

RAMAN, INFRARED AND ELECTRONIC SPECTRA OF ACENAPHTHYLENE

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ABSTRACT

Raman, infrared and electronic spectra of acenaphthylene have been recorded and studied. The Raman spectrum was recorded on a Spex 1400 II double monochromator using Spectra-Physics 125 He-Ne laser source. The infrared spectra were recorded on a Perkin-Elmer 13U double beam infrared spectrophotometer in nujol mull, CCl_4 solution and in thin film. Detailed assignment of the observed vibrational bands have been made.

The ultraviolet absorption spectra of the molecule in vapour and solution phases have been recorded. The vapour phase spectra were recorded on Zeiss Q-24 medium quartz spectrograph and Hilger E_1 large quartz spectrograph. Three systems of absorption bands lie in the regions 31212-35207, 35447-37815 and 41309-42040 cm^{-1} . The absorption spectrum of the molecule in solution has been recorded on a Cary 14R spectrophotometer in the region 2000-4000 Å. The observed data have been compared with those of Gordon and Yang.

INTRODUCTION

THE molecule acenaphthylene resembles very closely naphthalene loosely coupled with ethylene. The vibrational spectra of acenaphthylene, therefore, are expected to show the characteristics of both naphthalene and ethylene. No detailed work, as regards the Raman and infrared spectra of acenaphthylene has so far been reported. The electronic spectrum of acenaphthylene has recently been studied by Gordon and Yang¹ in vapour and pure crystal phases and in single crystal matrices of acenaphthylene. Bree *et al.*² have also described the absorption of acenaphthylene in durene matrices. Heilbronner *et al.*³ identified, from theoretical calculations, five electronic absorption systems in the near ultraviolet spectrum and determined their relative polarisation and discussed the nature of the electronic excitation. The present investigation deals with the ultraviolet absorption spectra of the molecule in vapour and solution phases. The results have been compared with those of Gordon and Yang¹ and several ambiguities have been noted in the vibrational analysis made by them. Vibrational assignment of the naphthalene molecule has been made extensively by a number of workers⁴⁻⁶. Their work as also the data on Raman and infrared bands of ethylene molecule⁷ have helped us in interpreting the vibrational bands of acenaphthylene.

EXPERIMENTAL PROCEDURE

The chemical acenaphthylene was of E-Merck grade and was purified by the process of sublima-

tion. The Raman spectrum of the compound was recorded with the help of the Spex 1400 II double monochromator using Spectra-Physics 125 He-Ne laser source. The exciting radiation was 6328 Å of neon. The infrared spectra in the region 700-4000 cm^{-1} were recorded on a Perkin-Elmer 13U double beam spectrophotometer in nujol mull, carbon tetrachloride solution and in thin film. The thin film of the compound was prepared by making a concentrated solution of the substance in carbon tetrachloride, a small amount of which was allowed to spread out on a NaCl window. CCl_4 evaporated soon leaving a thin and uniform layer of the substance on the window. While recording the spectra, the prominent peaks were examined again at the lowest speed for recording subsidiary peaks and for accurate measurements.

The ultraviolet absorption spectrum in solution was recorded with the help of a Cary 14R spectrophotometer in the region 2000-4000 Å. Concentration of the solution was in the order of 10^{-4} to 10^{-3} molar and ethanol was used as the solvent. The absorption spectrum in the vapour phase was recorded on a Zeiss Q-24 medium quartz spectrograph and also on a Hilger E_1 large quartz spectrograph. The absorption cell used was one meter long with quartz to pyrex graded seal at each end and it was kept inside a calibrated furnace. Beckman hydrogen lamp was used as the source in the medium quartz and xenon lamp was used as source in E_1 spectrograph. Exposure times varied from 2 to 4 hours with a slit of width 0.05 mm. Kodak B 10 plates were used. Three systems of bands were

developed at temperatures 45, 50 and 60° C. The Raman and infrared spectra are shown in Fig. 2, while the ultraviolet absorption spectrum of the compound is shown in Fig. 3.

