

# THE RAMAN AND INFRARED SPECTRA OF PENTAFLUOROTHIOPHENOL

K. SINGH, S. C. SRIVASTAVA AND I. S. SINGH

Department of Physics (Spectroscopy Section), Banaras Hindu University, Varanasi-5

## ABSTRACT

The Raman spectrum with polarization measurement of pentafluorothiophenol (liquid) has been recorded on a Spex-spectrophotometer model 1400 using a He-Ne laser source. The infrared spectrum of this sample has been recorded in liquid phase on a Perkin-Elmer 621 grating spectrophotometer at high resolution. Assignments of the observed frequencies assuming  $C_{2v}$  symmetry for the molecule have been presented.

## INTRODUCTION

ASSIGNMENTS have been made for a number of fluorinated benzenes<sup>1-5</sup>. In a recent review on the vibrational spectra of fluorinated organic compounds Brown and Morgan<sup>6</sup> have drawn attention to the lack of information on complete vibrational assignments of substituted pentafluorobenzenes. The vibrational spectra of the parent compound hexafluorobenzene have been studied and assignments of the observed frequencies have been proposed<sup>5</sup>. The vibrational spectra of several pentafluorobenzene derivatives have also been studied<sup>7-13</sup>. Recently the vibrational spectra of pentafluorostyrene have been studied and assignments of the observed frequencies have been proposed<sup>14</sup>. In the present paper the results obtained in a study of the vibrational spectra of pentafluorothiophenol in liquid phase have been presented.

## EXPERIMENTAL

The pure sample for the present work was obtained from Koch-Light Laboratory, England. The Raman spectrum (in liquid phase) with polarization measurements was recorded on a spex-spectrophotometer model 1400 equipped with a He-Ne laser source. The accuracy of measurements is estimated to be within  $2\text{ cm}^{-1}$ . The infrared spectrum of the compound (in liquid phase) was recorded on a Perkin-Elmer 621 grating spectrophotometer in the region  $250\text{--}4000\text{ cm}^{-1}$ . A KBr cell of  $0.1\text{ mm}$  path-length was used to record the spectrum below  $700\text{ cm}^{-1}$ . For above  $700\text{ cm}^{-1}$  a thin liquid film between two NaCl windows was used.

## RESULTS AND DISCUSSION

The pentafluorothiophenol molecule has approximately  $C_{2v}$  symmetry. The 33 normal vibrations of  $C_6F_5SH$  are distributed among the symmetry classes as follows:

$$12 a_1 + 11 b_1 + 3 a_2 + 7 b_2$$

The 30 fundamental vibrations of  $C_6F_5X$  molecule (where X is an atom) divide among the symmetry classes of the point group  $C_{2v}$

$$11 a_1 + 10 b_1 + 3 a_2 + 6 b_2$$

as follows:

Thus the SH group gives rise to one  $a_1$  vibration (SH stretching mode), one  $b_1$  vibration (SH in-plane-bending mode) and one  $b_2$  vibration (SH out-of-plane bending mode). The vibrations belonging to species  $a_1$ ,  $b_1$  and  $b_2$  are active in both the infrared and Raman spectra. But the vibrations belonging to  $a_2$  species are active only in the Raman spectrum. The vibrations of  $a_1$  species are polarized whereas the vibrations belonging to  $a_2$ ,  $b_1$  and  $b_2$  species are depolarized in the Raman spectrum,  $a_1$  and  $b_1$  species represent in-plane vibrations whereas  $a_2$  and  $b_2$  species represent out-of-plane vibrations.

