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FTIR AND FTR SPECTRAL STUDIES ON 4-VINYL CYCLOHEXENE

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ABSTRACT

FTIR and FTR spectra of 4-Vinyl Cyclohexene 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 distributions associated with normal modes are also reported here. The assignment of fundamental vibrational frequencies for 4-vinyl cyclohexene agree with the calculated frequencies.

Keywords: Vibrational spectra; Normal coordinate calculation; 4-Vinyl cyclohexene.

INTRODUCTION

4-vinyl cyclohexene, derivative of cyclohexene is a colourless liquid and it has a boiling point of 127°C and flash point of 16°C. It is moderately soluble in water. It is a stable and flammable. It is incompatible with strong oxidizing agents, peroxide catalysts but air-sensitive. It is flammable, dangerous (fire risk) and it is harmful by ingestion or inhalation. This alicyclic organic chemical compound has great importance in polymers and organic synthesis. It has been used as a chemical intermediate for production of flame retardants, flavours and fragrances, in the manufacture of polyolefins, as a solvent and in the manufacture of its diepoxide.

Mash, Eugene, Waller and Stephen[1] reported the syntheses and spectroscopic characterizations of oxidative metabolites of 4-vinyl cyclohexene. Its mixture diluted with argon was heated to temperature in the range of 880 - 1230 K behind reflected shock waves. Profiles of IR-laser absorption were measured at 3.39 mm[2]. Co-polymerisation of ethylene and 4-vinyl cyclohexene by various metallocenes was carried out by Kims & others[3]. Pancir and Turecek reported the mechanism of the retro-Diels-Alder reaction in 4-vinylcyclohexene[4]. The infrared (3200-30 cm^{-1}) spectra of gaseous and solid, the Raman spectra (3200-30 cm^{-1}) of the liquid and solid vinyl silyl bromide have been recorded[5].However, there is no report in the literature about the vibrational spectra and analysis of 4-vinylcyclohexene. In the present study, the results and analysis of FTIR and FT Raman spectra of this compound is reported for first time. The assignments have been made and further verified through normal-coordinate calculations.

EXPERIMENTAL

FTIR spectra of 4, vinylcyclohexene is recorded on Brucker IFS 66V FTIR spectrometer in the region 4000 - 200 cm^{-1}. FT Raman spectra of the same compound is 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 ± 1 cm^{-1}. The structure of 4, vinyl cyclohexene is shown in Figure 1. The recorded FTIR and FT Raman spectra of 4, vinyl cyclohexene is shown in Figure 2.

Theoretical Considerations

4, Vinyl Cyclohexene belongs to C_s point group having 54 normal modes of vibrations and they are distributed as $\Gamma_{vib} = 36\ a' + 18\ a''$. The vibrations of the type a′ belongs to in-plane and those of a″ belongs to out-of-plane. All the frequencies are assigned to various fundamental modes and compared with those obtained for some related molecules.

The potential energy distribution is evaluated using the refined force constants to test the validity and precision of the present assignment. The close agreement between the observed and calculated frequencies confirm the validity of the present assignment.

Normal Coordinate Analysis

The simplified general valance force field (SGVFF) is found to be very effective for the polyatomic molecules. In the present work, SGVFF has been employed to obtain normal frequencies. The initial set of force constants are refined by damped least-square technique, keeping few interaction constants fixed throughout the refinement process to obtain a close fit between the observed and calculated frequencies. This set of force constants is subsequently used to evaluate potential energy distribution. The normal coordinate calculations were performed by utilising the program of Fuhrer et al.[6] with suitable modifications for computing the G and F matrices and for adjusting a set of independent force constants. The structural parameters necessary for these compounds are taken from Sutton's table[7] and structurally related similar molecules. The normal coordinate calculations have also been performed to obtain vibrational frequencies and the potential energy distribution for the various modes.

In the normal coordinate analysis, the potential energy distribution from each internal coordinates to the total potential energy associated with particular normal coordinate of the molecule. The vibrational assignments for all the in-plane and out-of-plane vibrations of Raman and infrared frequencies are made on the basis of data available in the literature for related molecules, intensities and potential energy distribution.

