

THE RAMAN SPECTRA OF SOME SIMPLE MOLECULES.

(Dimethyl Ether, Phosgene, *n*-Butane, Ethylene Diamine, Ethylene Glycol, Ethylene Dichloride, Ethylene Dibromide, Acetylene Tetrachloride, Acetylene Tetrabromide and Hexachloroethane.)

BY R. ANANTHAKRISHNAN.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received March 7, 1937.

(Communicated by Sir C. V. Raman, Kt., F.R.S.; N.L.)

1. Introduction.

THE results reported in the following pages are the outcome of a systematic study of the Raman spectra of certain relatively simple organic molecules which the author undertook some time back. Both from the theoretical as well as from the chemical standpoint, the importance of accurate data relating to the Raman spectra of such molecules, including the exact knowledge of the state of polarisation of the modified frequencies appearing in them, cannot be overemphasised. Although the vibrational Raman spectra of practically all the substances considered here have been repeatedly examined by previous investigators, polarisation data are lacking in many cases, where precisely such data appears to be of great importance. It was the desire to fill this existing gap that prompted the author to take up this investigation.

On the theoretical side, we are still not in a position to be able to compute the exact degree of depolarisation of a vibrational Raman line even in the case of very simple molecules. The polarisation rules enunciated by Placzek (1934) are based purely on the symmetry characters of the vibration concerned, and state that,

- (i) the degree of depolarisation ρ of those Raman lines which arise from *totally symmetric* vibrations is zero in the case of molecules possessing cubic symmetry (e.g., CH_4 , SF_6 , etc.), while for other molecules, ρ can take any value between 0 and $\frac{6}{7}$;
- (ii) all the vibrational Raman lines which pertain to those fundamental vibrations of the molecule which are *not totally symmetric* will be depolarised ($\rho = \frac{6}{7}$);
- (iii) *degenerate* vibrations are always depolarised.

We thus see that in so far as the assignment and classification of the Raman frequencies of a molecule are concerned,—barring those molecules which presumably possess cubic symmetry—it is generally more important to know whether they are polarised ($\rho < \frac{2}{3}$) or depolarised ($\rho = \frac{2}{3}$), rather than knowing the exact degree of depolarisation of the individual vibrational Raman lines. Indeed, the *exact* quantitative estimate of ρ involves extreme labour in the case of those molecules whose spectra comprise a large number of frequencies showing a wide range of intensities. The errors of photometry involved in the comparison of two lines of very different intensities are much more than those involved in the comparison of two lines of comparable intensities. For precisely the same reason, it is very often found (see Tables VI and VII) that while the quantitative estimate of the degree of depolarisation shows considerable discrepancies between different authors, the broad classification of the observed frequencies as polarised and depolarised, invariably shows very good agreement. In the present investigation, therefore, the author has followed the latter procedure, since it enables the study of a large number of substances without undue expense of time and labour. This was also the procedure adopted by the author (1936) in his investigations on the polarisation of the Raman lines of certain substances reported by him in previous papers wherein he pointed out remarkable regularities in the spectra of molecules such as $\text{H}\cdot\text{C}\cdot(\text{CH}_3)_3$, $\text{N}(\text{CH}_3)_3$, $\text{H}\cdot\text{C}\cdot\text{Cl}_3$, etc.

2. *Experimental.*

Dimethyl ether, phosgene and *n*-butane were condensed from commercial cylinders into thick-walled pyrex glass tubes of suitable size using a bath of alcohol and solid carbon dioxide; they were distilled several times in vacuum before sealing them off in the experimental tubes. The six ethane derivatives which are liquids at room temperature, and hexachloroethane which is a solid were Kahlbaum's purest chemicals. Ethylene dichloride, ethylene dibromide and acetylene tetrachloride were subjected to preliminary treatment in a fractionating column, and were subsequently distilled several times in vacuum into Wood tubes of pyrex glass (about 100 c.c. capacity) with flat end windows. Acetylene tetra-bromide was coloured light yellow, presumably due to dissolved bromine, but the distillate collected in vacuum by heating the surface of the liquid with a small flame was perfectly colourless. Glycol was distilled in a similar manner. In the case of ethylene diamine, only 5 grams of the substance were available, but there was no difficulty in photographing its spectrum.

