

Vibrational analysis of 1-chlorononane

Devinder Singh^{1*}, Neena Jaggi² & Nafa Singh³

¹Department of Physics, Dyal Singh College, Karnal 132 001

²Department of Physics, National Institute of Technology, Kurukshetra 136 119

³Department of Physics, Kurukshetra University, Kurukshetra 136 119

* E-Mail: ds_kuk@yahoo.com

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Fourier transform infrared and Raman spectra of the organic compound 1-chlorononane have been recorded in its liquid state at ambient temperature in the ranges 4000-400 cm^{-1} and 3200-150 cm^{-1} , respectively. A detailed vibrational analysis in terms of assignment of the observed vibrational bands of 1-chlorononane has been done to different modes of vibrations for its four most probable conformations with symmetries C_s and C_1 in its liquid phase with the aid of normal co-ordinate calculations. The normal co-ordinate calculations have been carried out utilizing the computer program MOLVIB. The potential energy distribution has also been calculated for each mode of vibration.

Keywords: FT-IR, Raman, Normal co-ordinate calculations, 1-Chlorononane

1 Introduction

The organic compound 1-chlorononane (1-CLN) is a colourless and transparent liquid at ambient temperatures. It has versatile synthetic applications in polymer, pharmaceutical and chemical industry. The vibrational spectra of long chain polyatomic molecules such as 1-CLN are quite complicated and depend upon the molecular state, molecular conformations, molecular symmetry, molecular force-field and temperature¹. Thus, the analysis of vibrational spectra plays a vital role in the elucidation of the molecular structure and gives a dynamical picture of the molecule. Although several haloalkanes have been studied in the past by several researchers² and more recently by LaPlante and Stidham *et al*³⁻⁶.

Normal co-ordinate calculations have been employed in the vibrational spectral analyses of the polyatomic molecules during the past few decades⁷ and are commonly used to study complex molecules⁸⁻¹⁰ now-a-days. Experimental considerations alone cannot yield the unique assignments of the observed vibrational frequencies to specific modes of vibration of complex molecules like 1-CLN. Therefore, normal co-ordinate analysis is used to study the vibrational spectra.

In the present study, Fourier transform infrared (FT-IR) and Raman spectra of 1-CLN have been recorded in its liquid state at ambient temperature. Assignments of the observed infrared and Raman

frequencies of this molecule have been done to different modes of vibration for its most probable conformations in its liquid phase with the aid of normal co-ordinate calculations.

2 Experimental Details

The spectroscopic grade pure sample of 1-CLN with stated purity of 99% has been procured from Sigma-Aldrich Company, USA and used as such without further purification. The FT-IR spectrum of the sample was recorded in the wavelength region 4000-400 cm^{-1} on Perkin-Elmer Spectrum-One Fourier transform infrared spectrometer equipped with a global source and deuterated triglycine sulphate (DTGS) infrared detector using KBr pellets. The Raman spectra of the compound were recorded in the wavelength region 3200-150 cm^{-1} on a Spex-1877, triple monochromator laser Raman spectrometer equipped with CCD detector at liquid N_2 temperature using Ar^+ laser with 488 nm as the exciting line. The resolution of spectrometers was maintained at 2 cm^{-1} . The FT-IR and Raman spectra of 1-CLN are shown in Figs 1 and 2, respectively.

3 Normal Co-ordinate Calculations

The normal co-ordinate calculations have been carried out for the four most probable conformations of the molecule 1-CLN in its liquid phase, as are found in several similar halogenated alkanes^{2,11}. Among these, the most symmetric conformation I has