Potential Energy Distribution

The check whether the chosen set of assignments contribute maximum to the potential energy associated with normal coordinates of the molecules, potential energy distribution (PED) has been calculated using the relation-

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

where F_{ii} are the force constants defined by damped least square technique, L_{ik} the normalized amplitude of the associated element (i,k) and λ_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 infrared, Raman frequencies and the calculated frequencies along with the PED of various modes of vibration of 4, Vinyl Cyclohexene are presented in table. The assignment of frequencies is made as follows.

Stretching vibrations

C-H Stretching: The strong infrared band at 3081 cm^{-1} and very strong Raman band at 3082 cm^{-1} have been assigned to C-H asymmetric stretching in CH_2. The C-H symmetric stretching in CH_2 is assigned to very strong band at 3025 cm^{-1} both infrared and Raman. The PED calculation for asymmetric stretching mode in CH_2 indicates that 71% is contributed by asymmetric C-H vibration and 19% is contributed by C = C stretching. Similarly for symmetric stretching mode in CH_2, PED shows that 82% is contributed by CH vibration and 10% is contributed by C = C stretching.

In cyclohexene, the C-H stretching absorptions are usually observed below 3000 cm^{-1}. The absorption bands observed at 2725, 2775, 2831, 2857, 2888 and 2975 cm^{-1} in the infrared spectrum and 2844, 2913 and 2986 cm^{-1} in the Raman spectrum are assigned to C-H stretching vibrations in the present case. The PED shows that all are pure modes except at the assigned frequencies of 2986 and 2888 cm^{-1} which are mixed modes. There are little contributions due to C-C stretching. The calculated wavenumbers agree with the observed frequencies and with the literature values[8].

CH - CH_2 Stretching: The vinyl functional group CH = CH_2 stretching generally occurs in the range 3150 - 3000 cm^{-1}. In the present case, this stretching is assigned to strong infrared band at 3000 cm^{-1}

which agrees with the calculated frequency at 2999 cm^{-1}. The PED calculation reveals that this is a mixed mode. The 64% contribution is from CH = CH_2 stretching and 14% contribution from C-C stretching.

C-C Stretching: The C - C stretching vibrations of the 4, vinylcyclohexene are assigned to 1038, 1075, 1138, 1175 and 1196 cm^{-1} fine absorption bands. The assigned frequencies are in good agreement with the calculated frequencies as given in the table1. The calculated frequencies of C - C stretching at 1174, 1031 and 1031cm^{-1} are not pure modes. They are mixture of C-H stretching as per the PED calculation.

In plane and out of plane bendings

CH_2 deformation and rocking: The strong infrared at 1431 cm^{-1} and weak Raman at 1420cm^{-1} has been assigned to CH_2 deformation. The medium infrared at 1419 cm^{-1} and weak Raman at 1410 cm^{-1} has been assigned to CH_2 rocking. These frequencies agree with the calculated and literature values[9].

C-H bending: The bands observed at 1213, 1244 1263, 1275, 1295, 1300, 1338, 1390 and 1450 cm^{-1} have been assigned to C-H in plane bendings while the bands observed at 725, 750, 800, 869, 907, 925, 950, 963 and 975 cm^{-1} are assigned to C-H out of plane bending vibrations. These frequencies agree quite well with the calculated values as listed in the table.

CCC in plane and out of plane bendings: CCC in plane bending vibrations is assigned at 575 and 512 cm^{-1} while CCC out of plane bending vibrations is assigned to 275, 325, 350 and 400 cm^{-1}.

CCC ring breathing and trigonal bending: The CCC ring breathing mode and CCC trigonal bending are assigned to the bands at 850 and 996 cm^{-1}. These vibrations appear in the expected range and find support from literature values[10-12].

CH_2 Wagging and twisting: CH_2 wagging and CH_2 twisting have been assigned to 400 and 381 cm^{-1} which agree with calculated values.