The traces of the Raman and infrared spectra are reproduced in Figs. 1 and 2 (a, b)

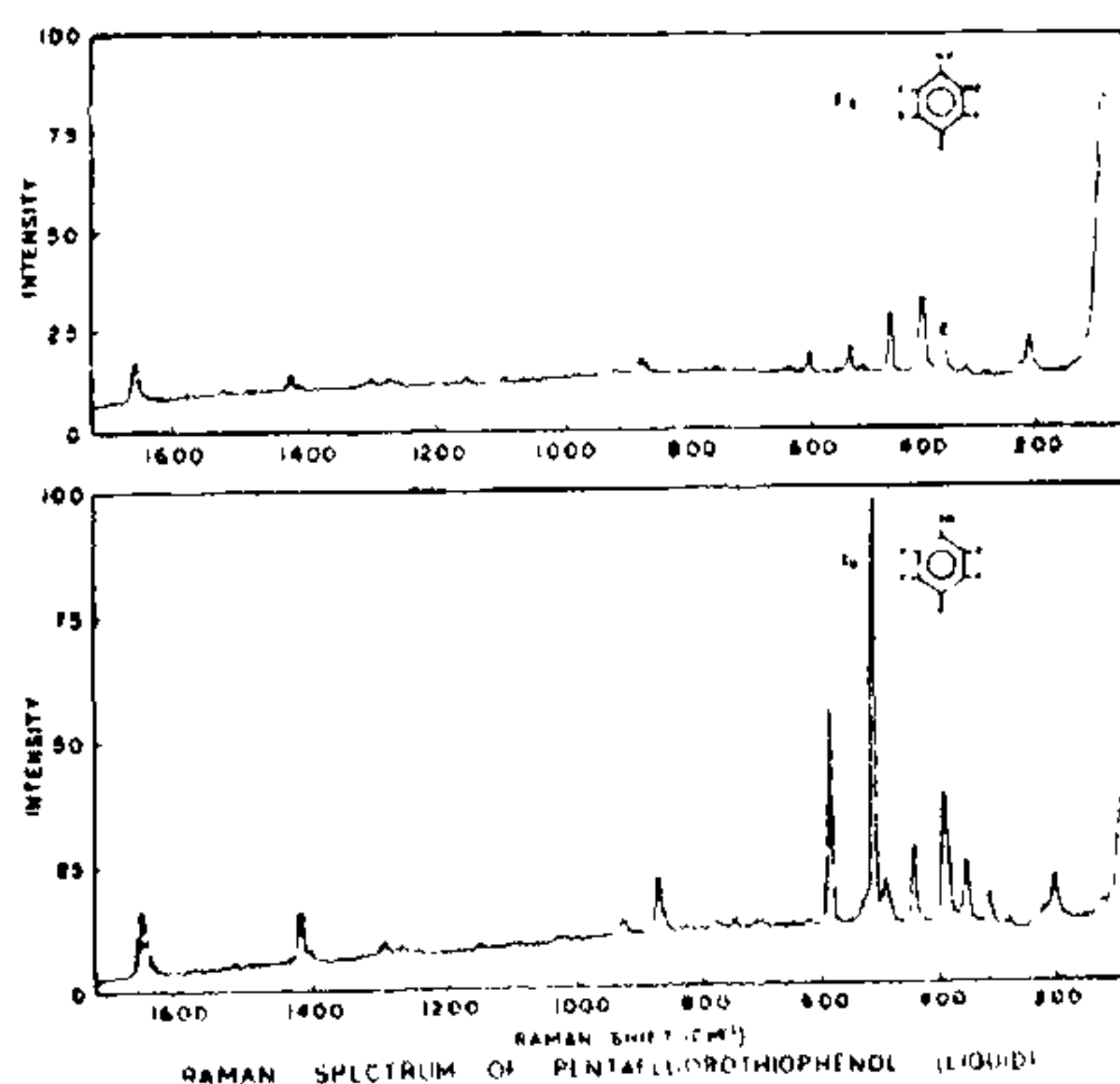
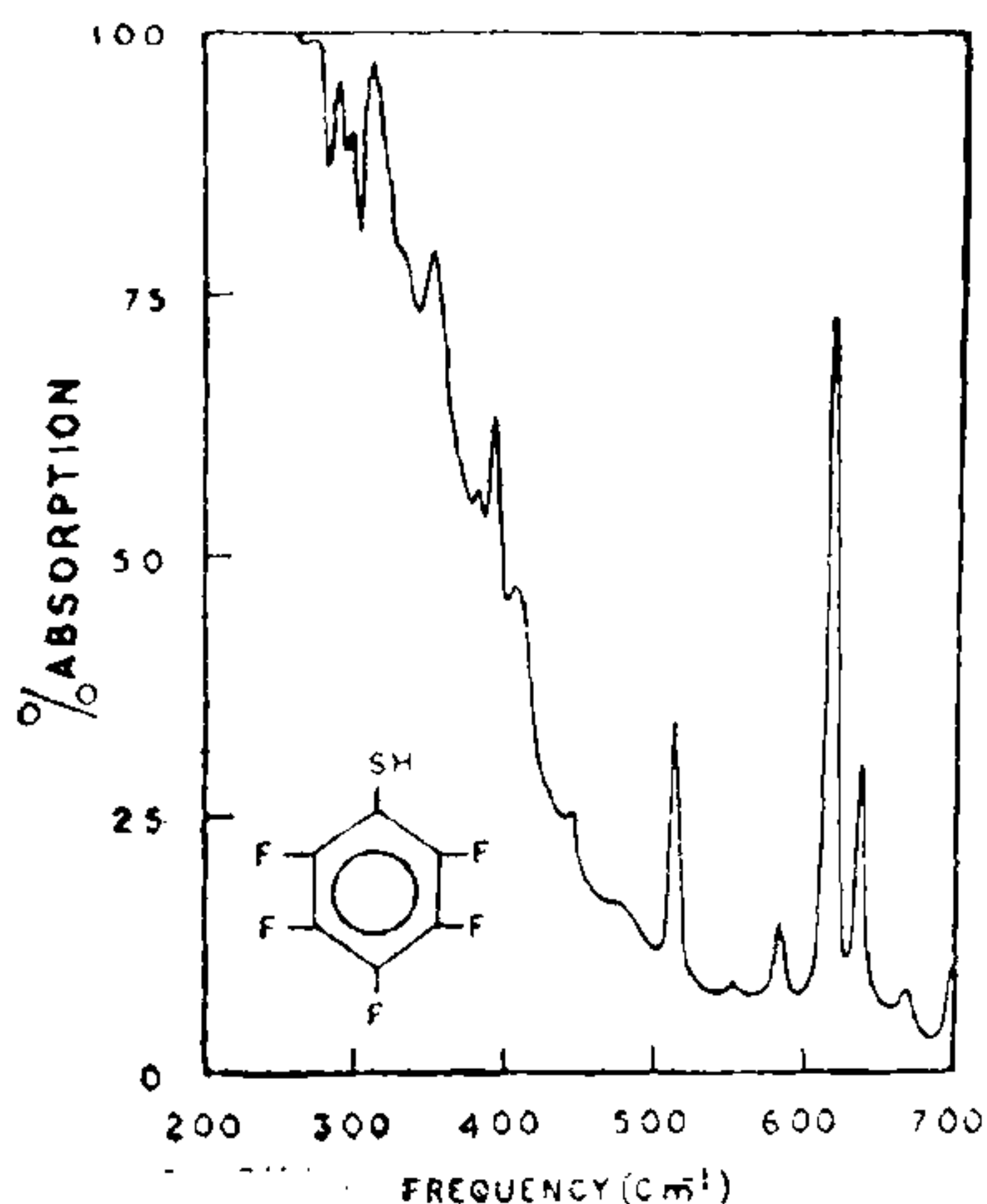


