RAMAN AND INFRARED SPECTRA OF ETHYLENE GLYCOL

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Abstract

The Raman spectrum of ethylene glycol has been investigated in the liquid and solid states and also in aqueous solutions. The infrared absorption spectrum of the liquid has been recorded. 27 Raman lines and 17 infrared maxima in the liquid state and 20 Raman lines in the solid state have been reported. Detailed vibrational assignments have been given. Two strong polarised Raman lines of the liquid which have no corresponding infrared absorption bands, and which disappear on solidification, have been attributed to the trans configuration of the glycol molecule. From a comparative study of the various spectra, it is concluded that in the liquid state, glycol exists as a mixture of the two rotational isomers (trans and gauche) whereas in the solid state only the gauche form is present. In very dilute aqueous solutions, the predominant molecular form is the gauche form.

1. Introduction

It is well known that substituted ethanes exhibit the phenomenon of rotational isomerism. Spectroscopic studies based on Raman effect and infrared absorption of these substances offer an elegant means for investigating the presence or otherwise of isomers in them. The Raman spectra of 1, 2, disubstituted ethanes have been investigated by many authors in both the liquid and solid states. These are summarised by Mizushima (1954) in his book on the *Internal Rotations and Structure of Molecules*. Among the disubstituted ethanes, ethylene glycol, $CH_2(OH) \cdot CH_2OH$, forms a particularly interesting substance from the spectroscopic point of view as it is supposed to contain an intramolecular hydrogen bond.

The Raman spectrum of ethylene glycol has been the subject of investigation for many workers and the literature on this subject up to 1948 has

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been referred to in a paper by Narayanaswamy (1948). He recorded the Raman spectrum of ethylene glycol using λ 2536·5 excitation. Later, Hariharan (1954) from our Laboratory studied the polarisation characteristics of the Raman lines of glycol. The only investigation reported so far on the Raman spectrum of solid glycol is that by Nakamura (1939).

The infrared absorption spectrum of glycol was studied by Kuhn (1952) and by Kuhn, Luttke and Mecke (1959). Kambayashi and Nukada (1963) have investigated the vibrational spectrum of glycol and concluded that in the liquid state, the molecules of glycol existed only in one configuration namely the gauche form.

We have re-examined the Raman spectra of glycol and its aqueous solutions using λ 2536·5 excitation. We have also recorded the Raman spectrum of solid glycol at about — 70° C. using λ 4046 and 4358 radiations as exciter. The results are presented here.

2. EXPERIMENTAL DETAILS

The experimental work on the Raman spectra of glycol and its aqueous solutions using the λ 2536·5 excitation was carried out in the Physics Department of the Indian Institute of Science, Bangalore. The Wood's tube was made of fused silica of good optical quality. A Hilger medium quartz spectrograph with a slit width of 0·04 mm. was employed to record the spectrum. For Ilford Zenith astronomical plates exposures of twenty-four hours had to be given in order to get intense spectrograms. Aqueous solutions of glycol with four different concentrations were prepared with the percentage by volume of glycol having values 50, 25, 125 and 6·25, and their Raman spectra were recorded. A Hilger E_1 quartz spectrograph was also used to get spectrograms under high dispersion.

The Raman spectrum of glycol in the solid state was recorded using a Cary Model 81 Recording Raman Spectrometer. This part of the work was carried out in the Department of Chemistry, Cornell University, Ithaca, USA. The sample of glycol contained in a Wood's tube was cooled by circulating cold air at liquid nitrogen temperature. The actual temperature of the sample was about — 70° C. and the solid was in the form of a translucent mass.