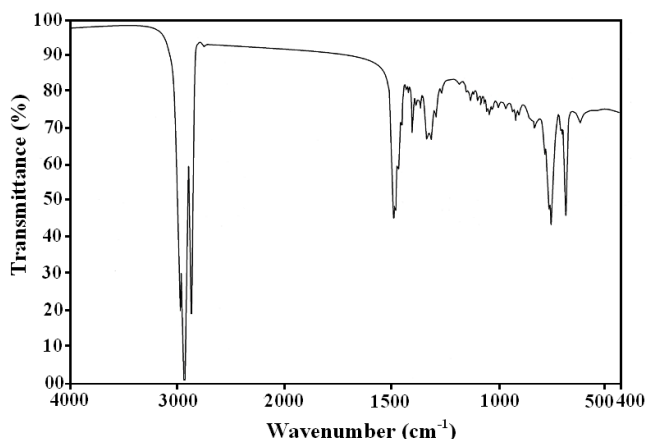


Fig. 1 — FT-IR spectrum of 1-chlorononane

a *trans* configuration. This conformation of 1-CLN has Cl atom co-planar with C-C skeleton and belongs to C_s point group as shown in Fig. 3(I). The other conformations II, III, and IV as shown in Figs 3(II), (III) and (IV), respectively possess C_1 symmetry. In the conformation II called *gauche*, the Cl atom lies above the C-C skeletal plane, while in the conformation III the methyl group attached to the C_8 atom has been rotated about C_7-C_8 bond to occupy the position of H_{15} . In conformations IV, the Cl atom is above (or below) the C-C skeletal plane and the methyl group attached to C_8 is rotated about the C_7-C_8 bond to occupy the position of H_{15} (or H_{16}).

The molecular parameters used are C-C = 1.54 Å, C-H = 1.09 Å, C-Cl = 1.77 Å and all the bond angles assumed as 109.47° . Internal co-ordinates and symmetry co-ordinates of the molecule for the four conformations were constructed utilizing the approach of Snyder and Schachtschneider⁷.

The total number of modes of vibration for the molecule 1-CLN corresponding to the 29 atoms present in it is 81. The number of genuine normal modes of vibrations present in two symmetry species a' and a'' of conformation I with C_s symmetry has been calculated as 46 and 35, respectively¹². These modes are both Raman active as well as infrared active. The 81 modes of vibration calculated for the conformations II, III, and IV each with symmetry C_1 belong to only one symmetry species i.e. a . All of these modes are allowed in both, infrared and Raman spectra.

The normal co-ordinate calculations have been carried out using the computer program¹³ MOLVIB and utilizing the force-field obtained in the study of 1-chlorooctane¹⁴. The force-field was then refined to fit the calculated frequencies with the observed

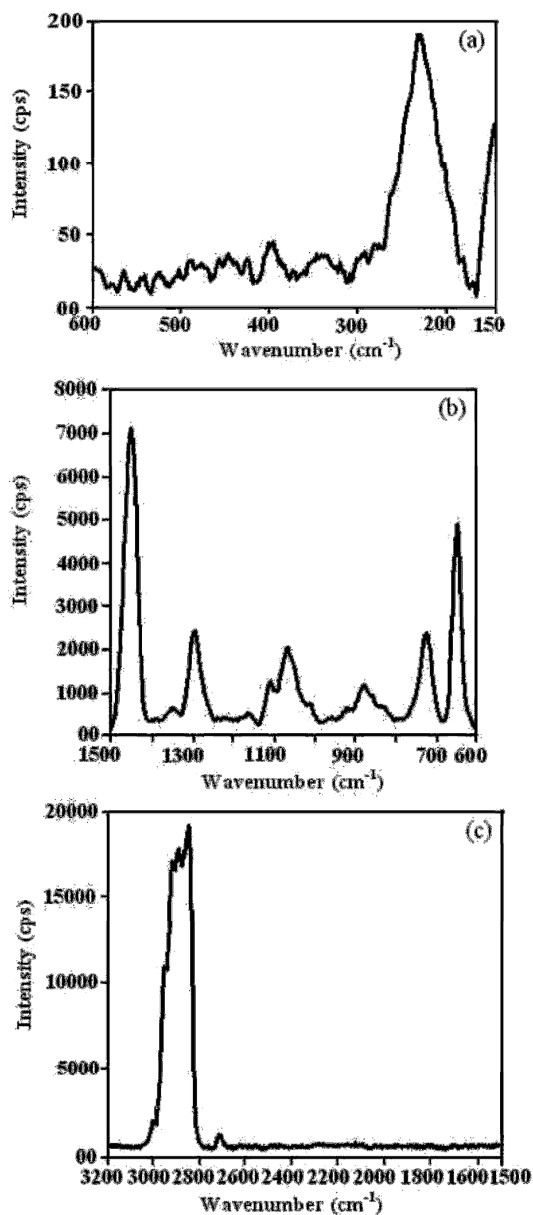


Fig. 2 — Raman spectra of 1-chlorononane in the range (a) 150-600 cm^{-1} , (b) 600-1500 cm^{-1} and (c) 1500-3200 cm^{-1}

frequencies for this molecule using the computer program¹³ MOLFIT. The force-field after a number of iterations generated frequencies is in close agreement with the observed ones within an average error of ± 5.1 cm^{-1} . The percentage potential energy distribution (PED) over the symmetry co-ordinates for the calculated frequencies has also been calculated.

