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VIBRATIONAL SPECTRA AND NORMAL COORDINATE ANALYSIS OF ACETIC ACID CYCLOHEXYL ESTER

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ABSTRACT

FTIR and FTR spectra of acetic acid cyclohexyl ester have been recorded in the regions 200 - 4000 cm^{-1} and 30 - 4000 cm^{-1}. The vibrational analysis has been carried out by assuming C_s symmetry. The observed frequencies were assigned to various modes of vibrations on the basis of intensity, frequencies from allied molecules and normal coordinate calculations. The potential energy distribution associated with normal modes are also reported here. The assignment of fundamental vibrational frequencies for acetic acid cyclohexyl ester agree with the calculated frequencies.

Keywords: Vibrational spectra; Normal coordinate calculation; Acetic acid cyclohexyl ester.

INTRODUCTION

Acetic acid cyclohexyl ester, derivative of acetic acid, is a colourless liquid with characteristic odour. It has boiling point 177°C. It is immiscible in water. It is soluble in alcohol but insoluble in water and combustible. Besides, it reacts with strong oxidants causing fire and explosion hazard. Acetic acid cyclohexyl esters are used in large quantities as solvents for plastics, lacquers, resins and gums. It is used as solvent for nitrocellulose, cellulose ether, bitumens, metallic soaps, basic dyes, blown oils, crude rubber, many natural and synthetic resins and, gums and lacquers. The X-ray structures proton and carbon-13 NMR spectra have been obtained by Baldwin and others[1] for two dicyclohexyl esters and one tricyclohexyl esters. Cyclohexyl azide is synthesized and the vibrational spectrum is recorded in several phases including liquid at various temperatures, amorphous and crystalline at 90K[2]. Senyavin and others[3] reported the vibrational spectra, structure and force fields of perfluorinated cyclo and bicycloalkanes.However, there is no report about the vibrational spectra and analysis of acetic acid cyclohexyl ester in the literature. Hence, an attempt has been made in the present work to record the FTIR and FTR spectra of acetic acid cyclohexyl ester and to study the complete vibrational analysis for the first time.

EXPERIMENTAL

FTIR spectra of acetic acid cyclohexyl ester were recorded on Brucker IFS 66V FTIR spectrometer in the region 4000 - 200 cm^{-1}. FT Raman spectra of the same compound were also recorded on the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.06 μm line with a scanning speed of 30 cm^{-1} min^{-1} of spectral width 20 cm^{-1}. The frequencies for all sharp bands were accurate to $\pm$ 1 cm^{-1}. The molecular structure of this compound is given in Figure 1. The recorded spectrum of acetic acid cyclohexyl ester is shown in Figure 2.

Theoretical considerations:

The geometrical symmetry possessed by the molecule helps to determine and classify the actual number of fundamental vibrations of the system. The observed spectrum is explained on the basis of C_s point group symmetry. The 66 fundamental vibrations are distributed as $\Gamma_{vib} = 46a' + 20\ a''$. All the modes are active in both Raman and infrared. Assignments have been made on the basis of relative intensities, magnitudes of the frequencies and polarization of the Raman lines. The vibrational assignments are discussed in terms of the potential energy distribution which are obtained from the evaluated potential constants.

Normal coordinate Analysis:

With the modified computer program developed in this laboratory on the basis of Fuhrer et al., program[4], normal co-ordinate analysis were carried out using Wilson's F-G matrix method. The simple general valence force field was adopted for both in plane and out of plane vibrations. The structural parameters are taken from related molecules and Sutton's table[5]. The initial set of force constants were refined by keeping a few interaction constants fixed throughout the refinement process. The assignment to all the in plane and out of plane fundamentals are made on the basis of intensities of Raman and IR bands, normal coordinate analysis and on comparison with those of similar molecules.

Potential Energy Distribution:

A normalised potential energy distribution can be expressed as

$$\mathrm{PED} = \frac{F_{ii} L^2_{ik}}{\lambda_k}$$

where $\mathbf{F_{ii}}$ are the force constants defined by damped least square technique, $\mathbf{L_{ik}}$ the normalized amplitude of the associated element (i,k) and $\boldsymbol{\lambda_k}$ the eigen value corresponding to the vibrational frequency of the element k.The PED contribution corresponding to each of the observed frequencies over 10% are alone listed in the present work.

RESULTS AND DISCUSSION

The observed frequencies along with their relative intensities of acetic acid cyclohexyl ester and probable assignments are presented in table. The assignment of frequencies is made as follows.

