

## Vibrational spectra of $\alpha$ - and $\beta$ -naphthaldehydes

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The infrared spectra of  $\alpha$ - and  $\beta$ -naphthaldehydes in the frequency range 200-4000  $\text{cm}^{-1}$  and their Raman spectra in the frequency range 40-4000  $\text{cm}^{-1}$  have been recorded together with the depolarization ratio of the Raman lines in case of  $\alpha$ -naphthaldehyde. The observed frequencies have been assigned to all the fifty four modes of vibration in each of the two molecules by assuming  $C_2$ -symmetry.

### 1. INTRODUCTION

A lot of work have been reported on the electronic and vibrational spectra of single ring aldehydes, while work on condensed ring aldehydes seems to be meagre. The infrared studies of  $\alpha$ - and  $\beta$ -naphthaldehydes reported by earlier workers (Moyer 1950, Pinchas 1957, Singh *et al* 1969) were confined to a limited spectral region and to the discussion of a few modes of vibration only. The Raman spectra of these compounds have not been reported by any one of the earlier workers. In view of the above facts, it seems worthwhile to study the Raman and infrared spectra of these compounds in greater detail. The study is expected to give further information on the vibrational frequencies of mono-substituted naphthalenes on one hand and the effect of  $\alpha$ - and  $\beta$ -substitutions on the other.

During the present course of investigation, the I.R. spectra of  $\alpha$ - and  $\beta$ -naphthaldehydes in the frequency range 200-4000  $\text{cm}^{-1}$  and their Raman spectra in the range 40-4000  $\text{cm}^{-1}$  have been recorded together with the depolarization factor of the Raman lines in the case of  $\alpha$ -naphthaldehyde. Attempts have been made to identify all the fifty four modes of vibration in each of the two molecules.

### 2. EXPERIMENTAL

Both the compounds were Fluka made pure quality, supplied by J. Kundan & Co., Bombay (India). The infrared spectra of the compounds were recorded on Carl-Zeiss UR-10 and Perkin-Elmer 521 and 621 infrared spectrophotometers. In case of  $\beta$ -naphthaldehyde, the solid sample was mullied with hexachloro-1-3 butadiene, mineral oil (Nujol) and KBr powder, while liquid absorption cells were used for  $\alpha$ -naphthaldehyde. Infrared spectra of  $\alpha$ - and  $\beta$ -naphthaldehydes are shown in figures 1 and 2 respectively.

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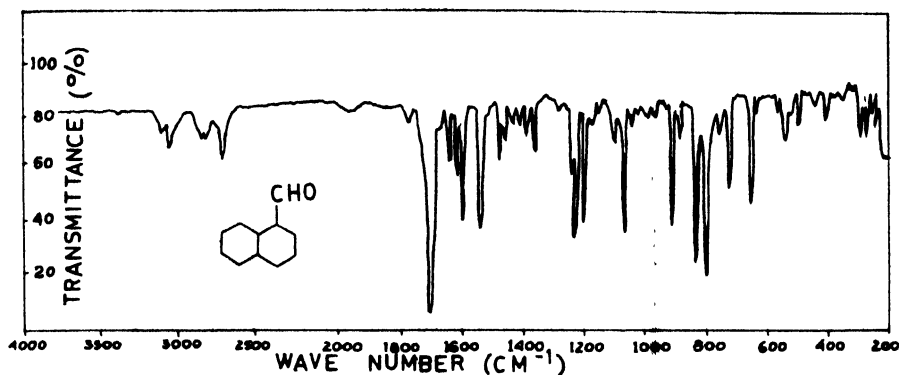


Fig. 1. Infrared spectrum of  $\alpha$ -Naphthaldehyde (liquid) recorded with Perkin-Elmer 621-infrared spectrophotometer.