4 Results and Discussion

The observed infrared and Raman frequencies of 1-CLN, their relative intensities and the corresponding calculated frequencies for all the four

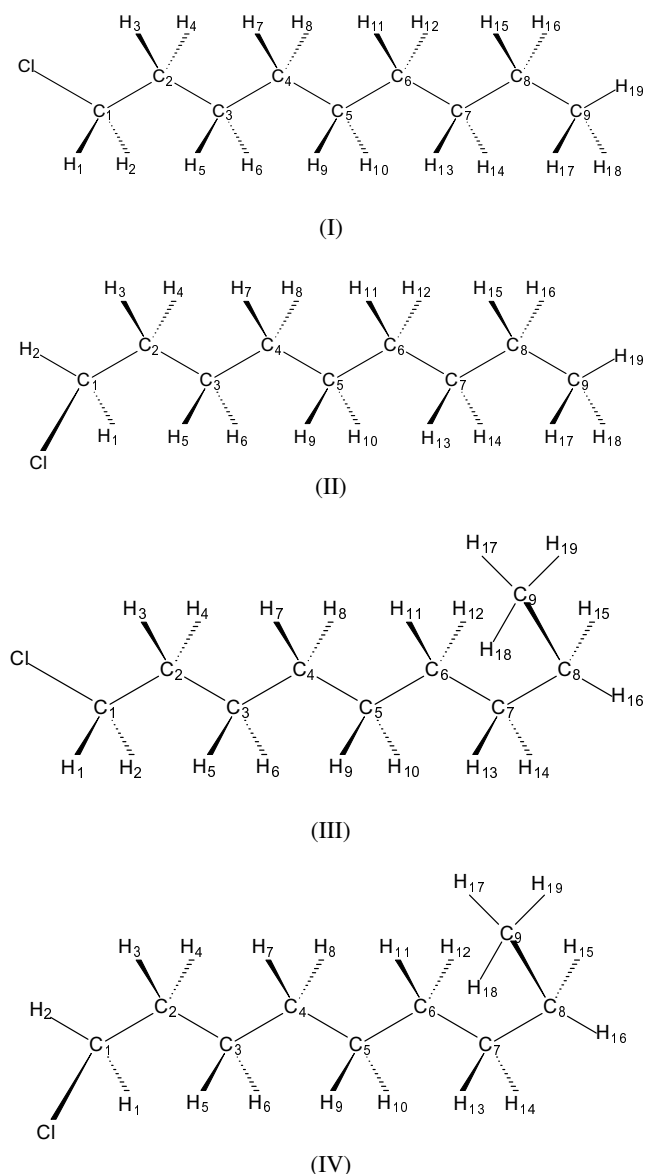


Fig. 3 — Structures of different conformers of 1-chlorononane

conformers and the modes of vibration along with their PED are presented in Table 1.

The assignments of the observed frequencies to different modes of vibration have been made on the basis of normal co-ordinate calculations and the PED. Table 1 clearly presents that while most of the prominent infrared and Raman bands could be correlated with the calculated frequencies of the molecule with C_s symmetric conformation, yet some other strong Raman bands at 1291, 1106, 1064, 875, 651, 445, 401 and 229 cm^{-1} and intense infrared bands at 1309 and 654 cm^{-1} could be correlated only with the calculated frequencies for other conformations of the molecule. This shows that 1-

CLN exists in different conformations in its liquid state at ambient temperatures. However, all the infrared and Raman bands of the molecule in the liquid phase could be correlated with the calculated frequencies for the above mentioned four conformers belonging to C_s and C_1 symmetries. It is seen from Table 1 that five Raman bands at 828, 454, 384, 340 and 236 cm^{-1} and two infrared bands at 1050 and 827 cm^{-1} solely belong to calculated frequencies of conformation I, while an infrared band at 754 cm^{-1} and five Raman bands at 875, 507, 308, 204 and 172 cm^{-1} belong to conformation II only. Similarly, three infrared bands at 1309, 1121 and 730 cm^{-1} and three Raman bands at 445, 424 and 331 cm^{-1} are found to correspond to the calculated frequencies of the conformation III. Furthermore, three infrared bands at 1157, 869 and 801 cm^{-1} and nine Raman bands at 1157, 1106, 1006, 494, 401, 346, 266, 229 and 184 cm^{-1} are assigned to conformation IV only.

