Infrared and Raman spectra and vibrational assignment of methylene cyclopropane- h_6 and $-d_6$

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Received June 30, 1970

Infrared spectra have been recorded in the range 4000 to 20 cm^{-1} for methylene cyclopropane- h_6 and $-d_6$ in the gas phase, and from 4000 to 200 cm^{-1} for methylene cyclopropane- h_6 in the liquid phase. Raman spectra have been recorded for the liquid phases of both species. The fundamental modes of vibration have been assigned using i.r. band contours and Raman depolarization ratios, with the exception of the i.r. inactive A_2 modes which were not observed. An interesting feature is the occurrence of remarkably small isotope shifts for certain modes.

Canadian Journal of Chemistry, 48, 3889 (1970)

Introduction

Vibrational assignments have been made for only a relatively small number of molecules containing the cyclopropane ring (1-10). Apart from cyclopropane, complete assignments have been published for cyanocyclopropane (7), methyl cyclopropane (8), and bromocyclopropane (9). The remainder of the work on cyclopropane derivatives has been directed mainly toward determining characteristic frequencies for the cyclopropane ring (10). The symmetry of the three molecules studied (7-9) in detail is low, hindering the definitive assignment of the spectra from purely spectroscopic evidence. The relatively high symmetry, C_{2v} , of methylene cyclopropane makes this molecule a desirable one to study in order to support the assignments with purely spectroscopic evidence, and hence to obtain definitive information to further our knowledge of the vibrations of the cyclopropane ring. It is of particular interest to observe the changes in the ring vibrations and force constants caused by the presence of the very distorted sp² hybridization on the ring C-1. The detailed assignment of methylene cyclopropane is, further, of interest in connection with the deuterium isotope effects in the formation of methylene cyclopropane- d_2 and $-d_4$ from methylene pyrazoline- d_2 and $-d_4$ (11).

Since the initial preparation of methylene cyclopropane by Gragson *et al.* (12) in 1951, its vibrational spectrum has been investigated in the i.r. and Raman by Blau (13) who attempted the assignment of the 24 normal modes. Blau used an approximate normal coordinate calculation to help in making assignments and, later, Loewenstein (14) used a more general force-field and made some reassignment of the spectra. Neverthe-

less it was not possible for these authors to make a complete assignment of the spectrum. There is no published information on the vibrational spectrum of methylene cyclopropane- d_6 .

In this paper the assignment of the i.r. and Raman spectra of methylene cyclopropane- h_6 and $-d_6$ are discussed. The results of normalcoordinate calculations upon these molecules will be submitted to this journal shortly.

Experimental

Methylene cyclopropane and methylene cyclopropaned₆ were prepared by the pyrolysis of 1-methylene pyrazoline, h_6 and d_6 respectively, at 200 °C (11). Gas liquid chromatography using a $\beta_1\beta_1$ -oxydipropionitrile column at 20 °C revealed no impurities for the hydrogen isotope. The n.m.r. spectra gave no indication of impurity for the h_6 isotope, but indicated 0 to 3% of H in the d_6 isotope, distributed randomly between the ethylenic and methylenic positions. This undoubtedly indicates between 0 and 18% of C₄D₅H impurity in the C₄D₆. No other impurity could be detected, except for a trace of water.

The i.r. spectra between 200 and 4000 cm⁻¹ were taken with a Beckman I.R. 12 spectrophotometer. The instrument was calibrated using standard gases (15) and the Beckman fiducial marker accessory. The frequencies quoted are accurate to ± 0.5 cm⁻¹ up to 2000 cm⁻¹ and ± 1 cm⁻¹ above 2000 cm⁻¹. The resolution was generally better than 1 cm⁻¹ between 4000 and 650 cm⁻¹ and better than 2.5 cm^{-1} between 650 and 200 cm⁻¹. The i.r. spectra between 30 and 200 cm⁻¹ were obtained using a Beckman-R.I.I.C. FS 720 interferometer, and using a sine plus cosine Fourier transform. The gas cells had a 10 cm path length and were fitted with either cesium iodide or polyethylene windows. The gas pressures were between 2 and 60 cm of mercury for C_4H_6 and between 2 and 20 cm of mercury for C_4D_6 . The gas temperature was usually + 37 °C, but was about -40 °C for a few spectra recorded to check for hot bands and difference bands. Liquid spectra of C_4H_6 were taken from 200 to 4000 cm⁻¹ in a low temperature cell with CsI windows, using a .005 in. spacer.

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FIG. 1. Raman spectrum of C_4H_6 (upper), and C_4D_6 (lower), liquids at about 22 °C.

