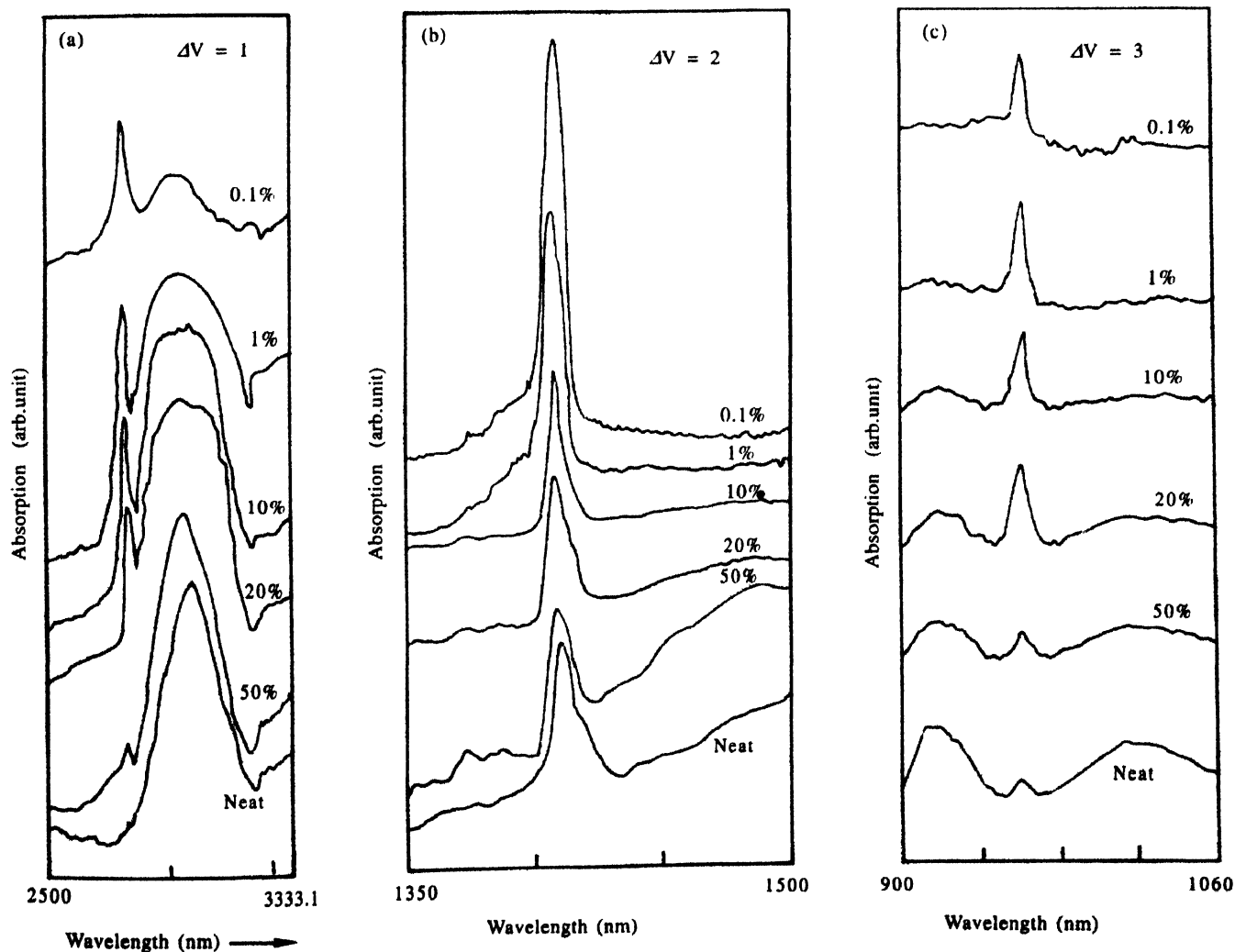The frequencies of the bands for different transitions

Figure 1. The shift of the free OH peak for different bands in isopropanol when diluted with CCl$_4$.

Table 2. Transition frequencies and widths (both in cm⁻¹) for different transitions for OH (associated and free) stretch vibrations in methanol, ethanol, n-propanol and isopropanol molecules.