Stretching vibrations:

C-H stretching:

The infrared bands at 3010 cm^{-1} and 2944 cm^{-1} have been assigned to C-H asymmetric stretching in CH_3. The C-H symmetric vibration in CH_3 is assigned to Raman band at 2931 cm^{-1}. The PED obtained for this CH symmetric stretching mode in CH_3 shows that it is pure mode with 94% is contributed by symmetric C-H vibration. This molecule gives rise to eleven C-H stretching modes which are assigned to 2677, 2688, 2700, 2712, 2756, 2788, 2800, 2844, 2855, 2868 and 2905 cm^{-1}. As expected the PED shows that these CH stretching modes are dominated by pure stretching characters except at 2855 cm^{-1} and 2712 cm^{-1} where there are little contributions from CC stretching along with C-H stretching. These values are good agreement with the calculated frequencies and literature values.

C = O and C - O Stretching:

All esters have two strong characteristic bands one due to the C = O stretching vibration and the other due to the C-O stretching vibration[6]. The C = O and C-O stretching modes are assigned at infrared band at 1738 cm^{-1} and at 1538 cm^{-1} which agree with calculated values.

C - C Stretching:

The six C - C stretching vibrations of the acetic acid cyclohexyl ester give rise to six absorption bands, which can be assigned to 1050, 1075, 1100, 1119, 1145 and 1156 cm^{-1}. The PED calculation shows that the calculated frequencies at 1069 cm^{-1} and 1041 cm^{-1} of C-C stretchings are not pure mode whereas they are in a mixed mode. These are combinations of C - C stretching and C - H stretching modes.

In plane and out of plane bendings:

CH – bending:

The bands observed at 1195, 1243, 1256, 1269, 1300, 1315, 1331, 1343, 1359, 1370 and 1381 cm^{-1} are assigned to C-H in plane bendings while the bands observed at 650, 800, 818, 838, 863, 900, 913, 925, 943, 956 and 968 cm^{-1} are assigned to C - H out of plane banding vibrations. These frequencies agree quite with the calculated values as listed in the Table 1.

CCC in plane and out of plane bendings:

Three CCC in plane bending vibrations are assigned at 605, 625 and 720 cm^{-1} while CCC out of plane bending vibrations are assigned at 356, 343 and 300 cm^{-1}. These are good agreement with calculated frequencies.

CH_3 deformation and rocking vibration:

The strong infrared band at 1456 cm^{-1} and very strong Raman band at 1438 cm^{-1} have been assigned to CH_3 deformation and CH_3 rocking. The weak infrared at 438 cm^{-1} and Raman band at 388 cm^{-1} have been assigned to CH_3 wagging mode and CH_3 torsion.

CCC ring breathing and trigonal bending:

The skeleton of the molecule also gives some characteristic absorption wave number such as ring breathing and CCC trigonal bending. In the present case, these are assigned at 856 cm^{-1} and 1019 cm^{-1} which agree quite well with literature values[7-9].

CONCLUSION

A complete vibrational spectra and analysis is reported in the present work for the first time for acetic acid cyclohexylester. The close agreement between the observed and calculated frequencies confirms the validity of the present assignment.

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Table-1: Observed, calculated frequencies (cm^{-1}), vibrational assignments and potential energy distribution of Acetic acid cyclohexyl ester

Species	Observed frequency / Intensity		Calculated wavenumber	Assignment	% PED
	Infrared	Raman			
a′	3010 w	-	3006	asymmetric stretching in CH_3	87 ν_{asCH}
a′	2944 vs	-	2942	asymmetric stretching in CH_3	92 ν_{asCH}
a′	-	2931 vw	2929	CH symmetric stretching in CH_3	94 ν_{syCH}
a′	-	2905 m	2901	C-H stretching	84 ν_{CH}
a′	2868 vs	-	2859	C-H stretching	81 ν_{CH}
a′	-	2855 m	2850	C-H stretching	79 ν_{CH} + 12 ν_{CC}
a′	2844 vs	-	2839	C-H stretching	86 ν_{CH}
a′	2800 vw	-	2804	C-H stretching	88 ν_{CH}
a′	-	2788 vw	2779	C-H stretching	74 ν_{CH}
a′	-	2756 vw	2751	C-H stretching	83 ν_{CH}
a′	-	2712 w	2108	C-H stretching	72 ν_{CH} + 17 ν_{CH}
a′	2700 vw	-	2694	C-H stretching	84 ν_{CH}
a′	-	2688 w	2681	C-H stretching	81 ν_{CH}
a′	-	2677 w	2671	C-H stretching	88 ν_{CH}
-	2113 vw	-	-	1100 + 1025	-
a′	1738 vs	1732 m	1731	C = O stretching	86 $\nu_{C=O}$
a′	1538 w	-	1530	C - O stretching	89 $\nu_{C=O}$
a′	1467 s	1468 w	1462	O - C stretching	71 $\nu_{C=O}$ + 19 ν_{C-CH_3}
a′	1456 v	-	1451	CH_3 deformation	74 δ_{CH_3} + 24 ρ_{CH_3}
a′	-	1438 vs	1429	CH_3 rocking	72 ρ_{CH_3} + 26 δ_{CH_3}