Raman spectra were recorded on a Perkin-Elmer L.R.-1 spectrophotometer using a 7 mW He-Ne laser and 90° excitation. The instrument was calibrated using carbon tetrachloride and benzene Raman lines, and the frequencies quoted are accurate to ± 5 cm⁻¹. The resolution was better than 10 cm⁻¹. The Raman samples were liquid and were contained in thick-walled glass tubing, about 1 mm i.d., flattened and polished at the ends, and sealed by a stopcock capable of sealing a few atmospheres internal pressure. The sample temperature was about 22 °C. Late in the course of this work a Raman spectrophotometer became available consisting of a Carson's Laboratories model 10SP Ar⁺/Kr⁺ laser, a Spex model 1401 monochromator, a cooled FW130 photomultiplier. and photon counting electronics. The Raman spectrum of C4H6 was obtained with this instrument and, using the 4880 Å Ar⁺ line at about 140 mW power output, spectra with a resolution of about 1 cm⁻¹ and a frequency accuracy of $\pm 1 \text{ cm}^{-1}$ were obtained. The sample was the liquid at about 22 °C, sealed into a m.p. capillary tube. The Raman spectrum for C₄H₆ reported in this paper is that obtained from this instrument, while the spectrum for C₄D₆ is that obtained from the Perkin-Elmer L.R. 1. The spectrum of C_4D_6 could not be re-run on the new instrument because no sample was available at that time.

Results

The Raman spectra are shown in Fig. 1, and the frequencies are listed in Table 1. The i.r. spectrum of the gas is shown in Fig. 2 for C_4H_6 between 200 and 4000 cm⁻¹, and in Fig. 3 for C_4D_6 between 200 and 3200 cm⁻¹. No features, apart from the broad, unresolved, pure-rotational absorption, were found for either isotope below 200 cm⁻¹. The spectrum of liquid C_4H_6 is shown in Fig. 4. Table 2 presents the frequencies of the i.r. absorption features for gaseous and liquid C_4H_6 , along with a description of the gas phase band contour, and the proposed assignment. For C_4D_6 , too little material was available to permit spectra of the liquid to be recorded. Table 3 presents the frequencies of the i.r. absorption features for gaseous C₄D₆, along with a decription of the band contours, and the proposed assignment. In Tables 2 and 3 weak combination or overtone bands have been included only if an identifiable band contour was observed. Figs. 5-10 show the i.r. spectra of gaseous C_4H_6 or C_4D_6 in specific regions, and show the proposed resolution of multiple bands into A-, B-, or C-type band contours. For convenience, Table 4 presents a brief symmetry coordinate description of each mode next to the mode number. This description does not, in most cases, accurately describe the normal coordinate. The numbering of the modes follows Herzberg (16).

Our i.r. spectra of C_4H_6 gas are more extensive and were run at higher resolution than those of Blau, but show essentially the same features, subject to resolution differences, except that we do not observe the band at 695 cm⁻¹ reported by him. Blau's Raman spectrum of C_4H_6 contains a number of features, at 596, 663, 922, 969, and 1476 cm⁻¹ that we have not observed. We believe that we would have observed them had they been present in our sample. The i.r. spectra reported



FIG. 2. The i.r. spectrum of C_4H_6 gas at about 34 °C. The gas pressures are: curve A, 580 mm of Hg; curve B, 250 mm of Hg; curve C, 60 mm of Hg. The path length is 10 cm.

here for liquid C_4H_6 , and for gaseous C_4D_6 , and the Raman spectrum of C_4D_6 reported here, are, to our knowledge, the first to be published.

Discussion

(a) Molecular Structure and Infrared Band Contours

The structure of methylene cyclopropane has been determined by Laurie and Stigliani (17) by microwave spectroscopy; the only assumption required was that the ethylenic carbon-hydrogen bond length is 1.088 Å (17). The molecule belongs to the $C_{2\nu}$ point group (16). Taking the ring plane to be the xz plane, the 24 normal modes form the following representation of the group:

$8A_1 + 4A_2 + 7B_1 + 5B_2$

The Raman depolarization ratios help to identify the A_1 modes, the bands unique to the Raman spectrum arise from the A_2 modes, and the band contours in the i.r. spectrum of the gas characterize the absorption by the A_1 , B_1 , and B_2 modes.

The i.r. band contours may be calculated (18) from a knowledge of the moments of inertia. Using Laurie and Stigliani's (17) data we calculate the moments of inertia of C_4D_6 to be 37.6, 92.5, and 116.8, a.m.u. Å², and the band contours to be of Ueda and Shimanouchi's (18) type 17 for both C_4H_6 and C_4D_6 .

The A_1 , B_1 , and B_2 modes may thus be

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FIG. 3. The i.r. spectrum of C_4D_6 gas at about 34 °C. The gas pressures are: curve A, 200 mm of Hg; curve B, 100 mm of Hg. The path length is 10 cm.

identified by their A, B, C band contours respectively.

(b) Assignment for C_4H_6

(i) C—H Stretching Vibrations

The i.r. active fundamentals to be assigned are an A_1 and a B_1 ethylenic mode and A_1 , B_1 , and B_2 methylenic modes. The ethylenic B_1 and the methylenic B_2 modes are expected at a higher frequency than the other three modes, as they arise from the asymmetric stretch of the CH₂ group. The spectrum from 2900 to 3150 cm⁻¹ is shown in Fig. 5.

