

THE RAMAN SPECTRA OF ACETYLCHLORIDE, ACETYLBROMIDE AND ETHYLBROMIDE AT LOW TEMPERATURES

By B. M. BISHUI *

(Received for publication, Aug. 3, 1948)

Plate XV

ABSTRACT. The Raman spectra of acetylchloride, acetylbromide and ethylbromide in the liquid and solid states have been investigated. It has been observed that all the prominent Raman lines of these liquids appear in the case of the solid state. It is concluded therefore that there are no rotational isomers in these liquids. There are, however, two extra lines in the Raman spectrum of each of these substances and it is pointed out that these may be due to formation of associated groups of molecules in the liquid and solid states of these substances.

INTRODUCTION

In continuation of the investigations on the Raman spectra of organic substances in the solid state at low temperatures by the present author and also in collaboration with Sirkar, (1943, 1945, 1946a, 1946b, 1948a, 1948b, 1948c) the Raman spectra of acetylchloride, acetylbromide and ethylbromide have been studied in the solid state at low temperatures. From a systematic investigation of a large number of organic compounds, it has previously been observed that some changes in intensities and frequencies of some of the Raman lines take place, when particular organic liquids are solidified at low temperatures. These changes observed in the case of substituted ethanes have been explained by previous workers (Mizushima *et al.* 1934, 1936, 1938) on the hypothesis that rotation isomers co-exist in the liquid state and molecules of only one configuration are present in the solid state of these compounds. It has been observed by the author (Bishui, 1948b) that there are some difficulties in such an explanation in the case of 1,1-dichloroethane, because although this substance cannot have two stable rotational isomers; it gives too many Raman lines in the liquid state to be accounted for by the single configuration of the molecule. In order to understand this phenomenon more clearly the investigation of Raman spectra of a large number of substituted ethane compounds has been undertaken and in the present paper the results obtained in the case of the three compounds mentioned above are discussed. The Raman spectra of these substances in the liquid state have also been studied carefully in order to compare them with those observed in the case of the solid state and the polarisation of the Raman lines due to the liquid state has been studied qualitatively.

* Fellow of the Indian Physical Society.

EXPERIMENTAL

The method for studying the Raman spectra of these substances at low temperatures was the same as that was used by Sirkar and Bishui (1943). The liquids from Kahlbaum's and Merck's original sealed bottles were procured from old stock and redistilled in vacuum. A double walled tube of Pyrex glass containing the distilled liquid was held in a vertical position with its lower portion immersed in the liquid oxygen contained in a transparent Dewar vessel. The solidification of the liquid took place very slowly when the interspace of the double-walled tube was evacuated with a Cenco Hyvac pump. Light from two vertical mercury arcs condensed by two six-inch glass condensers was focussed on the substance from opposite sides.

