

RAMAN EFFECT IN CERTAIN DERIVATIVES OF CYCLOHEXANE.

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INTRODUCTION.

It is well known that the ortho-, meta- and para-xylenes show different Raman Spectra. H. Mlodzianovska (*Zeit. f. Physik.*, 1930, 65, 124) investigated the influence of the position of groups in a series of disubstituted benzene derivatives on the Raman Spectra and has shown that some of the frequencies are common to all the isomerides, some to ortho and meta, meta and para or ortho and para and some are peculiar to each isomeride. Ganesan and Thatte (*Zeit. f. Physik.*, 1931, 70, 131) have obtained identical Raman Spectra with the ortho-, meta- and para-toluidines, in contradiction with the results of H. Mlodzianovska in the three toluidines. Recently M. E. High (*Phys. Rev.*, 1931, 38, 1837) has shown in four such series of isomers, a regular increase in the value of the lower frequencies in the order ortho, meta and para.

The purpose of the present investigation is to study the Raman Spectra of the ortho-, meta- and para-compounds in order to see whether the position of the substituted groups influences the Raman Spectrum of a molecule. For this, compounds belonging to the cyclohexane series were chosen because they were free from such troubles as the discolouration due to exposure to light or the photochemical decomposition such as occurring in the toluidines; etc.

The following table gives the physical properties of the substances investigated. The densities and refractive indices were determined at 25° and 30° calculated for 20° in order to compare with the figures given in literature (Landolt Börnstein & International Critical Tables).

Ganesan and Venkateswaran (*Ind. Jour. Phys.*, 1929, 4, 195) and Petrikaln and Hochberg (*Phys. Chem.*, 1929, B. 3, 226) have examined the cyclohexane and the latter authors have examined the cyclohexanol also in an incomplete manner. During the progress of this work J. Weiler (*Z. Physik.*, 1931, 69, 586) published his results on the Raman Spectra in cyclohexane and cyclohexene.

Since the completion of our work, the Raman Spectra of cyclohexane and some of its derivatives have been examined by Krishnamurti (*Ind. Jour. Phys.*, 1932, 6, 543), Godchot and co-workers (*Comptes Rendus*, 1932, 194, 176 and 1574) and Wood and Collins

TABLE I.

	D _{20/4}		N _{D20}		B.P. (685 mm.)
	Authors	Literature	Authors	Literature	
Cyclohexane	0.7846	0.779	1.4244	1.427	77°·5
Methylcyclohexane ..	0.7755	0.764	1.4231	1.423	97°·0
<i>m</i> -Dimethylcyclohexane	0.7768	0.771	1.4242	1.429	117°·5
Cyclohexene	0.8349	0.810	1.4454		81°·0
Cyclohexyl acetate ..	0.9669		1.4417		87° (35 mm.)
Cyclohexyl propionate ..	0.9539		1.4403		93° (35 mm.)
Cyclohexanol	0.9516	0.949	1.4654	1.4659	156°
<i>o</i> -Methylcyclohexanol ..	0.9354	0.928	1.4607	1.463	160°
<i>m</i> -Methylcyclohexanol ..	0.9246	0.917	1.4560	1.458	167°·5
<i>p</i> -Methylcyclohexanol ..	0.9202	0.917	1.4567	1.455	169°
Cyclohexanone	0.9665	0.949	1.4503	1.4526	70° (45 mm.)
<i>o</i> -Methylcyclohexanone	0.9325	0.930	1.4477		67° (23 mm.)
<i>m</i> -Methylcyclohexanone	0.9184	0.914	1.4460		70° (25 mm.)
<i>p</i> -Methylcyclohexanone	0.9171	0.912	1.4441		68° (23 mm.)

(*Phys. Rev.*, 1932, 42, 386), that of cyclohexane by Wood and Collins (*loc. cit.*) and Morris (*Ibid.*, 1931, 38, 141). The work of these authors is more or less in agreement with ours.

Recently Miller and Piaux (*Compt. Rend.*, 1933, 197, 412) have investigated the Raman Spectra of the *cis* and *trans* space isomers of ortho-dimethyl cyclohexane prepared by fractionating the product of hydrogenation of orthoxylene. The derivatives examined by us are probably mixtures of *cis* and *trans* compounds. All these authors have obtained Raman lines only with the 4046 and 4358 mercury lines. In this investigation, Raman lines with the 3125, 3131, and the triplet 3650, 3654 and 3662 mercury lines have been obtained for cyclohexane, methylcyclohexane, methylcyclohexanol and cyclohexene by using quartz tube.