Two regions of absorption are noted: the higher frequency band consisting of a B- and a C-type contour, while the one at lower frequency contains one B and two A bands. The assignment of the C-type band at 3069.5 cm^{-1} to the B₂ methylenic stretch, v_{20} , and the B feature at 3086.2 cm^{-1} to the B₁ ethylenic stretch, v₁₃, follows immediately. The other B_1 mode (B_1 methylenic stretch, v_{14}) is found at 2996.0 cm⁻¹. The A_1 feature at 3008.3 cm⁻¹ is assigned to the A_1 ethylenic stretch, v_1 , and the A_1 band at 2999.3 cm⁻¹ to the A₁ methylenic stretch, v_2 , for the following reasons: (a) The Raman line at 2988 cm^{-1} is considerably more intense than that at 2997 cm⁻¹. Both lines are strongly polarized and therefore arise from A_1 modes. Somewhat intuitively, one expects the methylenic stretch to cause a greater polarizability change than the ethylenic stretch, and therefore to yield a more intense Raman line. Thus we assign the methylenic stretch to low frequency of the ethylenic stretch.

TABLE 1

 C_4H_6* $C_4D_6^{\dagger}$ Depolarization Depolarization Frequency[‡] Intensity Frequency[†] Intensity ratio ratio 288 0.75 0.75 2 253 ĩ 3 356 0.75 0.7 304 0.75 1 0.65 0.75 0.35 724 4 642 1 1.5 i.5 3 890 0.75 708 804 1000 0.1 1Ŏ 1034 10 900 0.1 0.75 0.1 0.1 1125 0.1 946 1.5 1019 1048 1144 0.6 0.75 1411 1435 0.75 1 0.4 1 0.3

1172

1725

1753

2202

2258

2310

Raman spectrum	of C_4H_6 a	nd C₄D ₆ liquid

•	Frequencie	s accurate to	± 1	cm ⁻¹ .

0.1 0.5

0.05

0.4 2.5 1.2

0.3

0.1

0.1

0.1

0.1

0.75

2

†Frequencies accurate to ± 5 cm⁻¹.

1453

1736

1784

1805

2988

2997

3060

(b) The higher frequency A_1 band is the more intense in the i.r., and, from the assumed geometry of the molecule, the bond moment approximation, assuming equal bond moments for all C—H bonds, predicts that the ethylenic stretch has a greater dipole moment change along the zaxis than the methylenic stretching mode, and therefore has a greater absorption intensity.

The i.r. inactive A_2 vibration expected near v_{20} or v_{13} may contribute to the broad depolarized Raman feature at 3050 to 3080 cm⁻¹, but, because this is not resolved, we cannot make a reliable assignment of this mode.

(ii) The C = C Stretching Vibration

In the range 1600 to 2000 cm^{-1} , only two strong A-type features are found in the i.r. spectrum, at 1786.0 and 1742.2 cm^{-1} (Fig. 6). One of these features must be due to the C = Cstretch, v_3 . The lower frequency feature, at 1742.2 cm⁻¹, corresponds to a medium intensity Raman peak (polarized), while the 1786.0 cm^{-1} feature gives rise to only a very weak band in the Raman. On this basis, we prefer the assignment of v_3 to 1742.2 cm⁻¹, and assign the 1786.0 band to $2v_{22}$, enhanced by Fermi resonance with v_3 . The high frequency for a C=C stretching mode, 1742.2 cm⁻¹, undoubtedly arises primarily from the large kinetic coupling with the symmetric ring stretching mode which, itself, arises from the large angle ($\sim 150^{\circ}$) between the C==C bond and the ring C-C bonds. A similar effect is known to exist for C=O stretching modes (19).

15

1

9

0.5

0.3

1.5

0.1

0.1

0.3

0.03

0.75

0.1

(iii) The Ring Vibrations

Three ring vibrations are expected: the A_1 symmetric stretching mode (the ring breathing mode), the B_1 asymmetric stretching mode, and the A_1 deformation mode. The ring breathing mode (v_6) is readily identified at 1034 cm⁻¹ by its very strong Raman intensity, and by the A-type band at 1037.4 cm^{-1} in the i.r. (Fig. 7). The second Q branch at 1030.3 cm^{-1} decreases in intensity relative to that at 1037.4 cm^{-1} when the gas is cooled and is believed to be a hot band, probably originating from the 279.6 cm^{-1} energy level. The remaining A_1 and B_1 modes must be at considerably lower frequencies than 1037.4 cm^{-1} . The only A-type band meeting this requirement is at 723.8 cm⁻¹ and we assign this to the A_1 ring deformation mode (v_8). The B₁ asymmetric ring stretching mode should be between the two A_1 modes, and is assigned at 895 cm⁻¹ (Fig. 8), to the only B-type band in this region.

