

Infrared and Raman studies of some naphthols

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Abstract. Vibrational spectra of α -naphthol, β -naphthol and β -naphthol-OD have been recorded in the solid and solution phases. A number of bands, common to all the three compounds, have been correlated with earlier naphthalene assignments and an attempt has been made to identify certain frequencies with vibrational modes that are centred in the substituents OH and OD. The C_s symmetry is assumed for each molecule.

Keywords. Infrared spectroscopy; Raman spectroscopy; vibrational analysis; vibrational spectra; naphthols.

1. Introduction

Singh and Singh (1970) have proposed a tentative assignment of the infrared bands ($700\text{--}4500\text{ cm}^{-1}$) of α - and β -naphthols to the various normal modes of vibration. Recently, Sharma and Singh (1977) have reinvestigated the infrared spectra ($200\text{--}4000\text{ cm}^{-1}$) of these molecules in the solid phase, and carried out the vibrational assignments of all the fundamental vibrations following the Raman data reported by Luther and Drewitz (1962) and the reliable spectroscopic studies on the parent molecule naphthalene [phosphorescence spectrum by Hanson (1969), Raman scattering tensors for single crystals by Hanson and Gee (1969), and high resolution studies by Hollas (1962)]. However, the far-infrared spectrum (below 200 cm^{-1}) in the solid phase and the mid-infrared spectrum as well as the Raman spectrum in the solution phase of the above molecules have not yet been reported. Moreover, the earlier studies have not considered the effect of molecular association which usually occurs in all the molecules containing the hydroxyl group (or groups). Such types of vibrational studies for the deuterated β -naphthol have not been made so far.

The present work was undertaken to provide rather a complete and more accurate infrared and Raman data of all the three molecules to identify the various vibrational modes and to correlate these with the modes in naphthalene. The frequency assignments in the ground state are also of importance in the vibronic analysis of the electronic spectra of these substances recorded in the vapour phase (to be reported separately). The deuterated β -naphthol-OD has been taken, because by comparing the spectra it might be possible to get some results which would help accurate assignment of the observed frequencies.

2. Experimental details

Pure samples of α - and β -naphthols were of BDH make, and were recrystallized twice with 30% dilute alcohol. The sample of the deuterated (OD) β -naphthol was prepared from the normal β -naphthol. The crystallized β -naphthol was converted first into the β -naphthol acetate. This was treated with NaH and dry benzene, and then hydrolyzed with heavy water to give the required sample.

The mid infrared spectra (200–4000 cm^{-1}) of the compounds in the solid state were recorded in nujol mull and KBr pellets, with a Perkin-Elmer-621 infrared spectrophotometer, and the far infrared spectra (95–500 cm^{-1}) were measured in the polyethylene pellets on a Beckman IR-11 spectrophotometer. A Cary model 82 Raman spectrophotometer was employed to measure the Raman spectrum of each compound in the region 0–4000 cm^{-1} . The sensitivity and scanning time were varied to obtain optimum resolution and presentation. The 4880 Å argon ion laser line was used as the excitation source with approximately 50 mW power at the sample. The infrared spectra of these samples in ethanol (500–4000 cm^{-1}) were recorded on a Nicolet 7199 spectrophotometer and those in CH_2Cl_2 (620–4000 cm^{-1}) on Perkin Elmer-621 spectrophotometer. Raman spectra of the α - and β -naphthols in the solution (20% sample in ethanol) were measured from 100 to 3100 cm^{-1} with a Spex Raman spectrophotometer.

3. Description of observed spectra

The survey scans of the infrared and Raman spectra (from which the vibrational frequencies are now reported). Some characteristic features of these spectra may be summarized as follows:

(i) Both the α - and β -naphthols show sharp and distinct Raman bands in the regions 0–1600 cm^{-1} and 3000–3100 cm^{-1} . The bands observed in β -naphthol are generally weak and therefore show a relatively small number of bands as compared to α -naphthol.

(ii) The apparent intensity and half-band width of most of the bands in the infrared spectrum depend on concentration of the sample. Therefore, to get good spectral records the proportion of the samples in the proper matrices (polyethylene, KBr, CH_2Cl_2 , etc.) was varied till optimum conditions were achieved.

