Vibrational Spectra and Structure of Four-Membered Ring Molecules*

2-Chlorocyclobutanone and 2-Chloro-2, 4, 4-Trideuterocyclobutanonet

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The infrared spectra of 2-chlorocyclobutanone and 2-chloro-2.4, 4-trideuterocyclobutanone in the liquid and vapor phases have been recorded from 4000 to 250 cm⁻¹. The far-infrared spectrum of 2-chlorocyclobutanone vapor has been recorded from 33 to 600 cm⁻¹. The Raman spectra of the two isotopic species in the liquid state have also been measured. An assignment of the fundamental vibrational frequencies is presented. The ring-puckering mode gave rise to lines at 178 and 170 cm⁻¹ in the Raman spectrum of 2-chlorocyclobutanone and 2-chloro-2,4,4-trideuterocyclobutanone, respectively, and the qualitative nature of the potential function governing this vibration is discussed. The NMR spectra of both isotopic species have likewise been recorded. From the interpretation of the data, the 2-chlorocyclobutanone molecule appears to be essentially planar with only one geometrical configuration which is in marked contrast to the conformers previously reported for this molecule.

INTRODUCTION

The assignment of the thirty fundamental modes of chlorocyclobutane was presented by Durig and Morrissey (1). A vibrational assignment has also been given for the cyclobutanone molecule by Frei and Günthard (2). A microwave study has shown the chlorocyclobutane molecule to be puckered with an average dihedral angle of $20 \pm 1^{\circ}$ [Ref. (3)]. An infrared investigation has presented strong evidence of a "near-planar" conformer which is believed to have an appreciable abundance ($\sim 20\%$) at room temperature (4)–(6). On the other hand, cyclobutanone has been shown to have an average dihedral angle of 0° and is therefore considered planar (7). The potential functions governing the ringpuckering fundamentals of chlorocyclobutane and cyclobutanone are substantially different, as expected. A single-minimum, asymmetric, potential func-

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tion has been found to govern the ring-puckering vibration of chlorocyclobutane (1), (8), whereas the ring-puckering vibration of cyclobutanone has been shown to be well described by a pure quartic potential function (9).

To facilitate a study of the combined effects of chlorine substitution along with a carbonyl group upon the fundamental vibrations of the four-membered ring, we have investigated the vibrational spectra of 2-chlorocyclobutanone and 2-chloro-2,4,4-trideuterocyclobutanone. Additional interest in this molecule arises from a recent publication by Conia and Gore (10) who proposed the existence of the conformers for 2-chlorocyclobutanone.

EXPERIMENTAL

2-Chlorocyclobutanone was prepared by the reaction of sulfuryl chloride with cyclobutanone (10). The procedure of Conia and Gore was modified by allowing the reactants to stir for 30 hours instead of 15 hours at room temperature, and by using a 1-to-1 equivalent ratio of cyclobutanone to SO_2Cl_2 . After the CCl_4 solvent was removed by distillation, the reactants were separated on a 20-ft. Carbowax vpc column at a column temperature of 150°C. The desired product was passed through the column a second time to assure high purity. The sample of 2-chloro-2,4,4-trideuterocyclobutanone was prepared as above by the reaction of cyclobutanone-d₄ with SO_2Cl_2 . The preparation of 2,2,2',2'-tetradeuterocyclobutanone has been reported previously (2). Isotopic purity of the partially deuterated 2-chlorocyclobutanone was shown by the nmr spectrum to be >99 %.

Infrared spectra of the two isotopic species, in both the liquid and vapor phases, were measured from 4000 to 250 cm⁻¹ with a Perkin-Elmer Model 521 spectrophotometer which was purged with nitrogen and calibrated by the usual procedure (11). Vapor and liquid phase spectra were recorded with cells which had CsI windows. Infrared spectra of the pure solid phases were obtained by means of a liquid-nitrogen cryostat with a sample temperature of approximately -185° C. Since no new data were obtained from the solid, the spectra are not reproduced. Original tracings of the infrared spectra of 2-chlorocyclobutanone, and 2-chloro-2,4,4-trideuterocyclobutanone are shown in Fig. 2, the frequencies of the observed bands are listed in Tables I and II.



FIG. 1. Drawing illustrating notation used to distinguish carbon atoms.