The spectra of the liquids were photographed in the usual manner, partly on a Hilger two-prism spectrograph, and partly on a Fuess spectrograph

of larger dispersion. Hexachloroethane which is a solid at room temperature, was investigated by the technique of complementary filters. The duration of exposure varied very much from substance to substance, and was minimum in the case of the halogen derivatives of ethane which yielded very intense Raman spectra with an exposure of a few hours. In the case of $\text{Br}_2 \cdot \text{HC} \cdot \text{CH} \cdot \text{Br}_2$, the incident light was filtered by a saturated solution of NaNO_2 , to prevent decomposition of the substance. In those cases where polarisation has been studied, the liquids were illuminated by condensed light from a quartz mercury lamp, and the horizontal and vertical components of the transversely scattered radiation were photographed separately and simultaneously in the usual manner by the interposition of a double-image prism in the path of the scattered light.

3. Results.

In spite of repeated distillation, ethylene diamine and ethylene glycol were somewhat fluorescent; the spectra of the other substances, however, were absolutely free from background. The following tables give the Raman frequencies, with the estimated intensities (visual) and polarisation characters. In every case, results of recent investigations by other workers are also added for comparison.

P = polarised ($\rho \ll \frac{2}{3}$)

D = depolarised ($\rho \approx \frac{2}{3}$)

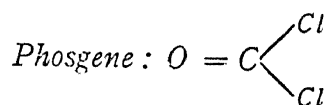
PP — indicates a line which is highly polarised, the depolarisation factor being estimated to be generally less than 20 per cent.

TABLE I.

Dimethyl ether : H₃C · O · CH₃

Dadiou and Kohlrausch (1931)	Sirkar (1932)	Author
		160 ($\frac{1}{2}b$) P
	333 (0)	300 (<i>obd</i>) P
	416 (0)	412 (<i>1b</i>) P
924 (2)	921 (2)	916 (<i>b</i>) P
	1102 (0)	1105 ?
(1150) (1)	..	1155 ($\frac{1}{2}b$) D
1452 (<i>1vb</i>)	1454 (<i>1b</i>)	1445 (<i>6vb</i>) D
2814 (5)	2814 (7)	2810 (10) P
(2862) (2)	2869 (3)	2863 (6) P
2914 (2)	2921 (3)	2916 (5) P
2953 (2)	2952 (3)	2951 (4) P
2990 (2)	2989 (3)	2986 (6) P

TABLE II.



Dadiou & Kohlrausch	$\Delta \nu$ Int.	300 5	444 4	570 10	834 $\frac{1}{2}b$	1810 4
Author	$\Delta \nu$ Int. <i>p</i>	302 6 P	442 5 D	573 10 PP	832 2 <i>b</i> D	1807 5 P

TABLE III.

n-Butane : $H_3C \cdot H_2C \cdot CH_2 \cdot CH_3$.

Bhagavantam (1931)	Murray and Andrews (1933)	Kohlrausch and Köppel (1934)	Author
..	..	220 (0) ?	..
320 (0)	338 (0)	319 ($\frac{1}{2}$)	319 ($\frac{1}{2}$) P
430 (6)	428 (3)	426 (5)	430 (5) P
793 (4)	787 (2)	785 (2)	786 (3) P
834 (10)	832 (6)	838 (8)	{ 828 (8) 837 (8) P
960 (3)	951 (1)	952 (1)	953 (2b) D
983 (3)	980 (1)	978 (1)	979 (2s) P
1060 (6)	1058 (3)	1057 (4b)	1056 (4s) P
1067 (0)	1070 (0)	..	1070 (1b) P
1146 (4)	1149 (1)	1145 (2)	1144 (3s) P
1303 (3b)	1293 (1b)	1302 (2b)	1302 (2b) D
1453 (4)	1450 (3b)	1450 (7vb)	1445 (10vb) D
2665 (1)	2670 (0)	2663 ($\frac{1}{2}$)	2663 ($\frac{1}{2}$) P
2706 (1)	2702 (0)	2705 (2)	2701 (1) P
273 (2)	2739 (1)	2733 (5b)	2730 (4) P
2864 (4)	2864 (5)	2857 (10)	2858 (10) P
2879 (8)	2879 (10)	2875 (15)	2879 (15) P
2910 (3)	2912 (3)	2908 (8)	2910 (6b) P
2938 (6)	2949 (8)	2936 (15)	2940 (12) P
2964 (3)	2963 (3)	2966 (9)	2967 (10) D ?

TABLE IV.
Ethylene diamine : $H_2N \cdot H_2C \cdot CH_2 \cdot NH_2$.