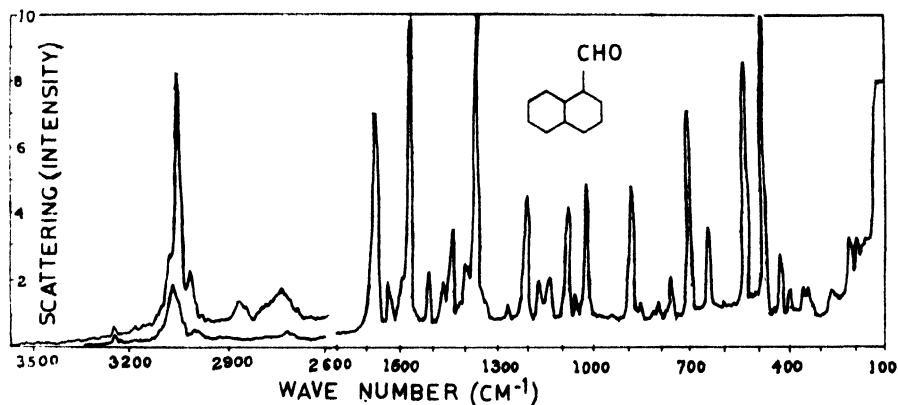


Fig. 2. Infrared spectrum of  $\beta$ -Naphthaldehyde mullied with mineral oil recorded with Perkin-Elmer 621-infrared spectrophotometer.

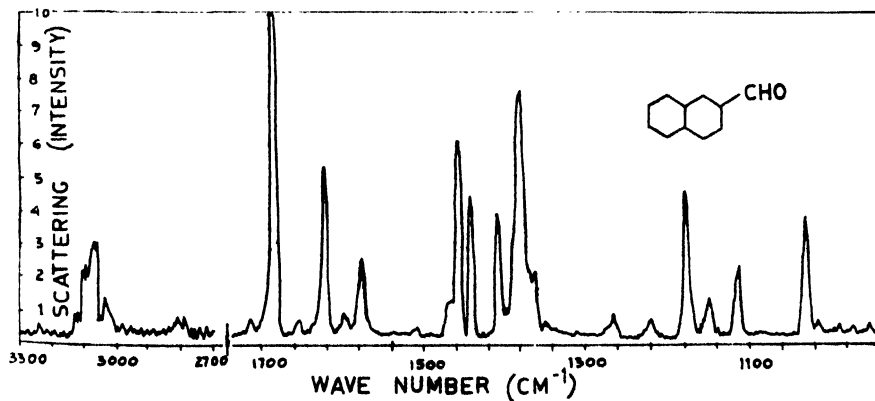


Fig. 3. Raman spectrum of  $\beta$ -Naphthaldehyde (liquid) recorded with Jarrell-Ash model 25-300 Laser Raman spectrometer.

The Raman spectra of the two compounds were recorded with Jarrel-Ash Model 25-300 Laser Raman Spectrometer. The excitation sources used were the 6328Å (He/Ne laser) and 5145Å (Ar<sup>+</sup> ion laser). In case of  $\alpha$ -naphthaldehyde the values of the depolarization factor of the Raman lines were calculated from two spectra run under the identical conditions, except for rotation of the incident polarization from 90° to 45° of the half-wave plate. The Raman spectra of  $\alpha$ - and  $\beta$ -naphthaldehydes are given in figures 3 and 4a, 4b respectively.

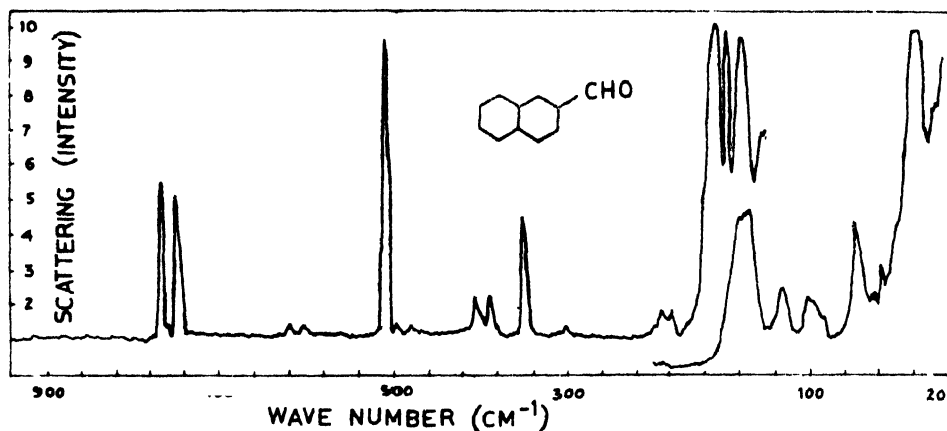


Fig.4(a). Raman spectrum of  $\beta$ -Naphthaldehyde (solid) recorded with Jarrell-Ash model 25-300 Laser Raman spectrometer.