a′	1381 vs	-	1378	C-H in plane bending	88 β_{CH}
a′	-	1370 w	1361	C-H in plane bending	92 β_{CH}
a′	1359 s	-	1352	C-H in plane bending	84 β_{CH}
a′	-	1343 w	1340	C-H in plane bending	87 β_{CH}
a′	1331 m	1331 w	1324	C-H in plane bending	70 β_{CH} + 24 β_{CC}
a″	1315 m	-	1306	C-H in plane bending	81 β_{CH}
a′	-	1300 w	1304	C-H in plane bending	84 β_{CH}
a′	-	1269 w	1260	C-H in plane bending	69 β_{CH} + 26 β_{CC}
a′	-	1256 m	1248	C-H in plane bending	80 β_{CH}
a′	-	1243 m	1239	C-H in plane bending	72 β_{CH} + 24 β_{CO}
a′	-	1195 w	1189	C-H in plane bending	79 β_{CH}
a′	1156 m	-	1151	C-C stretching	79 ν_{CC}
a′	-	1145 m	1138	C-C stretching	86 ν_{CC}
a′	1119 vs	1119 vw	1111	C-C stretching	82 ν_{CC}
a′	1100 m	1100 vw	1091	C-C stretching	81 ν_{CC}
a′	-	1075 vw	1069	C-C stretching	69 ν_{CC} + 20 ν_{CH}
a′	-	1050 vw	1041	C-C stretching	74 ν_{CC} + 18 ν_{CH}
a′	1039 vw	-	1030	C-CH_3 stretching	58 $\nu_{C\text{-}CH_3}$ + 26 $\nu_{C=O}$ + 14 $\nu_{C\text{-}O}$
a′	1019 s	1019s	1010	CCC trigonal bending	88 β_{CCC}
a″	968 vs	-	959	C-H out of plane bending	81 η_{CH}
a″	956 s	-	950	C-H out of plane bending	79 η_{CH}
a″	943 s	-	936	C-H out of plane bending	86 η_{CH}
a″	-	925 vw	919	C-H out of plane bending	66 η_{CH} + 28 η_{CC}
a″	913 m	-	907	C-H out of plane bending	81 η_{CH}
a″	900 s	900 w	894	C-H out of plane bending	69 η_{CH} + 21 η_{CC}
a″	863 w	-	858	C-H out of plane bending	74 η_{CH}
a′	-	856 v	850	CCC ring breathing	91 β_{CCC}
a″	838 m	838 w	828	C-H out of plane bending	79 η_{CH}
a″	818 w	-	809	C-H out of plane bending	68 η_{CH} + 30 η_{CC}
a″	800 vw	800 vs	790	C-H out of plane bending	74 η_{CH} + 16 η_{CC}
a′	750 vw	-	739	C=O in plane bending	86 $\beta_{C=O}$
a′	720 vw	-	709	C-O in plane bending	69 $\beta_{C\text{-}O}$ + 12 $\beta_{C=O}$
a′	720 vw	-	-	CCC in plane bending	
a″	650 m	650 mw	646	C-H out of plane bending	74 η_{CH}
a′	625 vw	619 m	615	O-C in plane bending	74 $\beta_{C\text{-}O}$ + 12 $\beta_{C=O}$
a′	625 vw	619 m		CCC in plane bending	
a′	605 m	-	600	CCC in plane bending	81 β_{CCC}
a″	550 w	550 m	541	C=O out of plane bending	76 $\eta_{C=O}$ + 11 $\eta_{C\text{-}O}$
a″	481 vw	-	470	C-O out of plane bending	62 $\eta_{C\text{-}O}$ + 22 $\eta_{C=O}$
a′	456 vw	456 vw	448	C-CH_3 in plane bending	54 $\beta_{C\text{-}CH_3}$ + 18 $\beta_{C=O}$ + 11 $\beta_{C\text{-}O}$
a″	438 w	438 w	430	CH_3 wagging	66 ω_{CH_3} + 30 τ_{CH_3}
a″	388 vw	388 vw	378	CH_3 torsion	69 τ_{CH_3} + 29 ω_{CH_3}
a″	356 w	350 w	331	CCC out of plane bending	74 η_{CCC}
a″	-	343 w	330	CCC out of plane bending	69 η_{CCC} + 10 η_{CH}
a″	300 vs	300 vs	288	CCC out of plane bending	61 η_{CCC} + 20 η_{CH}
a″	-	281 vw	271	O-C out of plane bending	64 $\eta_{C\text{-}O}$ + 26 $\eta_{C=O}$ + 10 $\eta_{C\text{-}CH_3}$
a″	-	238 vw	221	C-CH_3 out of plane bending	52 $\eta_{C\text{-}CH_3}$ + 30 $\eta_{C=O}$ + 12 $\eta_{C\text{-}O}$