The spectrograph used was Hilger's E 316. The letters used in the tables indicate the exciting mercury lines as given in the following table:

TABLE II.

Wave-lengths and symbols of the mercury arc lines.

Wave-length in Å	Wave-number cm. ⁻¹	Symbol
4358.3	22938	a
4347.5	22995	b
4339.2	23039	c
4077.8	24516	d
4046.6	24705	e
3662.9	27293	f
3654.8	27353	g
3650.2	27388	h
3341.6	29917	A
3131.6	31923	B
3125.6	31985	C
3021.6	33085	D
2967.2	33692	E

The Raman frequencies of the different cyclohexane derivatives are given in the following tables with their intensity and exciting lines shown within brackets, the data obtained by other workers being also shown for comparison.

TABLE III.
Cyclohexane.

Petrikaln and Hochberg ¹	Ganesan and Venkateswaran ²	Daure ³	Weiler ⁴	Authors
..	383(0) (ae)	..	365(0) (ae)	393(1) (ae)
..	420(0) (ae)	430(ae)	424(0) (ae)	431(1) (aef)
..	478(0) (e)
..	608(0) (ae)
801(5) (ae)	800(4) (abcde)	800(ae)	803(4) (ade)	808(6) (abcdefghBC)
895(1) (a)	896(0) (e)	..
925(1) (a)
..	971(0) (a)	..
..	992(2) (abcde)
1030(4) (ae)	1028(2) (ade)	1030(ae)	1029(2) (acde)	1036(5) (abegABC)
1082(5) (a)
1162(5) (a)	1157(1) (ae)	1160(ae)	1156(1) (abde)	1162(2) (deh)
1267(4) (ae)	1268(3) (ae)	1270(ae)	1263(1) (ade)	1270(5) (efghABC)
1350(4) (a)	1346(2) (ae)	1360(ae)	..	1354(2) (eAC)
1442(4) (ae)	1445(3) (ace)	1440(ae)	1444(1) (ace)	1448(5) (aefhABC)
..	..	2660(ae)	..	2675(2) (e)
..	..	2700(ae)
2867(5) (ae)	2853(4) (adefh)	2860(ae)	2850(4) (adefgh)	2856(6) (adeBCD)
..	2890(1) (de)
..	2921(3) (defh)	..	2920(2) (adefgh)	..
2944(4) (ae)	2935(3) (adefgh)	2931(ae)	2941(2) (adefgh)	2938(6) (adefghBD)

¹ Petrikaln and Hochberg, *Zeit. f. Phys. Chem. B.*, 1929, 3, 217 and 405.

² Ganesan and Venkateswaran, *Ind. Jour. Phys.*, 1929, 4, 196.

³ Daure, *Annales de Phys.*, 1929, 12, 375.

⁴ Weiler, *Zeit. f. Physik.*, 1931, 69, 586.

TABLE IV.
Cyclohexene.

Lespieau and Bourguel ⁵	Weiler ⁶	Authors
..	173(0) (a)	..
..	292(0) (ae)	..
396(a)	393(1) (ace)	400(3) (aB)
..	..	467(1) (a)
..	494(1) (alce)	501(1) (aefg)
..	649(0) (ae)	651(1) (aefh)
..	731(0) (e)	735(1) (aeg)
825(a)	826(4) (abcde)	832(5) (abcdeghBC)
..	879(1) (ade)	883(2) (aegh)
..	905(1) (ae)	909(2) (ae)
..	963(1) (ade)	969(2) (aehABC)
1029(a)	1036(1) (ade)	1043(0) (ef)
1072(a)	1058(1) (ade)	1072(3) (aefhABC)
..	..	1144(1) (e)
1219(a)	1220(1)	..
..	..	1231(4) (aeABC)
1276(a)	1266(2) (abcde)	1274(3) (egh)
..	..	1355(1) (ehC)
1429(a)	1430(2) (ae)	..
1462(a)	1448(1) (alce)	1447(4) (aefghABC)
1654(a)	1650(2) (ae)	1655(4) (aghABCD)
2807(a)	2835(3) (aefgh)	2842(2) (ehCD)
2868(a)	2862(2) (ade)	2876(1) (CD)
..	2884(2) (aef)	2887(2) (aeD)
2916(a)	2914(2) (adeh)	2919(2) (hBCD)
2944(a)	2940(2) (aefgh)	2946(5) (adeghBCD)
3024(a)	3024(3) (aefgh)	3033(4) (aefhBCDE)

⁵ Lespieau and Bourguel, *C. R.*, 1930, 190, 1504.

⁶ Weiler, *Zeit. f. Physik.*, 1931, 69, 586.