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FIG. 2. Top: Infrared spectrum of 2-chlorocyclobutanone liquid recorded between CsI plates. Bottom: Infrared spectrum of 2-chloro-2,4,4-trideuterocyclobutanone liquid recorded neat between CsI plates.

The far infrared spectrum of 2-chlorocyclobutanone was measured with a Beckman Model IR-11 spectrophotometer which was calibrated with atmospheric water vapor and the assignments of Randell *et al.* (12). The spectrum of the vapor was recorded at a sample pressure of 5 mm in an 8.2-m cell equipped with polyethylene windows. A reproduction of the original spectrum is illustrated in Fig. 3 and the frequencies obtained are listed in Table I.

Raman spectra of the liquid phase samples were recorded with a Cary Model 81 Spectrophotometer equipped with a helium-neon laser.¹ Data taken from original tracings of the Raman spectra of 2-chlorocyclobutanone and 2-chloro-2,4,4-trideuterocyclobutanone are listed in Tables I and II. All reported frequencies are believed to be accurate to within ± 2 cm⁻¹.

The nmr spectra of 2-chlorocyclobutanone and 2-chloro-2,4,4-trideuterocyclobutanone are reproduced in Fig. 4. A Varian Model A-60 nmr spectrometer was used. The samples were studied in CCl_4 solutions with TMS and $CHCl_3$ as internal standards.

The basic structural parameters of the cyclobutanone molecule (2) were em-

Infrared (cm ⁻¹)	Rel. Int.	Raman (cm ⁻¹)	Rel. Int.	Assignment
3646(b)	VW			$v_{1} + v_{21} = 3641$
				$v_3 + v_{21} = 3654$
3582	w			$2v_{6} = 3598$
3013(sh)	w	3020(sh)	W	ν ₁
		2995(sh)	W	×2
2967	m	2965(sh)	W	_ ۷ ₃
		2954(sh)	w	الر
2940(sh)	VW	2940	S	ν ₅
2874(sh)	VW			$v_6 + v_{1l_1} = 286l_1$
				$2v_7 = 2896$
2777	VW			$v_6 + v_{17} = 2774$
2485	v w			$v_6 + v_{21} = 2486$
2132	VW			$v_7 + v_{21} = 2135$
1968	W	x		$v_{10} + v_{20} = 1971$
1890(sh)	VW			$v_{11} + v_{21} = 1891$
1799	VVS	1800	m	` 6
1 750(sh)	VW			$v_{16} + v_{20} = 1748$
1620	W			
17178	m	1447	W	۷ ₇
1394	s	1394	W	8
1251(sh)	W	1254	W	v ₉
1225(sh)	m			v ₁₀
1204	s	1205	W	v 11
1188(sh)	A ft	x		1 2
11 65(sh)	A M	· 1		* 13
1096(sh)	VW			$v_{21} + v_{24} = 1099$
1069(ъ)	¥۶	· .		۳ <u>۱).</u>

Table I. Infrared and Raman Data of 2-chlorocyclobutanone Liquid^a

Infrared (cm ⁻¹)	Rel. Int.	Raman (cm ⁻¹)	Rel. Int.	Assignment
1034(sh)	m	1036	m	۳ 15
1002(sh)	W	1000	¥W	1 6
975	s	974	m	۲7
893(sh)	m	894	S	1 8
872	s	873(sh)	W	v 19
746	w	747	m	* 20
710(sh)	VW			$v_{23} + v_{27} = 710$
687	S	689	S	v 21
598(b)	S	600	m	۲ 22
534	m	534	m	v ₂₃
412	m	411	m	٧ 21 ₄
307	m	30 6	m	2 25
277	vw	270	W	۲ 26
172	m	178	S	2 7

Table I. (continued)

a s, m, w, v, sh, and b denote strong, medium, weak, very, shoulder and broad, respectively.

ployed in the product rule calculations. Although these parameters are only approximate for the 2-chlorocyclobutanone molecule, the product rule thus obtained fits the observed data quite well.

DISCUSSION AND ASSIGNMENT OF FUNDAMENTALS

The 2-chlorocyclobutanone molecule contains no elements of symmetry, and is therefore described by point group C₁. Each of its 27 fundamental vibrations is both infrared and Raman active. No information may be gained from depolarization measurements because of the absence of molecular symmetry—all lines will be polarized. The absence of symmetry has also limited the number of useful vapor-band contours, yet a comparison of the observed data with those obtained for other similar molecules (1), (2), (13), along with isotopic shifts make a reliable vibrational assignment possible.