(iii) Out of the seven C-H stretching vibrations expected for each naphthol, only one to three vibrations could be observed in the infrared spectrum. The bands in the spectral region 1600–2800 cm^{-1} , where mainly combinations and overtones of the fundamental frequencies are expected to appear with relatively weak intensity, were best developed when the samples were suspended in nujol mull. However, the bands in the above cited region for the deuterated β -naphthol were better developed in KBr pellets, rather than in nujol mull.

(iv) In the condensed phase a single (broad and asymmetric) peak of about 300 cm^{-1} half-intensity width is observed at $\sim 3200 \text{ cm}^{-1}$ for the α - and β -naphthols. For the deuterated β -naphthol-OD, this band is shifted to $\sim 2400 \text{ cm}^{-1}$ with about 100 cm^{-1} half intensity width. In dilute solution, the above band is modified to give rise to two or three distinct bands.

4. Vibrational assignments

If the substituent group OH or OD is assumed to lie in the plane of the carbon rings of naphthalene, all the three molecules would belong to C_s point group. In this symmetry classification, of the 51 total normal modes of vibration for each naphthol, 35 are symmetric with respect to the plane of symmetry (a' species) and the remaining 16 modes are antisymmetric (a'' species). According to the relevant infrared and Raman selection rules, both types of vibrations are active in the Raman as well as the infrared spectrum. The planar vibrations (a') should give rise to polarized Raman lines and the non-planar vibrations (a'') to depolarized Raman lines. In the absence of depolarization ratios of the Raman lines and band contour shapes of the vapour phase infrared bands, the present vibrational analysis has been made on the basis of only band intensities and group frequency correlations. Data on the vibronic analyses of the vapour phase electronic absorption spectra (Pandey 1982) and the partial vibrational analyses of the infrared and Raman data (Sharma and Singh 1977) of these and similar other molecules have also been used in our studies. The results obtained are summarized in tables 1-3. The scheme of Mulliken (1955) has

Table 1. Vibrational frequencies and their assignments for α -naphthol

Raman frequencies (cm^{-1})		Infrared frequencies (cm^{-1})			Assignments
Solid	Ethanol	Polyethylene pellet and nujol mull	KBr pellet [Sharma, <i>et al.</i> (1977)]	Ethanol	
1	2	3	4	5	6
46(es)					Lattice vibration
58(s)					$\nu_{41}-\nu_{30}$
89(s)					$\nu_{30}-\nu_{43}$
101(vs)		101*(ms)			
168(ms)	157(msd)	170*(ms)			$\nu_{51} \phi(\text{CC})$
—	246(ew)	240*(s)	—		$\nu_{50} \phi(\text{CC})$
—	270(w)	268*(ms)	—		$\nu_{49} \gamma(\text{C-OH})$
279(ms)	—	285*(s)	—		$\nu_{48} \phi(\text{CC})$
—	—	335**(ms)	350(ew)		$\nu_{35} \alpha(\text{CCC})$
423(ew)	—	420(ms)	—		$\nu_{47} \phi(\text{CC})$
466(ms)	468(ms)	460*(w)	460(ew)		$\nu_{46} \phi(\text{CC})$
483(ms)	480(sh)	473**(ms)	478(ms)		$\nu_{45} \phi(\text{CC})$
—	—	481**(ms)	482(ms)		$\nu_{34} \alpha(\text{CCC})$
527(vw)	530(wb)	525(msb)	520(w)	530(ew)	$\nu_{33} \alpha(\text{CCC})$
572(sh)	575(ms)	570(vs)	570(s)	575(w)	$\nu_{44} \phi(\text{CC})$
578(ms)	—	578(sh)	578(ms)	—	$\nu_{32} \beta(\text{C-OH})$
—	—	619(msd)	—	—	$\nu_{43} \gamma(\text{OH})$
—	—	627(w)	630(ms)	630(ew)	$\nu_{31} \alpha(\text{CCC})$
714(es)	712(vs)	710(ms)	710(s)	705(vw)	$\nu_{30} \nu(\text{CC})$ [ring breathing]
735(w)	—	731(sh)	—	730(ew)	$\nu_{42} \gamma(\text{CH})$
770(ew)	—	763(vs)	770(sh)	765(vs)	$\nu_{41} \gamma(\text{CH})$
789(vw)	—	787(vs)	790(vs)	790(vs)	$\nu_{29} \alpha(\text{CCC})$
799(vw)	—	794(sh)	—	—	$\nu_{40} \gamma(\text{CH})$
859(ew)	—	856(w)	860(ms)	850(vw)	$\nu_{39} \gamma(\text{CH})$
879(ms)	880(s)	875(w)	878(vs)	875(ms)	$\nu_{28} \alpha(\text{CCC})$