FIG. 1

respectively. Fundamental frequencies are given in Table I.



INFRARED SPECTRUM OF  
PENTAFLUORO - THIO - PENOL  
0.1 m.m.

FIG. 2 (a)

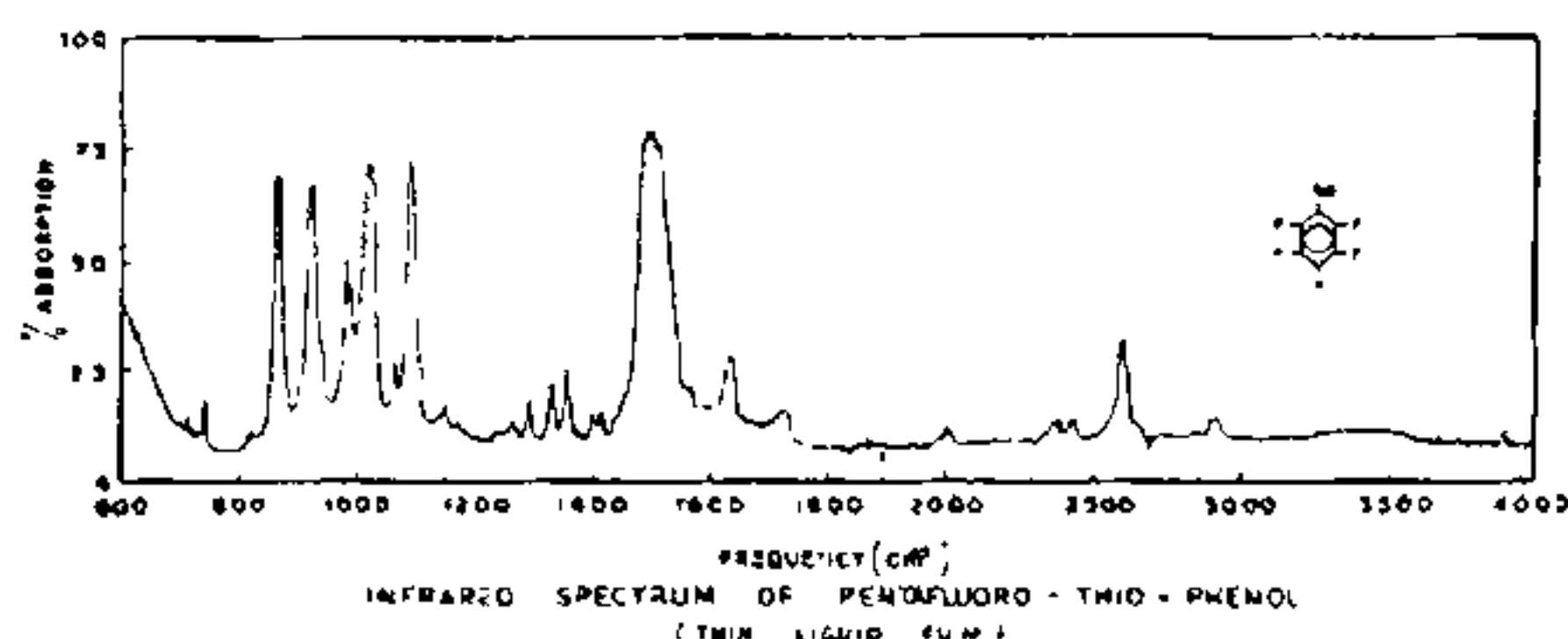


FIG. 2 (b)

#### ASSIGNMENTS

##### $a_1$ Class

The twelve vibrations belonging to  $a_1$  class of  $C_6F_5SH$  molecule include three  $C=C$  stretching, three  $C-F$  stretching, one  $(C_6F_5)-SH$  stretching, two  $C-C-C$  in-plane-bending, two  $C-F$  in-plane-bending and one  $S-H$  stretching vibrations. The Raman lines 1646, 1513, 1414, 1295, 866, 584, 512, 392, 310 and 272  $cm^{-1}$  have been assigned to this class, since they are polarized. The frequencies 1646  $cm^{-1}$  (S-R and  $m$ -IR), 1513  $cm^{-1}$  ( $vw$ -R and  $vs$ -IR) and 512  $cm^{-1}$  ( $vvs$ -R and  $ms$ -IR) have been assigned to  $C=C$  stretching modes. These vibrations have been derived from 1655  $cm^{-1}$  ( $e_{2g}$ ), 1530  $cm^{-1}$  ( $e_{1u}$ ) and 559  $cm^{-1}$  ( $a_{1g}$ ) vibrations respectively of  $C_6F_6$ . When the symmetry is reduced from  $D_{6h}$  to  $C_{2v}$ , the doubly degenerate species  $e_2$  and  $e_{1u}$  split up into

