Indian J. Phys **47**, 494–498 (1973)

A note on the assignment of the vibrational frequencies of 1, 2-dibromopropane

J. SOM AND G. S KASTHA

Optics Department, Indian Association for the Cultivation of Science, Calcutta-32

(*Received* 9 *October* 1972)

From a comparative study of the Raman and infrared spectra of 1,2-dibromopropane in the liquid and solid states obtained from this investigation and those reported by previous workers a complete assignment of the observed frequencies of the molecules of 1,2-dibromopropane has been given in terms of modes of vibration of all the three rotational isomeric forms of the molecule

INTRODUCTION

The existence of three rotational isomeric forms of the molecules of 1,2-dibromopropane was established by several workers from studies of the Raman and infrared spectra of the compound. They concluded that all the three forms are present in the vapour phase and the configuration in which the two Br-atoms are trans to each other has the lowest energy (Pozdyshev *et al* 1957, Nakamura 1957). In the liquid state also all the three rotamers are present but only the trans form of the molecule is observed in the solid state (Nakamura 1957). The above conclusions were arrived at from a partial analysis of the vibrational spectra of 1,2-dibromopropane in the region of C-Br stretching vibrations but no report on the complete assignment of all the observed vibration frequencies of the molecule has yet appeared. The vibrational assignment of 1,2-dichloropropane which is similar to 1,2-dibromopropane has been made only recently (Dempster *et al* 1971) The purpose of this note is to report an analysis of the vibrational spectrum of 1,2-dibromopropane.

EXPERIMENTAL

Pure 1,2-dibromopropane procured from Schuchardt (Germany) was subjected to repeated distillation under reduced pressure before being used in the investigation. The Raman spectrum of the compound in the solid state at 93°K and the qualitative depolarization character of the Raman lines of the liquid were obtained with a Fuess glass spectrograph in the usual manner. The Raman and infrared spectra of the liquid were reinvestigated so that the frequencies observed in the present investigation may be compared with those reported by previous workers (Pozdyshev *et al* 1957).

RESULTS

The Raman frequency shifts of 1,2-dibromopropane with their polarization characters and relative visual intensities together with the wavenumbers of the infrared absorption maxima and their approximate strengths are given in table 1. The data on the infrared absorption spectrum of the compound in the liquid and solid states given by Pozdyshev *et al* (1957) are also included in the table. The assignment of the vibration frequencies given in the last column of the same table have been made with the help of all the relevant data entered in the table. These are discussed in the following paragraphs

DISCUSSION

The molecules of 1,2-dibromopropane, as already mentioned, exist in three isomeric forms analogous to those observed in the molecules of 1,2-dichloropropane. The three forms, respectively, termed trans (t), gauche-1 (g_1) and gauche-2 (g_2) are shown schematically in figure 1.

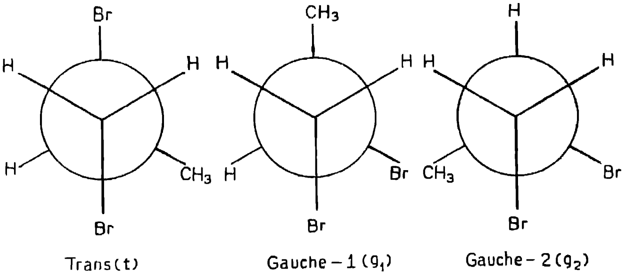

Fig. 1

The energies of the three conformers of the free molecules of 1,2-dibromopropane are in the order $E_t < E_{g1} < E_{g2}$ (Pozdyshev *et al* 1957). The energy difference between the forms t and g_2 is the highest and the form g_2 is present in very small amount in both vapour and liquid phases but in the solid state only the form t is present (Nakamura 1957). Thus the Raman lines and infrared bands due to the solid phase are attributed to the trans isomer of the molecule. It may be noted from table 1 that many vibrational frequencies found in the Raman and infrared spectra of the solid are also present in the corresponding spectra of the liquid and in such cases many of them have been assigned to all the three isomers.

In the present molecule many of the vibration frequencies of the CH_3, CH_2 and CH groups and also the skeletal C–C stretching vibrations are similar to those of 1,2-dichloropropane (Dempster *et al* 1971) and their assignments made from a direct comparison are given in table 1. In the following paragraphs the assignments of the frequencies due to the C–C–C and C–C–Br deformation modes are briefly discussed The assignments of the C–Br stretching vibrations have been discussed by Nakamura (1957) All the assignments are shown in table 1