The nomenclature illustrated in Fig. 1 is utilized to distinguish the carbon atoms and it will be initially assumed that the carbon ring is planar to facilitate

Infrared (cm ⁻¹)	Rel. Int.	Raman (cm ⁻¹)	Rel. Int.	Assignment
3640(ъ)	VV W			$v_1 + v_{21} = 3632$
3567	W			$2v_6 = 3594$
3013(sh)	W	3014	m	۲,
29 66	m	2968	S	^٧ 3
2915(sh)	vw			$v_6 + v_8 = 2907$
2867(sh)	ΨW			$v_6 + v_{11} = 2872$
2247(sh)	vvω	22 46	S	پ 2
2213	w	2214	S	پ
2185(sh)	VW	2186(sh)	m	ν ₅
21 59(sh)	VVW			$v_6 + v_{2l_4} = 2157$
1797	۷¥s	1796	m	v 6
1720(sh)	VW			ν ₁₁ , ν ₁₇ + ν ₂₀ = 1718
1447	m	1447	m	۷ 7
1253(sh)	VW			$v_{10} + v_{24} = 1253$
1224	¥	1225	W	¥9
11/13	m			v 13
1110(sh)	w			4
1085(sh)	W			v ₇ - v ₂₄ = 1087
1075	VS	1075	W	ັນ
1052(sh)	vw			ν ₆ - ν ₂₀ = 1052
1037	٧s	1035	Ŵ	1 15
973	3	973	W	v 11, v 17
952(sh)	VW			۷ ₁₂
893	m			۲ 10
835	m	834	S	v 18
798	m	794	m	1 6
745	m	744	s	٧ 20

Table II. Infrared and Raman Data of 2-chloro-2,4,4-trideuterocyclobutanone.^a

Infrared (cm ⁻¹)	Rel. Int.	Raman (cm ⁻¹)	Rel. Int.	Assignment
649(sh)	W	650(b)	W	۳ <u>ا</u> 9
638(sh)	ጥ ዋ			?
619	m	618	w	۲ ₂₁
556	S	554	s	4 22
488	TTI	485	m	۲ 23
360	VŴ	362	5	v 24
301	S	301	ΨW	v ₂₅
		263	¥W	*2 6
		170	٧S	v 27

Table II (continued)

a S, m, w, v, sh, and b denote strong, medium, weak, very, shoulder, and broad, respectively.



Fig. 3. Redrawn far-infrared spectrum of 2-chlorocyclobutanone vapor recorded at a sample pressure of 5 mm in an 8.2-m path cell at 80° C.

the discussion of the assignments. However, in a latter section it will be shown that this assumption is valid. The topics of discussion will be covered in the following order: CH stretching vibrations, CH bending vibrations, carbonyl and CCl vibrations, and ring deformations.



FIG. 4. Top: NMR spectrum (expanded scale) of complex triplet arising from the α -proton of 2-chlorocyclobutanone. Bottom: A. NMR spectrum of 2-chloro-2,4,4-trideuterocyclobutanone; B. NMR spectrum of 2-chlorocyclobutanone.

CARBON-HYDROGEN STRETCHING MODES

There are five CH stretching fundamentals for the 2-chlorocyclobutanone molecule and two CH stretching modes in the α, γ -deuterated isomer. The two CH stretching modes which these isotopic species have in common are the inphase and out-of-phase stretching of the β -methylene group. The bands resulting from these vibrations are found at 2966 and 3013 cm⁻¹, respectively, in the in-