Kohlrausch and Köppl (1935)	Author	Kohlrausch and Köppl (1935)	Author
	186 ($\frac{1}{2}b$,	1346 (2)	1360 (2 <i>b</i>)
322 (00)	333 ($\frac{1}{2}b$)	1453 (5 <i>b</i>)	1445 (6 <i>b</i>)
468 (2)	467 (3)		2661 ($\frac{1}{2}b$) ?
	510 (0)	2730 ($\frac{1}{2}$)	2743 (1 <i>b</i>)
837 (3)	836 (5 <i>b</i>)	2855 (7)	2848 (10 <i>b</i> <i>d</i>)
	987 (0) ?	2891 (6)	2898 (8 <i>b</i>)
	1051 (1 <i>b</i>)	2928 (7 <i>b</i>)	2932 (8 <i>b</i>)
1092 (3 <i>b</i>)	1093 (3)	3296 (7 <i>b</i>)	3299 (8 <i>b</i>)
	1240 (0)	3362 (5 <i>b</i>)	3366 (6 <i>b</i>)
1299 (2)	1296 (2)		

TABLE V.
Ethylene glycol : $HO \cdot H_2C \cdot CH_2 \cdot OH$.

Kohlrausch and Köppl (1935)	Author	Kohlrausch and Köppl (1935)	Author
342 (00)	340 (1 <i>b</i>) P	..	1227 ($\frac{1}{2}b$) ?
478 ($\frac{1}{2}$)	475 (2) P	1258 (1)	1260 (3 <i>b</i>) D
512 (00)	520 (1) D	1457 (4 <i>b</i> ,	1450 (8 <i>b</i>) D
862 (5 <i>b</i>)	865 (8) P	2709 ($\frac{1}{2}$)	2712 (1 <i>b</i>) P
	900 (1) D	2866 (7 <i>vb</i>)	2860 (10 <i>b</i>) P
1033 (1)	1035 (2 <i>b</i>) D	2926 (8 <i>vb</i>)	2945 (10 <i>vb</i>) P
1059 (1)	1060 (2 <i>b</i>) D ?		~3400 (2 <i>vb</i>) P
1086 (2 <i>b</i>)	1090 (4) P		O-H band width ~ 300 $cm.^{-1}$

TABLE VI.
Ethylene dichloride : $Cl \cdot H_2C \cdot CH_2 \cdot Cl$.

Trumpy (1935)	Kohlrusch and Ypsilanti (1935)	Cheng (1935)	Mizushima, Morino and Noziri (1936)	Author
$\Delta\nu$ ρ	$\Delta\nu$	$\Delta\nu$ ρ	$\Delta\nu$	$\Delta\nu$ ρ
	125 (3)		124(2b)	123 (4b) D
260 ($\frac{1}{2}$) P ?	265 (2)	264 (1) 0.52	265 (1)	263 (2) P
300 (5) 0.3	301 (7)	298 (5b) 0.3	301 (5)	302 (8) P
410 (1) 0.87	410 (3)	410 (1) 0.91	412 (2)	411 (3) D
651 (10) 0.18	652 (9)	653 (5) 0.16	652 (8)	654 (10) PP
672 (1) 0.88	675 (4)	676 (2) D ?	676 (2)	675 (3) D
754 (12) 0.26	751 (12)	749 (12b) 0.41	753 (10b)	754 (15b) P
880 (0) D	875 (1)	879 (1) 0.76	878 (1)	880 (1) D
940 (3) 0.5	942 (2)	940 (1) 0.17	941 (2)	940 (2) P
		990 (0) —		
		1022 ($\frac{1}{2}$) 0.83		
	1048 (2)	1047 (1) 0.55	1050 (0)	1052 (1) P
	1143 ($\frac{1}{2}$)	1141 ($\frac{1}{2}$) 0.89	1145 (1)	1144 ($\frac{1}{2}$) D
	1205 (2)	1204 (1) 0.36	1206 (0)	1206 (2) D
	1260 (2)	1264 (0) —	1263 (1)	1262 (1) D
	1303 (4)	1300 (3) 0.29	1303 (3)	1302 (3) P
	1429 (4b)	1433 (2b) 0.8	1428 (3)	1429 (3) D
1440 (36) 0.83				1440 ($\frac{1}{2}$) D
				2844 (1) ?
	2871 (1)		2872 (0)	2872 (1) P
2953 (15) 0.15	2956 (10)	2953 (8) 0.08	2955 (8)	2956 (12b) PP
3000 (3) 0.85	3001 (5)	2998 ($\frac{1}{2}$) D	2999 (4b)	3002 (4b) D

TABLE VII.
Ethylene dibromide: $Br \cdot H_2C \cdot CH_2 \cdot Br$.