CONCLUSION

A complete vibrational spectra and analysis is available in the present work for the first time for 4-Vinyl Cyclohexene. The close agreement between the observed and calculated frequencies confirm the validity of the present assignment.

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Table-1: Observed, calculated frequencies (cm^{-1}), vibrational assignments and potential energy distribution of 4, Vinylcyclohexene

Species	Observed frequency / Intensity		Calculated wavenumber	Assignment	% PED
	Infrared	Raman			
a′	3081 s	3082 vs	3079	metric stretching in CH_2	71 ν_{asCH} + 19 $\nu_{C=C}$
a′	3025 vs	3025 vs	3021	metric stretching in CH_2	82 ν_{symCH} + 10 $\nu_{C=C}$
a′	3000 s	3000 m	2999	$_2$ stretching	64 $\nu_{CH=CH_2}$ + 14 $\nu_{C\text{-}C}$
a′	-	2986 w	2981	tching	81 ν_{CH} + 10 ν_{CC}
a′	2975 s	-	2970	tching	88 ν_{CH}
a′	2913 vs	2913 s	2906	tching	92 ν_{CH}
a′	2888 vs	2881 m	2879	tching	79 ν_{CH} + 12 ν_{CC}
a′	2857 s	2857 m	2852	tching	94 ν_{CH}
a′	-	2844 s	2838	tching	89 ν_{CH}
a′	2831 vs	-	2828	tching	86 ν_{CH}
a′	2775 w	2775 vw	2771	tching	93 ν_{CH}
a′	2725 w	2725 vw	2719	tching	91 ν_{CH}
-	2663	-	-	295	-
-	1825 w	-	-	7	-
a′	-	1650 vs	1642	tching	89 $\nu_{C=C}$ + 11 ν_{CH}
a′	1450 m	1450 w	1452	lane bending	72 β_{CH} + 10 β_{CC}
a′	1431 s	1420 w	1411	rmation	71 δ_{CH} + 20 ρ_{CH}
a′	1419 m	1410 w	1409	ing	69 ρ_{CH} + 26 δ_{CH}
a′	1388 w	1390 m	1384	lane bending	84 β_{CH}
a′	1338 w	1338 m	1321	lane bending	88 β_{CH}
a′	-	1300 vs	1302	lane bending	79 β_{CH} + 12 β_{CC}
a′	1294 w	1295 w	1290	lane bending	91 β_{CH}
a′	1275 w	-	1269	lane bending	68 β_{CH} + 21 β_{CH}
a′	-	1263 s	1258	lane bending	61 β_{CH} + 19 β_{cc}
a′	1250 w	1244 m	1242	lane bending	74 β_{CH} + 14 β_{cc}
a′	1212 w	1213 s	1211	lane bending	78 β_{CH}
a′	-	1196 vs	1191	tching	84 ν_{CC}
a′	1175 w	-	1174	tching	76 ν_{CC} + 14 ν_{CH}
a′	1138 w	1132 w	1128	tching	89 ν_{CC}
a′	1075 w	1075 w	1069	tching	92 ν_{CC}
a′	1038 m	1038 s	1031	tching	61 ν_{CC} + 24 ν_{CH}
a′	1025 w	-	1019	etching	59 $\nu_{C\text{-}CH}$ + 21 $\nu_{=CH_2}$ + 10 ν_{CC}
a′	996 s	1000 w	998	onal bending	89 β_{CCC}
a″	-	975 w	969	of plane bending	74 η_{CH} + 11 η_{CC}
a″	963 m	-	958	of plane bending	88 η_{CH}
a″	-	950 w	941	of plane bending	86 η_{CH}
a″	-	925 s	919	of plane bending	90 η_{CH}
a″	907 vs	912 m	908	of plane bending	81 η_{CH}
a″	869 s	869 s	861	of plane bending	72 η_{CH} + 12 η_{CH}
a′	-	850 w	841	g breathing	92 β_{CCC}
a″	800 w	800 w	794	of plane bending	64 η_{CH} + 16 η_{CCC}
a″	750 w	750 w	742	of plane bending	71 η_{CH} + 10 η_{CH_2}
a″	725 s	725 vs	718	of plane bending	72 η_{CH} + 14 η_{CC}
a′	663v s	663 m	657	$_2$ in plane bending	58 $\beta_{CH=CH_2}$ + 26 β_{CC}