two components  $a_1$  and  $b_1$ . The frequencies 1414  $cm^{-1}$  (s-R and w-IR) and 1295  $cm^{-1}$  ( $vw$ -R and w-IR) have been assigned to  $C-F$  stretching modes derived from 1490  $cm^{-1}$  ( $a_{1g}$ ) and 1323  $cm^{-1}$  ( $b_{1u}$ ) frequencies respectively of  $C_6F_6$ . The third  $C-F$  stretching vibration belonging to  $a_1$  class derived from 1157  $cm^{-1}$  ( $e_{1u}$ ) of  $C_6F_6$  could not be observed in the Raman spectrum but the very strong infrared band appearing at 1090  $cm^{-1}$  may be assigned to this mode. The assignment of this frequency to  $a_1$  species is in agreement with the assignments proposed for  $C_6F_6Br$  and  $C_6F_5I^8$ . The frequency 866  $cm^{-1}$  ( $m$ -R and  $vs$ -IR) may be assigned to  $(C_6F_5)-SH$  stretching mode. The frequencies 584  $cm^{-1}$  ( $vs$ -R and  $mw$ -IR) and 392  $cm^{-1}$  (s-R and  $ms$ -IR) have been assigned to  $C-C-C$  in-plane-bending modes derived from 640  $cm^{-1}$  ( $b_{1u}$ ) and 443  $cm^{-1}$  ( $e_{2g}$ ) frequencies of  $C_6F_6$ . The other component of the  $e_{2g}$  mode is depolarized and is assigned to  $b_1$  species. The two  $C-F$  in-plane-bending vibrations belonging to this class have been identified at 310  $cm^{-1}$  (w-R and  $vs$ -IR) and 272  $cm^{-1}$  ( $vw$ -R and  $vs$ -IR). These modes have been derived from 315  $cm^{-1}$  ( $e_{1g}$ ) and 264  $cm^{-1}$  ( $e_{2g}$ ) frequencies of  $C_6F_6$ . The  $S-H$  stretching vibration is generally weak in the infrared spectrum<sup>15-19</sup> and appears in the region 2500-2600  $cm^{-1}$ . We have assigned the frequency 2600  $cm^{-1}$  observed with medium intensity in the infrared spectrum to this mode.

##### $b_1$ Class

The eleven vibrations belonging to  $b_1$  class of  $C_6F_5SH$ . The  $S-H$  stretching vibration is generating, two  $C-F$  stretching, one  $C-C-C$  in-plane-bending, three  $C-F$  in-plane-bending and one  $S-H$  in-plane-bending vibrations. The depolarized Raman lines 1269, 1148, 1018, 857, 744, 444 and 202  $cm^{-1}$  have been assigned to  $b_1$  class vibrations. The frequency 1269  $cm^{-1}$  ( $vw$ -R and  $vvw$ -IR) has been assigned to  $C=C$  stretching mode corresponding to 1253  $cm^{-1}$  ( $b_{2u}$ ) frequency of  $C_6F_6$ . The other two  $b_1$  class  $C=C$  stretching frequencies are derived from 1655  $cm^{-1}$  ( $e_{2g}$ ) and 1530  $cm^{-1}$  ( $e_{1u}$ ) modes of  $C_6F_6$ . In the present investigation the  $b_1$  components of these modes could not be observed in the Raman spectrum. However, the frequency 1500  $cm^{-1}$ , which appears in the infrared spectrum with very high intensity, has been correlated with the  $b_1$  component of the  $e_{1u}$  mode (1530  $cm^{-1}$ ) whereas the  $C=C$  stretching frequency corresponding to 1655  $cm^{-1}$  frequency could not be assigned. It may be