TABLE V. *Raman Spectra of Cyclohexane and its Derivatives.*

Cyclohexene	Cyclohexane	Methylcyclohexane	m-Dimethylcyclohexane	Cyclohexanol	o-Methylcyclohexanol	m-Methylcyclohexanol
400(8)	393(3)					
	431(3)	414(2)	427(4)			426(4)
467(3)		454(2)			443(2)	457(4)
501(3)						
		551(2)	549(5)	558(2)	522(6) 575(2)	551(4)
651(3)						
735(3)	808(10)	773(10)	767(7)	798(8)	768(6)	773(6)
832(10)		848(4)	847(3)	853(2)	843(2)	
883(4)		895(4)				
909(4)			955(2)			
969(4)		972(4)	992(3)		986(4)	974(4)
1043(0)	1036(8)	1036(4)	1066(7)	1028(6)	1039(2)	1044(4)
1072(7)					1087(2)	
1144(3)	1162(3)	1165(4)	1170(6)	1147(2)	1145(4)	1151(2)
1231(0)	1270(8)	1267(4)	1223(2)	1259(6)	1254(6)	1257(4)
1274(7)			1269(3)			
1355(3)	1354(3)	1348(4)	1353(6)	1364(2)	1354(4)	1354(4)
1447(10)	1448(8)	1452(8)	1456(7)	1446(8)	1458(8)	1448(6)
1641(10)						
	2675(3)				2665(2)	
2842(4)						
2876(3)	2856(10)	2855(10)	2855(10)	2859(10)	2865(8)	2862(8)
2887(4)						
2919(4)						
2946(4)	2938(10)	2934(10)	2936(10)	2939(10)	2936(10)	2933(10)
3033(4)						

TABLE V. Raman Spectra of Cyclohexane and its Derivatives.—(Contd.)

<i>p</i> -Methyl cyclohexanol	Cyclohexyl acetate	Cyclohexyl propionate	Cyclohexanone	<i>o</i> -Methyl cyclohexanone	<i>m</i> -Methyl cyclohexanone	<i>p</i> -Methyl cyclohexanone	Vibrator
		269(2)					
	303(4)	304(2)	314(2)	312(2)			
394(2)				411(2)	400(3)	386(6)	
			423(4)				
482(4)		462(2)					
			499(2)		511(3)	500(6)	
	559(2)			577(5)			
649(2)			656(6)	663(8)	641(8)	692(4)	
779(6)	806(6)	806(6)	756(6)	725(8)	751(8)	750(8) 808(4)	Ring
			843(6)	843(5)	827(5)		
	901(2)	910(2)			883(3)		
	970(2)		955(2)	988(5)	961(5)		
1051(4)	1033(6)	1032(4)	1030(6)	1053(3)	1051(3) 1086(3)	1013(6) 1088(4)	
1151(2)	1164(2)	1160(2)	1131(4)	1133(3)	1120(5)	1125(4) 1191(2)	
1228(4) 1252(2)	1264(4)	1264(4)	1230(2) 1266(2)	1254(2)	1219(5) 1271(3)	1248(2)	
1359(4)	1348(2)	1369(2)	1322(4) 1362(2)	1317(5)	1333(5)	1321(2)	
1457(6)	1450(6)	1449(6)	1451(8)	1451(8)	1425(3) 1458(8)	1463(6)	CH ₂
			1714(8)	1712(8)	1708(8)	1715(6)	C=O ketone C=O ester
	1742(2)	1733(2)					
2862(8)	2865(8)	2863(8)	2869(10)	2859(10)	2872(8)	2879(0)	C ₆ H ₁₁ → H
2944(5)	2939(10)	2943(10)	2957(10)	2943(8)	2947(10)	2955(8)	C → H ≥ C → H

DISCUSSION.

The results are summarised in Table V. In the following discussion attempt has been made to identify the prominent Raman lines with the vibrations of the linkages taking into consideration data obtained under the same conditions of dispersion and resolution. The more detailed discussion can be made only after preparing these compounds in a pure condition and using a spectrograph with a higher dispersion.