The infrared absorption spectrum of liquid glycol was recorded using a Perkin Elmer 337 grating infrared spectrometer. The sample was kept in the form of a thin film in between two KBr plates. The region investigated was from 400 to 4000 cm.$^{-1}$

3. RESULTS

An enlarged photograph of the Raman spectrum of liquid ethylene glycol along with its microphotometer record is reproduced in Fig. 1 on Plate VIII. The values of the frequency shifts are marked in the figure. The infrared absorption spectrum of the liquid is reproduced in Fig. 2. The actual curve has been redrawn on a uniform scale. The Cary record of the Raman spectrum of the solid is not reproduced as the same was taken with different amplifications for the different regions. The frequency shifts of the Raman lines for the liquid and solid and frequencies corresponding to infrared absorption maxima for the liquid are entered in Table I. The figures in brackets represent the visually estimated intensities of the Raman lines.
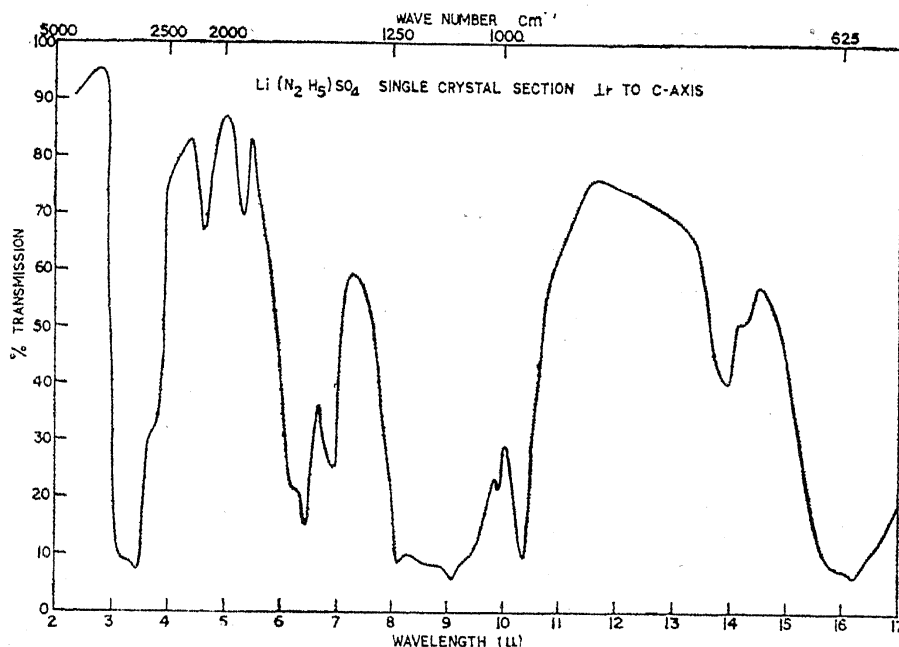

FIG. 2. Infrared absorption spectrum of liquid glycol.

The polarisation data of Hariharan (1954) are indicated against the prominent Raman lines in column 1 of Table I, as ' P ' for polarised and ' D ' depolarised. These data were also confirmed by taking recordings in the Cary instrument using suitably oriented polaroids.

Twenty-seven Raman lines and a wing extending up to about 220 cm.$^{-1}$ from the exciting line have been recorded in the case of the liquid, *i.e.*, three more lines than those reported by Narayanaswamy (1948) using the same excitation. In the case of the solid at $-70°$ C. only twenty lines have been identified. In the latter case the low frequency shift lines could not be recorded with the Cary instrument mainly due to poor transparency arising

Table I

Raman and infrared spectra of ethylene glycol

Raman spectrum		I.R. spectrum	Assignment
Liquid	Solid		
0–220	...	..	wing
311 (0, b)	...	..	C–C–O torsion
348 (3) P	347	...	C–$\hat{\text{C}}$–O bending
481 (5) P	...	—	do.
525 (3, b) D	520	524 W	do.
557 (0)	...	...	...
803 (1)	...	..	CH_2 rocking
863 (10) P	870	864 m	C–C stretching
886 (4) D	885	882 s	CH_2 rocking
1044 (6, b) D	1045	1040 vs	C–O stretching
1069 (7, b) P		...	do.
1093 (10) P	1090	1085 vs	do.
1117 (2)	...	..	CH_2 twisting
1224 (2, b)	{1217 {1238	1200 mb	do.
1264 (6, b)	1276	1250 Wb	CH_2 wagging
1294 (6, b)	1304	..	do.
1395 (2, b)	{1360 {1382b	1330 s	do.
		1410 sb	C–$\hat{\text{O}}$–H bending
1465 (10) D	{1462 {1490	1462s	CH_2 bending
..	..	1660 W	..
1941 (0, b)	..	1940 Wb	1093 + 863
2095 (0, b)	..	2115 Wb	2 × 1044 1224 + 863
2161 (0, b)	..	..	1294 + 863
2367 (0, b)	..	..	1465 + 806
2460 (1, b)	..	..	1465 + 1044, 1264 + 1224
2527 (0)	..	..	1465 + 1069
2719 (5) P	..	2715 W	O–H stretching (H-bonded)
2876 (10, b) P	2881	2870 vs	C–H stretching sym.
2940 (10, vb) P	{2933 {2953	2935 vs	C–H stretching anti-sym.
3390 (band) P	{3310b {3365b	3350vsb	O–H stretching (H-bonded)