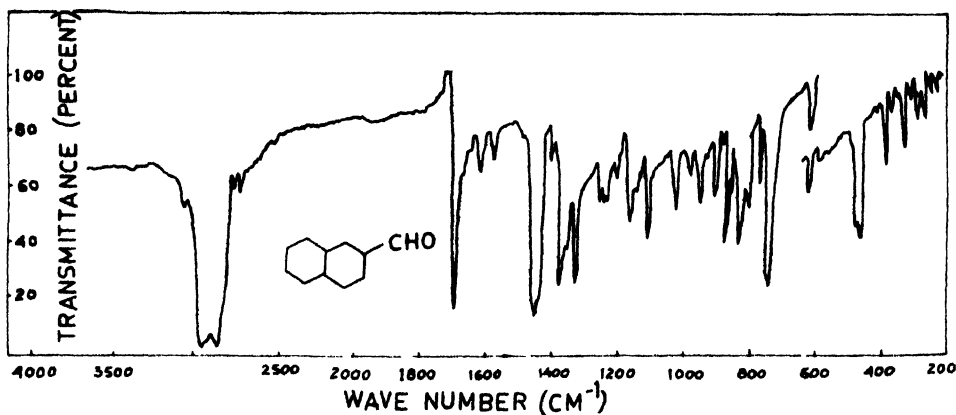


Fig. 4(b). Fig. 4(a) continued.

### 3. RESULTS

Frequencies of all the bands observed in the infrared and Raman spectra of each of the compounds along with their intensities and depolarization factors are given in table 1. In case of  $\alpha$ -naphthaldehyde molecule, 83 and 65 bands were

Table 1. Infrared and Raman frequencies of  $\alpha$ - and  $\beta$ -naphthaldehyde in  $\text{cm}^{-1}$ 

$\alpha$ -naphthaldehyde		$\beta$ -naphthaldehyde	
Infrared	Raman	Infrared	Raman
205(4)	155(3)	273(1.5)	40(10)
210(4)	162(3.5)d	280(1)	55(1)
215(4)	190(3)d	295(1.5)	60(.5)
235(1.5)	218(3)d	305(1)	71(10)
243(2)	265(1.5)d	312(1)	98(9.5)
252(1)	349(2)	325(1)	115(9.5)
265(2)	360(2)d	350(2.5)	134(10)
270(1.5)	403(2)d	355(1)	184(2)
275(2)	433(2.5)d	368(1)	192(2)
285(.5)	468(1.5)d	388(3)	200(1.5)
296(0)	498(9)d	415(1)	210(1)
308(0)	513(1.5)sh	423(1.5)	301(.5)
322(0)	524(1)sh	455(1.5)	351(4.5)
324(0)	533(2)d	473(6)	372(.5)
334(0)	548(7.5)	481(5)	388(2)
340(0)	618(1)	515(2)	404(2)
350(.5)	648(3.5)	575(2)	480(.5)
358(0)	675(1)	600(3)	500(.5)
365(2)	710(7)	628(4)	516(9.5)
374(0)	737(1)d	720(2)sh	602(.5)
384(0)	768(2)	745(7)	628(.5)
404(2)	793(1)	770(4)	756(4.5)
434(1)	802(.5)	820(5)	764(1.5)
470(0)sh	860(1)	835(6)	770(5)
478(.5)	883(4.5)	856(4)	870(.5)
500(2)	920(5)d	870(6)	912(.5)
512(1)sh	955(.5)d	890(2.5)	952(.5)
524(2)	980(.5)d	907(4)	972(.5)
548(1.5)	1020(4.5)	945(2.5)	984(.5)
620(1)	1055(1)d	952(3)	990(.5)
650(5.5)	1078(4)	962(4.5)	1010(.5)
711(4.5)	1118(.5)	983(3.5)	1023(4)
738(2)	1143(1.5)d	992(3)	1119(2.5)
772(9)	1165(2)	1008(5)	1144(1.5)
802(8)	1214(4.5)	1018(3)	1168(4)
861(2)	1226(1.5)sh	1118(6)	1215(.5)
886(6.5)	1265(1)	1140(4)	1258(1)
920(1)	1296(0)	1165(5)	1348(.5)
958(1)	1370(10)d	1210(3.5)	1368(.5)
978(1)	1393(2)sh	1245(4.5)	1379(7.5)
1010(1)	1412(1)	1255(4.5)	1408(4)
1021(2)	1442(3)	1347(7)	1442(4.5)
1032(1)	1460(1.5)	1365(6)	1460(6)
1056(7)	1510(1.5)	1375(8)	1508(.5)
1076(2)	1572(9.5)d	1400(3)	1528(0)