Table 1. (Continued)

1	2	3	4	5	6
952(vw)	950(ew)	944(vw)	950(w)	—	ν_{38} γ (CH)
960(ew)	—	958(w)	960(ms)	955(ew)	ν_{37} γ (CH)
981(vw)	—	986(ew)	980(sh)	—	ν_{36} γ (CH)
1016(ms)	1013(w)	1013(ms)	1020(s)	1010(ms)	ν_{27} α (CCC)
1046(ms)	1043(w)	1041(ms)	1048(s)	1040(s)	ν_{26} ν (CC)
1084(ms)	1080(ms)	1083(ms)	1085(vs)	1080(s)	ν_{25} β (CH)
1144(ms)	1140(w)	1145(msb)	1150(ms)	1145(s)	ν_{24} β (CH)
1168(w)	—	1163(vw)	—	1160(ew)	ν_{23} β (CH)
1208(vw)	—	1206(w)	—	—	$\nu_{40} + \nu_{47}$
1213(sh)	—	1212(w)	1210(ms)	1206(vw)	ν_{22} β (CH)
1231(sh)	—	1226(sh)	—	1220(sh)	$\nu_{30} + \nu_{33}$
1239(ms)	1240(wb)	1238(ms)	1240(s)	1235(w)	ν_{21} β (CH)
1270(ms)	—	1267(ms)	1270(vs)	1270(s)	ν_{20} β (CH)
1279(sh)	—	1280(sh)	1280(sh)	—	ν_{19} (C-OH)
1310(ewd)	—	1307(msd)	1310(s)	1300(sh)	ν_{18} β (OH)
1362(ms)	1360(sh)	1358(sh)	1362(s)	—	ν_{17} ν (CC)
1370(ms)	—	1372(s)	1370(s)	1365(ms)	ν_{16} ν (CC)
1386(es)	1380(vs)	1382(s)	1390(vs)	1385(vs)	ν_{15} ν (CC)
1408(ew)	—	1406(ew)	—	1405(sh)	ν_{14} ν (CC)
1458(s)	1453(ms)	1457(vs)	1455(ms)	1450(ms)	ν_{13} β (CH)
1469(ms)	1470(sh)	1474(sh)	—	1475(ew)	$\nu_{41} + \nu_{30}$
1526(sh)	—	1512(vw)	1510(w)	1520(w)	ν_{12} ν (CC)
1581(s)	1580(ms)	1578(ms)	1580(s)	1580(s)	ν_{11} ν (CC)
1593(sh)	1592(sh)	1596(ms)	1600(s)	1595(ms)	ν_{10} ν (CC)
—	—	1630(vw)	1630(w)	1625(vw)	ν_9 ν (CC)
—	—	1675(wb)	—	—	$\nu_{15} + \nu_{45}$
—	—	1807(w)	—	—	$\nu_{15} + \nu_{47}$
—	—	1830(wb)	—	1830(ewb)	$\nu_{16} + \nu_{46}$
—	—	1990(w)	—	—	$\nu_{16} + \nu_{46}$
—	—	2310(w)	—	—	$\nu_{11} + \nu_{42}$
—	—	2345(w)	—	—	$\nu_{11} + \nu_{41}$
—	—	2740(w)	—	2750(ew)	$2\nu_{16}$
—	—	2780(msd)	—	2800(ew)	$2\nu_{15}$
2990(ewd)	—	—	—	—	ν_8 ν (CH)
3012(ew)	—	—	—	—	ν_7 ν (CH)
3027(w)	—	3030(ms)	—	—	ν_6 ν (CH)
3041(ew)	—	—	—	—	ν_5 ν (CH)
3060(s)	3060(ms)	3060(ms)	3050(ms)	3050(ms)	ν_4 ν (CH)
3074(sh)	—	—	—	—	ν_3 ν (CH)
3078(sh)	—	—	—	—	ν_2 ν (CH)
—	—	3240(sb)	3230(vsb)	—	ν_1 ν (OH)
—	—	—	—	—	(polymer)
—	—	3440(msb)	—	3460(ewb)	ν_1 ν (OH)
—	—	—	—	—	(dimer)
—	—	—	—	3550(ew)	ν_1 ν (OH)
—	—	—	—	—	(monomer)

*Frequency observed in polyethylene pellet.