b= broad, P= polarised, D = depolarised, vs= very strong, s =strong, w= weak, m= medium.

from the whitish nature of the solid. The Raman lines of the liquid are generally broader than those of the solid. Five broad and intense lines appearing in the spectrum of the liquid are split up into two each in the spectrum of the solid. In the region from 500 cm.$^{-1}$ to 3400 cm.$^{-1}$ the infrared spectrum of the liquid exhibits 17 maxima which correspond to the appropriate Raman frequencies.

The wing accompanying the Raman spectrum of the liquid exhibits a structure due to the superposition of lines at 110, 180 and 211 cm.$^{-1}$ The kink next to the exciting line is due to a bogus band.

4. DISCUSSION

(*a*) *Vibrational Assignments.*—Before taking up the question of rotational isomerism, let us consider the vibrational assignments of the observed Raman lines in the liquid. The Raman lines and the infrared absorption maxima are broad because of the highly associated nature of the liquid. The O–H stretching vibration appears as a broad band extending from about 3250 cm.$^{-1}$ to about 3550 cm.$^{-1}$ in the Raman spectrum. Its appearance in this region suggests that the O–H stretching vibration is influenced by hydrogen bonding. The C–O–H in plane bending vibration is assigned to the broad Raman line with centre around 1395 cm.$^{-1}$ and the infrared band with centre around 1410 cm.$^{-1}$ The corresponding out of plane vibration is expected to occur near 700 cm.$^{-1}$ This may be assigned to the very broad infrared absorption starting at around 730 cm.$^{-1}$ The corresponding band is not observed in the Raman spectrum.

The C–H stretching vibrations occur as two broad bands at 2876 and 2940 cm.$^{-1}$ in both the Raman and infrared spectra. The CH_2 bending vibration is located at 1465 cm.$^{-1}$ The corresponding Raman band is depolarised. The symmetric polarised Raman line due to the CH_2 bending may either be coincident with this Raman line or may be superimposed on the broad band due to C–O–H bending. The CH_2 wagging and twisting vibrations are assigned as shown in Table I. These were done by comparison with the spectra of 1, 2-dihaloethanes given by Mizushima (1954). The CH_2 rocking vibration is expected to give rise to frequencies in the range 700–1000 cm.$^{-1}$ In the Raman spectrum there are 3 lines, one very weak at 803 cm.$^{-1}$, an intense polarised line at 863 cm.$^{-1}$ and a depolarised line of moderate intensity at 886 cm.$^{-1}$ In the infrared the latter two lines appear but the order of their intensities is reversed. Now, it is a fact of observation, that the CH_2 rocking frequencies do not give rise to strong Raman lines, whereas the same vibrations appear with considerable intensity in the infra-