(iv) The CH₂ Deformation Vibrations

The ethylenic CH₂ group gives rise to an A₁ deformation, an A₂ torsion, a B₁ rocking, and a B_2 wagging mode. The A_1 and B_2 modes are well characterized in substituted ethylenes (20, 21) at 1410 to 1420 cm⁻¹, and near to 890 cm⁻¹ respectively. We therefore assign the A-type feature at 1411.0 cm⁻¹ (Fig. 6) to the A_1 ethylenic

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FIG. 4. The i.r. spectrum of C_4H_6 liquid at about -45 °C. The exact path length is unknown but is less than or equal to 0.005 in.

deformation (v_5) , and the intense C-type band at 890.5 cm⁻¹ to the B₂ ethylenic wag (v_{22}) (Fig. 8).

The A_2 torsion is not observed in the Raman spectrum. The B_1 rocking motion of the ethylenic group is not so uniquely determined. Early work, summarized by Sheppard and Simpson (20), placed this mode at around 1280 cm⁻¹ in disubstituted ethylenes of the type RR'C==CH₂. Torkington (22) preferred the assignment of the ethylenic rock to 1062 cm⁻¹ in isobutene and 1040 cm⁻¹ in propene. Meyer and Gunthard, in a study of 2-bromo-propene (23), assign this mode to a band at 925 cm⁻¹. A recent study of isobutene (21) in the gas, liquid, and solid states assigns the A_1 ethylenic deformation to 1416 cm⁻¹ and the B_1 ethylenic rock to 975 cm⁻¹. In view of this uncertainty we discuss this assignment with the other B_1 modes later.

The methylenic CH₂ groups give rise to an A₁ and a B₁ deformation, an A₁ and a B₁ wag, an A₂ and a B₂ twist, and an A₂ and a B₂ rock. The A₁ deformation is found near 1475 cm⁻¹ (1, 5) in cyclopropane, and at 1490 cm⁻¹ in ethylene oxide (24). The i.r. spectrum of methylene cyclopropane shows a weak A-type band at 1436.5 cm⁻¹ (Fig. 6) coincident with a polarized Raman line, and a very weak Q branch (A or C band contour) at ~ 1500 cm⁻¹, where no Raman band was detected. The Raman activity of the 1436.5 cm⁻¹ feature suggests it arises from a fundamental transition and we assign it to the A₁ methylenic deformation (v₄). The band at 1508 cm⁻¹ may be due to $2v_{23}$. The only remaining A₁

TABLE 2

Infrared absorption frequencies* of methylene cyclopropane-h6

TABLE 3

Infrared absorption frequencies* of methylene cyclopropane-d₆ vapor

Gas† frequer	Icy	Band contour	Liquid‡ frequency	Assignment
279.6	mw	С	290	V24
355	w	в	355	V19
723.8	m	Α	725	ν ₈
728	vw	Α		hot band?
748.6	тw	С	748	V23
888.0	vw	С		hot band
890.5	vs	С	889	V22
895		в	~900	V ₁₈
951	vw	С	950	$v_8 + v_{24}$
1000.0	vw	Α		hot band
1002.6	m	Α	999	ν ₇
1030.3	mw	С		hot band
1037.4	ms	Α	1036	V6
	ms			V10
1073.0	ms	С	1072	V21
1125.3	ms	в	1122	V17
1244	vvw	B		?
1280.5	vw	Ē	1279	$v_{24} + v_{7}$
1354.4	mw	B	1357	V16
1410	m	B	1397	V15
1411.0	wm	Ā	1409	Ve
1436.5	wm	Ă	1434	V.
~ 1500	w	Å ?	1497	$2v_{2}^{4}$
1742.2	s	A	1737	2423. Vo
1786 0	s	A	1777	2
1822	w	Å	1814	λ_{22}
1896	vw	Ŕ	1888	$v_{23} + v_{21}$
1948	VW	Δ	1000	$v_7 + v_{18}$
~ 1980	VW	Δ	1984	21 21
2138	VVVVV	Δ	2142	207
2160	V V VV	Å	2142	$2v_{21}$
2248	¥ • • •	R	2241	2_{1}^{23} , 5_{2}^{1}
2350	VNV	A 2	2340	$2v_{17}$
2467	¥ ¥¥	Δ.	2452	V6 1 V16
2996 0	5	R	8	V16 T V17
2000 3	3 m	A D	8	V14
3008 3	Ne	Å	8	v ₂
3060.5	v 5 e	ĉ	8	v ₁
3086.2	3	р р	8	V ₂₀
22/19	5	D A	2250	V13
3/35	v w	AL D	3330	$v_{20} + v_{24}$
3665	vw		2420	: 2
3820	w	A .	2000	
3020	vw.	A C	2021	$v_{20} + v_{23}$
	vvw	ر ر		$v_{18} + v_{9}(A_2)$

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*Frequency units are cm⁻¹. †At about 30 °C. ‡At -40 °C. \$The bands were too intense to measure.

mode, the A_1 wag, is found at 1002.6 cm⁻¹ characterized by a polarized Raman band and an A-type i.r. absorption (Fig. 7).