Trumpy (1935)		Kohlrausch and Yp-lanti (1935)	Cheng (1935)		Mizushima, Morino & Noziri (1936)	Author	
$\Delta\nu$	ρ	$\Delta\nu$	$\Delta\nu$	ρ	$\Delta\nu$	$\Delta\nu$	ρ
		90 (2)			90 (0b)	92 (2b)	D
189 (8)	0.29	190 (12)	187 (10b)	0.5	189 (9)	189 (10)	P
		245 (1)	235 ($\frac{1}{2}$)	0.55	232 (0b)	228 (1b)	P
		358 (3)	356 (1)	0.86	356 (1)	320 (0)	?
						358 (2)	D
						470 (0)	?
554 (3)	0.07	557 (8)	552 (5)	0.19	552 (5)	551 (8)	PP
		589 (4)	583 (2)	D?	586 (2b)	580 (2b)	D
657 (20)	0.33	660 (15b)	658 (15b)	0.43	660 (10b)	659 (15b)	P
						790 (0)	?
		843 (0)				834 ($\frac{1}{2}$)	D
		904 (1)	897 (1)	0.44	897 (0)	895 (1)	P
			934 ($\frac{1}{2}$)	0.5	930 (0b)	930 (1b)	P?
1048 (2)	D?	1057 (5)	1047 (4)	0.85	1053 (4)	1051 (6)	D
		1108 (0)	1098 ($\frac{1}{2}$)	0.89	1091 (0)	1086	??
		1178 ($\frac{1}{2}$)	1165 (0)	—		1169 ($\frac{1}{2}$)	D
						1187 (0)	D
1252 (9)	0.38	1255 (10)	1251 (10b)	0.59	1254 (6)	1256 (10b)	P
					1276 (1)	1295 (1s)	P
		1421 (2)	1419 ($\frac{1}{2}$)	0.75	1418 (1)	1419 (1)	D
1440 (2)	0.7	1440 (3)	1434 (2b)	0.86	1440 (2b)	1436 (2)	D
		2864 (1)				2852 (1)	PP
2950 (8)	0.15	2954 (5)	2950 (2)	0.22	2953 (3)	2950 (6)	PP
2968 (8)	D	2969 (8)	2965 (8b)	0.08	2971 (5)	2970 (8)	PP
		3013 (2)	3012 (1)	D	3013 (2)	3012 (2b)	D
		3041 (2)	3039 (1)	D			

TABLE VIII.

Acetylene tetrachloride : $Cl_2 \cdot HC \cdot CH \cdot Cl_2$.

Trumpy (1935)		Kohlrausch and Ypsilanti (1935)	Mizushima, Morino and Noziri (1936)	Author
$\Delta \nu$	ρ	$\Delta \nu$	$\Delta \nu$	$\Delta \nu$
		89 (10b)	91 (10b)	92 (8b)
171 (5)	0.62	178 (7)	179 (6)	173 (6b)
		224 (2)	226 (2)	222 (2)
238 (4)	0.60	239 (7)	243 (6)	242 (6s)
289 (4)	D ?	290 (8)	289 (7)	289 (7s)
		324 (1)	327 (0)	324 (00d) ? ?
350 (8)	0.14	354 (8) (doublet)	353 (8)	353 (10)
			364 (3)	366 (7s)
		400 (3)	402 (0)	(400) (00) ? ?
540 (2)	D	544 (6)	547 (4)	544 (6)
641 (6)	0.05	647 (11)	650 (10)	647 (10)
		758 (5)	764 (3)	764 (5)
799 (7b)	0.51	795 (12)	802 (11)	799 (10b)
		1017 (3)	1016 (1)	1013 (1)
1210 (1)	D	1214 (4)	1218 (3)	1219 (3)
		1242 (1)	1242 (1)	1240 (1)
		1276 ($\frac{1}{2}$)	1280 (1)	1280 (1)
		1303 ($\frac{1}{2}$)	1306 (1)	1310 (1)
2980 (9)	0.3	2982 (8b)	2986 (10)	2986 (10)

TABLE IX.

Acetylene tetrabromide : Br₂·HC·CH·Br₂.