red. On this basis, it is highly improbable that the 863 cm.$^{-1}$ Raman line arises from CH_2 rocking vibration. Moreover, the C–C stretching frequency is expected to appear in this region also. In aliphatic alcohols it is seen that the C–C stretching appears consistently in the region 800–900 cm.$^{-1}$ (Krishnan, 1961). It is reasonable therefore to expect that the C–C stretching frequency in glycol should also appear in this region. Hence, the 863 cm.$^{-1}$ Raman line is assigned to the C–C stretching vibration. Its polarisation is also in conformity with this assignment, since the C–C stretching frequency should be polarised, whatever the molecular configuration. Then, the weaker 886 cm.$^{-1}$ Raman line and the very weak 803 cm.$^{-1}$ Raman line can be assigned to CH_2 rocking vibrations. It is interesting to note that the reversed intensities of the 886 and 863 cm.$^{-1}$ lines in the infrared are in conformity with the above arguments. Furthermore, in the case of ethylene fluoride, which has approximately the same molecular weight Klaboe and Nielsen (1960) assigned the two observed Raman lines at 858 (P) and 886 (D) cm.$^{-1}$ to C–C stretching and CH_2 rocking vibrations respectively. Kurodo and Kubo (1957) and Miyake (1959) assigned both the frequencies 886 and 863 cm.$^{-1}$ to CH_2 rocking frequencies. From the arguments cited above, their assignments have to be revised.

The weak Raman line at 311 cm.$^{-1}$ is assigned to a C–C–O torsional mode. A number of weak Raman lines are observed in the region from 1600–2800 cm.$^{-1}$ They belong to the second order spectrum and the corresponding assignments are indicated in the last column.

The existence of hydrogen bonds in the liquid would give rise to new hydrogen bond stretching modes and the three low frequency lines at 110, 180 and 211 cm.$^{-1}$ have to be assigned to such modes. Similar observations have been made by Gross (1959) in formic acid and by Krishnan (1961) in methyl and ethyl alcohols. The corresponding region of the Raman spectrum of the solid if recorded would furnish further confirmations of the above assignments.

(b) *Rotational Isomers.*—It is known that most of the disubstituted halogen ethanes exist in the liquid state as a mixture of molecules having the two configurations namely the trans and the gauche forms. In the case of ethylene glycol conflicting views have been expressed by workers regarding the composition of the two forms. From polarisation studies Hariharan (1954) concluded that it is a mixture of the two isomers. Kuhn, Lüttke and Mecke (1959) came to the same conclusion from infrared studies, whereas the Japanese workers concluded that liquid glycol contained only one of

the isomers. Let us examine the present results from the point of view of the existence of one or more isomers both in the liquid and solid states.

On comparing the Raman spectra of the liquid and the solid given in Table I, it is noticed that the two intense polarised lines at 481 cm.$^{-1}$ and 1069 cm.$^{-1}$ appearing in the liquid spectrum are absent in the solid spectrum. It may be inferred from this that there is a change in the molecular configuration on solidification.

Electron diffraction study of glycol vapour by Bastiansen (1949) showed the existence of a peak in the diffraction pattern corresponding to the gauche form having a dihedral angle of 74°. The other molecular parameters obtained by him are as follows:

$$C\text{-}O = 1\cdot43\,\text{Å}, \quad C\text{-}C = 1\cdot52 \pm 0\cdot02\,\text{Å} \quad C\text{-}\hat{C}\text{-}O = 109°\,5'.$$

Also the two O–H groups are near enough to form an intramolecular hydrogen bond of length $2\cdot96 \pm 0\cdot02\,\text{Å}$. The two possible configurations of the glycol molecule are indicated in Fig. 3. The gauche form has the symmetry C_2, while the trans form has symmetry C_{2h}.
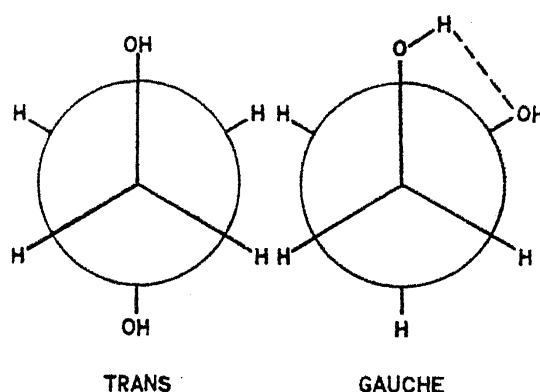

Fig. 3. Rotational isomers of ethylene glycol.