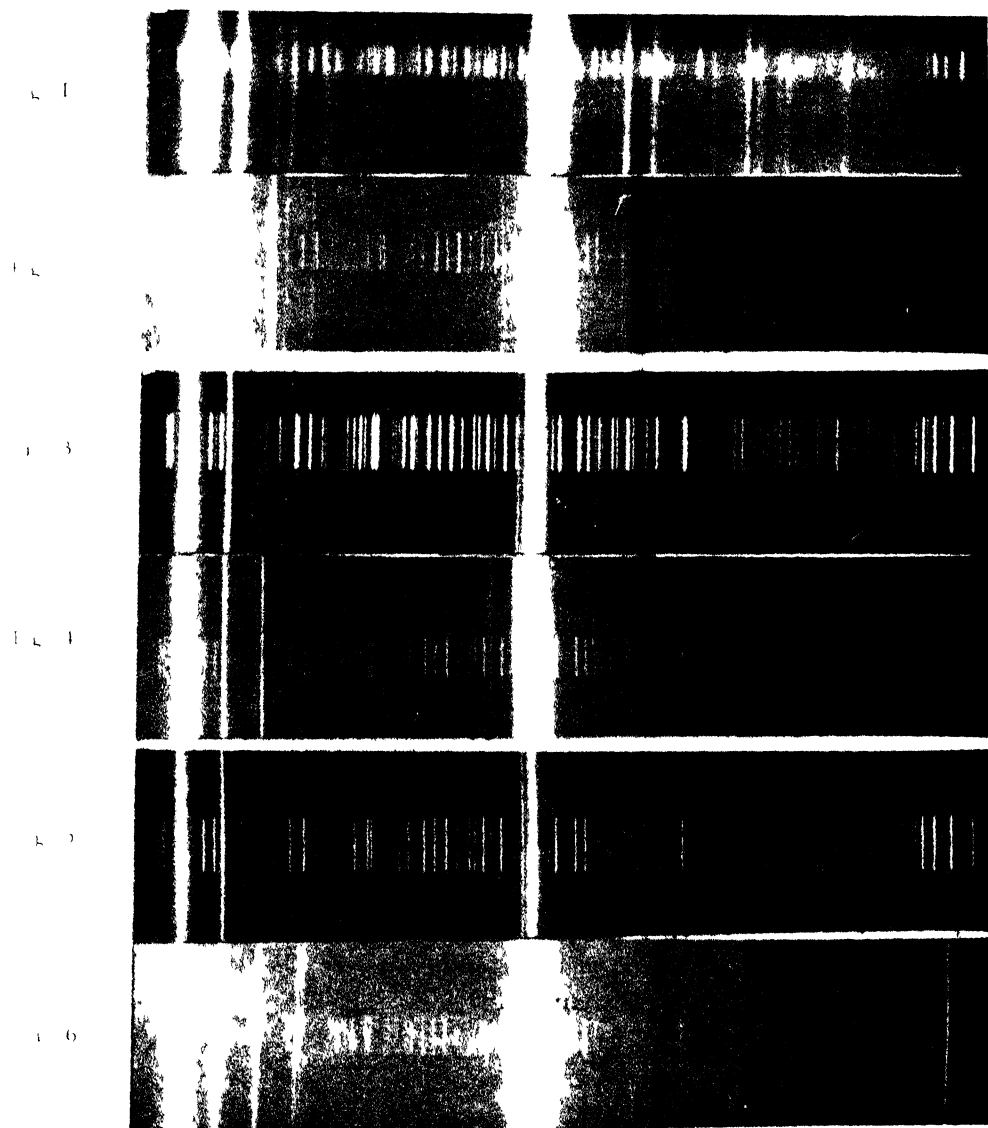
A Fuess glass spectrograph having the dispersion of 14 \AA per m.m. in the region of 4046 \AA used in the previous investigations was used in the present investigation also. A blue-violet glass filter was placed in the path of the incident light in order to diminish the continuous background in the blue-green region. The polarisation of the Raman lines due to the liquid state was studied in each case by photographing simultaneously the vertical and the horizontal components of the scattered light with the help of a double image prism. Light from a mercury arc focussed with the help of a condenser was used as the incident light in this case also.

RESULTS AND DISCUSSION

The spectrograms for the liquid and the solid states are reproduced in the Plate XV. The results are given in Tables I, II and III. The first column of each table contains the results reported by some of the previous workers. The data for the solids obtained in the present investigation are given in the last column. The polarisation of the lines is indicated by the letter P and total depolarisation by D. The approximate visually estimated intensities are given in the parenthesis.

Acetyl Chloride. The Raman spectrum of acetyl chloride was studied formerly by Kohlrausch *et al* (1933) and others. The results obtained by the former authors agree fairly well with those obtained in the present investigation. The weak line 236 cm^{-1} reported by them, however, has not been observed in the present investigation. The lines 956 cm^{-1} , 136 cm^{-1} , 1427 cm^{-1} , 2996 cm^{-1} and 3025 cm^{-1} are found to be totally depolarised. This fact suggests that the molecule has an element of symmetry which is evidently a plane of symmetry containing the C, O and Br atoms.

In the solid state at -170°C some of the Raman lines shift a little from their original positions. The line at 596 cm^{-1} due to the C-Cl valence oscillation shifts to 586 cm^{-1} but the line at 356 cm^{-1} due evidently to C-Cl deformation oscillation remains practically in the same position. The line 1810 cm^{-1} due to C=O valence oscillation and the line 2996 cm^{-1} due to the



Raman Spectra

Fig. 1	Acetylchloride	at about		32°C
Fig. 2	,		-	170 C
Fig. 3	Acetyl bromide	at about	+	32 C
Fig. 4	,	,	-	170 C
Fig. 5	Ethylbromide	at about		32 C
Fig. 6	,			170°C

TABLE I
Acetyl Chloride H_3CCOCl .