Sample	$1 \leftarrow 0$	$2 \leftarrow 0$	$3 \leftarrow 0$	$4 \leftarrow 0$
Methanol	3349.0	6627.9	9612.7	12418.9
	300*	450*	690*	
	3652.0#	7136.0#	10467.0#	
Ethanol	3350.2	6634.9	9640.1	12434.2
	310*	480*	750*	
	3641.0#	7113.0#	10428.0#	
n-Propanol	3350.0	6641.6	9659.2	12449.9
	310*	490*	730*	
	3628.0#	7120.0#	10433.0#	
Isopropanol	3350.5	6650.5	9665.3	12430.0
	320*	490*	760*	
	3634.0#	7101.0#	10413.0#	

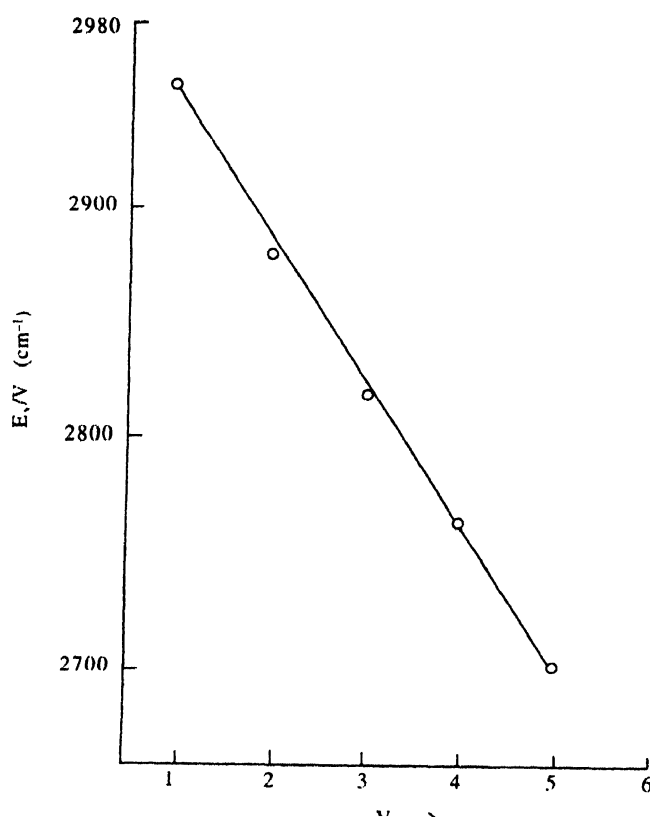#:Free OH stretch vibration.

*: Denotes the FWHM.

Table 3. Transition frequencies (in cm⁻¹) for different transitions under different dilutions with CCl₄ and hexane.

Isopropanol

Concentration of alcohol(%)	$1 \leftarrow 0$	$2 \leftarrow 0$	$3 \leftarrow 0$
100	3634.0	7101.0	10413.0
50	3640.3	7103.0	10413.0
	(3643.9)	(7116.0)	(10420.0)
20	3645.9	7105.0	10413.0
	(3647.8)	(7119.5)	(10425.1)
10	3649.0	7105.4	10413.0
	(3655.4)	(7124.0)	(10427.3)
1	3651.0	7107.0	10413.0
	(3665.1)	(7126.5)	(10428.2)
0.1	3654.0	7110.0	10413.0
	(3670.9)	(7130.4)	(10435.3)

: Values in the parenthesis () are for hexane dilution.

in the four molecules are tabulated in Table 1. A Morse plot of E_v/v versus v for CH stretch in isopropanol is shown in Figure 2. The vibrational frequency and the anharmonicity constant for the CH and OH stretch (for free as well as associated) vibrations have been calculated using the relation,

$$E_v = Av + Bv^2, \tag{1}$$

Figure 2. A Morse plot E_v/v versus v for CH stretch vibration of isopropanol.

where $B = -w_e x_e$, and the constant $A = w_e - w_e x_e$.