TABLE I  
Vibrational frequencies and their assignments for pentafluorothiophenol

Raman shift (cm <sup>-1</sup> )	Raman Int.	Dep. ratio	I.R. Freq. (cm <sup>-1</sup> )	I.R. Int.	Assignment
111	vw	0.87 D	..	..	$a_2, b_2$ C—F o.p. bending
202	m	0.90 D	..	..	$b_1$ C—F i.p. bending
214	w	0.88 D	..	..	$b_2$ C—F o.p. bending
272	vw	0.50 P	272	m	$a_1$ C—F i.p. bending
			287	ms	$b_2$ C—(SH) o.p. bending
			295	m	$b_1$ C—F i.p. bending
310	w	0.43 P	310	vs	$a_1$ C—F i.p. bending
351	m	0.92 D	350	s	$b_2$ C—F o.p. bending
375	vw	0.86 D	..	..	$a_2$ C—F o.p. bending
392	s	0.57 P	392	ms	$a_1$ C—C—C i.p. bending
444	ms	0.88 D	443	m	$b_1$ C—C—C i.p. bending
491	m	0.23 P	491	sh	..
512	vvs	0.07 P	512	ms	$a_1$ C—C stretching (ring)
584	vs	0.12 P	585	mw	$a_1$ C—C—C i.p. bending
618	vw	1.2 D	616	ms	$b_2$ C—C—C o.p. bending
648	vvw	..	..	..	$a_2$ C—C—C o.p. bending
667	vvw	..	670	vw	$b_2$ S—H o.p. bending
708	vvw	..	712	vvw	$b_2$ C—C—C o.p. bending
744	vvw	0.90 D	740	vw	$b_1$ C—F i.p. bending
857	vvw	0.87 D	857	sh	$b_1$ S—H i.p. bending
866	m	0.33 P	866	vs	$a_1$ (C <sub>6</sub> F <sub>5</sub> )—SH stretching
923	w	0.50 P	922	s	$a_1$ C—SH bending
1018	vvw	D?	1020	vvs	$b_1$ C—F stretching
..	..	..	1090	vs	$a_1$ C—F stretching
1148	vvw	1.0 D	1146	vw	$b_1$ C—F stretching
1269	vw	0.86 D	1263	vvw	$b_1$ C=C stretching
1295	vw	0.78 P	1291	vw	$a_1$ C—F stretching
1414	s	0.30 P	1412	vw	$a_1$ C—F stretching
..	..	..	1500	vvs	$b_1$ C=C stretching
1513	vvw	0.75 P	1511	vs	$a_1$ C=C stretching
1646	s	0.53 P	1635	m	$a_1$ C=C stretching
			2600	m	$a_1$ S—H stretching

N.B.—i.p.=in-plane, o.p.=out-of-plane, m=medium, w=weak, v=very, sh=shoulder,  
D=Depolarized, P=Polarized, s=strong, I.R.=Infrared, Int.=Intensity.

mentioned that the same frequency has been assigned to both  $a_1$  and  $b_1$  components in the vibrational study of C<sub>6</sub>F<sub>5</sub>X<sup>8</sup> (X=Cl, Br, I) and C<sub>6</sub>F<sub>5</sub>CN<sup>9</sup> corresponding to the  $e_2$  mode. The frequencies 1148 cm<sup>-1</sup> (vvw-R, vw-IR) and 1018 cm<sup>-1</sup> (vvw-R, vvs-IR) have been assigned to C—F stretching modes derived from 1157 cm<sup>-1</sup> ( $e_{2g}$ ) and 1011 cm<sup>-1</sup> ( $e_{1u}$ ) frequencies of C<sub>6</sub>F<sub>6</sub>. The frequency 857 cm<sup>-1</sup> (vvw-R, w sh-IR) has been assigned to S—H in-plane-bending mode. The frequency 444 cm<sup>-1</sup> (ms-R, m-IR) has been assigned to C—C—C in-plane-bending mode derived from 443 cm<sup>-1</sup> ( $e_2$ ) frequency of C<sub>6</sub>F<sub>6</sub>. The frequencies 744 cm<sup>-1</sup> (vvw-R, vw-IR) and 202 cm<sup>-1</sup> (m-R) have been assigned to C—F in-plane-bending modes derived from 691 cm<sup>-1</sup> ( $a_{2g}$ ) and 208 cm<sup>-1</sup> ( $b_{2u}$ ) frequencies of C<sub>6</sub>F<sub>6</sub>. The medium strong infrared band appearing at 295 cm<sup>-1</sup> may be assigned to the third C—F in-plane-bending mode derived from 315 cm<sup>-1</sup> ( $e_{1u}$ ) frequency of C<sub>6</sub>F<sub>6</sub>. The assignment of this frequency to  $b_1$  species is in agreement with the assignment proposed for C<sub>6</sub>F<sub>5</sub>CN<sup>9</sup>.