Liquid at room temperature		Solid at about -170°C
Kohlraush <i>et al</i> (1933)	Present author	Present author
236 (o) e,
348 (5) k, f, e, c	354 (3) e, k, P	356 (1) e, k
134 (12) k, i, g \pm f \pm e, C	437 (20) e \pm , k; P	430 (5) e, k
590 (10b) k, i, f, e, c.	596 (8b) e \pm , k, i; P	586 (31) e, k
955 (2) k, e,	956 (2) e, k; D	951 (0) e, k
1038 (0) k, e;	1036 (0) e, k ?
1006 (1) k, e,	1102 (1b) e, k; P	1102 (1) e, k
1328 (0) k, e.	1360 (1) e, k, D
1358 (1) k, e
1418 (3) k, e	1127 (1) e, k; D	1423 (2b) e, k
1793 \pm 8 (1b) e,	1810 (6b) e, P	1791 (2) e
2935 (12) q, p, k, i, e	2939 (10) e, i, k; P	2937 (8) e, k
2991 (2) q, k,	2996 (3) e, k; D	2986 (3) e, k
3016 (4) k, e	3025 (4) e, k, D	3025 (5) e, k.

antisymmetric C-H valence oscillation shift respectively to 1791 cm^{-1} and 2986 cm^{-1} in the solid state. No new lines are observed to appear in the neighbourhood of the Rayleigh line at the low temperature. The lines 1036 cm^{-1} and 1360 cm^{-1} are weak in the spectrogram due to the liquid and they are not observed in the case of the solid probably because they are masked by the continuous background which is rather strong in the spectrogram due to the solid. It can thus be seen from Table I that not a single prominent line disappears in the solid state in this case.

The number of Raman lines having frequency shifts below 1200 cm^{-1} is six in the present case but the number of lines in this region due to the vibration of the C-COCl is expected to be five, the sixth line due to C=O valence oscillation being that at 1810 cm^{-1} . Further the CH_3 group is expected to yield only one totally depolarised line due to antisymmetric C-H valence oscillation. Actually such lines at 2996 cm^{-1} and 3025 cm^{-1} are observed in the present case. Hence there are at least two extra lines in the Raman spectrum of acetyl chloride which cannot be accounted for if we assume that the liquid contains only single molecules of a particular configuration. Since no prominent lines disappear when the liquid is frozen,

TABLE II
Acetylbromide H_3CCOBr .

Liquid at room temperature		Solid at about -170°C
Kohlraush <i>et al</i> (1934)	Present author	Present author
...	246 (1) e, k ?
303 (9) k, f, \pm e, a	305 (5) e, e, k P	305 (2) e, k
339 (15sb) k, f, \pm e, c, b	345 (10) e, e \pm , k P	340 (5) e, k
555 (8b) k, i, g, f, \pm e, c, b, a	560 (8) e, e \pm , k, i P	555 (4) e, k
944 (0) k, e	950 (2b) e, k ?
981 (c) k, e
1081 (3b) k, f, e	1088 (1b) e, k ; P	1082 (0) e, k
1350 (1) k, e	1300 (3) e, k P	1300 (0b) e, k
1414 (2b) k, e	1425 (3b) e, k ; D	1420 (1b) e, k
1809 \pm 10 (2b) e	1820 (1b) e P	1820 (0) e
2931 (6) q, p, k, i, e	2938 (8) e, k, i, P	2934 (5) e, k
2987 ($\frac{1}{2}$) k	3000 (3) e, k, D	2982 (3) e, k
3010 (3b) k, e	3015 (3) e, k ; D	3010 (3) e, k

it is evident that the presence of rotational isomers cannot be postulated in the present case. Hence we are left with the explanation that both in the liquid and solid states the molecules of acetyl chloride are in associated state giving rise to extra Raman lines.

Acetylbromide. The Raman spectrum of this liquid was studied previously by Kohlraush *et al* (1934). A comparison of the data given in the first two columns of Table II shows that some of the frequency shifts observed by the present author are a little higher than those observed by the previous authors. The line 246 cm^{-1} observed in the present investigation was not recorded by the previous authors and the line 981 cm^{-1} reported by the previous authors has not been observed in the present investigation. In the solid state at about -170°C some minor changes take place. The frequency of the line at 560 cm^{-1} due to C-Br valence oscillation is lowered a little with the solidification of the substance. The line 1425 cm^{-1} due to C-H deformation vibration undergoes changes both in intensity and in frequency. The frequencies of the lines 345 cm^{-1} , 560 cm^{-1} , 1088 cm^{-1} , 3000 cm^{-1} and 3015 cm^{-1} diminish a little in the solid state but that of the line 1820 cm^{-1} remains unchanged. In this case also there are six Raman lines having frequency shifts below 1200 cm^{-1} and arguments similar to those advanced

TABLE III
Ethylbromide C₂H₅Br.