**Frequency observed in both polyethylene and nujol mull.

Note: (i) The notations ϕ , ν , α , β and γ denote non-planar torsional modes, bond stretching, angle deformation, in-plane bending on twist of the bonds on angles, respectively.

(ii) The symbols written in small brackets against the frequencies stand for the relative intensities of the corresponding bands. The description of these symbols is as follows: es = extremely strong; vs = very strong; s = strong; ms = medium strong; msd = medium strong and diffuse; msb = medium strong and broad; w = weak; vw = very weak; ew = extremely weak; sh = shoulder.

Table 2. Vibrational frequencies and their assignments for β -naphthol.

Raman frequencies (cm^{-1})		Infrared frequencies (cm^{-1})			Assignments
Solid	Ethanol	Polyethylene pellet and nujol mull	Ethanol	CH_2Cl_2	
1	2	3	4	5	6
40(sh)					$\nu_{39} - \nu_{29}$
48(ms)					
63(s)					$\nu_{28} - \nu_{29}$
104(vs)	—	102*(ms)			$\nu_{29} - \nu_{42}$
157(ewd)	—	160*(ms)			$\nu_{51} \phi(\text{CC})$
—	—	190*(sb)			
—	—	240*(vs)			$\nu_{50} \phi(\text{CC})$
—	—	285*(vs)			$\nu_{49} \phi(\text{CC})$
—	—	309*(msb)			$\nu_{48} \gamma(\text{C-OH})$
—	—	331*(vs)			$\nu_{35} \alpha(\text{CCC})$
408(ew)	403(w)	415(vw)			$\nu_{47} \phi(\text{CC})$
445(w)	435(w)	451***(w)			$\nu_{46} \phi(\text{CC})$
470(ew)	470(ms)	468(ms)			$\nu_{45} \phi(\text{CC})$
480(ew)	485(ew)	480(vs)			$\nu_{34} \alpha(\text{CCC})$
527(w)	525(ms)	526(w)	520(ew)		$\nu_{33} \alpha(\text{CCC})$
—	—	550(wb)	—		$\nu_{32} \beta(\text{C-OH})$
—	—	580(w)	570(ew)		$\nu_{44} \phi(\text{CC})$
—	—	626(msb)	620(w)	630(ew)	$\nu_{31} \alpha(\text{CCC})$
—	—	—	—	690(vs)	$\nu_{43} \gamma(\text{OH})$
					[monomer]
720(ew)	715(ew)	716(vw)	710(vw)	715(vsb)	$\nu_{42} \gamma(\text{CH})$
—	—	740(vs)	740(s)	735(vs)	$\nu_{41} \gamma(\text{CH})$
—	—	751(sh)	—	750(sh)	$\nu_{40} \gamma(\text{CH})$
771(s)	766(vs)	766(ew)	770(w)	—	$\nu_{30} \nu(\text{CC})$
					[ring breathing]
—	800(vw)	810(ms)	805(ms)	801(ms)	$\nu_{29} \alpha(\text{CCC})$
—	830(ew)	841(ms)	840(s)	835(s)	$\nu_{28} \gamma(\text{CH})$
—	876(ms)	875(w)	865(ms)	865(wb)	$\nu_{28} \alpha(\text{CCC})$
—	—	906(w)	900(w)	893(ms)	$2\nu_{46}$
—	—	949(sh)	—	945(sh)	$\nu_{38} \gamma(\text{CH})$
960(ew)	958(vw)	958(w)	955(w)	953(ms)	$\nu_{37} \gamma(\text{CH})$
—	—	980(ew)	—	985(ew)	$\nu_{36} \gamma(\text{CH})$
1015(w)	1015(ms)	1015(ew)	1010(vw)	1010(vw)	$\nu_{27} \alpha(\text{CCC})$
—	1045(vw)	1038(ew)	1040(ms)	1040(ew)	$\nu_{26} \nu(\text{CC})$
—	1089(vw)	1095(ewd)	1085(w)	—	$\nu_{30} + \nu_{35}$
—	—	1110(ms)	1115(w)	1114(ms)	$\nu_{25} \beta(\text{CH})$
1140(ew)	—	1130(ms)	1140(vw)	1130(ms)	$\nu_{24} \beta(\text{CH})$
1148(ew)	—	1145(wd)	1150(ew)	—	$\nu_{41} + \nu_{47}$
1172(ewd)	—	1170(msb)	1170(ms)	1168(vsb)	$\nu_{23} \beta(\text{CH})$
—	1217(ew)	1218(ms)	1215(ms)	1213(ms)	$\nu_{22} \beta(\text{CH})$
—	1240(ew)	1238(w)	1235(ms)	1240(w)	$\nu_{21} \beta(\text{CH})$
—	—	1248(sh)	1265(ms)	1250(w)	$\nu_{20} \beta(\text{CH})$
—	1270(vw)	1270(msb)	1280(w)	1270(wb)	$\nu_{19} \nu(\text{C-OH})$
—	—	1283(wb)	1290(wb)	1285(wb)	$\nu_{18} \beta(\text{OH})$
—	—	1320(wb)	—	1325(sh)	$\nu_{41} + \nu_{44}$
1360(ew)	1365(sh)	1362(sh)	1360(w)	1360(ms)	$\nu_{17} \nu(\text{CC})$
1370(sh)	—	1370(vs)	—	1370(sh)	$\nu_{16} \nu(\text{CC})?$
1382(s)	1380(vs)	1386(wb)	1380(w)	1378(ms)	$\nu_{15} \nu(\text{CC})$