The C-H stretch modes of vibration belonging to the CH_2Cl , CH_3 and CH_2 groups for all the four conformations of the molecule have been calculated in the frequency range 2998-2853 cm^{-1} as pure modes. Among these, the asymmetric modes of vibration appear with relatively higher values in the order $\text{CH}_2\text{Cl} > \text{CH}_3 > \text{CH}_2$ followed by symmetric C-H vibrations occupying lower positions in the spectra in the same order. Most of these calculated frequencies find a correlation with the strongly observed infrared and Raman bands in the range 2996-2856 cm^{-1} . These results are alike to those reported earlier for similar molecules¹⁴⁻¹⁸.

The bending vibrational frequencies for the CH_2Cl , CH_3 and CH_2 groups have been calculated in the range 1470-1414 cm^{-1} for each conformation as nearly pure modes. Most of these frequencies are assigned to observe infrared and Raman bands in the range 1466-1414 cm^{-1} . However, the CH_3 symmetric bending mode of vibration for conformations I, II, III and IV has been calculated at 1344, 1343, 1345 and 1343 cm^{-1} , respectively. This mode of vibration has been assigned to an observed Raman band at 1347 cm^{-1} . These values are in agreement with those for similar molecules already studied^{3-6,11,15-20}.

The next lower range of frequencies consists of wagging, twisting and rocking modes of vibration. It has been found that most of the modes of vibration calculated in the finger print region of the molecule are sensitive to conformational changes in the structure. The wagging mode of vibration calculated

Table 1 — Observed and calculated frequencies, modes of vibrations and potential energy distribution of 1-CLN^a