We now consider the three B_1 modes: methylenic deformation, methylenic wag, and ethylenic rock. The spectrum shows two undisputable B contours at 1125.3 cm⁻¹ (Figs. 2 and 7) and 1354.4 cm^{-1} (Figs. 2 and 6). In addition to these there is a very weak B contour at 1244 cm^{-1} (Fig. 2). The presence of a further B-type band at \sim 1410 cm⁻¹ is suggested by the i.r. bandshape in the region

Gas freque	s ncy	Band contour	Assignment
240	mw	С	V24
304	vw	Ř	V10
537.5	mw	Ē	V 73
541.5	vw	Ĉ	hot band?
637.0	m	Ā	Vs
639.5	vw	A	hot band
650.5	vvw	С	$v_6 - v_{24}$
705.0	vs	С	v ₂₂
735	m	В	V18
804.2	vw	Α	ν ₇
835.5	w	С	V ₂₁
882	vw	С	$v_{24} + v_8$
895	mw	Α	V ₆
1017	m	В	V ₁₇
1043	mw	A?	$v_{19} + v_{18}?$
1047	mw	С	$v_{24} + v_7$
1073	S	В	V16
1122	W	В	V15
1139	w	Α	ν ₅
1168	W	Α	V4
1410	mw	B?	impurity
1727.7	ms	A	V ₃
1758.0	m	A	$v_{17} + v_{18}$
1805	vw	В	$v_{16} + v_8$
2179.0	m	В	V14
2202.3	ms	Ą	V ₂
2239.5	w	A	hot band
2241.7	s	A	ν_1
2315.2	s	<u>C</u>	V ₂₀
2321.1	S	B	V ₁₃
3038	mw	Α	impurity

*Frequency units are cm⁻¹.

TABLE 4

Symmetry co-ordinate description of the normal modes

v ₁	A ₁ Symmetric ethylenic stretch
ν ₂	A ₁ Symmetric methylenic stretch
ν ₃	C=C Stretch
V4	A ₁ Methylenic deformation
ν ₅	A ₁ Ethylenic deformation
V ₆	A ₁ Ring stretch
V ₇	A ₁ Methylenic wag
V ₈	A ₁ Ring deformation
Vg	A ₂ Methylenic stretch
v_{10}	A_2 Methylenic twist
V11	A ₂ Methylenic rock
V12	A_2 Ethylenic torsion
v ₁₃	B ₁ Asymmetric ethylenic stretch
V14	B_1 Symmetric methylenic stretch
V15	B ₁ Methylenic deformation
V16	B ₁ Ethylenic rock
V17	B ₁ Methylenic wag
V18	B ₁ Ring deformation
V19	In-plane C=C-C deformation
V ₂₀	B ₂ Asymmetric methylenic stretch
V21	B_2 Methylenic twist
V22	Ethylenic wag
V23	B ₂ Methylenic rock
V24	Out-of-plane C-C-C deformation

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FIG. 5. The i.r. spectrum (solid line) of C_4H_6 gas, between 2920 and 3140 cm⁻¹, at about 34 °C, 10 cm path length. The dashed lines represent our proposed separation of the bands into A-, B-, and C-type contours.

1390 to 1450 cm^{-1} (Fig. 6), which is not consistent with there being just two A_1 fundamentals plus two A_1 hot bands in this region. Further, the Raman line at 1411.0 cm⁻¹ (Fig. 1) is depolarized, suggesting the presence of a non-A₁ vibration at this frequency, in addition to the A_1 vibration observed in the i.r. Further, in the spectrum of the liquid (Fig. 4), there is a clearly separated band at 1397 $\rm cm^{-1}$, in addition to bands corresponding to the A_1 features. We therefore assign the 1410 cm^{-1} B-type i.r. band to the B₁ methylenic deformation. The in-phase and out-of-phase methylenic deformations are therefore separated by 27 cm^{-1} , which is similar to the separation in ethylene oxide (24) and cyclopropane (1, 5)(20 and 41 cm^{-1} respectively).

In cyclopropane, the a_2' and e' methylenic wags are assigned at 1070 cm⁻¹ and 868 cm⁻¹ respectively (5). The A₁ wag in C₄H₆ corresponds more clearly to the e' mode in C₃H₆ and the B₁ wag to the a_2' mode. Therefore we expect the B₁ methylenic wag to occur at a higher frequency than the A₁ wag (1002.6 cm⁻¹). The B-type band at 1125.3 cm⁻¹ is therefore assigned to the B₁ methylenic wagging vibration, v_{17} , and the B_1 ethylenic rocking vibration, v_{16} , can only be assigned to the band at 1354.4 cm⁻¹. This is a high frequency for such a vibration, but this assignment appears to be forced on us. There is a weak B-type band at ~ 1244 cm⁻¹ that was considered to possibly arise from the ethylenic rock, but it is absent in the spectrum of the liquid, and seems unlikely to arise from a fundamental transition.