RESULTS AND DISCUSSION

Acenaphthylene is assumed to have symmetry C_{2v} so that in accordance with the recommendation of the Joint Commission of Spectroscopy⁸, Z-axis is the highest symmetry axis, i.e., the C_{2v} axis, ZY is the molecular plane and X-axis is perpendicular to the molecular plane as shown in Fig. 1.

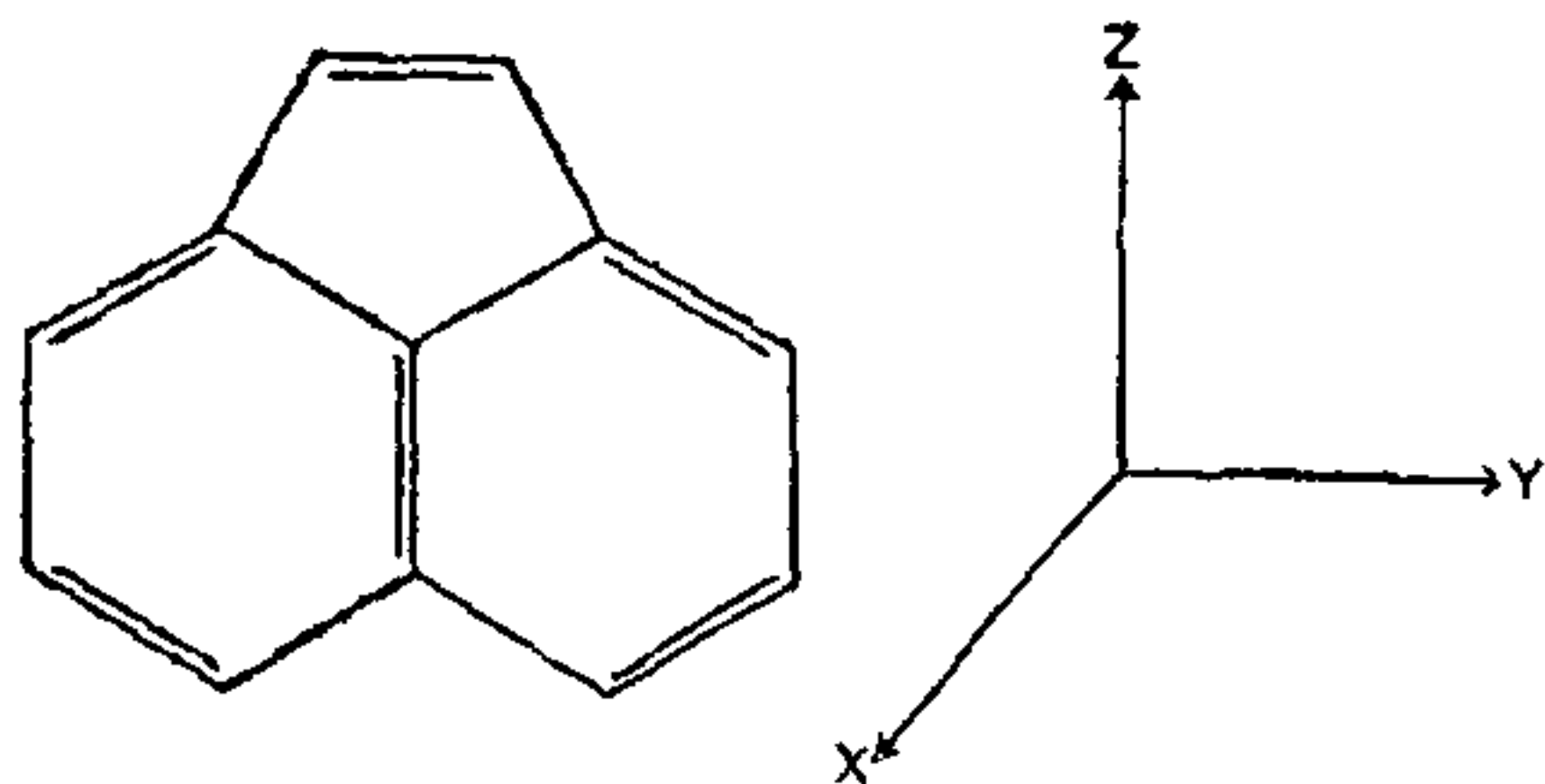


FIG. 1. Molecular structure of acenaphthylene.