Table 1—(continued)

$\alpha$ -naphthaldehyde		$\beta$ -naphthaldehyde	
Infrared	Raman	Infrared	Raman
1118(1)	1590(1.5)sh	1458(9)	1577(2.5)
1144(2)	1622(1.5)	1505(2)	1598(.5)
1170(6.5)	1684(6.5)	1530(2)	1628(5)
1217(7)	1765(.5)	1535(2)	1656(.5)
1230(4)	2505(0)	1572(2)	1695(10)
1265(1)	2560(.5)	1578(2)	1712(.5)
1290(.5)	2680(0)	1593(3)	2720(1.5)
1342(2)	2730(1.5)	1622(3)	2740(1.5)
1371(2)	2760(0)	1642(2.5)	2765(1.5)
1395(1.5)	2840(.5)	1700(8)	2840(2.5)
1410(1.5)	2860(1)	1770(1)	2850(2.5)
1420(1)sh	2920(.5)	1800(1)	2940(1)
1442(2.5)	2945(0)	1825(1)	2970(1)
1460(3.5)	2975(.5)	1942(2)	3015(2.5)
1510(6.5)	3015(2)	1965(.5)	3030(5) <sub>i</sub>
1574(6)	3060(10)	2285(2)	3060(10)
1592(4)	3085(3)sh	2500(.5)	3075(8)
1621(3)	3145(.5)	2720(4)	3090(3)sh
1655(2)sh	3182(.5)	2760(3.5)	3250(1)
1688(10)	3242(.5)	2850(9.5)	3290(.5)
1765(1.5)		2920(10)	
1830(1)		2960(.5)	
1842(1)sh		3060(4.5)	
1938(1)		3160(.5)	
2130(.5)		3360(3)	
2630(.5)		3385(0)	
2730(3)			
2760(2.5)sh			
2785(2)sh			
2840(3)			
2860(3)			
2960(2)			
3020(0)sh			
3058(3)			
3095(3)			
3190(0)			
3270(.5)			
3366(2)			

*Note* :—d-depolarized, sh-shoulder,

Numericals in paranthesis indicate the relative intensity of the corresponding band.

measured in infrared and Raman spectra respectively, while in the case of  $\beta$  compound the number of corresponding bands measured were 71 and 66 respectively. Assignments of various fundamental frequencies to different modes of vibration alongwith their correlation with those of naphthalene and formaldehyde are given in table 2.

 Table 2. Fundamental frequencies ( $\text{cm}^{-1}$ ) of  $\alpha$ - and  $\beta$ -naphthaldehydes