The B₂ methylenic twisting and rocking vibrations give rise to two C-type features at 1073 cm⁻¹ (Figs. 2 and 7) and 748.6 cm⁻¹ (Fig. 2). The relative positions of these motions have been established unambiguously in cyclobutane (25) and in studies on solid cyclopropane (4), and we therefore assign the twist (v₂₁) to 1073.0 cm⁻¹ and the rock (v₂₃) to 748.6 cm⁻¹.

The two remaining i.r. active fundamentals, a B_1 in-plane, and a B_2 out-of-plane, ==CH₂ wagging vibration, have yet to be assigned. A C-type contour is observed at 279.6 cm⁻¹ with a weak B-type contour at 355 cm⁻¹ (Fig. 2). These modes are better resolved in the liquid spectrum

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v/cm^{−1}



(Fig. 4) and confirm the presence of a band centered at 355 cm^{-1} in the gas spectrum. Both modes are observed in the Raman spectrum and are depolarized (Fig. 1). The in-plane wag (v_{19}) is thus assigned to the band at 355 cm^{-1} and the out-of-plane motion (v_{24}) to that at 279.6 cm⁻¹.

The A_2 modes were not observed in this work.

(c) Assignment of C_4D_6

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(i) C-D Stretching Vibrations

These occur between 2340 and 2160 cm⁻¹ (Fig. 9) and can be assigned by direct comparison with the assignment of the light compound as: B₁ ethylenic stretch, v_{13} , 2321.1 cm⁻¹; B₂ methylenic stretch, v_{20} , 2315.2 cm⁻¹; A₁ ethylenic stretch, v_1 , 2241.7 cm⁻¹; A₁ methylenic stretch, v_2 , 2202.3 cm⁻¹; B₁ methylenic stretch, v_{14} ,

2179.0 cm⁻¹. The A_2 methylenic stretch was not observed.

v/cm⁻¹

(ii) C=C Stretching Vibration

As in the spectra of C_4H_6 , two A_1 features are found in the i.r. at 1758.0 and 1727.7 cm⁻¹ (Fig. 3) and in the Raman (Fig. 1). The higher frequency band is weaker in both the i.r. and Raman and may be due to a combination of two intense B-type modes at 1017 and 735 cm⁻¹, enhanced by Fermi resonance. We thus assign v_3 , C=C stretch, to 1727.7 cm⁻¹. The shift of this mode on deuteration (1742.2 to 1727.7 cm⁻¹) is remarkably small, but these assignments appear to be the most reasonable for each compound. If 1742.2 cm⁻¹ is accepted for C_4H_6 , the C_4D_6 frequency may be expected at about 1660 cm⁻¹, and there is clearly no band of significant







FIG. 7. The i.r. spectrum (solid line) of C_4H_6 gas, between 970 and 1150 cm⁻¹, at 34 °C, 10 cm path length. The dashed lines represent our proposed separation of the two A-type contours between 970 and 1060 cm⁻¹. The C-type band at 1073 cm⁻¹ and the B-type band at 1125 cm⁻¹ are self-evident.



FIG. 8. The i.r. spectrum (solid line) of C_4H_6 gas, between 820 and 960 cm⁻¹, at 34 °C. 10 cm path length. The dashed lines represent our proposed resolution of the band into a B- and a C-type contour.

intensity in that region. Conversely, if 1727.7 cm^{-1} is accepted for C₄D₆, the C₄H₆ frequency would be expected near to 1810 cm⁻¹. While weak bands do occur in this region it does not seem reasonable to prefer them to the strong 1742.2 cm⁻¹ band for this assignment.

(iii) The Ring Vibrations

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By analogy with C_4H_6 we assign the feature at 900 cm⁻¹ (Fig. 1), the most intense Raman band, to the ring breathing mode, v_6 . There is a somewhat imperfect A-type band in the i.r. at 895 cm⁻¹ (Fig. 3), consistent with this assignment. The A₁ ring deformation (v_8) is assigned to the well-defined A-type i.r. band at 637.0 cm⁻¹, which is nearly coincident with a partly polarized Raman band. The B₁ ring deformation (v_{18}), is assigned to the only B-type i.r. band between the two A₁ frequencies, at 735 cm⁻¹.

(iv) The CD_2 Deformation Vibrations

We must assign an A_1 deformation, an A_2 torsion, a B_1 rock, and a B_2 wag for the ethylenic group, and an A_1 and a B_1 deformation, an A_1 and a B_1 wag, an A_2 and a B_2 twist, and an A_2 and a B_2 rock for the methylenic groups.

There are clearly C-type bands (Fig. 3) at 537.5 cm^{-1} , 705.0 cm^{-1} , 835.5 cm^{-1} , and 882 cm^{-1} . The strongest of these bands, at 705.0 cm^{-1} is assigned to the ethylenic wagging mode (v_{22}) , which usually yields strong i.r. absorption, at any rate in non-deuterated ethylenes (20, 21), and does so in C₄H₆ (see Discussion, section *b*, *iv*). For the same reasons as in C₄H₆ (Discussion, section *b*, *iv*) we assign the lower frequency band, 537.5 cm^{-1} to the methylenic rock (v_{23}) and we assign the B₂ methylenic twist (v_{21}) to the more intense of the remaining C-type bands, at 835.5 cm^{-1} .