The constants thus obtained along with error for the CH and the OH stretch vibrations are given in Tables 4 and 5 respectively. From these Tables, it is clear that the CH stretch vibration remains unchanged on dilution. The frequencies for the OH vibration, however increases appreciably as we go from associated to free OH. The anharmonicity constant on the other hand is reduced from 100 to 80 cm⁻¹. This clearly indicates that the potential for free O-H is less anharmonic than for the associated one, which is one of the consequences of the hydrogen bonding. Concentration versus frequency shift (Δv) for isopropanol for $\Delta v = 1$ and $\Delta v = 2$ is also shown in Figure 3.
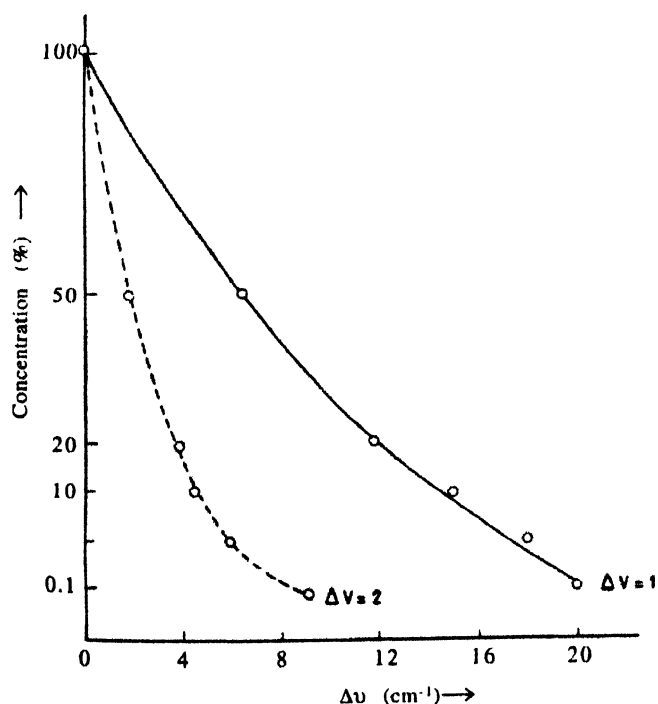
Table 4. Vibrational frequencies and anharmonicity constants (in cm⁻¹) for C-H stretch vibrations in methanol, ethanol, n-propanol and isopropanol.

Sample	A (cm⁻¹)	$B = -w_e x_e$ (cm⁻¹)	$w_e = A - B$ (cm⁻¹)	$D_e = w_e^2/w_e x_e$ (eV)
Methanol	3030.2 ± 6.7	72.6 ± 1.6	3102.8 ± 8.2	4.1 ± 0.1
Ethanol	3033.0 ± 6.7	68.5 ± 1.6	3101.5 ± 8.3	4.3 ± 0.1
n-Propanol	3035.8 ± 8.4	72.9 ± 2.5	3108.7 ± 10.9	4.1 ± 0.1
Isopropanol	3056.9 ± 7.8	74.3 ± 1.4	3131.2 ± 9.2	4.1 ± 0.0

Table 5. Vibrational frequencies and anharmonicity constants (in cm⁻¹) for O-H (associated and free) stretch vibrations in methanol, ethanol, n-propanol and isopropanol.

Sample	A (cm⁻¹)	$B = -w_e x_e$ (cm⁻¹)	$w_e = A - B$ (cm⁻¹)	$D_e = w_e^2/w_e x_e$ (eV)
Methanol	3490.6	96.1	3586.7	4.1
	±14.0	±4.1	±18.1	±0.1
	3730.1♥	80.4♥	3810.5♥	5.6♥
	±1.1	±0.7	±1.7	±0.0
Ethanol	3497.15	96.4	3593.5	4.1
	±15.6	±4.5	±20 1	±0.1
	3720.7♥	81.7♥	3802.4♥	5.5♥
	±1.4	±0.5	±1.9	0.0
n-Propanol	3500.8	96.1	3596.9	3.9
	±16.5	±4.8	±21.3	±0.2
	3712.9♥	78.2♥	3791.1♥	5.7♥
	±4.9	±1.9	±6.9	±0.05
Isopropanol	3515.7	100.9	3616	4.0
	±19.6	±5.7	±25.3	±0.21
	3712.8♥	80.7♥	3793.4♥	5.5♥
	±1.4	±0.5	±1.9	±0.0

♥· Represents the value for free alcohols.