a′	650 vs	-	642	plane bending	$64\ \beta_{C\text{-}CH} + 12\ \beta_{CH_2} + 19\ \beta_{CC}$
a″	-	638 w	630	$_2$ out of plane bending	$56\ \eta_{CH=CH_2} + 24\ \eta_{CC}$
a′	575 m	581 vw	572	lane bending	$71\ \beta_{CCC} + 19\ \beta_{CH}$
a″	538 s	531 vw	532	t of plane bending	$49\ \eta_{C=C} + 21\ \eta_{CH} + 20\ \eta_{CH_2}$
a′	510 s	512 vs	504	lane bending	$84\ \beta_{CCC} + 10\ \beta_{CH}$
a″	475 vs	475 vs	468	t of plane bending	$53\ \eta_{C\text{-}CH} + 21\ \eta_{CH_2} + 19\ \eta_{CC}$
a″	400 s	400 ws	402	gging	$58\omega_{CH_2} + 31\tau_{CH_2}$
a″	400 s	400 ws		of plane bending	-
a″	381 m	381 w	371	sting	$64\tau_{CH_2} + 29\ \omega_{CH_2}$
a″	350 s	350 vs	342	of plane bending	$71\ \eta_{CCC} + 12\ \eta_{CH}$
a″	-	325 s	318	of plane bending	$86\ \eta_{CCC} + 12\ \eta_{CH}$
a″	275 w	-	264	of plane bending	$60\ \eta_{CCC} + 24\ \eta_{CH=CH_2} + 10\eta_{CH}$

a′ - in-plane vibrations, a″ - out-of plane vibrations.
Abbreviations used: w - weak; m - medium; s - strong; vw - very weak; vs - very strong.

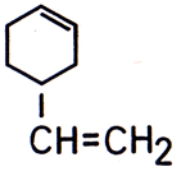

Fig.-1: structure of 4, vinylcyclohexene

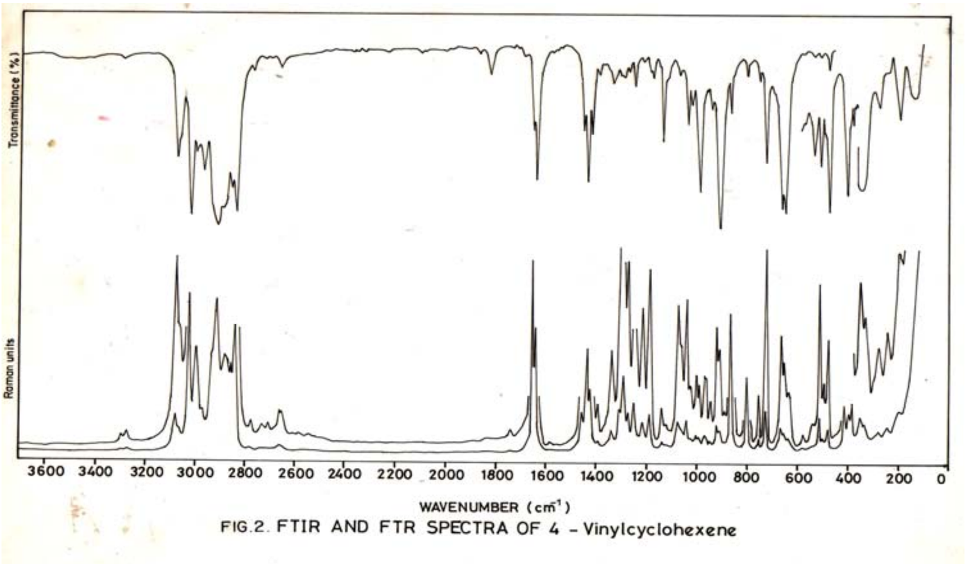

FIG.2. FTIR AND FTR SPECTRA OF 4 – Vinylcyclohexene

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