The three B_1 modes must be assigned to the three B-type bands, at 1122, 1073, and 1017 cm⁻¹ (Figs. 3 and 10). The 1122 and 1073 cm⁻¹ bands are assigned to the B_1 methylenic deformation (v_{15}) and the ethylenic rock (v_{16}) respectively. This assignment yields a 20.5 and 20.7% respectively isotope shift on deuteration. The 1017 cm⁻¹ feature must then be assigned to the B_1 methylenic wagging mode (v_{17}) . This assignment implies a surprisingly small isotope shift of 9.6% for this mode, compared with 19.8% for the A_1 methylenic wag. However, the product rule is

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FIG. 9. The i.r. spectrum of C_4D_6 gas, between 2140 and 2380 cm⁻¹, at about 34 °C, 10 cm path length. The dashed lines represent our proposed separation of the bands into A-, B-, and C-type contours.

well satisfied by this assignment, and there is no viable alternative.

The three A₁ modes are less easy to assign confidently. The remaining A-type bands in the i.r. spectrum are all very weak (Figs. 3 and 10), and we must use the Raman polarization data as an aid to assignment. There are weak A-type infrared bands at 1168 (Fig. 10), 1139 (Fig. 10), and 804.2 cm⁻¹ (Fig. 3), all of which correspond to polarized Raman lines. There are also two Q branch lines at 1043 and 1047 cm⁻¹ which can best be separated into a C-type band at 1047 cm⁻¹ and an A-type band at 1043 cm^{-1} (Fig. 10). There is a partly polarized Raman band at 1048 cm^{-1} which could arise from overlapping A- and C-type bands, or could arise from a single A-type band. The i.r. Q branches at 1047 and 1043 cm^{-1} could be assigned as an A-type band plus a hot band. At any rate there is clearly an A-type band at 1043 or 1047 cm^{-1} , or both.

The 804.2 cm⁻¹ band is assigned to the A_1 methylenic wag (v_7) and the A_1 methylenic deformation (v_4) is assigned to the 1168 cm⁻¹ band. In cyclopropane (5) and ethylene oxide (24)

the symmetric methylenic deformation is strong in the Raman of the deuterated derivative, in contrast with its Raman intensity for the light species, perhaps because of coupling with the symmetric ring stretching mode. The occurrence of the same Raman intensity change supports the assignment of the symmetric CH_2 deformation at 1436.5 cm⁻¹ in C₄H₆ and 1168 cm⁻¹ in C₄D₆.

The A₁ ethylenic deformation can be assigned to the A₁ bands at 1139 cm⁻¹ or at 1043 cm⁻¹. We prefer to assign it to the 1139 cm⁻¹ band because of (a) the large isotopic shift (26%) if we assign it at 1043 cm⁻¹ (compared to 21% in propylene (26)), and (b) there being no clear explanation of the 1139 cm⁻¹ feature in terms of combinations, while the 1043 cm⁻¹ band can be assigned as $v_{19} + v_{18}$, which is expected at 1039 cm⁻¹. However, as will be seen in section 4d this assignment does not fit the product rule well, while assigning the A₁ ethylenic deformation to 1043 or 1047 cm⁻¹ does fit the product rule well.

No evidence as to the frequencies of the A_2 modes was obtained.

The two remaining modes, the in-plane (B_1)



FIG. 10. The i.r. spectrum of C_4D_6 gas, between 980 and 1180 cm⁻¹ at about 34 °C, 10 cm path length. The dashed lines represent our proposed separation of the band into A-, B-, and C-type contours.

(v_{19}), and out-of-plane (B_2) (v_{24}), wagging of the =CD₂ group are observed as the weak B-type band at 304 cm⁻¹, and the medium C-type band at 240 cm⁻¹ respectively.

(v) Impurity Bands

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The i.r. bands at 3030 and 1410 cm⁻¹ and the Raman band at 946 cm⁻¹ can not be readily assigned to C_4D_6 and are believed to arise from impurities. Because of these bands, and because of some very small isotopic shifts implied by the above assignments, we examined our C_4D_6 carefully for impurities (see Experimental), and have found no evidence for any impurity other than 18% or less of C_4D_5H . Further study of C_4D_6 was prevented by the very limited supply of sample, and the considerable difficulty of making more.

(d) Product Rule

The "product rule" for the A_1 modes, using the above assignment is 4.71 (5.33 theoretical). This implies either (1) large anharmonic effects influence the frequencies of the A_1 modes or (2) a

wrong assignment. The latter may be the more likely, because the product rule factor becomes 5.2 if v_5 is assigned at 1047 cm⁻¹ in C₄D₆ instead of at 1139 cm⁻¹. However this assignment leaves the more intense 1139 cm⁻¹ band unassigned and creates anomalies in the relative frequencies of the different CD₂ deformation modes in C₄D₆. We regard the assignment of v_5 in C₄D₆ as uncertain between these two options.