Raman and infrared spectra.—The fifty-four normal modes of vibrations can be divided among the symmetry species as $19 a_1 + 8 a_2 + 18 b_1 + 9 b_2$ where, a_1 , b_1 and b_2 are infrared active, and all are active in Raman. Table I gives the assignment of the prominent vibrational frequencies observed in the Raman and infrared spectra of the molecule. Some characteristic bands are discussed below.

Out of eight infrared active C–H mode vibrations, four vibrations with frequencies 3050, 3005, 2950, and 2848 cm^{-1} have been observed giving rise to four bands and they have been identified as fundamentals a_1 , b_2 , b_2 and a_1 respectively. The frequencies 3050, 3005, and 2950 cm^{-1} may be correlated to the frequencies of 3063 (a_1), 3014 (b_{2u}) and 2947 (b_{2u}) cm^{-1} , respectively of the naphthalene molecule. The frequency 2848 cm^{-1} presumably corresponds to an ethylenic C–H stretching mode of vibration, which may be correlated to the frequency 2880 cm^{-1} in ethylene⁷. The frequency 3005 cm^{-1} gives rise to a strong band. In the infrared spectrum of ethylene, there appears a very strong band at 2989 cm^{-1} which has been interpreted as due to C–H stretching mode of b_{3u} type. Thus the above frequency of 3005 cm^{-1} may also be interpreted as due to ethylenic C–H stretching mode. In the Raman spectrum, the frequencies corresponding to C–H stretching mode of vibrations have been identified at 3055 (a_1), 2947 (b_2), 2934 (a_1), 2918 (a_1) and 2876 (a_1) cm^{-1} .

The bands at 1604 and 1538 cm^{-1} (in nujol) are very strong and sharp. They are classified as b_2 and a_1 types of vibrations, corresponding to the

frequencies 1595 (b_{2u}) and 1578 (a_g) cm^{-1} of naphthalene. Similarly the band with frequency 1372 cm^{-1} is very strong and therefore has been conveniently assigned as due to C–C stretching mode which corresponds to the band at 1387 (b_{2u}) cm^{-1} of naphthalene.

The frequency 1635 cm^{-1} (in nujol and CCl_4) probably corresponds to an ethylenic C–C stretching mode. In the Raman spectrum of ethylene⁷ there is a strong band at 1623 cm^{-1} assigned as C–C stretching mode of a_g type.

The medium strong bands at 1450 and 1437 cm^{-1} (in CCl_4) have been tentatively assigned as due to C–H in-plane and out-of-plane bending modes of vibrations. In nujol mull, they have the magnitudes 1445 and 1438 cm^{-1} whereas in solid film there is only one band at 1444 cm^{-1} . In naphthalene, there is only one band at 1440 cm^{-1} , which is actually a doublet classified as H(II) and H(I) bending vibrations having symmetries b_{3g} and b_{1g} . On this basis, the two bands at 1450 and 1437 cm^{-1} may be assigned as in-plane and out-of-plane bending modes of vibrations, corresponding to the unresolved bands at 1440 (b_{3g}) and 1440 (b_{1g}) cm^{-1} of naphthalene. In case this was correct, then there is considerable splitting of the two bands. It is noted that b_{1u} mode which becomes a_2 in C_{2v} symmetry is inactive in infrared. The present observation, however, shows that a_2 mode of vibration appears in CCl_4 and nujol mull but is absent in the infrared spectrum of thin film. Thus the symmetry of the vibrational mode of 1438 cm^{-1} may be actually different from a_2 . In Raman spectrum, this frequency appears as a strong band at 1438 cm^{-1} . The frequency 1450 cm^{-1} observed in Raman and infrared spectra has been correlated with the excited state frequency of 1406 cm^{-1} observed in the ultraviolet spectrum of the compound in solution phase. Gordon and Yang¹ have identified the corresponding frequency of 1378 cm^{-1} as a C–C stretching mode. However, the study of the Raman and infrared spectra of ethylene⁷ shows that ethylenic C–C stretching mode actually does not lie in this region. The only ethylenic C–C stretching mode has already been assigned to the frequency 1635 cm^{-1} .