Trumpy (1936)	Gockel (1935)	Author	Trumpy (1936)	Gockel (1935)	Author
	61 (2)	61 (6b) D			740 (0) P
	115 (5)	113 (4) D ?			800 (0) D
147 (0) P	148 (5)	148 (4s) P		1012 (1)	1012 (3) PP
175 (2) 0.86	181 (6)	176 (5) D		1035 (0)	1030 (1) P
		184 (1) D	1140 (1) P ?	1139 (0)	1133 (1) D
		197 (½) D		1150 (2)	1151 (2) D
220 (4) 0.15	220 (8)	219 (10s) PP		1198 (4)	1196 (4s) P
		242 (1s) PP		1236 (0)	1222 (½) P
450 (1) D	452 (4)	449 (4) D			1250 (½d) D
532 (3) 0.09	538 (6)	537 (8) PP		1282 (½)	1281 (1) P
665 (1) P	665 (4)	664 (4) PP			1405 (½d) P
707 (6) 0.68	713 (8)	713 (15b) P	2985 (3) 0.37	2981 (4b)	2986 (4) P

TABLE X.

Hexachloroethane : Cl₃C·Cl₃.

Mizushima and Morino (1936)	$\Delta\nu$	223	336	430	853	
	Int.	5	5	8	5	
Author	$\Delta\nu$	220	344	431	852	980
	Int.	2	3	8s	5b	2

4. Discussion of Results.

(1) *Dimethyl ether*: $H_3C \cdot O \cdot CH_3$.—From the study of electron diffraction in the vapour of di-methyl ether, Sutton and Brockway (1935) determined the following constants for the molecule of this substance :

angle $\hat{C}OC = 110^\circ \pm 4^\circ$.

$d_{c-o} = 1.44 \pm .03 \text{ \AA}$; $d_{c-c} = 2.39 \pm .05 \text{ \AA}$.

If we regard the CH_3 groups as units, the molecule of dimethyl ether has the symmetry C_{2v} of the bent AB_2 molecule (*e.g.*, SO_2). Of the three fundamental frequencies of such a molecule, two are totally symmetric ($\rho < \frac{6}{7}$) and the third one anti-symmetric ($\rho = \frac{6}{7}$). Polarisation results enable us to identify the three frequencies. Employing Mecke's rotation, we have

$\omega_1 = \nu(\sigma) = 1155$; $\omega_2 = \nu(\pi) = 916$; $\omega_3 = \delta(\pi) = 412$.

From these three frequencies determined spectroscopically, and the molecular constants determined by electron diffraction, it is possible to make a rough computation of the C—O and C—C force constants.

(2) *Phosgene*, $O = C \begin{matrix} \diagup Cl \\ \diagdown Cl \end{matrix}$.—Brockway, Beach and Pauling (1935) found

from the study of electron diffraction that the molecule of phosgene has got a planar configuration with the symmetry C_{2v} , and the molecular constants $d_{c-o} = 1.28 \pm .02 \text{ \AA}$, $d_{c-cl} = 1.68 \pm .02 \text{ \AA}$ and angle $Cl \hat{C} Cl = 117^\circ \pm 2^\circ$. Henri and Howell (1930) made an elaborate study of the ultra-violet absorption spectrum of phosgene vapour. Kohlrausch and Pongratz (1934) have discussed the vibrational Raman spectrum of this substance and have given the following diagrammatic representation of the normal modes of vibration.

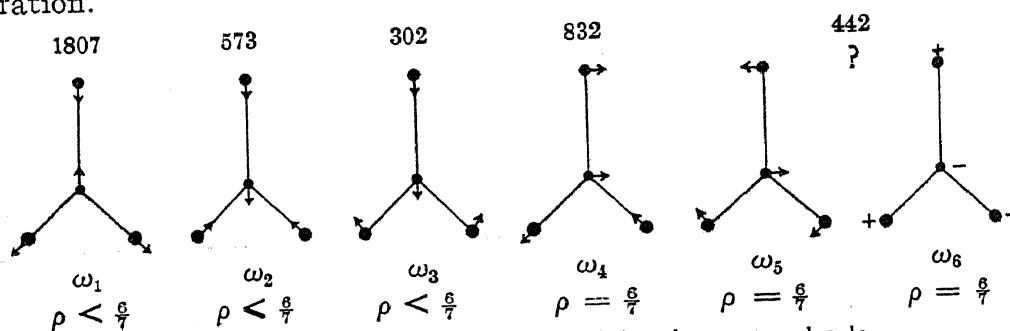


FIG. 1. Normal modes of vibration of the phosgene molecule.