#### $a_2$ Class

Out of three  $a_2$  vibrations, one vibration is derived from 595 cm<sup>-1</sup> ( $e_{2u}$ ) C—C—C out-of-plane-bending mode of C<sub>6</sub>F<sub>6</sub> and two vibrations are derived from 370 cm<sup>-1</sup> ( $e_{1g}$ ) and 125 cm<sup>-1</sup> ( $e_{2u}$ ) C—F out-of-plane-bending modes of C<sub>6</sub>F<sub>6</sub>. In the present investigation the frequency 648 cm<sup>-1</sup> (vvw-R) has been assigned to C—C—C out-of-plane-bending mode. The frequencies 375 cm<sup>-1</sup> (vw-R) and 111 cm<sup>-1</sup> (vw-R) are depolarized and have been assigned to C—F out-of-plane-bending modes. The depolarization ratio of 648 cm<sup>-1</sup> frequency could not be determined due to its weakness. All of these vibrations are active in the Raman spectrum only as expected.

#### $b_2$ Class

The seven vibrations belonging to  $b_2$  class include two C—C—C, three C—F, one C—(SH) and one S—H out-of-plane-bending vibrations. The frequencies 708 cm<sup>-1</sup> (vvw-R, vvw-IR) and 618 cm<sup>-1</sup> (vw-R, s-IR) have

been assigned to C-C-C out-of-plane-bending vibrations. These are derived from  $714\text{ cm}^{-1}$  ( $b_{2g}$ ) and  $595\text{ cm}^{-1}$  ( $e_{2u}$ ) frequencies of  $\text{C}_6\text{F}_6$ . The frequencies  $351\text{ cm}^{-1}$  (m-R, s-IR),  $214\text{ cm}^{-1}$  (w-R) and  $111\text{ cm}^{-1}$  (vw-R) have been assigned to C-F out-of-plane-bending modes. These vibrations have been derived from  $370\text{ cm}^{-1}$  ( $e_{1g}$ ),  $215\text{ cm}^{-1}$  ( $a_{2u}$ ) and  $125\text{ cm}^{-1}$  ( $e_{2g}$ ) frequencies of  $\text{C}_6\text{F}_6$ . The frequency  $667\text{ cm}^{-1}$  (vw-R, vw-IR) has been assigned to S-H out-of-plane-bending mode. In thio-benzoic acid<sup>20</sup> the frequency  $680\text{ cm}^{-1}$  has been assigned to this mode. The medium strong infrared band at  $287\text{ cm}^{-1}$  may be assigned to C-(SH) out-of-plane-bending mode. Although this frequency has not been observed in the Raman spectrum, the magnitude is of the right order. The frequency  $111\text{ cm}^{-1}$  has been assigned to both  $a_2$  and  $b_2$  species.

#### ACKNOWLEDGEMENTS

The authors are indebted to Prof. Jacob Shamir of Hebrew University, Jerusalem, Israel, for obtaining the Raman spectrum of the sample through S. R. Singh. We are also thankful to Prof. G. B. Singh, Head, Chemistry Department, Banaras Hindu University, for permission to use P.E. 621 infrared spectrophotometer. One of us (K. Singh) is thankful to U.G.C., New Delhi, for financial assistance.