FOUR-MEMBERED RING MOLECULES

Table III. Vibrational Assignments for 2-chlorocyclobutanone

	Approximate Description of Vibration	2-chlorocyclobutanone (cm ⁻¹) ^a	2-chloro-2,4,4-trideutero- cyclobutanone(cm ⁻¹) ^a
י1	β-CH ₂ out-of-phase stretching	3013	3013
v ₂	a-CH stretching	2995*	221,7
×3	β -CH ₂ in-phase stretching	2967	2966
ب 4	Y-CH ₂ out-of-phase stretching	2954*	2213
v 5	γ -CH ₂ in-phase stretching	2970	2185
v 6	C=0 stretching	1799	1797
۷ ₇	β -CH ₂ deformation	1448	1447
۷ 8	$Y-CH_2$ deformation	1394	1110
v ₉	β-CH ₂ twisting	1251	1224
v 10	a-CH (L) b endin _s	1225	893
ب	Y-CH2 wagging	1204	(975)
۲ 12	Y-CH ₂ twisting	1188	952
" 13	β-CH ₂ wagging	1165	1143
v 14	ring deformation	1069	1075
v 15	ring deformation	1034	1037
v 16	a-CH (11) bending	1002	798
۷ ₁₇	ring deformation	975	973
v 18	ring "breathing"	893	835
7 19	Y-CH ₂ rocking	872	649
ν ₂₀	p-CH ₂ rocking	746	745
۷ ₂₁	ring deformation	687	619
v 22	C-Cl stretching	598	556
v 23	C = 0 (11) bending	534	488
۷ ₂₄	$C=0 (\bot)$ bending	412	362 [*]

and 2-chloro-2, h, h-trideuterocyclobutanone.

Table III (continued)

	Approximate Description of Vibration	2-chlorocyclobutanone (cm ⁻¹) ^a	2-chloro-2,4,4-trideutero- cyclobutanone(cm ⁻¹) ^a
ν ₂₅	C-X (1) bending	307	301
v 26	C-X () bending	275*	2 53 [*]
v 27	ring-puckering	178*	170*

^a Numbers in parentheses are estimated values.

* Asterisk denotes Raman frequencies - all other values are infrared frequencies of the liquid.

frared spectrum of α, γ -trideuterocyclobutanone liquid. The analogous absorptions of the light compound were located at 2967 and 3013 cm⁻¹, respectively. The α -CHCl stretching mode is assigned to the Raman line at 2995 cm⁻¹ and shifts to 2247 cm⁻¹ upon deuterium substitution. The similar CHCl stretching fundamental of chlorocyclobutane, with a frequency of 3005 cm⁻¹, supports this assignment (1). The in-phase and out-of-phase stretching modes of the γ -methylene group are assigned to the Raman lines at 2940 and 2954 cm⁻¹, respectively; deuterium substitution results in shifts to 2186 and 2214 cm⁻¹, respectively. The distinction between in-phase and out-of-phase stretching of each methylene group has been made on the basis of relative intensity considerations. Namely, the in-phase mode is expected to exhibit greater intensity in the Raman spectrum than in the infrared spectrum, and further, the out-of-phase vibrations normally occur at higher frequencies than do their in-phase counterparts.

CARBON-HYDROGEN BENDING VIBRATIONS

Each of the two methylene groups contributes a deformation, a wagging, a twisting, and a rocking mode to the CH bending fundamentals. The band positions of analogous modes of the β - and γ -groups, however, are expected to be separated somewhat due to the differences in their immediate environments. The bending modes associated with the β -methylene group should absorb at the same relative frequencies in the two isotopic species; whereas bands arising from the γ -group shift to lower values with deuteration. The deformation, twisting, wagging, and rocking of the β -group are assigned to bands at 1448, 1251, 1165, and 746 cm⁻¹, respectively, in the infrared spectrum of 2-chlorocyclobutanone. The corresponding values observed for the deuterated molecule are 1447, 1224, 1143 and 745 cm⁻¹. The wagging and twisting modes of the light molecule appear to be coupled slightly with other modes which have nearly the same energy as is evidenced by their small shift with deuteration; the deformational and rocking modes, however, appear to be fairly "pure" and not mixed.

The deformation, wagging, twisting, and rocking fundamentals of the γ -group are assigned to infrared bands at 1394, 1204, 1188, and 872 cm⁻¹, respectively. Deuterium substitution causes these bands to shift to 1110, 973, 952, and 649 cm⁻¹.

The two α -CH bending modes are assigned to bands at 1225 and 1002 cm⁻¹ in the infrared spectrum of the liquid, and shift to 893 and 798 cm⁻¹ upon deuteration. Once again, a correspondence is found with the values of 1263 and 975 cm⁻¹ measured for the similar vibrations of the α -CHCl group in chlorocyclobutane.¹ The 1225 cm⁻¹ band corresponds to a CH bending which is perpendicular to the assumed molecular plane of the ring, whereas the 1002 cm⁻¹ band results from a CH motion that is parallel to this plane.