There are six distinct vibrations all of which are allowed in the Raman effect as well as in the infra-red. ω_1 , ω_2 and ω_3 are totally symmetric, and hence should be polarised in the Raman effect ; ω_4 , ω_5 and the perpendicular vibration ω_6 should be depolarised. The Raman spectrum of phosgene, however,

shows only five characteristic frequencies. Kohlrausch and Pongratz have given a tentative classification of these frequencies which requires modification in view of the author's polarisation measurements. Of the three totally symmetric vibrations, ω_1 , ω_2 and ω_3 , we see that ω_1 and ω_2 are primarily valence oscillations, while ω_3 is a deformation oscillation. Polarisation measurements enable us to identify these three frequencies as,

$$\omega_1 = 1807 ; \omega_2 = 573 ; \omega_3 = 302.$$

Of the other three vibrations, ω_4 is of the valence type and hence can be identified with the Raman line at 832 cm.^{-1} ω_5 and ω_6 are deformation oscillations; a unique assignment of the depolarised frequency 442 cm.^{-1} to one or other of these two vibrational modes is not possible.

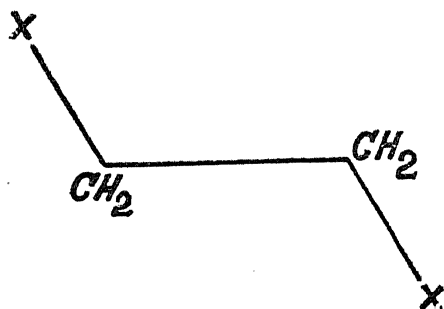
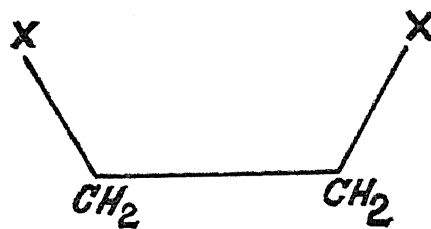
The Ethane derivatives, $X \cdot H_2C \cdot CH_2 \cdot X$ and $X_2 \cdot HC \cdot CH \cdot X_2$.—The Raman spectra of the ethane derivatives are of great interest because classical organic chemistry postulates the existence of "free rotation" about the C—C bond in the case of such compounds. Chemical evidence in support of the postulate of "free rotation" is, however, only of an indirect nature since it depends upon the non-existence—from the chemical standpoint—of stereo-isomeric compounds of the type $X_2 \cdot HC \cdot CH \cdot X_2$, $X \cdot H_2C \cdot CH_2 \cdot X$, etc. Of course, this does not preclude the possibility that such isomers do exist, if the chemical methods are incapable of isolating them in the free state. During the last few years, the application of physical and mathematical methods to the problem has made it clear that "free rotation" in the sense postulated by classical organic chemistry does not exist, and can at best be only a limiting case of very high temperatures. Theoretical investigation of the intra-molecular potential of ethane and its symmetrically substituted derivatives has shown that the *trans*-configuration has the minimum potential energy, while the *cis*-configuration corresponds to a maximum in the potential energy curve plotted as a function of the azimuth of the two rotating groups. This means that the *trans*-configuration is the most stable one, while the *cis*-configuration is the least stable. Between these two extreme limits, there are, in general, other configurations for which the potential energy curve exhibits minima of a more, or less pronounced character depending upon the nature of the substituents.

Study of electron diffraction by Wierl (1932), and of X-ray diffraction by Ehrhardt (1932) in the vapours of ethylene dichloride and ethylene dibromide, made it clear that the *trans*-configuration alone could not explain the observed results. Mizushima, Morino and Higasi (1934) made an elaborate study of the variation of the dipole moment of these two substances with temperature in different solvents. They found a systematic increase

of the dipole moment with temperature in the case of the chloride as well as of the bromide. Since the *trans*-configuration has no dipole moment, while a departure from this configuration gives rise to a finite dipole moment, these authors explained their results by postulating hindered rotation of the two groups about the *trans*-configuration, the amplitude of the oscillatory rotation increasing with temperature. This postulate had also been found to be sufficient to explain the results of X-ray and electron diffraction.