Fundamentals of naphthalene <sup>+</sup>	$\alpha$ -naphthaldehyde		$\beta$ -naphthaldehyde		Species	Probable modes of vibration
	Infrared	Raman	Infrared	Raman		
176 ( $b_{1u}$ )		162		134	$a''$	Wing-wagging
195 ( $b_{2g}$ )		190		192	$a''$	Skeletal bending
285 ( $b_{3g}$ )	215	218		210	$a''$	Skeletal bending
359 ( $b_{2u}$ )	350	349	350	351	$a'$	Skeletal distortion
400 ( $a_u$ ) <sub>j</sub>	404	403		404	$a''$	Skeletal distortion
476 ( $b_{1u}$ )	470	468	473		$a''$	Skeletal bending
506*( $b_{1g}$ )	500	498	481	480	$a'$	Skeletal distortion
512 ( $a_g$ )	548	548	515	516	$a'$	Skeletal distortion
562 ( $b_{3u}$ )	512	513		500	$a'$	Skeletal distortion
618 ( $b_{2u}$ )	620	618	600	602	$a'$	Skeletal distortion
698 ( $a_u$ )	524	533	575		$a''$	Skeletal distortion
730 ( $a_u$ )		675	720		$a''$	C-H bending
758 ( $a_g$ )	711	710	770	770	$a'$	Ring breathing
770 ( $b_{3g}$ )	738	737		756	$a''$	Skeletal bending
782 ( $b_{1u}$ )	772	768	745		$a''$	C-H bending
874†( $b_{1g}$ )		793		764	$a'$	C-H bending
877 ( $b_{3u}$ )	888	883	870	870	$a'$	Skeletal distortion
915 ( $a_u$ )	861	860	890		$a''$	C-H bending
943‡( $b_{2g}$ )	920	920	907	912	$a''$	C-H bending
958 ( $b_{1u}$ )	958	955	952	952	$a''$	C-H bending
1025 ( $a_g$ )	1021	1022	1018	1023	$a'$	C-H bending
1099 ( $b_{3g}$ )	978	980		972	$a''$	C-H bending
1144 ( $b_{3u}$ )	1118	1118	1118	1119	$a'$	C-H bending
1145*( $a_g$ )	1076	1078	992	990	$a'$	C-H bending
1158 ( $b_{2g}$ )	1144	1143	1140	1144	$a''$	C-H bending
1210 ( $b_{3u}$ )	1170	1165	1165	1168	$a'$	C-H bending
1267 ( $b_{2u}$ )	1230		1265		$a'$	C-H bending
1320 ( $b_{1g}$ )	1265	1265	1255	1258	$a'$	Skeletal distortion
1380 ( $a_g$ )	1371	1370	1375	1379	$a'$	C-C stretching
1387 ( $b_{2u}$ )	1342		1347	1348	$a'$	C-C stretching

Table 2—(continued)

Fundamentals of naphthalene <sup>+</sup>	$\alpha$ -naphthaldehyde		$\beta$ -naphthaldehyde		Species	Probable modes of vibration
	Infrared	Raman	Infrared	Raman		
1438 ( $b_{1g}$ )	1410	1412		1408	$a'$	C-C stretching
1460 ( $a_g$ )	1460	1458	1460		$a'$	C-C stretching
1483 ( $b_{1g}$ )	1442	1442		1442	$a'$	C-C stretching
1506 ( $b_{2u}$ )	1510	1510	1505	1508	$a'$	C-C stretching
1577 ( $a_g$ )	1574	1572	1572	1577	$a'$	C-C stretching
1592 ( $b_{2u}$ )	1592	1590	1593		$a'$	C-C stretching
1624( $b_{1g}$ )	1621	1622	1622	1628	$a'$	C-C stretching
1715 ( $b_{3u}$ )	1655		1642		$a'$	C-C stretching
2978 ( $b_{1g}$ )		2975		2970	$a'$	C-H stretching
2987 ( $b_{1u}$ )	2860		2920		$a'$	C-H stretching
3027 ( $b_{2u}$ )	2960		2960		$a'$	C-H stretching
3031 ( $a_g$ )	3020	3015		3015	$a'$	C-H stretching
3060 ( $a_g$ )	3058	3060	3060	3060	$a'$	C-H stretching
3060 ( $b_{2u}$ )	3095			3090	$a'$	C-H stretching
3092 ( $b_{1g}$ )		3085		3075	$a'$	C-H stretching
	365	360	388	388	$a''$	C-substituent bending
	1056	1055	1008	1010	$a'$	C-substituent bending
	1217	1214	1210	1215	$a'$	C-substituent stretching
1743**( $a_1$ )	1688	1684	1700	1695	$a'$	C = O stretching
1503**( $a_1$ )	1395	1993	1400		$a'$	C-H deformation
1167**( $b_2$ )	802	802	835		$a''$	C-H bending
1281**( $b_1$ )	650	648	628	628	$a'$	C-H bending
2780**( $a_1$ )				98	$a''$	Torsional vibration
				115		
2874**( $b_1$ )	2730	2730	2730	2720	$a'$	C-H stretching