The agreement between the observed and calculated values in the B_1 block is satisfactory, 4.55 and 4.76 respectively. This is within the usual range of anharmonic effects, and supports the assignment above.

In the B₂ block the observed "product rule" is 3.46 vs. 3.39 calculated. This implies an overall small negative anharmonicity. The ethylenic wagging mode has been shown to have a negative anharmonicity in asymmetrically disubstituted ethylenes (20) and it is reasonable to suppose that the other out of plane motion (v_{24}) will behave similarly to give the small net negative anharmonicity required to fit the product rule exactly.

We thank Dr. R. J. Crawford for the C_4D_6 and for some of the C₄H₆ used in this study. Mr. R. S. Swindlehurst recorded the n.m.r. spectra. The work was supported by the National Research Council of Canada.

1. A. W. BAKER and R. C. LORD. J. Chem. Phys. 23, 1636 (1955).

- 1636 (1955).
 P. M. MATHAI, G. G. SHEPHERD, and H. L. WELSH. Can. J. Phys. 34, 1448 (1956).
 Hs. H. GUNTHARD, R. C. LORD, and T. K. MCCUB-BIN, JR. J. Chem. Phys. 25, 768 (1956).
 C. BRECHER, E. KRIKORIAN, J. BLANC, and R. S. HALFORD. J. Chem. Phys. 35, 1097 (1961).
 J. L. DUNCAN and D. C. MCKEAN. J. Mol. Spec-trosc. 27, 117 (1968).
 J. B. BATES, D. E. SANDS, and W. H. SMITH. J. Chem. Phys. 51, 105 (1969).
 L. H. DALY and S. E. WIBERLEY. J. Mol. Spectrosc. 2, 177 (1958).

- 177 (1958).
 L. M. SVERDLOV, N. P. KRAINOV, and N. I. PROKO-FEVA. Fiz. Probl. Spektrosk. Akad. Nauk. S.S.S.R., Mater. Soveshch., Leningrad, 1, 363 (1960); Chem.
- Mater. Sovesnein, Leningrad, 1, 363 (1960); Chem. Abstr. 59, 12303a.
 W. G. ROTHSCHILD, J. Chem. Phys. 44, 3875 (1966).
 H. E. SIMMONS, E. P. BLANCHARD, and H. D. HARTZLER. J. Org. Chem. 31, 295 (1966), and references quoted therein. Also W. G. ROTHSCHILD. J. Chem. Phys. 44, 1712 (1966).
 R. J. CRAWFORD and D. M. CAMERON. J. Amer. Chem. Soc. 99, 2580 (1966).
- Chem. Soc. 88, 2589 (1966).
 12. J. T. GRAGSON, K. W. GREENLEE, J. M. DERFER, and C. E. BOORD. J. Amer. Chem. Soc. 75, 3344 (1953).

- E. J. BLAU. University Microfilms. Mic. 58-730: 1953. Ph.D. Thesis, Ohio State University, Colum-
- bus, Ohio, 1953.
 W. B. LOEWENSTEIN. University Microfilms. Mic. 60–82. Ph.D. Thesis, Ohio State University, Columbus, Ohio, 1954.
 I.U.P.A.C. Tables of wavenumbers for the calibration of infrared energy Physics. Butterworthe Scientific
- of infrared spectrometers. Butterworths Scientific Publications, Ltd., London, 1961.
- G. HERZBERG. Infrared and Raman spectra. D. Van 16.
- Nostrand Company, Inc., New York, 1945. V. W. LAURIE and W. M. STIGLIANI. J. Amer. Chem. Soc. 92, 1485 (1970). T. UEDA and T. SHIMANOUCHI. J. Mol. Spectrosc. 17.
- 18. 28, 350 (1968).
- J. O. HALFORD. J. Chem. Phys. 24, 830 (1956); P. VON R. SCHLEYER and R. D. NICHOLAS. J. Amer. 19. Chem. Soc. 83, 182 (1961).
- 20. N. SHEPPARD and D. M. SIMPSON. Quart. Rev. 6, 1 (1952).
- 21. W. LUTTKE and S. BRAUN. Ber. Bunsenges. 71, 34
- W. LUTRE and S. BRAUN. Ber. Builsenges. 71, 34 (1967).
 P. TORKINGTON. J. Chem. Phys. 17, 1279 (1949).
 R. MEYER and Hs. H. GUNTHARD. Spectrochim. Acta, 23 (A), 2341 (1967).
 R. C. LORD and B. NOLIN. J. Chem. Phys. 24, 656
- (1956).
 25. R. C. LORD and D. G. REA. Unpublished; cited by R. C. LORD and I. NAKAGAWA. J. Chem. Phys. 39,
- 2951 (1963), and in ref. 1. R. C. LORD and P. VENKATESWARLU. J. Opt. Soc. Amer. 43, 1079–1085 (1953). 26.