a′ - in-plane vibrations, a″ - out-of plane vibrations.

Abbreviations used: w - weak; m - medium; s - strong; vw - very weak; vs - very strong.

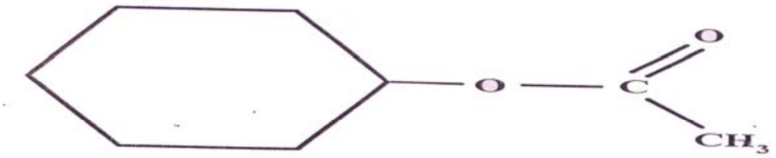

Fig.1 Structure of acetic acid cyclohexylester

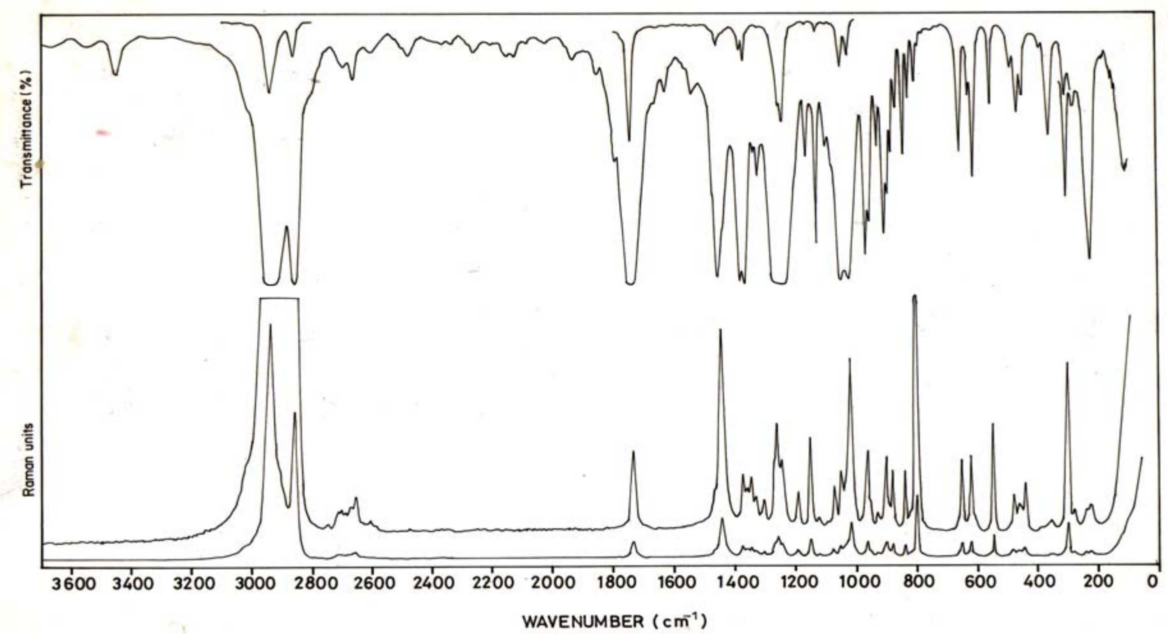

FIG.2. FTIR AND FTR SPECTRA OF Acetic acid cyclohexyl ester

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A scientific truth does not triumph by convincing its opponents and making them see the light, but rather because its opponents eventually die and a new generation grows up that is familiar with it.

-Max Planck