Mizushima, Shimanouchi, Nakagawa and Miyaki (1953) have indicated a method of calculating the skeletal frequencies of rotational isomers in the case of disubstituted ethanes using Wilson's F–G matrix method. We have also adopted the same technique for evaluating the normal frequencies of vibration of the two isomers of glycol neglecting the motion of the hydrogen atoms. The force constants assumed were the same as those used by Mizushima and others. They are in units of 10^5 dynes/cm. as follows:

$$K_{CH_2\text{-}CH_2} = 3\cdot7, K_{CH\text{-}OH} = 4\cdot6,$$

$$H_{CH_2\text{-}CH_2} = {}_{CH_2\text{-}OH} = 0\cdot20 \text{ and } F_{CH2\text{-}OH} = 0\cdot65.$$

The calculated frequencies are entered in Table II and the corresponding observed Raman frequencies are also given in the same table. The matching up was done on the following basis:

Table II

The calculated and observed skeletal frequencies of ethylene glycol

Configuration	species	Description of vibration	Calculated cm.$^{-1}$	Observed cm.$^{-1}$
Trans	Ag	C–O stretching	1105	1069
C$_2$		C–C stretching	940	863
		C–Ĉ–O bending	416	481
	Bu	C–O stretching	1073	1085
		C–C–O–bending	337	...
Gauche	A	C–O stretching	1098	1093
C$_2$		C–C stretching	928	863
		C–Ĉ–O bending	358	348
	B	C–O stretching	1033	1044
		C–C–O bending	502	525

For the trans isomer which has a centre of symmetry, the Raman and infrared frequencies should be mutually exclusive. The liquid spectrum exhibits two Raman lines at 481 and 1069 cm.$^{-1}$ which are absent in infrared absorption. These two lines have therefore been assigned to the vibration of the trans isomer. The C–C stretching mode gives rise to a polarised Raman line. There is only one polarised Raman line at 863 cm.$^{-1}$ assignable to C–C stretching. It is therefore assumed that the C–C stretching mode has nearly the same frequency for both the isomers and is therefore assigned to both the isomers. In view of the various approximations involved in the calculations, the agreement between the observed and calculated frequencies can be considered as fairly satisfactory.

In order to check up the correctness of the assignments given in Table II for the skeletal modes, the sum rule for the rotational isomers enunciated by Mizushima and others (1953) is applied. The sum rule states

$$\sum_{i=1}^{n} v_i{}^2 = \text{a constant}$$

Using the data given in Table II we have calculated $\sum v_i{}^2$ for both the isomers. For gauche form, the value is $34\cdot05\times10^5$ and for the transform it is $33\cdot78\times10^5$. They are nearly equal showing thereby the correctness of the assignments.

Comparing the Raman spectra of the liquid and solid and the infrared absorption spectrum of the liquid, it may be concluded that in the liquid state both the configurations exist while in the solid state, glycol exists only in the gauche form. It has not been possible to estimate the relative proportions of the isomers present in the liquid at ordinary temperatures.

In most of the dihalogene ethanes, the stabler form in the solid state is the trans configuration (Mizushima, 1954). From what has been said above it is clear that in solid glycol the stabler form is the gauche configuration. It can be seen from Fig. 3 that the gauche form contains an intramolecular hydrogen bond with an O–O distance of $2\cdot96$ Å This accounts for the lowering of the frequency of the O–H stretching mode and its appearance as a broad band with a maximum at about 3390 cm.$^{-1}$ in the Raman spectrum of liquid glycol. In the solid state this band is split up into a doublet due to intermolecular interaction.