<sup>+</sup>Denotes the frequencies taken from Mitra & Bernstein (1959)

\*\*Denotes the frequencies of formaldehyde.

\*Data from Hollas (1962).

†From Luther (1955).

‡From Lippincott & O'Reilly (1955).

#### 4. DISCUSSION

If the substituent CHO is treated as lying in the plane of the ring, both the molecules belong to  $C_s$ -point group and the fifty four modes of vibration in the two molecules are attributed as ; 37 totally symmetric ( $a'$  class) and 17 non-totally symmetric ( $a''$  class) of vibrations. According to the selection rules, both of these types of vibrations will be Raman as well as infrared active.

Considering the naphthaldehyde molecule as a substituted naphthalene on one hand and a substituted formaldehyde on the other, the observed fundamental frequencies in the spectra of the two molecules can be discussed into two separate heads; (A) Naphthalene group frequencies and (B) Formaldehyde group frequencies.

(A) *Naphthalene Group Frequencies*

*C-H Stretching* : The frequencies of 3059 and 3060  $\text{cm}^{-1}$  in  $\alpha$ - and  $\beta$ -naphthaldehydes respectively, appear with the most intense Raman lines in C-H stretching region of the spectra. These are correlated to 3060  $\text{cm}^{-1}$   $a_g$ -type frequency of naphthalene, which has also been reported to be appearing with similar intensity. Other frequencies of 2975, 3018 and 3085  $\text{cm}^{-1}$  in  $\alpha$ -compound and 2970, 3015 and 3075  $\text{cm}^{-1}$  in  $\beta$ -compound, which are either prominent in the Raman spectrum or appear in the Raman spectrum only, are correlated to the Raman active frequencies of 2978, 3031 and 3092  $\text{cm}^{-1}$  in naphthalene respectively.

*C-C Stretching* : While assigning the fundamentals of naphthalene molecule, all the previous workers in the field have chosen 1577  $\text{cm}^{-1}$  for an  $a_g$ -class, even though it appears as a strong depolarized line. Lippincott & O'Reilly (1955), Mitra & Bernstein (1959) have also given argument in favour of a strong depolarized line for a totally symmetric mode in preference to a weak polarised one. On the above ground, the frequencies at 1371 and 1573  $\text{cm}^{-1}$  in  $\alpha$ -naphthaldehyde and 1377 and 1575  $\text{cm}^{-1}$  in  $\beta$ -naphthaldehyde, which appear with matching intensities in the Raman spectrum of the respective compounds, are correlated to 1380 and 1577  $\text{cm}^{-1}$  frequencies of naphthalene.

Frequencies at 1342, 1510, 1591 and 1655  $\text{cm}^{-1}$  in  $\alpha$ -naphthaldehyde and 1347, 1507, 1593, 1642  $\text{cm}^{-1}$  in  $\beta$ -naphthaldehyde which appear either in the infrared spectra only or they are more intense in the infrared spectra in comparison to their counter parts in Raman spectra have been correlated to 1387, 1506, 1592 and 1715  $\text{cm}^{-1}$  infrared frequencies of naphthalene respectively.

Other important frequencies of this mode which deserve special reference are the frequencies corresponding to 1460  $\text{cm}^{-1}$  strong Raman active frequency of naphthalene. Lippincott & O'Reilly and Mitra & Bernstein have assigned 1460  $\text{cm}^{-1}$  frequency as an overtone ( $2 \times 700$ ); contrary to this we have taken 1460  $\text{cm}^{-1}$  in naphthalene and its counterparts in the two molecules as fundamentals on the basis of their intensities in each spectrum. Luther *et al* (1962) and Hollas (1962) have favoured this view.