1. Nielson, J. R., Liang, C. and Smith, D. C., *Discussions Faraday Soc.*, 1950, 9, 177.
2. Ferguson, E. E., *J. Chem. Phys.*, 1953, 21, 886.
3. —, Hudson, R. L., Nielson, J. K. and Smith, D. C., *Ibid.*, 1953, 21, 1457.
4. —, —, — and —, *Ibid.*, 1953, 21, 1464.
5. Steele, D. and Whiffen, D. H., *Trans. Faraday Soc.*, 1959, 55, 369.
6. Brown, J. K. and Morgan, K. J., *Advances in Fluorine Chemistry*, Edited by Stacey, M., Tatlow, J. C. and Sharpe, A. G., 1965, 4, 253.
7. Steele, D. and Whiffen, D. H., *Spectrochim. Acta*, 1960, 16, 368.
8. Long, D. A. and Steele, D., *Ibid.*, 1963, 19, 1955.
9. Shurvell, H. F., Blair, A. S. and Jakobsen, R. J., *Ibid.*, 1968, 24 A, 1257.
10. Bailey, R. T. and Hasson, S. G., *Ibid.*, 1968, 24 A, 1891.
11. Mooney, E. F., *Ibid.*, 1968, 24 A, 1999.
12. Ammini Amma, R., Nair, K. P. R. and Rai, D. K., *Ind. J. Pure and Appl. Phys.*, 1969, 7, 519.
13. Hyams, I. J., Lippincott, E. R. and Bailey, R. T., *Spectrochim. Acta*, 1966, 22, 695.
14. Singh, K. and Singh, I. S., *Curr. Sci.* (under publication).
15. Scott, D. W., McCullough, J. P., Hubbard, W. N., Hossenlopp, I. A., Frow, F. R. and Guy Waddington, *J. Am. Chem. Soc.*, 1956, 78, 5463.
16. Sheppard, N., *Trans. Faraday Soc.*, 1950, 46, 429.
17. Bell, F. K., *Chem. Ber.*, 1927, 60 B, 1749.
18. —, *Ibid.*, 1928, 61 B, 1918.
19. Williams, *Phys. Rev.*, 1938, 54, 504.
20. Murthy, A. S. N., Rao, C. N. R., Rao, B. D. N. and Venkateswarlu, P., *Trans. Faraday Soc.*, 1962, 58, 855.

## POLYPHENOLS OF THE LEAVES OF *MAJORANA HORTENSIS*

S. SANKARA SUBRAMANIAN AND A. G. R. NAIR

Department of Chemistry, Jawaharlal Institute of Postgraduate Medical Education and Research, Pondicherry-6

AND

ELOY RODRIGUEZ AND TOM J. MABRY

The Cell Research Institute and Department of Botany, University of Texas at Austin, Texas, U.S.A.

#### ABSTRACT

A new flavone designated majoranin, shown to be 4',5,1-trihydroxy-3',6,8-trimethoxy flavone and the 7-glucuronides of dinatin and diosmetin have been isolated from the leaves of *Majorana hortensis*, which also contain a high proportion of hydroquinone.

**M**AJORANA *HORTENSIS* Moench.<sup>1,2</sup> (syn. *Origanum majorana* Linn., fam. Labiatae), a perennial herb commonly grown for its aroma and used as a flavouring agent, stimulant, carminative and emmenagogue, has been earlier known to contain ursolic acid and a bitter substance. Its volatile oil is composed of carvacol, terpineol, camphor and borneol. In

continuation of our chemical studies on *Mentha spicata*<sup>3</sup> and *Anisochilus carnosus*<sup>3</sup> of the same family, we have systematically examined the leaves of *M. hortensis* for flavonoids, and the results are recorded in brief.

Fresh leaves of *M. hortensis* were extracted thrice under reflux with hot 80% ethanol, and the combined extract concentrated in vacuo to