In the liquid spectrum one notices a strong Raman line at 2719 cm.$^{-1}$ which is absent in the solid spectrum and is also absent in the very dilute aqueous solution. This line should therefore be attributed to the trans form. Molecules belonging to this configuration can form hydrogen bonds through the hydroxyl group with their neighbours. Since it is known, that glycol is a strongly associated liquid these intermolecular hydrogen bonds are expected to be very strong. The frequency of the O–H stretching mode will be very much reduced and it appears at 2719 cm.$^{-1}$

Effect of Dilution.—In order to investigate the effect of solvent like water on the Raman frequencies, the spectra of aqueous solutions of glycol containing 50%, 25%, $12\cdot5\%$ and $6\cdot25\%$ by volume of glycol have been recorded using $\lambda\,2536\cdot5$ excitation. The microphotometer records of the spectrograms are reproduced in Fig. 4 along with that of pure glycol. Records were also taken with the Cary instrument for two concentrations of the aqueous solution, namely 20% and very dilute. The 1000–1100 cm.$^{-1}$ region of the
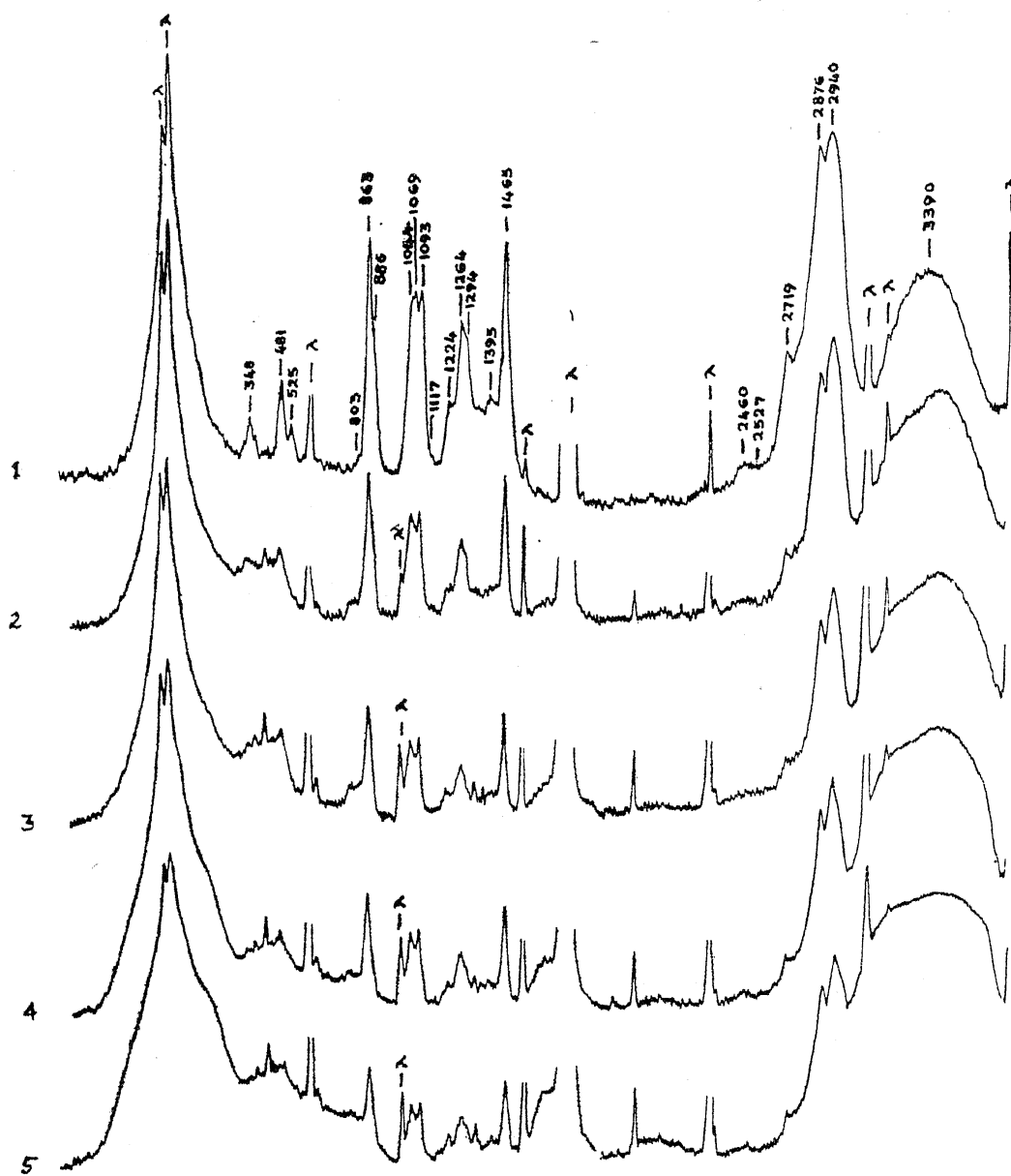
FIG. 4. Microphotometer records of the Raman spectra of glycol and its aqueous solutions. Percentage of glycol: (1) 100%, (2) 50%, (3) 25%, (4) 12·5% and 6·25% by volume.