CARBONYL AND CHLORINE VIBRATIONS

The C=O stretching fundamental gives rise to the very intense infrared band at ~1800 cm⁻¹ in the spectrum of both isotopic species. The two carbonyl bending vibrations are assigned to the infrared bands at 534 (parallel to the plane) and 412 cm⁻¹ (perpendicular to the plane) (2); these bands shift to 488 and 360 cm⁻¹ with deuteration. The C-Cl stretching fundamental is assigned to the intense, broad infrared band at 598 cm⁻¹ (the corresponding Raman line is found at 600 cm⁻¹) in the spectrum of 2-chlorocyclobutanone liquid and shifts to 556 cm⁻¹ with deuteration. The two C-Cl bending vibrations give rise to Raman lines at 307 and 270 cm⁻¹; deutcrium substitution produces very slight shifts to 301 and 263 cm⁻¹, respectively. The line of higher frequency is assigned to the perpendicular bending mode, whereas the 370 cm⁻¹ line is assigned to the parallel bending motion. The perpendicular and parallel bending motions of the halogen showed very strong and weak Raman lines, respectively, in the halocyclobutanes (1), (6), (13).

RING DEFORMATIONS

There are six fundamental vibrations which are associated with the carbonring skeleton of the molecule. If one assumes that the ring is planar or nearly so, then five of these modes can be thought of as oscillations within the plane, and the sixth as an out-of-plane bending mode. The five intraplanar fundamentals are assigned to the bands at 1069, 1034, 975, 893, and 687 cm⁻¹ in the infrared spectrum of the liquid. The corresponding bands of the deuterium-substituted molecule are located at 1075, 1037, 973, 835, and 619 cm⁻¹. The analogous vibrations of the 2-bromocyclobutane molecule were found at very nearly the same

¹ The helium-neon laser was purchased with funds from a National Science Foundation Grant, GP-7079.

frequencies (14). The 893- and 687-cm⁻¹ bands shift more than might be expected of ring modes, but it is suggested that these two modes are coupled with the bending vibrations of the methylene groups. The mixing of these two ring modes has been reported previously in the deuterated analogs of the halocyclobutanes (1), (13). It should also be pointed out that the intensity of the corresponding Raman lines leaves little doubt in the assignments of these two frequencies.

The out-of-plane ring-bending mode is the most interesting vibration of 2chlorocyclobutanone and it is normally referred to as the ring-puckering vibration. The ring-puckering fundamental of several four-membered ring systems has been studied in the past (1), (4), (6), (8), (9), (13), (14), and it is expected to be the band of lowest frequency. It is thus assigned to the strong Raman line at 178 cm^{-1} and the corresponding band in the infrared spectrum of the vapor is centered at 172 cm⁻¹. The band contour resembles a Type-A envelope with Pand R branches at 165 and 179 cm⁻¹, respectively (see Fig. 3). There are no apparent "hot bands" on either side of the fundamental transition. Therefore, it appears that the ring-puckering vibration for 2-chlorocyclobutanone is harmonic or nearly so. The deuterated compound displays the corresponding Raman line at 170 $\rm cm^{-1}$. The shift is much smaller than expected for the ring-puckering vibration, since for other four-membered ring molecules, the corresponding vibration showed a marked shift with isotopic substitution (9), (13). However, the shift is consistent with that found for the corresponding vibration in 2bromocyclobutanone (14) where it was postulated that this vibration consists of a large motion of the β -CH₂ group compared to the motion of the remaining part of the molecule.

SUMMARY AND CONCLUSIONS

Recently Conia and Gore published a lengthy report dealing with the chemistry of substituted cyclobutanones (10). In this report the data presented were interpreted as resulting from two equilibrium configurations, equatorial and axial, of the 2-chlorocyclobutanone molecule. Their evidence was based on infrared, ultraviolet, and NMR spectra, as well as measurements of dipole moments in different solvents.