The medium strong band at 2893 cm^{-1} probably corresponds to the second harmonic of the fundamental at 1438 cm^{-1} . Other C–H in-plane-bending modes identified are 1275 (b_2), 1256 (a_1), 1209 (b_2), 1178 (a_1), 1147 (a_1), 1096 (b_2) and 1122 (b_2) cm^{-1} observed in nujol mull. The corresponding Raman frequencies are 1290, 1259, 1223, 1178, 1156, 1099 and 1021 cm^{-1} respectively. Most of these frequencies can be correlated with the frequencies observed in

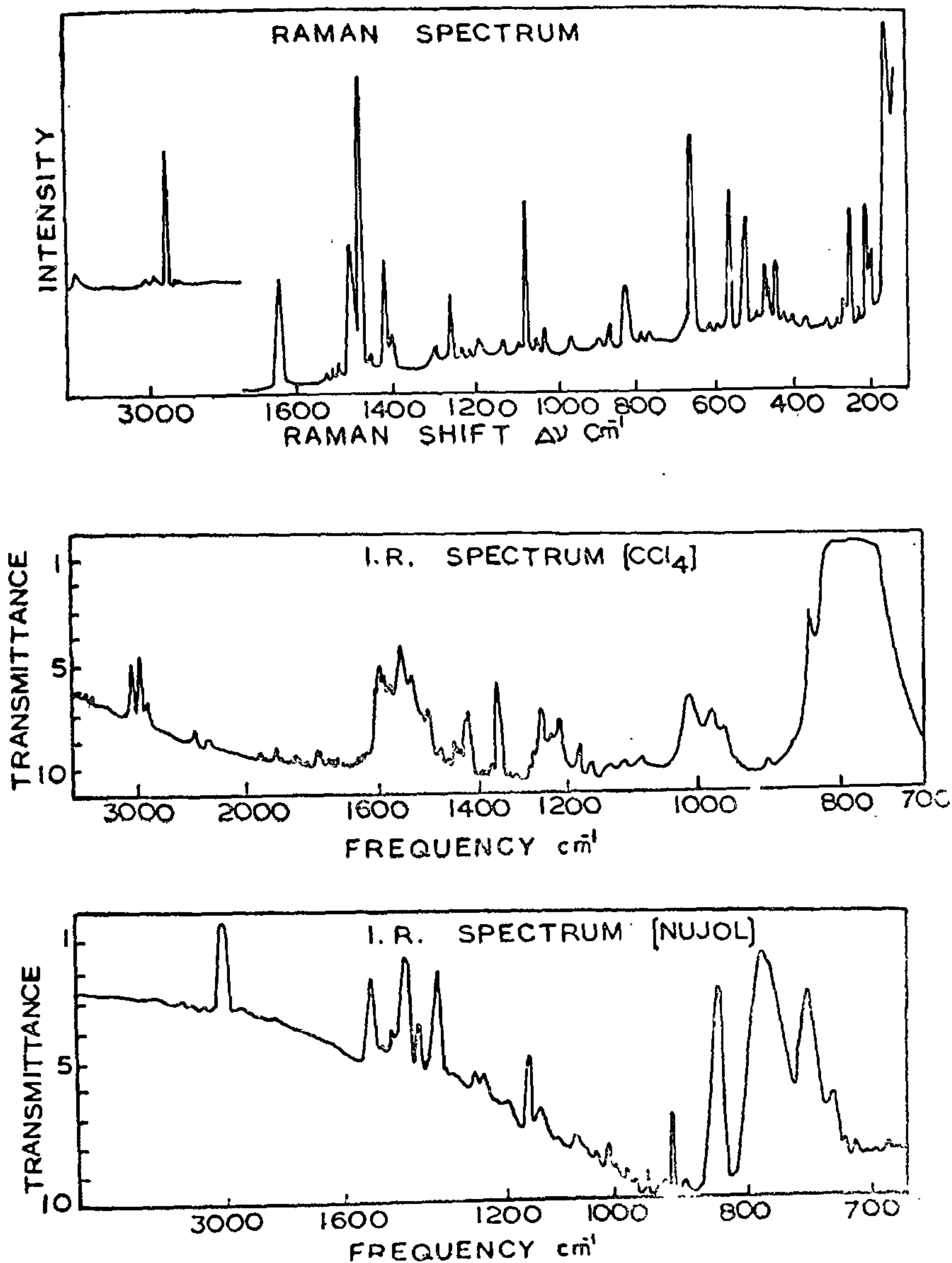


Fig. 2

the molecule of naphthalene. However, the frequency 1256 cm^{-1} does not have any corresponding naphthalene mode. Thus it is concluded that this mode is characteristic of the ethylenic group.

The ring breathing mode of vibration in acenaphthylene has been identified as the strong band at 1002 cm^{-1} in Raman spectrum and 1000 , 989 and 999 cm^{-1} observed in the infrared spectra in solid

film, CCl_4 and nujol respectively. In naphthalene the ring breathing mode has been conclusively identified at 1024 cm^{-1} ^{4,6} and in acenaphthene¹⁰ the ring breathing mode has been identified at 1045 cm^{-1} .