Observed frequencies(cm ⁻¹)		Calculated frequencies (cm ⁻¹), symmetry species, modes of vibrations and PED (%)							
Infrared	Raman	Conformation-I		Conformation-II		Conformation-III		Conformation-IV	
	2996 m	2998 a''	CH ₂ Clas(99)	2999 a	CH ₂ Clas(100)	2998 a	CH ₂ Clas(99)	2999 a	CH ₂ Clas(100)
2957 vs	2956 s sh	2957 a'	CH ₃ as(99)	2957 a	CH ₃ as(99)	2957 a	CH ₃ as(90)	2957 a	CH ₃ as(90)
2957 vs	2956 s sh	2956 a''	CH ₃ as(97)	2956 a	CH ₃ as(97)	2956 a	CH ₃ as(89)	2956 a	CH ₃ as(89)
		2941 a''	CH ₂ as(22)	2941 a	CH ₂ as(22)	2941 a	CH ₂ as(27)	2941 a	CH ₂ as(26)
		2940 a''	CH ₂ as(26)	2940 a	CH ₂ as(25)	2940 a	CH ₂ as(27)	2940 a	CH ₂ as(26)
2932 vvs		2937 a''	CH ₂ as(26)	2938 a	CH ₂ as(25)	2937 a	CH ₂ as(20)	2937 a	CH ₂ as(20)
2932 vvs		2935 a''	CH ₂ as(24)	2935 a	CH ₂ as(24)	2935 a	CH ₂ as(48)	2935 a	CH ₂ as(47)
2932 vvs		2932 a''	CH ₂ as(23)	2932 a	CH ₂ as(23)	2933 a	CH ₂ as(22)	2933 a	CH ₂ as(23)
	2929 vvs	2929 a''	CH ₂ as(24)	2929 a	CH ₂ as(24)	2930 a	CH ₂ as(26)	2930 a	CH ₂ as(26)
	2929 vvs	2928 a''	CH ₂ as(20)	2928 a	CH ₂ as(21)	2928 a	CH ₂ as(27)	2928 a	CH ₂ as(27)
	2903 vvs	2907 a'	CH ₂ Clss(99)	2907 a	CH ₂ Clss(99)	2907 a	CH ₂ Clss(99)	2907 a	CH ₂ Clss(99)
	2875 vvs	2875 a'	CH ₃ ss(98)	2875 a	CH ₃ ss(98)	2875 a	CH ₃ ss(98)	2875 a	CH ₃ ss(98)
	2875 vvs	2869 a'	CH ₂ ss(22)	2869 a	CH ₂ ss(21)	2869 a	CH ₂ ss(27)	2868 a	CH ₂ ss(27)
		2865 a'	CH ₂ ss(25)	2865 a	CH ₂ ss(25)	2864 a	CH ₂ ss(26)	2864 a	CH ₂ ss(28)
2856 vvs	2857 vvs	2862 a'	CH ₂ ss(25)	2862 a	CH ₂ ss(25)	2861 a	CH ₂ ss(25)	2860 a	CH ₂ ss(27)
2856 vvs	2857 vvs	2859 a'	CH ₂ ss(25)	2858 a	CH ₂ ss(24)	2859 a	CH ₂ ss(81)	2859 a	CH ₂ ss(82)
2856 vvs	2857 vvs	2856 a'	CH ₂ ss(23)	2856 a	CH ₂ ss(23)	2857 a	CH ₂ ss(24)	2857 a	CH ₂ ss(27)
2856 vvs	2857 vvs	2854 a'	CH ₂ ss(25)	2854 a	CH ₂ ss(24)	2855 a	CH ₂ ss(28)	2855 a	CH ₂ ss(26)
2856 vvs	2857 vvs	2853 a'	CH ₂ ss(22)	2853 a	CH ₂ ss(21)	2853 a	CH ₂ ss(27)	2853 a	CH ₂ ss(27)
1466 vvs		1468 a'	CH ₃ aδ(84)	1468 a	CH ₃ aδ(84)	1470 a	CH ₃ aδ(65)	1470 a	CH ₃ aδ(65)