*Ring Breathing* : The electronic and vibrational spectra of some mono-substituted naphthalenes reported earlier (Singh & Singh 1965, 1970, Sharma and Singh 1972) and the theoretical calculations made by Luther (1948) indicate that the value of this fundamental increases slightly on  $\beta$ -substitution, while it



decreases very much on  $\alpha$ -substitution. In naphthalene this mode of vibration has been indentified at  $758\text{ cm}^{-1}$ . On the basis of above argument the frequencies at  $711$  and  $770\text{ cm}^{-1}$ . in  $\alpha$ - and  $\beta$ -compounds respectively, which appear more strongly in Raman than in I-R spectra, are assigned to this mode.

#### *Skeletal Distortion :*

This mode of vibration in naphthalene skeleton has been variously assigned between  $500$ - $900\text{ cm}^{-1}$ . During the high-resolution study of the electronic spectra of naphthalene, Craig et al (1961) and Hollas (1962) observed a strong frequency of  $506\text{ cm}^{-1}$  ( $b_{1g}$ -type) in addition to  $512\text{ cm}^{-1}$  ( $a_g$ -type) frequency which was observed only in combination. In the Raman spectrum of naphthalene, on the other hand, the latter appears as a strong polarised Raman line and the former one is absent. On the reduction of symmetry from  $D_{2h}$  to  $C_s$ , the two modes of  $b_{1g}$  and  $a_g$ -type are reduced to  $a'$ -type, and both of these modes are expected to appear in Raman as well as in the infrared spectra of mono-substituted naphthalenes. During the present course of investigation, the two frequencies of  $499$  and  $548\text{ cm}^{-1}$  appearing strongly in the Raman spectrum of  $\alpha$ -naphthaldehyde are correlated with  $506$  and  $512\text{ cm}^{-1}$  frequencies of naphthalene. This is in conformity with the vibrational spectra of  $\alpha$ -fluoro,  $\alpha$ -chloro- and  $\alpha$ -bromonaphthalenes reported earlier. In the case of  $\beta$ -naphthaldehyde the corresponding frequencies are assigned at  $481$  and  $516\text{ cm}^{-1}$  respectively, where the former appears weakly in comparison to its counterpart in the  $\alpha$ -compound.

#### *C-H In-Plane Bending :*

There are seven C-H in-plane bending modes of vibration in both the molecules, the values of which may lie between  $900$ - $1500\text{ cm}^{-1}$ . Two alternative assignments have been given for  $1025\text{ cm}^{-1}$  prominent frequency of naphthalene: and is C-C. stretching and the other C-H in-plane bending. We have preferred the latter assignment for this frequency in naphthalene as well as in other mono-substituted naphthalenes.

#### (B) *Formaldehyde Group Frequencies*

Colthup (1964) has quoted the range  $2700$ - $2900\text{ cm}^{-1}$  for the C-H valence vibration when the hydrogen atom is attached to a carbonyl group and Pozfosky et al (1951) found two bands near  $2700$  and  $2800\text{ cm}^{-1}$  for a number of aldehydes. During the present course of investigations also two bands have been observed in both the molecules. The bands at  $2730\text{ cm}^{-1}$  in  $\alpha$ -naphthaldehyde and  $2720\text{ cm}^{-1}$  in  $\beta$ -naphthaldehyde also assigned to characteristic C-H stretching mode of CHO group in the respective molecules, while those at  $2840$  and  $2845\text{ cm}^{-1}$  in  $\alpha$ - and  $\beta$ -compounds respectively, are assigned following Bauman (1957) as overtones of C-H bending vibrations of CHO group.

The out of plane bending vibration at  $1167\text{ cm}^{-1}$  of formaldehyde would be heavily reduced on account of the replacement of hydrogen atom by the naphthalene group. The strong bands at  $802$  and  $835\text{ cm}^{-1}$  in  $\alpha$ - and  $\beta$ -compounds respectively are correlated with this frequency.

The characteristic C = O stretching frequencies in the two isomers have been identified with the intense bands at  $1684$  and  $1688\text{ cm}^{-1}$  respectively.

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