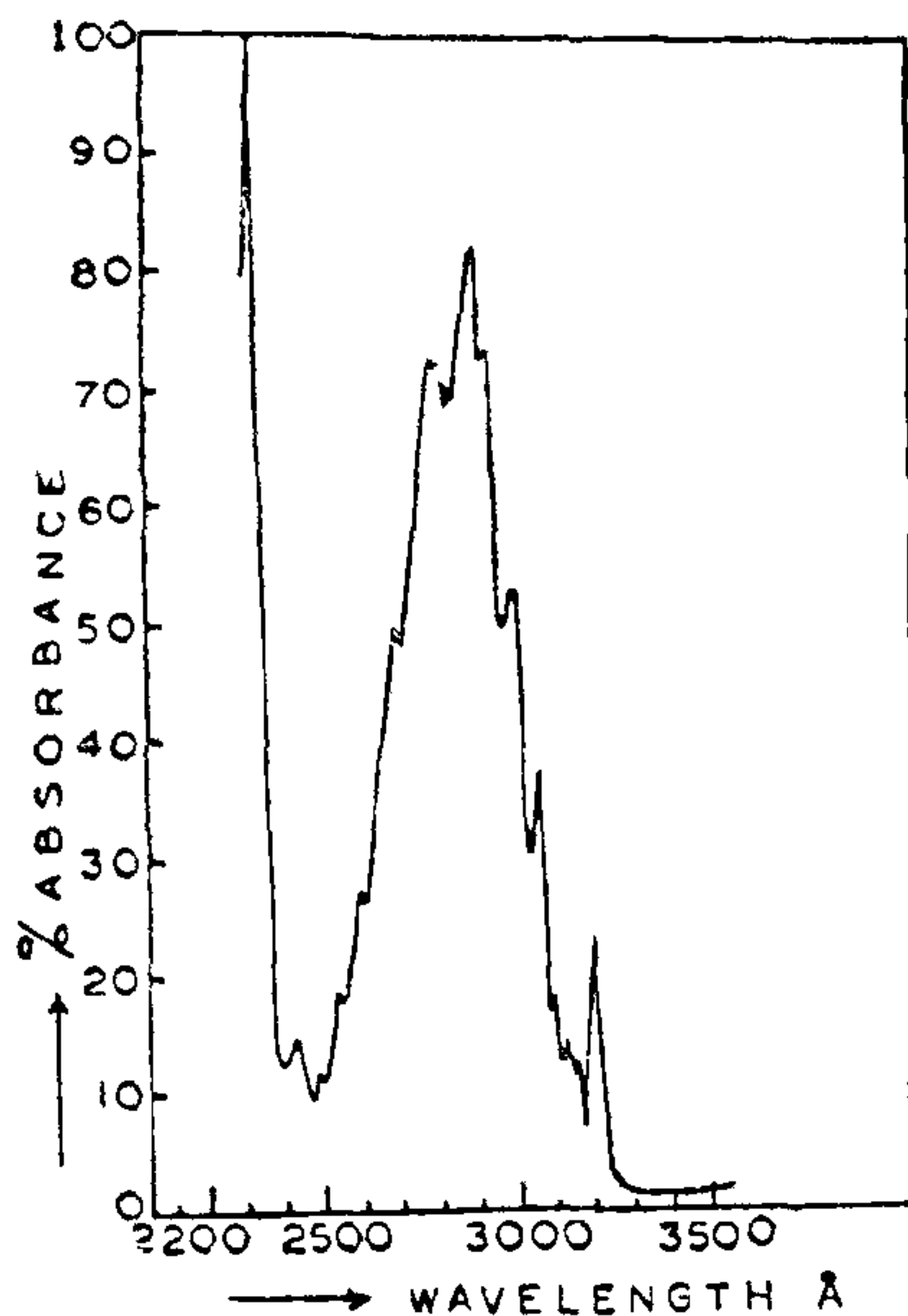


FIG. 3

The bands at 792 cm^{-1} in the Raman spectrum and 787 and 784 cm^{-1} in infrared spectrum are very strong and have been assigned to C-H out-of-plane bending mode of vibrations. This is identical to the strong naphthalene band at 782 cm^{-1} (b_{1u}). The other remaining C-H out-of-plane modes are assigned as shown in Table I. In assigning these bands, aid has mainly been taken from the vibrational assignment of acenaphthene¹⁰ and naphthalene³⁻⁵.

It has been mentioned in the introduction that acenaphthylene resembles very closely to naphthalene loosely coupled to ethylene. The present observations in the Raman and infrared spectra partially support this view. In Raman spectrum of ethylene molecule there are three strong and polarised lines at 3019.3 , 1623.3 and 1342.4 cm^{-1} . The first is essentially a C-H stretching vibration, the second a C-C stretching and the third a symmetrical CH₂ deformation. Out of these three, only the second one has been observed in the Raman and infrared spectra of the molecule of acenaphthylene.

Electronic spectra.—Three systems of absorption, classified as I, II and III, have been observed in the

solution spectrum of the molecule in the present work. It is observed that systems I and II overlap considerably. As a result, in solution spectrum they appear with absorption maximum near about 2900 Å . System (III) is very strong with maximum appearing at 2327 Å . Table II gives the absorption maxima observed with their assignments, in the ultraviolet absorption spectrum of acenaphthylene in solution phase.

The vibrational analysis in Table II is similar to that reported by Gordon and Yang¹. However, the electronic origins are not the same. In vapour phase, three absorption systems appear in the region 31212 – 35207 , 35447 – 37815 and 41309 – 42040 cm^{-1} at different temperatures. These correspond to the systems (I), (II) and (III) respectively in the solution spectrum. It is to be noted that the other two systems at 4660 and 3390 Å reported by Heilbronner *et al.*³ could not be recorded in the present investigation. The temperature of the absorption cell was raised to as high as 150°C but it could not show any absorption on the higher wavelength side. It may thus be possible that the higher wavelength ultraviolet band systems reported by Gordon and Yang develop due to some impurities.