According to Sacshe-Mohr multiplaner strainless ring structure cyclohexane can exist as a *chair* and a *cradle* form which will create two differently situated C-H linkages. This fact taken along with the *cis-trans* isomerism in the disubstituted derivatives shows the complexity of the problem and is probably the cause of disagreeing physical data of these substances. Because of the possibility of isomerism the study of Raman Spectra of cyclohexane compounds is considerably more interesting than the corresponding study of benzene derivatives. The strong frequency 3060 in benzene due to aromatic C-H linkage is absent in all the compounds and two prominent frequencies 2850 and 2950 due to aliphatic C-H are present. These two frequencies may be due to the vibration of C→H and C₆H₅→H with the same value for the binding energy. In cyclohexene the frequency 2850 is split up into three components 2835, 2868 and 2882 and the second frequency 2930 is split up into two components 2919 and 2946, the increased number of frequencies being due to the presence of C=C in the ring creating two differently placed C-H linkages. Besides aliphatic C-H frequencies present in cyclohexene, a strong line also appears at 3033 which may be identified as due to the H-C≡ linkage. This frequency is not due to the aromatic C-H because it is also present in amylene.

The frequency 1450 originating from the transverse vibration of C-H in CH₂ is strongly present in all the compounds. In cyclohexene a strong frequency appears at 1655 originating from the C=C linkage. The two esters cyclohexyl acetate and propionate show a frequency at 1735 which is due to C=O group in esters. The cyclohexanone and ortho-, meta- and para- methyl cyclohexanones show a strong frequency at 1705 which is due to the presence of the C=O group in a ketone. The C=O frequency in esters has a higher value than the C=O frequency in ketones (*cf.* Dadiou and Kohlrausch, *Ber.*, 1930, 63, 251).

The shifts 1100–1450 which are usually regarded as due to transverse oscillation of hydrogen show the characteristics of *cis* and *trans* isomers in the ortho-dimethyl cyclohexane investigated by Miller and Piaux (*loc. cit.*), 1164 cm.⁻¹ and 1355 cm.⁻¹ being characteristic of *trans* and 1260 cm.⁻¹ and 1053 cm.⁻¹ of *cis*. It is interesting to note that in cyclohexane 1164 and 1355 have the same intensity while 1260 goes with 1036 cm.⁻¹ although the latter is regarded as due to C-C vibration.

It appears that the compounds isolated by Miller and Piaux are more likely to be the 'cradle' and 'chair' forms of the cyclohexane derivative rather than being space isomers.

The large number of frequencies in cyclohexene in the range 1100-1400 is due to the transverse vibrations of α and β C-H with respect to C=C present in this compound. The occurrence of similar frequencies in terpenes is due to the same cause and will be discussed in a later paper.

A strong frequency at about 800 is characteristic of the oscillation of a closed ring. Its values in different compounds are :

(1) Cyclohexane	808
(2) Methylcyclohexane	773
(3) <i>M</i> -Dimethyl cyclohexane		..	767
(4) Cyclohexene	832
(5) Cyclohexyl acetate	806
(6) Cyclohexyl propionate	806

In all the compounds there is a large number of frequencies, between approximately 200 and 1300 which are apparently due to the vibrations of carbon chains C-C, C-C-C, C-C-C-C and so on. This region is especially rich in lines in cyclohexene which may be due to the additional vibrations of the C=C against the rest of the carbon chains. The frequencies from 600-1300 may be due to the oscillations between the C-C bonds and those from 200-600, due to the C-C-C bonds.

Comparison of the ortho-, meta- and para-compounds. Methylcyclohexanols.

In methylcyclohexanols the frequencies higher than 1000 are all common to the three isomers. Moreover, the values of these frequencies for cyclohexanol also are the same as given below :

TABLE VI.

Cyclohexanol	Ortho-methyl-cyclohexanol	Meta-methyl-cyclohexanol	Para-methyl-cyclohexanol	Vibrator
1028	1039	1044	1051	C—C
1147	1145	1151	1151	
1259	1254	1257	1252	
1364	1354	1354	1359	—CH ₂ —
1446	1458	1448	1457	
2859	2865	2862	2862	C—H
2939	2936	2933	2944	

This shows that the higher frequencies in this series do not change in value to a measurable extent even if we pass from the cyclohexanol to the next member, methylcyclohexanol. The position of the substituted groups also does not influence the values of these frequencies.

The frequencies of the OH group.

In the cyclohexanol and methyl cyclohexanols, the OH group vibrates against the rest of the molecule giving rise to a particular frequency. The following are the values for these frequencies in different compounds, and A_0 the heat of dissociation of the R-OH linkage calculated from these frequencies.

		Observed frequency	Calculated A_0
(1)	Cyclohexanol ..	798	105.5
(2)	Ortho-methylcyclohexanol ..	768	100.5
(3)	Meta-methylcyclohexanol ..	773	101.7
(4)	Para-methylcyclohexanol ..	779	103.5

The heat of dissociation is of the same order as for aliphatic alcohols and the values are in harmony with the fact that orthosubstituted cyclohexanols are much more rapidly dehydrated than the corresponding para compounds (Vavon and Barbier, *Bull. Soc. Chim.*, 1931, (4) 49, 567).