In the infrared study of Conia and Gore, the position of the carbonyl stretching vibration was measured in solvents of varying polarity. Cyclobutanone, as well as 2-chlorocyclobutanone, was studied. It was proposed that there exists a dynamic equilibrium between axial and equatorial conformations of the 2chlorocyclobutanone molecule; the equilibrium shifted to the favor of the axial conformation in non-polar solvents at the expense of the equatorial form, and in polar solvents the opposite was the case. The carbonyl stretching frequency was found to increase as the polarity of the solvents decreased and this evidence was taken to mean that the axial form was becoming predominant. A total increase of 13 cm⁻¹ was observed for the carbonyl stretching frequency of 2-chlorocyclo-

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butanone in solvents ranging from dimethyl sulfoxide to cyclohexane; however, the frequency increase observed for cyclobutanone, using the same solvents, was 24 cm⁻¹. It is well established that cyclobutanone is planar (7), (9), so the authors feel that such an increase in the carbonyl frequency for the 2-chlorocyclobutanone molecule, which is less than that observed for cyclobutanone itself, does not confirm the presence of two conformers and evidently may be the result of simple solvent interaction. Similar considerations may be applied to the ultraviolet absorption data reported. Also reported were the NMR spin-spin coupling constants between the α - and β -protons of 2-chlorocyclobutanone. It was stated that the coupling constants of the α -proton were 9 cps (*cis*) and 7 cps (*trans*); this was given as evidence for the nonplanarity of the molecule since the values obtained for cyclobutanone were 8.2 cps (*cis*) and 8.2 cps (*trans*). The NMR spectra of 2-chlorocyclobutanone and its deuterated isomer have been recorded in this laboratory (see Fig. 4).

NMR spectra were also recorded with a Varian HA-100 high-resolution instrument at temperature intervals up to 70° C. It is interesting to note that the shoulders on the lines near 283 and 300 cps merged closer to the line centers with increasing temperatures, although relative line intensities appeared to be insensitive to the changes of the sample temperature. This merging effect is probably the result of a steadily changing environment of the α -proton. One explanation could be that the average dihedral angle of the ring is slightly altered as excited states of the ring-puckering fundamental become increasingly thermally populated. Recent workers (15), (16) have reported the vicinal cis and trans coupling constants of cyclobutanone to be approximately 10 and 6 cps, respectively, so that the comparison of 2-chlorocyclobutanone to cyclobutanone which was previously made (10) seems to be incorrect. It is evident that the NMR spectrum of 2-chlorocyclobutanone cannot be treated as one of first order, and that coupling across the ring appears to add a great deal of complexity to the data. Lambert and Roberts (17) have recently commented that the similarity in coupling constants (6.4-9.7 cps), found by Conia *et al.*, is very different from the wide range of hydrogen-fluorine couplings for cyclobutanes which are known to be puckered. Roberts and Lambert indicate that it is impossible to distinguish between statistical and dynamic planarity by coupling-constant considerations alone, and they suggest that the deviation from planarity in the cyclobutanones is expected to be small. The dipole moment evidence of conformers reported by Conia is based upon differences which seem to be as large as the experimental uncertainties involved with such measurements. For example, the precision of dipole-moment measurements in solution is altered by solvent effects, which introduce an absolute error up to 10% or more (19).

If the 2-chlorocyclobutanone molecule were substantially puckered as is the case for the chlorocyclobutane molecule, one might expect the ring-puckering fundamental to produce a broad band which resembles the 159 cm⁻¹ band

found for chlorocyclobutane. Also, evidence for the existence of two conformers should be indicated. The harmonic appearance of the band assigned to the ringpuckering vibration, along with the absence of gross differences between the liquid and low-temperature solid phase spectra of 2-chlorocyclobutanone, however, lead to the conclusions that there is but one equilibrium conformation of the molecule and that the ring is planar or very nearly so. The proximity of the C-Cl vibrations (especially the bending modes) to the ring-puckering fundamental, along with the absence of molecular symmetry, make a great amount of mixing between these "normal" modes very probable. As a result, the ringpuckering mode can have substantial contributions from the C-Cl motions and may not be adequately described as a "pure" ring-puckering vibration. Because the C=O bending motions show coupling with the α -CH and γ -CH₂ modes by shifting with deuteration, and the C-Cl bending and ring-puckering modes do not, it is felt that the latter modes are not coupled appreciably with those of the α -CH and β -CH₂ groups, or the C=O bending motions. The negligible shift of the ring-puckering frequency with trideuteration supports the hypothesis that the α -CH and γ -CH₂ groups do not contribute any significant vibrational amplitude to the resultant motion of the ring-puckering mode. The actual oscillations taking place during the ring-puckering vibration are believed to be composed mainly of motions of the β -CH₂ group with contributions from motions of the chlorine substituent. A normal coordinate calculation should be of value to determine the relative motions of the atoms during the normal vibrations.

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