		1465 a''	CH ₃ aδ(93)	1465 a	CH ₃ aδ(93)	1465 a	CH ₃ aδ(93)	1465 a	CH ₃ aδ(93)
		1460 a'	CH ₂ δ(74)			1460 a	CH ₂ δ(74)		
						1458 a	CH ₂ δ(55)	1458 a	CH ₂ δ(55)
1452 vs sh				1455 a	CH ₂ δ(76)			1455 a	CH ₂ δ(76)
	1450 vvs	1450 a'	CH ₂ δ(72)	1450 a	CH ₂ δ(72)				
						1437 a	CH ₂ δ(63)	1437 a	CH ₂ δ(63)
1442 vs sh									
1427 m sh		1431 a'	CH ₂ δ(27)	1431 a	CH ₂ δ(26)				
1427 m sh		1430 a'	CH ₂ δ(43)	1430 a	CH ₂ δ(43)	1430 a	CH ₂ δ(26)	1430 a	CH ₂ δ(25)
1427 m sh		1425 a'	CH ₂ δ(22)	1425 a	CH ₂ δ(21)	1427 a	CH ₂ δ(47)	1427 a	CH ₂ δ(45)
1427 m sh		1423 a'	CH ₂ δ(26)	1423 a	CH ₂ δ(29)	1423 a	CH ₂ δ(44)	1423 a	CH ₂ δ(45)
1427 m sh		1422 a'	CH ₂ δ(24)	1422 a	CH ₂ δ(18)	1422 a	CH ₂ δ(32)	1422 a	CH ₂ δ(29)
1414 vw		1414 a'	CH ₂ Clδ(72)	1416 a	CH ₂ Clδ(73)	1414 a	CH ₂ Clδ(72)	1416 a	CH ₂ Clδ(74)
	1386 vw	1386 a'	CH ₂ w(33)	1385 a	CH ₂ w(31)	1385 a	CH ₂ w(30)	1384 a	CH ₂ w(35)
1379 s		1381 a'	CH ₂ w(58)	1381 a	CH ₂ w(59)	1381 a	CH ₂ w(60)	1380 a	CH ₂ w(61)
		1373 a'	CH ₂ w(32)	1372 a	CH ₂ w(29)	1372 a	CH ₂ w(33)	1370 a	CH ₂ w(32)
1360 vvw		1356 a'	CH ₂ w(17)						
				1353 a	CH ₂ w(11)	1350 a	CH ₂ w(12)		
	1347 w	1344 a'	CH ₃ sδ(75)	1343 a	CH ₃ sδ(63)	1345 a	CH ₃ sδ(71)	1348 a	CH ₃ sδ(73)
								1343 a	CH ₂ w(19)
		1324 a'	CH ₂ w(11)	1324 a	CH ₂ w(29)				
								1314 a	CH ₂ w(23)
1309 s						1311 a	CH ₂ w(14)		
						1305 a	CH ₂ t(42)	1305 a	CH ₂ t(32)
		1302 a''	CH ₂ t(21)	1302 a	CH ₂ t(19)				
		1299 a''	CH ₂ t(43)	1299 a	CH ₂ t(34)	1299 a	CH ₂ t(42)	1299 a	CH ₂ t(42)
				1298 a	CH ₂ w(19)				
		1295 a'	CH ₂ w(24)						
	1291 vs					1290 a	CH ₂ t(38)	1290 a	CH ₂ t(36)
1284 s		1283 a''	CH ₂ t(45)	1283 a	CH ₂ t(43)				
1284 s		1281 a''	CH ₂ t(32)	1281 a	CH ₂ t(31)	1281 a	CH ₂ t(29)	1281 a	CH ₂ t(30)
						1265 a	CH ₂ t(34)	1266 a	CH ₂ t(34)
1258 s		1254 a''	CH ₂ t(20)	1253 a	CH ₂ t(27)				
						1245 a	CH ₂ t(17)	1247 a	CH ₂ t(13)
1239 w	1237 vvw			1242 a	CH ₂ Clw(47)			1240 a	CH ₂ Clw(32)
	1221 vvw	1215 a''	CH ₂ t(66)	1215 a	CH ₂ t(65)				
		1209 a'	CH ₂ Clw(81)			1209 a	CH ₂ Clw(77)		