The position of the substituted groups exerts an influence on the value of frequencies lower than 700, showing a regular increase in the values as we go from ortho to meta and meta to para as can be seen below:

(1)	Ortho-methylcyclohexanol ..	443	522
(2)	Meta-methylcyclohexanol ..	457	551
(3)	Para-methylcyclohexanol ..	482	649
(4)	Ortho-methylcyclohexanone ..	312	577
(5)	Meta " " ..	400	641
(6)	Para " " ..	500	692

Methylcyclohexanones.

In the methylcyclohexanones the frequencies can be classified into three groups:

- (i) Frequencies appearing in all three isomers.
- (ii) Frequencies appearing in any two either ortho and meta or meta and para or ortho and para compounds.
- (iii) Frequencies appearing only in one isomer.

All these frequencies in the three methylcyclohexanones along with the cyclohexanone are classified in the following table:

TABLE VII.
Classification of Frequencies of the Cyclohexanones.

Cyclohexanone	Ortho-methyl-cyclohexanone	Meta-methyl-cyclohexanone	Para-methyl-cyclohexanone	Vibrator
314	312			
423	411	400	386	C-C-C
499	577	511	500	
656	663	641		
756	725	751	692	
		827	750	
843	843		808	
955		883		C-C
	988	961		
1030			1013	
	1053	1051		
1081		1086	1088	
1131	1133	1120	1125	
1230		1219	1191	
	1254		1248	
1266		1271		
1322	1317	1333	1321	-CH ₂ -
1362		1425		
1451	1451	1458	1463	
1714	1712	1708	1715	C=O
2869	2859	2872	2879	C-H
2957	2943	2947	2955	

Recently L. Piaux (*Compt. Rend.*, 1933, 197, 1647) has reported on the Raman Spectra of *o*, *m* and *p* methylcyclohexanones. He attributes the absence of lines between 1600–1700 cm.⁻¹ to the small proportion of enolic forms in the ketones.

In a general way the Raman lines are in harmony with the fact that the chemical characteristics of cyclohexanones are closely parallel to aliphatic ketones.

Comparison with the Infra-red data.

In the following table, the frequencies of the Raman lines corresponding to those known infra-red spectra (J. Lecomte, *Compt. Rend.*, 1926, 183, 27) are given for comparison:

TABLE VIII.

Raman. Infra-red.

Cyclohexane		Methyl Cyclohexane		<i>m</i> -Dimethyl cyclohexane		Cyclohexanol	
3.40	3.26	3.41	3.16	3.41	3.16	3.40	3.15
3.50	3.60	3.50	3.58	3.50	3.62	3.5	3.5
3.74	3.90						
6.91	6.97	6.89	6.97	6.87	6.97	6.92	7.00
7.39	7.56	7.43	7.40	7.39	7.40	7.34	7.48
7.87	8.2						
9.69	9.6						

Cyclohexanone		Cyclohexene		Cyclohexyl acetate	
3.38	3.03	3.30	3.26	3.40	3.03
3.49	3.60	3.52	3.58	3.49	3.6
5.84	5.93	6.04	6.22	5.74	5.90
6.89	6.97	6.92	7.00	6.90	6.87
7.35	7.10	7.39	7.35	7.43	7.43
7.57	7.57	7.86	7.68	7.92	7.98
7.91	7.77				

Lecomte found in these compounds two strong zones of absorption at 3.5μ and 7μ separated by a region of feeble absorption, composed of feeble intensity bands. "In passing from benzene compounds to cyclohexane derivatives the two principal bands 3.3μ and 6.8μ (in benzene) become longer 3.6 and 6.97μ (in cyclohexane) and 7.00μ (in cyclohexene). Introduction of methyl group makes the band 7.40μ appear very strongly. The groups CO, OH and CO in cyclohexanone; cyclohexanol and its acetate render the spectrum very simple, the feeble bands at 3.5μ and 6.5μ being entirely suppressed."

SUMMARY.

In all the derivatives of cyclohexane, the C-H bond appears in the same position as in aliphatic compounds. In general the frequencies in the region 600-1300 are identified with the C-C bonds and those from 200-600 with the C-C-C bonds.

In the methylcyclohexanols, frequencies higher than 1000 are common to all three isomers, but the smaller shifts show a regular increase in their values in the order ortho, meta and para.

The methylcyclohexanones, in addition to the individual characteristic frequencies, show as in the methylcyclohexanols a regular gradation in the smaller shifts 200-700 and are further distinguished by some frequencies which are common to ortho and meta, meta and para, and ortho and para.

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