Kohlrausch (1932) was the first to draw attention to the importance of the study of the Raman spectra of the ethane derivatives from the standpoint of the problem of free rotation. In a series of papers published during the last two years, Kohlrausch and his collaborators (1935) on the one hand and Mizushima, Morino and co-workers (1935-36) on the other have discussed the Raman spectra of ethane derivatives in relation to the problem of free rotation. Unfortunately, their view-points are rather conflicting, and indeed do not admit of reconciliation. While Mizushima and Morino definitely eschew the *cis*-configuration because theoretically it is the least stable, Kohlrausch appears to be of opinion that it is necessary to postulate the co-existence of the *cis*- and *trans*-types of molecules to explain the spectra of ethane derivatives of the type $X \cdot H_2C \cdot CH_2 \cdot X$ where $X = CH_3, Cl, Br$, etc.

The theoretical discussion of the vibrations of a molecule of this type is considerably simplified if we treat it as a four-body problem, considering X and CH_2 as units. In such a case, the *trans*- and *cis*-configurations of the molecule will have all the four units in the same plane, and are represented diagrammatically by Fig. 2 *a* and Fig. 2 *b* respectively. The *trans*-configuration

FIG. 2 *a*FIG. 2 *b*

has a centre of symmetry, and hence according to Placzek's selection rules, all those vibrations which are anti-symmetric to the centre of symmetry—this is one-half the total number—are forbidden in the Raman effect. The *cis*-form on the other hand does not possess a centre of symmetry, and so all the vibrations are allowed in the Raman effect; one-half of this total

number will be depolarised. Thus in the simple case of the four-body problem, the *trans*-form of the molecule ought to show three Raman lines all of which are polarised, while the *cis*-form should give rise to six Raman lines of which three are depolarised.

According to Kohlrausch, all frequencies less than 1000 cm.^{-1} in the spectra of the 1, 2 di-halogen derivatives of ethane can be regarded as the chain frequencies, *i.e.*, frequencies pertaining primarily to the four-body configuration $\text{X}\cdot\text{C}\cdot\text{C}\cdot\text{X}$. In this frequency interval, the dichloro and dibromo ethanes show at least nine frequencies. A single molecular configuration alone cannot explain this total number of observed frequencies. We also see that some of these frequencies are depolarised. This indicates the presence of symmetry in the molecule, which is possible only if all the four units lie in the same plane. The total number of observed frequencies as well as their polarisation characters are intelligible in a general manner, if one postulates the co-existence of the *cis*- and *trans*-configurations.

The above arguments are of a very general nature. Kohlrausch and Ypsilanti (1935) have also proposed a classification of the frequencies below 1000 cm.^{-1} in the case of the molecules $\text{Cl}\cdot\text{H}_2\text{C}\cdot\text{CH}_2\cdot\text{Cl}$, $\text{Br}\cdot\text{H}_2\text{C}\cdot\text{CH}_2\cdot\text{Br}$, $\text{H}_3\text{C}\cdot\text{H}_2\text{C}\cdot\text{CH}_2\cdot\text{CH}_3$, etc., between the various vibrational modes of the probable *cis*- and *trans*-forms of such molecules. However, as they have remarked, the assignment proposed by them is not free from difficulties. It might be mentioned here that the identification of the Raman frequencies 92 cm.^{-1} of $\text{Br}\cdot\text{H}_2\text{C}\cdot\text{CH}_2\cdot\text{Br}$ and 263 cm.^{-1} of $\text{Cl}\cdot\text{H}_2\text{C}\cdot\text{CH}_2\cdot\text{Cl}$, to similar vibrational modes of these molecules, is inconsistent with the observed states of polarisation of these two lines, because, the latter is polarised while the former appears to be depolarised. From the present investigation, we also notice the significant fact that the number of depolarised frequencies in the case of *n*-butane is much less than in the case of the corresponding dihalogen compounds. While the entire butane spectrum shows only three or perhaps four depolarised frequencies, we see as many as ten depolarised Raman lines in the spectra of 1, 2 dichloro and dibromo ethanes.

Mizushima and Morino have pointed out that certain frequencies attributed by Kohlrausch to the *cis*-configuration of the molecules of ethylene dichloride and ethylene dibromide can be regarded as the anti-symmetric vibrations of the *trans*-configuration which, though normally forbidden in the Raman effect, appear in the spectra of these compounds because of the hindered rotation of the two groups about the *trans*-position. The symmetry of the *trans*-form of the molecule is virtually obliterated by such rotation so that all the vibrations of the *trans*-configuration are rendered

Raman-active. In support of this view, they adduce the experimental fact observed by them that such lines are absent in the Raman spectra of the solid ethylene dihalides, wherein, presumably all the molecules exist only in the *trans*-state, and hindered rotation about this configuration is inhibited.