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Table 1 — Observed and calculated frequencies, modes of vibrations and potential energy distribution of 1-CLN^a — *Contd*

Observed frequencies(cm ⁻¹)		Calculated frequencies (cm ⁻¹), symmetry species, modes of vibrations and PED (%)							
Infrared	Raman	Conformation-I		Conformation-II		Conformation-III		Conformation-IV	
				1205 <i>a</i>	CH ₂ Cl _t (74)			1206 <i>a</i>	CH ₂ Cl _t (57)
						1204 <i>a</i>	CH ₂ w(77)	1203 <i>a</i>	CH ₂ w(63)
		1200 <i>a</i> ''	CH ₂ Cl _t (84)			1200 <i>a</i>	CH ₂ Cl _t (84)		
		1184 <i>a</i> ''	CH ₂ t(57)			1184 <i>a</i>	CH ₂ t(57)		
				1179 <i>a</i>	CH ₂ t(45)			1180 <i>a</i>	CH ₂ t(52)
		1175 <i>a</i> ''	CH ₃ r(18)	1173 <i>a</i>	CH ₃ r(16)				
						1167 <i>a</i>	CH ₂ r(20)		
1157 w	1157 w							1164 <i>a</i>	CH ₂ w(19)
		1127 <i>a</i> '	CH ₂ w (47)						
1121 w				1117 <i>a</i>	CH ₂ w(39)	1123 <i>a</i>	CH ₂ w(38)	1116 <i>a</i>	CH ₃ r(12)
						1110 <i>a</i>	CH ₃ r(12)		
	1106 s							1108 <i>a</i>	CCs(19)
		1079 <i>a</i> '	CCs (15)	1079 <i>a</i>	CCs (10)				
		1079 <i>a</i> ''	CH ₃ r (34)	1078 <i>a</i>	CH ₃ r(21)				
		1075 <i>a</i> '	CCs(28)						
				1072 <i>a</i>	CCs(46)	1072 <i>a</i>	CCs (29)		
1067 vw						1068 <i>a</i>	CCs(16)	1069 <i>a</i>	CH ₂ r(12)
1067 vw								1067 <i>a</i>	CCs(48)
	1064 vs			1060 <i>a</i>	CCs(43)	1060 <i>a</i>	CCs(40)	1060 <i>a</i>	CCs(56)
		1058 <i>a</i> '	CCs(52)						
1050 vw		1050 <i>a</i> '	CCs(35)						
				1046 <i>a</i>	CCs(46)	1045 <i>a</i>	CCs(23)	1043 <i>a</i>	CCs(25)
						1032 <i>a</i>	CCs(62)	1033 <i>a</i>	CCs(55)
		1031 <i>a</i> '	CCs(23)	1030 <i>a</i>	CCs(34)				
1022 w		1019 <i>a</i> ''	CH ₂ r(19)	1018 <i>a</i>	CCs(46)				
				1014 <i>a</i>	CH ₂ r(16)				
1009 w		1010 <i>a</i> '	CCs(27)			1010 <i>a</i>	CCs(33)		
	1006 m							1007 <i>a</i>	CH ₂ r(16)
						987 <i>a</i>	CH ₃ r(23)	990 <i>a</i>	CCs(41)
		979 <i>a</i> '	CCs(84)			981 <i>a</i>	CCs(88)		
970 w				973 <i>a</i>	CCs(55)			975 <i>a</i>	CCs(51)
	956 w	952 <i>a</i> ''	CH ₂ r(18)	939 <i>a</i>	CH ₂ r(17)	950 <i>a</i>	CH ₂ r(17)	937 <i>a</i>	CH ₂ r(17)
934 w								915 <i>a</i>	CCs(37)
	917 w					915 <i>a</i>	CCs(37)	915 <i>a</i>	CCs(37)
900 w		909 <i>a</i> '	CCs(35)	909 <i>a</i>	CCs(35)				
889 m		885 <i>a</i> ''	CH ₂ Cl _r (15)			883 <i>a</i>	CH ₂ Cl _r (19)		
	875 s			872 <i>a</i>	CH ₂ r(21)				
869 w								869 <i>a</i>	CH ₂ r(23)
827 w	828 w	820 <i>a</i> ''	CH ₂ r(16)						
				812 <i>a</i>	CH ₂ r(15)	813 <i>a</i>	CH ₂ r(14)		
801 w						781 <i>a</i>	CH ₂ r(49)	808 <i>a</i>	CH ₂ r(10)
786 w								780 <i>a</i>	CH ₂ r(42)
				774 <i>a</i>	CH ₂ Cl _r (46)				
		764 <i>a</i> ''	CH ₂ r(24)	746 <i>a</i>	CH ₂ r(17)			764 <i>a</i>	CH ₂ Cl _r (35)
754 m sh						741 <i>a</i>	CH ₂ r(23)		
731 s sh						727 <i>a</i>	CCl _s (87)	727 <i>a</i>	CH ₂ r(26)
725 vs	724 vs	727 <i>a</i> '	CCl _s (87)						
		721 <i>a</i> ''	CH ₂ r(13)	712 <i>a</i>	CH ₂ r(22)				
						701 <i>a</i>	CH ₂ r(31)		
	692 w sh	694 <i>a</i> ''	CH ₂ r(24)	690 <i>a</i>	CH ₂ r(27)			695 <i>a</i>	CH ₂ r(33)
						682 <i>a</i>	CH ₂ r(36)		
654 vvs	651 vvs	682 <i>a</i> ''	CH ₂ r(33)	654 <i>a</i>	CCl _s (80)			654 <i>a</i>	CCl _s (80)
	507 vw			503 <i>a</i>	CCCδ(24)				

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Table 1 — Observed and calculated frequencies, modes of vibrations and potential energy distribution of 1-CLN^a — *Contd*

Observed frequencies(cm ⁻¹)		Calculated frequencies (cm ⁻¹), symmetry species, modes of vibrations and PED (%)							
Infrared	Raman	Conformation-I		Conformation-II		Conformation-III		Conformation-IV	
	494 w							497 <i>a</i>	CCCδ(23)
	486 vvw	487 <i>a'</i>	CCCδ(21)			488 <i>a</i>	CCCδ(20)		
				466 <i>a</i>	CCCδ(14)			476 <i>a</i>	CCCδ(32)
	454 s sh	458 <i>a'</i>	CCCδ(33)						
	445 s					439 <i>a</i>	CCCδ(29)		
	424 w sh					419 <i>a</i>	CCCδ(22)		
				410 <i>a</i>	CCCδ(37)				
	401 s							399 <i>a</i>	CCCδ(31)
	384 m	379 <i>a'</i>	CCCδ(27)						
	346 m							347 <i>a</i>	CCCδ(36)
	340 vvw	341 <i>a'</i>	CCClδ(23)						
	331 m					327 <i>a</i>	CCClδ(23)		
	308 w			305 <i>a</i>	CCCδ(32)				
	282 vw			281 <i>a</i>	CCCδ(20)	280 <i>a</i>	CCCδ(27)		
	266 w							269 <i>a</i>	CCCδ(20)
	236 s	243 <i>a'</i>	CCCδ(29)						
	229 ms							230 <i>a</i>	CCClδ(33)
	204 m sh			206 <i>a</i>	CCClδ(31)				
		198 <i>a'</i>	CCCδ(16)			196 <i>a</i>	CCCδ(18)		
	184 w							178 <i>a</i>	CCCδ(13)
	172 w			170 <i>a</i>	CCCδ(25)				
						155 <i>a</i>	CCCδ(31)		
		134 <i>a'</i>	CCCδ(27)						
								89 <i>a</i>	CCCδ(31)
				75 <i>a</i>	CCCδ(25)				
						65 <i>a</i>	CCCδ(29)		
		56 <i>a'</i>	CCCδ(25)						

