THE RAMAN SPECTRA OF ETHYLENE GLYCOL AND ETHYLENE CHLOROHYDRIN

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The Raman spectrum of ethylene glycol has been compared with that of ethylene chlorohydrin and from the polarisation data of earlier investigation it has been concluded that the molecules of the former exist in different isomeric forms in the liquid state due to intramolecular coupling effects. The new lines reported by Narayanaswamy (1948) in ethylene glycol under ultraviolet excitation have been confirmed excepting the one at 698 cm.$^{-1}$

1. Introduction

From a comparative study of the Raman spectra of ethylene chlorohydrin ($ClCH_2CH_2OH$) and *n*-propyl chloride ($CH_3CH_2CH_2Cl$) in the liquid and solid states Mizushima *et al.* (1940) concluded that the ethylene chlorohydrin molecule existed at least in two isomeric forms in the liquid state whereas in the solid state it existed only in one form. Similar results have been obtained in several substituted ethanes. In the present investigation the spectrum of ethylene glycol ($OHCH_2CH_2OH$) has been compared with that of ethylene chlorohydrin and the results are discussed in relation to the molecular configuration of the former.

2. Experimental

The experimental arrangement for recording the Raman spectra of the liquids is the same as that used by the author (Hariharan, 1954) in an earlier investigation. The pure liquids were further purified by vacuum distillation and intense spectra were obtained using Ilford Hypersensitive Panchromatic plates.

3. Results and Discussion

The Raman spectra of ethylene glycol and ethylene chlorohydrin are reproduced in Plate XXI and the frequency shifts are given in Table I. The results of Narayanaswamy (1948) for the former obtained with λ 2537 as exciter and of Mizushima *et al.* (1940) for the latter are also reproduced for comparison. The polarisation data are taken from Ananthakrishnan (1937) and Bishui (1948) respectively.

TABLE I

Raman spectrum of ethylene glycol			Raman spectrum of ethylene chlorohydrin		
Author cm.$^{-1}$	Narayanaswamy (1948) cm.$^{-1}$		Author cm.$^{-1}$		Mizushima *et al.* (1940) cm.$^{-1}$
..	Wing ± 130		162 (1)	P.	164 (1 *b*)
346 (2 *b*)	P. 344 (2*b*)		295 (3)	P.	296 (4)
475 (2)	P. 476 (3)		398 (4)	P.	396 (5)
511 (2)	D. 509 (3)		475 (4)	D.	476 (4)
..	698·4 (0)		662 (10 *b*)	P.	662 (10 *b*)
803 (0)	801·5 (1)		749 (6 *b*)	P.	750 (7 *b*)
863 (6)	P. 865 (8)		850 (6)	P.	850 (6)
890 (3)	D. 884 (3)		940 (5 *b*)	D.	942 (6 *b*)
1035 (5 *b*)	D. 1033·5 (6 *b*)		1033 (6)	P.	1034 (2)
1065 (5 *b*)	D. 1063 (6 *b*)		1058 (2)		1055 (2)
1092 (4)	P. 1092·6 (5)		1077 (3)		1078 (4)
1132 (2)	1133 (2)		1177 (3)		1179 (3)
1221 (3)	1224 (3)		1245 (4 *b*)	P.	1245 (5 *b*)
1285 (4)	D. 1281 (5)		1280 (2)		1283 (2)
1390 (1)	1396 (1)		1298 (2)		1298 (3)
1457 (6)	D. 1458 (8)		1381 (1)		1379 (1)
2715 (1)	P. 2726 (2)		1441 (5)	D.	1443 (6)
2886 (8 *b*)	P. 2885 (10 *b*)		1458 (6)	D.	1457 (7)
2930 (10 *b*)	P. 2932 (10 *vb*)		2725 (2 *b*)		2725 (3 *b*)
band 3400	P. band 3250–3600		2880 (5)	P.	2875 (7)
			2923 (5)	P.	2925 (6)
			2965 (10)	P.	2962 (10)
			3010 (6)	P.	3011 (8)

Using λ 2537 Hg resonance radiation for excitation Narayanaswamy (1948) has recorded new lines at 698·4, 801·5, 884, 1133 and 1396 cm.$^{-1}$ In the present investigation all these lines excepting the one at 698 cm.$^{-1}$ have been observed as faint lines. Due to the similarity in the molecular structure of these two compounds there are a number of coincidences in the frequencies observed. Among the more important lines observed the 662 cm.$^{-1}$ in ethylene chlorohydrin has been attributed by Mizushima *et al.* to the oscillation in the *trans*-form and the line 750 cm.$^{-1}$ to a similar mode in a different form in which the molecule approaches the *cis*-form due to intramolecular coupling between the hydroxyl hydrogen and the chlorine atoms. The latter line has been observed to disappear in the solid state, a result which is later contradicted by Bishui (1948) who explains the persistence of the line in the solid state as due to association of the molecules in the liquid state itself.

The effect of the intramolecular coupling is likely to influence the configuration of ethylene glycol also. The number of lines observed and their polarisation characters rule out the possibility of a simple *trans*-form. If the hydroxyl group is considered as a single atom the molecule will give 6 polarised and only 3 depolarised lines for the C_{2h} symmetry (*trans*-form) and 6 polarised and 12 depolarised lines for the C_{2v} symmetry (*cis*-form). Out of the 18 lines observed, 7 have been observed to be polarised and 6 depolarised. This shows that apart from the *trans*-form there may be other rotational isomers in the liquid state and these probably arise from the intramolecular coupling due to virtual bonds.

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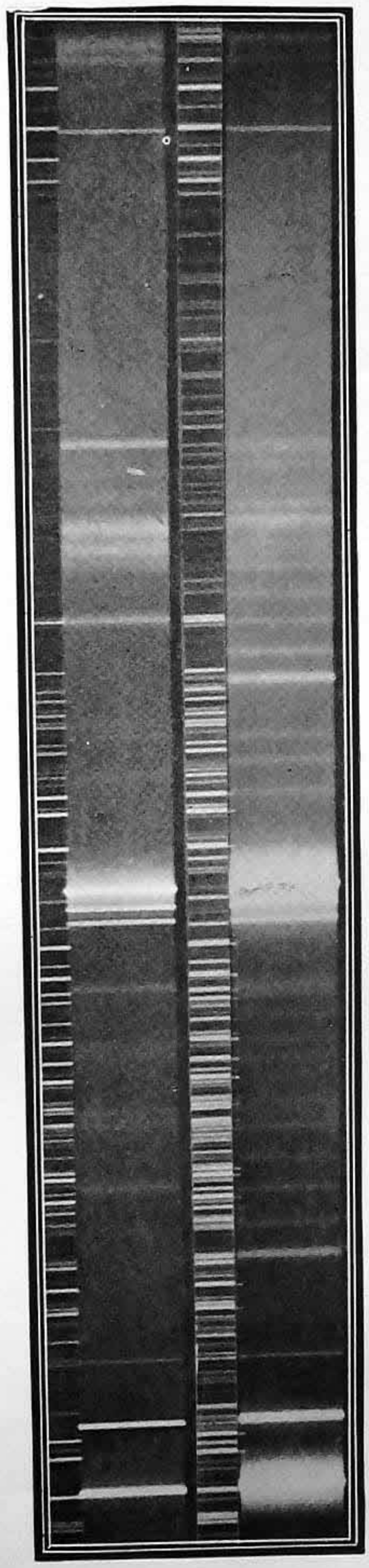

(*a*) (*b*)

(*a*) Raman spectrum of ethylene glycol. (*b*) Raman spectrum of ethylene chlorohydrin