Out of the three absorption band systems in the present work only the system (I) shows fine vibrational heads. Vibrational structures, however, are not resolved and hence detailed analysis was not possible. The strong band at 31489 cm^{-1} (3174.8 Å), has been identified as the (0,0) band of the system. The other bands have been assigned in terms of the excited state fundamental frequencies 152 , 300 , 455 , 670 , 1143 and 1390 cm^{-1} and ground state frequencies 122 and 220 cm^{-1} . The ground state frequency 220 cm^{-1} corresponds to the frequency 217 cm^{-1} observed in the fluorescence spectrum of the molecule reported by Pesteil *et al.*⁹. The excited state frequency 1390 cm^{-1} corresponds to the frequency 1406 cm^{-1} in the solution phase spectrum. This may be correlated with the frequency 1373 cm^{-1} observed in the crystal spectra¹. It was concluded by Heilbronner *et al.*³ that 0.32 of the electron density of an electron is transferred away from the ethylenic bond in this transition with the result that ethylenic bond length increases in the excited state.

Thus the frequency 1390 cm^{-1} cannot be interpreted as the C-C stretching in the excited state as was suggested by Gordon and Yang¹. The only ethylenic C-C stretching mode in the ground state has been identified at 1623 cm^{-1} ⁷. Thus the frequency 1390 cm^{-1} may be only interpreted as C-H in-plane bending mode. The corresponding ground state vibration observed in the infrared and Raman

TABLE I
Vibrational assignment of acenaphthylene

Raman	Infrared			Assignment
	Solid film	CCl ₄	Nujol	
3055 (s)	3060 (1)	3050 (1)	..	a ₁ ν (C—H)
	3009 (1)	3005 (1)	..	b ₂ ν (C—H)
2947 (w)	2953 (1)	2950 (3)	..	b ₂ ν (C—H)
2934 (s)	a ₁ ν (C—H)
2918 (s)	a ₁ ν (C—H)
2897 (vs)	2890 (2)	2893 (3)	..	a ₁ 2 × 14/5
2876 (ms)	2840 (1)	2848 (3)	..	a ₁ ν (C—H)
..	..	1635 (2)	1635 (1)	a ₁ ν (C—C)
1607 (vs)	1600 (10)	1604 (8)	1600 (9)	b ₂ ν (C—C)
..	1534 (2)	1528 (10)	1538 (2)	a ₁ ν (C—C)
1503 (ms)	1519 (3)	1500 (7)	1502 (2)	a ₁ ν (C—C)
1475 (vs)	1486 (3)	1480 (3)	..	b ₂ ν (C—C)
1450 (vs)	1444 (4)	1450 (3)	1450 (9)	b ₂ β (C—H)
1434 (sh)	..	1437 (4)	1438 (8)	a ₂ γ (C—H)
1430 (w)
1407 (w)
1370 (vs)	1368 (10)	1372 (7)	1372 (10)	b ₂ ν (C—C)
..	1297 (1)	1275 (3)	1275 (3)	b ₂ β (C—H)
1259 (ms)	1256 (3)	1255 (5)	1256 (3)	a ₁ β (C—H)
1223 (w)	..	1219 (4)	1209 (1)	b ₂ β (C—H)
1178 (ms)	1178 (4)	1175 (3)	1178 (5)	a ₁ β (C—H)
1156 (w)	1143 (2)	1153 (1)	1147 (3)	a ₁ β (C—H)
1099 (w)	..	1096 (1)	1096 (1)	b ₂ β (C—H)
1021 (s)	..	1015 (1)	1022 (3)	b ₂ β (C—H)
1002 (w)	1000 (1)	989 (4)	999 (2)	a ₁ ring breathing
..	910 (1)	899 (1)	898 (1)	b ₁ γ (C—H)
844 (s)	837 (10)	838 (5)	838 (10)	a ₁ α (C—C—C)
809 (w)	a ₂ γ (C—H)
792 (w)	784 (2)	..	787 (10)	b ₁ γ (C—H)
749 (w)	746 (5)	..	746 (8)	a ₁ α (C—C—C)
..	722 (5)	b ₁ γ (C—H)
..	..	675 (2)	675 (3)	b ₂ α (C—C—C)
580 (vs)	a ₁ α (C—C—C)
552 (vs)	b ₂ α (C—C—C)
475 (s)	a ₁ α (C—C—C)
447 (vs)	b ₁ δ (C—C—C)
402 (vw)	b ₂ α (C—C—C)
294 (vs)	a δ ₁ (C—C—C)
263 (vs)	b ₂ δ (C—C—C)
246 (sh)	b ₁ δ (C—C—C)
233 (s)	a ₁ δ (C—C—C)