Liquid at room temperature		Solid at about -170°C
Voge (1934)	Present author	Present author
290.5 (3)	296 (3) e, k; P	300 (6) e, k?
560.3 (10b)	563 (10) e±, k; P	554 (6) e, k
959.4 (2b)	964 (2b) e, k; P	957 (2) e, k
1062.8 (2)	1056 (2b) e, k; P	1050 (6) e, k
1244.7 (2)
1252.9 (2b)	1248 (2) e, k; P	1248 (1) e, k
1444.0 (2b)	1450 (3b) e, k; D	1445 (2b) e, k
2867.2 (2)	2870 (2b) e, k; P	2870 (1b) e, k
2924.1 (4)	2927 (5) e, k; P	2925 (5) e, k
2969.2 (2d)	2970 (1b) e, k; P	2968 (2) e, k
.....	2984 (3) e, k
	3010 (2b) e, k; D	3008 (1) e, k

in the case of acetylchloride lead to the conclusion that the molecules are strongly associated in the liquid and solid states and that there are no rotational isomers in the liquid state. In this case also there are several totally depolarised lines in the Raman spectrum of the liquid and therefore the molecule has an element of symmetry.

Ethylbromide. The data given in the first two columns of Table III show that almost all the lines due to the liquid have appeared in the solid state. The liquid was studied formerly by Dadiou, *et al* (1929) and later by Voge (1934). The data reported by the later author have been included in the first column of Table III for comparison. The line 1244.7 cm⁻¹, reported by the later author, has not been observed in the present investigation. The line 3010 cm⁻¹ which has been observed by the present author is not reported by any previous workers. The C-Br valence vibration has been diminished and its deformation vibration has been increased in the solid state. The C-C valence vibration has also undergone changes. The C-H valence vibrations have also changed with the solidification of the substance. The line 2970 cm⁻¹ has been split up into two lines at 2968 cm⁻¹ and 2984 cm⁻¹ respectively. The frequency of the C-H deformation vibration diminishes a little in the solid state. The number of lines below 1100 cm⁻¹ is four. But the group C-C-Br can yield only three lines in this region. The presence of an

extra line in this case also cannot be explained on the hypothesis of rotational isomers. The origin of this extra line can again be traced to the formation of the associated groups of molecules both in the liquid and solid states. Some of the Raman lines observed in this investigation are totally depolarised and this clearly shows that this molecule possesses an element of symmetry in the liquid state.

ACKNOWLEDGMENT

The author is indebted to Prof. S. C. Sirkar, D.Sc., F.N.I. for his kind interest and encouragement during the progress of the work and to Prof. M. N. Saha, F.R.S., for kindly allowing him to use the photo enlarger in the Palit Laboratory of Physics of the University College of Science, Calcutta.

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE,
210, BOWBAZAR STREET, CALCUTTA.

REFERENCES

- Bishui, B. M. (1948a), *Ind J. Phys.*, **22**, 167.
 ——— (1948b), *Ind J. Phys.*, **22**, 319.
 ——— (1948c), *Ind J. Phys.*, **22**, 333.
 Cleeton, C. E. and Dufford, R. T., (1931). *Phys. Rev.*, **37**, 362.
 Dadieu, A. and Kohlraush, K. W. F., (1929), *Wein. Ber.*, **38**, 635.
 Kohlraush, K. W. F. and Pongratz, A., (1933) *Z. Phys. Chem. (B)*, **22**, 373.
 ——— (1934). *Z. Phys. Chem. (B)*, **27**, 176.
 Mizushima, S. Morino Y. and Higasi, K. (1934). *Phys. Zeit.*, **36**, 905.
 ——— Norezi (1936), *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **29**, 63 and 88.
 ——— (1938a), *Proc. Ind. Acad. Sc.*, A, **8**, 315.
 Sirkar, S. C. and Bishui B. M. (1943), *Proc. Nat. Inst. Sc. India*, **9**, 287.
 ——— (1945), *Ind. J. Phys.*, **9**, 24.
 ——— (1946a), *Ind. J. Phys.*, **20**, 33.
 ——— (1946b), *Ind. J. Phys.*, **20**, 111.
 Voge, H. H. (1934), *Jour. Chem. Phys.*, **2**, 264.