However, as far as the present author can see, Mizushima, Morino and others have not accounted for the existence of the depolarised frequencies in the spectra of the liquid ethylene dihalides, on which Kohlrausch has based some of his main arguments. In later communications, they have also expressed the view that probably discrete rotational isomers are present in the liquid state. Although, the remarkable differences between the spectra of the solid and liquid ethylene dihalides discovered by them are very significant, it is necessary to make sure that the spectra of the solids reported by them are complete. Indeed, in the case of solid hexachloroethane, the frequency 980 cm.^{-1} is very clearly recorded in the spectrum of the solid photographed by the technique of complementary filters, while Mizushima and Morino failed to notice its presence in the solid spectrum.

The discussion of the spectra of acetylene tetrachloride and tetrabromide is more difficult, and is not possible at this stage. The author hopes to return to these questions on a future occasion.

In conclusion, the author's grateful thanks are due to Professor Sir C. V. Raman for his kind interest in the present work.

Summary.

The Raman spectra of dimethyl ether, phosgene, *n*-butane, ethylene diamine, ethylene glycol, ethylene dichloride, ethylene dibromide, acetylene tetrachloride, acetylene tetrabromide and hexachloroethane have been studied afresh. The Raman frequencies of phosgene have been classified with the aid of polarisation data. Polarisation measurements have also been made in the case of *n*-butane, ethylene glycol, ethylene dichloride, ethylene dibromide, and acetylene tetrabromide. A brief discussion of the spectra of the ethane derivatives in relation to the problem of "free rotation" is added.

REFERENCES.

- Ananthakrishnan, R., *Proc. Ind. Acad. Sci., A*, 1936, 3, 201, 528; *ibid.*, 4, 74, 82, 204; *ibid.*, 5, 76.
Bhagavantam, S., *Ind. Jour. Phys.*, 1931, 6, 595.
Brockway, L. O., Beach, J. Y., and Pauling, L., *Jour. Am. Chem. Soc.*, 1935, 57, 2693.
Cheng, H. C., *Jour. de Chim. Phys.*, 1935, 32, 715.
Dadiou, A., and Kohlrausch, K. W. F., *Mon. f. Chem.*, 1931, 57, 225.

- Ehrhardt, F., *Phys. Zeit.*, 1932, **33**, 605.
- Gockel, H., *Z. f. Phys. Chem.*, B, 1935, **29**, 79.
- Henri, V., and Howell, O. R., *Proc. Roy. Soc.*, A, 1930, **128**, 178, 190, 192.
- Kohlrausch, K. W. F., *Z. f. Phys. Chem.*, B, 1932, **18**, 61.
- Kohlrausch, K. W. F., and Köppl, F., *Z. f. Phys. Chem.*, B, 1934, **26**, 209.
- Kohlrausch, K. W. F., and Köppl, F., *Mon. f. Chem.*, 1935, **65-66**, 185.
- Kohlrausch, K. W. F., and Pongratz, A., *Z. f. Phys. Chem.*, B, 1934, **27**, 176.
- Kohlrausch, K. W. F., and Stockmair, W., *Z. f. Phys. Chem.*, B, 1935, **29**, 292.
- Kohlrausch, K. W. F., and Ypsilanti, P., Gr., *Z. f. Phys. Chem.*, B, 1935, **29**, 274.
- Mizushima, S., Morino, Y., and Higasi, K., *Sci. Pap. Inst. Phys. Chem. Res.*, 1934, **25**, 159.
- Mizushima, S., and Morino, Y., *Sci. Pap.*, 1934, **26**, 1; *ibid.*, 1936, **29**, 188.
- Mizushima, S., Morino, Y., and Noziri, S., *Sci. Pap.*, 1936, **29**, 63.
- Mizushima, S., Morino, Y., and Kozima, K., *Sci. Pap.*, 1936, **29**, 111.
- Murray, J. W., and Andrews, D. H., *Jour. Chem. Phys.*, 1933, **1**, 406.
- Placzek, G., *Handbuch der Radiologie*, Teil II, 1934.
- Sirkar, S. C., *Ind. Jour. Phys.*, 1932, **7**, 257.
- Sutton, L. E., and Brockway, L. O., *Jour. Ann. Chem. Soc.*, 1935, **57**, 473.
- Trumpy, B., *Z. f. Phys.*, 1935, **93**, 624; *ibid.*, 1936, **98**, 672.
- Wierl, R., *Ann. der Phys.*, 1932, **13**, 453.