^a Very very strong (vvs), very strong (vs), strong (s), medium strong (ms), medium (m), weak (w), very weak (vw), very very weak (vvw), shoulder (sh), asymmetric stretch (as), symmetric stretch (ss), stretch (s), asymmetric bending (aδ), symmetric bending (sδ), bending (δ) wagging (w), twisting (t), rocking, (r).

at 1311 cm⁻¹ exclusively for conformation III has been assigned to a strongly observed infrared band at 1309 cm⁻¹. The rocking modes of vibration calculated at 1164, 1007, 872 and 820 cm⁻¹ uniquely for different conformations are assigned to observed Raman bands at 1157, 1006, 875 and 828 cm⁻¹, respectively. Similarly, rocking modes of vibration calculated at 1164, 869, 820, 808, 746 and 741 cm⁻¹ uniquely for different conformations are assigned to observe infrared bands at 1157, 869, 827, 801, 754 and 731 cm⁻¹, respectively.

Eight C-C stretch modes of vibration of the molecule have been calculated mostly in the range 1108-909 cm⁻¹ for all the conformations as moderately mixed modes and are assigned to observe infrared and Raman bands in the range 1106-900 cm⁻¹. The present study manifests that these modes of vibrations are sensitive to conformational changes. The C-C stretch mode of vibration calculated at 1108 cm⁻¹ for conformation IV is

assigned to a strongly observed Raman band at 1106 cm⁻¹.

The C-Cl stretch modes of vibration are also found to be conformational sensitive. The present analysis reveals that these modes of vibrations are most diagnostic about the presence of more than one conformation. The C-Cl stretch mode of vibration for conformation I with symmetry *C_s* and conformation III with symmetry *C_i* has been calculated at 727 cm⁻¹ as almost pure mode. An intense Raman band at 724 cm⁻¹ and a strong infrared band at 725 cm⁻¹ are related to this mode. Similarly, the C-Cl stretch mode of vibration for conformations II and IV with symmetry *C_i* has been calculated at 654 cm⁻¹. A very strong Raman band at 651 cm⁻¹ and an intense infrared band at 654 cm⁻¹ are related with this mode. It is apparent from the study here that C-Cl stretch mode of vibration has been calculated at higher frequency when C-Cl bond lies in the -C-C- skeletal plane and at lower frequency when C-Cl bond lies

above or below the –C–C– skeletal plane. These outcomes are in concurrence with those reported in the literature for similar molecules^{3,11,18-20}.

The CCC and CCCI bending modes of vibration have been calculated within a wide range of 503–56 cm⁻¹ for all the four conformations and are found highly conformational sensitive. Most of these modes of vibrations for different conformations are assigned uniquely to observed bands. The CCCI mode of vibration calculated at 341 cm⁻¹ for conformation I, at 206 cm⁻¹ for conformation II, at 327 cm⁻¹ for conformation III and at 230 cm⁻¹ for conformation IV has been assigned to observed Raman bands at 340, 204, 331 and 229 cm⁻¹, respectively.

Eight torsional modes of vibrations for each conformation have been calculated at lowest frequencies as highly pure modes. However, these are not presented here as no measurements are done at these frequencies in the infrared and Raman spectra.

5 Conclusions

In the present study, the observed FT-IR and Raman bands of 1-CLN have been assigned to different modes of vibrations for four most probable conformations of the molecule using normal coordinate calculations. It has been established that these conformations co-exist in the liquid state of the compound under study at ambient temperatures, as some specific bands have been assigned exclusively to each of these conformations. The force-field of the molecule has been found quite reliable as the calculated frequencies of the molecule fit the observed ones within an average error of ± 5.1 cm⁻¹ and with a decent potential energy distribution.

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