spectrogram taken with Cary instrument is reproduced in Fig. 5. The most important change that one notices on dilution is a progressive decrease in intensity of the 481 and 1069 lines which are characteristic of the trans form. In the 400–500 cm.$^{-1}$ one can notice the appearance of a broad water band in the aqueous solution which has a disturbing effect on the 481 line. From the observed changes in the Raman spectrum, it may be concluded that the

proportion of the trans form progressively decreases on dilution and the gauche form gets stabilised. Similar behaviour is exhibited by ethylene chlorohydrin (Mizushima and others, 1940). Water being a polar solvent, apparently stabilises the gauche form which is also polar, through dipole-dipole interaction and eliminates the trans form which has no dipole moment.
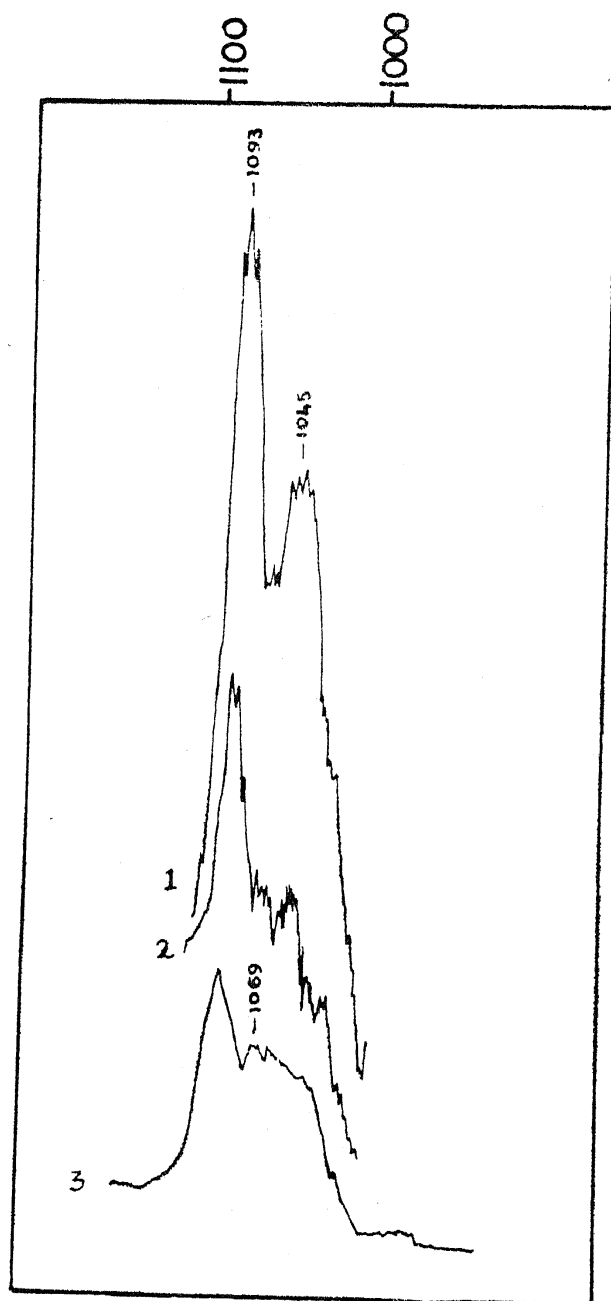

FIG. 5. Records of Raman spectra (in the region 1000–1100 cm.$^{-1}$) of (1) glycol, (2) 20% glycol solution and (3) very dilute glycol solution taken with Cary 81 Raman spectrophotometer.

5. ACKNOWLEDGEMENT

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