Table 6. Combination bands (in cm⁻¹) in all the four molecules and their assignments.

Isopropanol:

S. No.	Energy (cm⁻¹)	Assignments
1.	969	C-O stretching (v_{C-O})
2.	1102, 1131, 1163	CH₃ rocking
3.	1302, 1326, 1376	CH₂ waging
4.	1405	O-H in plane bending
5.	1453	CH₃ deformation
6.	1905	$u_{C-O}^{(0-2)}$
7.	2542	CH₃ deformation + CH₃ rocking
8.	2678	CH₂ waging + O-H in plane bending
9.	2880	CH₃ symmetric stretching
10.	4067	V_{CH} + CH₃ rocking
11.	4342	CH₃ symmetric stretching + CH₃ deformation
12.	4418	V_{CH} + CH₃ deformation
13.	4800	CH₃ symmetric stretching + two quantum of C-O stretching
14.	5675	V_{CH} + O-H in plane bending + CH₂ waging
15.	5909	$V_{CH}^{(asym)}$ + $V_{CH}^{(sym)}$
16.	7215	$V_{CH}^{(0-2)}$ + CH₃ deformation
17.	7380	$2V_{CH}$ + CH₃ deformation

Figure 3. Concentration *versus* frequency shift (Δv) for $\Delta v = 1$ and $\Delta v = 2$ of isopropanol.

Combination bands :

A large number of combination bands were also marked in

the NIR spectra of all these molecules. The combination bands for isopropanol is given in Table 6. The fundamental bands appearing in the 500–3500cm⁻¹ could be assigned easily with the help of earlier work [19–27] and they are given in Table 6, a similar is the situation with other alcohols. There appear overtone bands with appreciable intensity at 2046 cm⁻¹ and 2208 cm⁻¹ due to C-O and CH₃ rocking respectively in methanol. Similar bands are marked in other molecules also. The combination bands in the region >4000 cm⁻¹ are intense enough but unassigned in most of these molecules. For example, an intense band appears at 4056, 4069, 4060 and 4067 cm⁻¹ in these four alcohols considered, and they have been assigned due to {u_{CH} + CH₃ rocking} combination. Similarly, a band observed at 5901 cm⁻¹ in methanol, 5910 cm⁻¹ in ethanol, 5895 cm⁻¹ in n-propanol and at 5909 cm⁻¹ in isopropanol were assigned due to {$u_{CH}^{(asym)}$ + $u_{CH}^{(sym)}$}. Another band appearing near 7200 cm⁻¹ is due to combination of the first overtone of CH stretch {$u_{CH}^{(0-2)}$} with CH₃ deformation. Another band observed at 7327, 7380, 7371 and 7380 cm⁻¹ in the four molecules are interestingly due to (u_{CH} + u_{CH} + CH₃ deformation). We used these data to estimate the off-diagonal local-normal coupling coefficient X_c for the two

combination bands (v_{CH} + CH$_3$ rocking) and (v_{CH}+ CH$_3$ deformation).

The frequency for combination bands in the case of local-normal combination is given as

$$\Delta E (v_1, v_2; 0) = v_1 (A_1 + v_1 B_1) + v_2 (A_2 + v_2 B_2) + v_1 v_2 X_c, \qquad (2).$$

Table 7. Off-diagonal local-normal coupling coefficient X_c.

S. No.	Groups involved in coupling (v_{CH} + CH$_3$ rocking)	X_c
1.	Methanol	−8.0
2.	Ethanol	−11.0
3.	n-Propanol	−7.0
4.	Isopropanol	−10.0

Table 8. Off-diagonal local-normal coupling coefficient X_c.

S. No.	Groups involved in coupling (v_{CH} + CH$_3$ deformation)	X_c
1.	Methanol	−10.5
2.	Ethanol	−11.0
3.	n-Propanol	−12.5
4.	Isopropanol	−11.5

where A_1, B_1 and A_2, B_2 are the mechanical constants for the two vibrations and X_c is the coupling coefficient. The calculated value of the off-diagonal local-normal coupling coefficient for (v_{CH} + CH$_3$ rocking) and (v_{CH} + CH$_3$ deformation) for the four molecules are given in Tables 7 and 8 respectively.

Acknowledgment

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