TABLE 1 Raman shifts and infrared frequencies of 1,2-dibromopropane

Raman shifts (cm^{-1}) Present authors		Infrared frequencies (cm^{-1}) Present authors	Pozdyshev *et al* 1957		Possible Assignment
Liquid	Solid	Liquid	Liquid	Solid	
186 8P	186 (5)				C–C–Br def. t
294 6P	294 (4)				C–C–Br def. t
357 3P					C–C–Br dr. g_1, g_2 C–C–C–def. t
404 1					C–C–C def. g_1,
454 2					C–C–C def. g_2
525 4b P			530 549		C–Br stretch C–Br stretch g_1,
566 3 P	566 (1)		570	567 593	C–Br stretch t 2 × 294
650 10b,P	650 (8)	652 (s)	653	648	C–Br stretch t
		665 (m)			C–Br stretch g_1 g_2
		685 (w)			
		699 (w)			
		743 (ms)	752		CH_2 rock g_1, g_2
		761 (w,sh)		770	
			833	825	CH_2 rock, t
840 5 D	820 (2)	847 (m)	847	847	CH_2 rock t
		863 (w)	860		CH_2 rock g_1, g_2
895 6 D	895 (4)		898	901	CH_3 rock t
		904 (ms)	907		CH_3 rock g_1, g_2
		914 (w,sh)		916	
			982		C–C stretch g_1, g_2
1004 1 P		1006 (s)	996		C–C stretch g_1, g_2
1039 1 P		1043 (s)	1035	1034	C–C stretch t
			1093	1095	C–C stretch t

Table 1—contd.

Raman shifts (cm^{-1}) Present authors		Infrared frequencies (cm^{-1}) Present authors	Pozdyshev *et al* 1957		Possible Assignment
Liquid	Solid	Liquid	Liquid	Solid	
1120 1		1124 (m)	1116	1117	CH_3 rock t
			1138		CH_2 twist g_1, g_2
1157 3 P	1157 (1)	1161 (vsb)		1154	CH_2 twist t
			1174		CH_2 twist g_1, g_2
				1185	CH_2 twist t
			1203		CH def. g_1, g_2
1220 0		1216 (s)	1217	1212	(CH) def. t
1232 8 D	1232 (6)	1229 (ms)	1228	1235	CH_2 wag. t
		1246 (ms)			CH def g_1, g_2
1310 1		1317 (m)	1300		CH_2 wag. g_1, g_2
			1332		CH_2 wag. g_1, g_2
1340 1		1341 (vwb)		1347	(CH) def. t
			1372		
1380 1		1385 (vs)	1384	1382	Sym. CH_3 def. t
				1396	
1425 2D	1425 (1)	1429 (m)	1420	1432	CH_2 scissor t, g_1, g_2
1448 3b D	1448 (1)	1448 (s)	1448	1457	Asym. CH_3 def. t, g_1, g_2
2925 5P	2925 (3)	2923 (mb)			CH, CH_2 and CH_3 stretch } t, g_1, g_2
2965 6P	2965 (6)				

t—trans, g—gauche, P—polarised, D—depolarised, b—broad, s—strong, m—medium, w—weak, v—very, sh—shoulder.

C–C–C *deformation mode* :

The vibration frequencies due to this mode in 1,2-dichloropropane were not given by Dempster *et al* (1971) but Klaboe (1970) has identified this mode in 2-bromopropane at 403 cm^{-1}. Further, Trogrimsen & Klaboe (1970) reported the C–C–C bending vibrations in 1-propanethiol at 363 and 457 cm^{-1}. In the present molecule two weak Raman lines at 454 and 404 cm^{-1} and a medium weak line at 357 cm^{-1} have been observed in the spectrum of the liquid which most probably represent the deformation modes of vibration of the molecule. The absence of the first two Raman lines in the spectrum of the solid could not be definitely established because of their low intensities, but the third

Raman line seems to be absent in the solid state spectrum. The frequencies 454 and 404 cm^{-1} are assigned to all the three rotamers while the frequency 357 cm^{-1} may be attributed to the rotamers only. However, the frequency 357 cm^{-1} may be given an alternative assignment as discussed below

C–C–Br *deformation mode* ·

In 1,2-dibromoethane Mizushima (1954) identified the C–C–Br deformation modes in the trans isomer at 190 cm^{-1} while those due to the gauche form at 355 and 231 cm^{-1} In 2-bromopropane the frequencies of the C–C–Br deformation modes given by Klaboe (1970) are 282 and 290 cm^{-1}. In 1,2-dibromopropane there are two strong Raman lines 186 and 294 cm^{-1} which are also present in the spectrum of the solid and hence, are attributable to the C–C–Br deformation modes of the trans isomer.

As already pointed out the frequency 357 cm^{-1} may be assigned to a C–C–C deformation mode of the isomers However, following Mizushima, this may also represent the C–C–Br deformation vibration of the gauche isomers Both these assigments are shown in table 1

REFERENCES

Dempster A B Price K. & Sheppard N. 1971 *Spectrochim. Acta* **27A**, 1563.
Klaboe P. 1970 *Spectrochim. Acta* **26A**, 87.
Mizushima S 1954 *Structure of Molecules and Internal Rotation*, Academic Press, Inc., p. 197
Nakamura K 1957 *Nippon Kagaku Zasshi* **78**, 1158
Pozdyshev V A Pentin Yu. A. & Tatevskii V M. 1957 *Optika. i spectroscopiya* **3**, 211
Torgrimsen T. & Klaboe P. 1970 *Acta. Chem. Scan.* **24**, 1139.