ν = stretching; β = in-plane-bending; γ = out-of-plane bending,
α = in-plane skeletal deformation and δ = out-of-plane skeletal deformation.

TABLE II

Ultraviolet absorption spectrum of acenaphthylene in solution

System	Wavenumber cm^{-1}	Analysis
(I) ..	31166 vs	0, 0
	455 w	455
	687 s	687
	1130 w	455 + 687
	1406 vs	1406
	2072 s	1406 + 687
	2990 sh	1406 + 1130 + 456
	3398 vs	
	4052 vw	
(II) ..	35703 s	0, 0
	99 s	99
	1113 sh	1113
	2240 sh	2 × 1113
	3619 w	
	4532 w	
	5423 s	
(III) ..	42962 vs	0, 0

s = strong, w = weak, vs = very strong, vw = very weak, sh = shoulder.

spectra is 1450 cm^{-1} and identified as the b_2 fundamental. The bands with frequency 670 cm^{-1} in vapour and 687 cm^{-1} in solution may be correlated to the strong band at 749 cm^{-1} in the Raman spectrum of the compound. It is also probably a characteristic of the ethylenic group. The corresponding frequency in ethylene molecule is 720 cm^{-1} . The frequency 1143 cm^{-1} may be interpreted as a_1 fundamental with its ground state counterpart at 1156 cm^{-1} observed in the Raman spectrum of the molecule. Table V gives the proposed vibrational analysis of the ultraviolet bands of system (I). The (0, 0) bands of the different systems of acenaphthylene in vapour, solution and crystal are compared in Table III, and the fundamental frequencies observed in the ultraviolet spectra in different phases are compared in Table IV.

TABLE III

(0, 0) bands of the different systems of acenaphthylene

System	Vapour phase (Present work)	Solution phase (Present work)	Crystal
I	31489	31166	30675
II	35842	35703	..
III	41399	42962	..

TABLE IV

Fundamental frequencies observed in the ultraviolet spectra of acenaphthylene

Vapour	Solution	Crystal (1)	Ground state frequencies (Raman & I.R.)	Assignment
455	455	456	746	$a_1 \alpha$ (C-C-C)
670	687	651	1156	$a_1 \beta$ (C-H)
1038	1113	1142	1450	$b_2 \beta$ (C-H)
1143	1406	1373		

TABLE V

Ultraviolet absorption spectrum of acenaphthylene vapour (3200 Å system)

Wave number cm^{-1}	Analysis
- 220 ms	.. -220
- 122 w	.. - 122
- 35 w	.. -3 × 12
- 23 ms	.. -2 × 12
- 12 s	.. -12
31489 vs	.. 0, 0
14 w	.. 14
152 w	.. 152
300 s	.. 2 × 152
455 w	.. 455
601 w	.. 455 + 152
670 vs	.. 670
773 w	.. 455 + 2 × 152
916 w
1038 s	.. 1038
1143 s	.. 1143 $a_1 \beta$ (C-H)
1155 ms	.. 670 + 455
1390 ms	.. 1390 $b_2 \beta$ (C-H)
1518 w
1675 w
1852 vs	.. 1390 + 455

s=strong, ms=medium strong, vs = very strong.
w=weak, vw=very weak, a=in-plane-bending.

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