Table 2. (Continued)

1	2	3	4	5	6
1405(ewd)	1395(ew)	1403(wb)	1395(w)	1410(ew)	$\nu_{14} \nu(\text{CC})$
1450(ewd)	1450(ms)	1443(sh)	—	1443(ms)	$\nu_{41} + \nu_{42}$ [Reson.]
1471(ms)	1470(ms)	1473(ms)	1460(ms)	1462(ms)	$\nu_{13} \beta(\text{CH})$
—	—	1485(wb)	1485(vw)	1477(vw)	$2\nu_{41}$
—	—	1507(w)	1510(s)	1505(ms)	$\nu_{12} \nu(\text{CC})$
1578(w)	1575(w)	1578(wb)	1580(w)	1579(ms)	$\nu_{11} \nu(\text{CC})$
1589(w)	—	1595(ms)	1600(s)	1598(s)	$\nu_{10} \nu(\text{CC})$
1635(vwb)	1628(vw)	1630(ms)	1625(vs)	1623(s)	$\nu_9 \nu(\text{CC})$
—	—	1636(sh)	—	1633(sh)	$\nu_{28} + \nu_{29}$
—	—	1625(ewb)	—	—	$\nu_{39} + \nu_{29}$
—	—	1672(ewb)	—	—	$2\nu_{39}$
—	—	1685(ewb)	—	—	$\nu_{28} + \nu_{29}$
—	—	2025(ew)	—	—	$2\nu_{27}$
—	—	2280(ewd)	—	2300(wb)	$2\nu_{24}$
—	—	2400(vwb)	—	—	$\nu_9 + \nu_{30}$
—	—	2460(vwb)	—	2460(ew)	$\nu_9 + \nu_{39}$
—	—	2585(wd)	—	—	$2\nu_{18}$
—	—	2650(vwd)	2650(ew)	2650(ew)	$\nu_9 + \nu_{27}$
3010(ew)	—	3005(ms)	—	—	$\nu_8 \nu(\text{CH})$
3016(ew)	3020(ew)	—	—	—	$2\nu_{12}$
3029(ew)	—	—	—	—	$\nu_7 \nu(\text{CH})$
3040(ew)	3040(ew)	—	—	3035(w)	$\nu_8 \nu(\text{CH})$
3054(ms)	—	—	3050(ms)	—	$\nu_6 \nu(\text{CH})$
3059(ms)	3060(ms)	3060(ms)	—	3065(w)	$\nu_4 \nu(\text{CH})$
3073(sh)	—	—	—	—	$\nu_3 \nu(\text{CH})$
3079(sh)	—	3080(vw)	—	—	$\nu_2 \nu(\text{CH})$
—	—	3180(msb)	3150(msb)	—	$2\nu_{11}$
—	—	3250(msb)	—	—	$\nu_1 \nu(\text{OH})$ [polymer]
—	—	3350(msb)	—	3350(wd)	$\nu(\text{OH})$ bonded or combination band.
—	—	3400(w)	—	3400(wd)	
—	—	3450(vw)	3450(vwb)	3450(wd)	$\nu_1 \nu(\text{OH})$ [dimer]
—	—	—	3550(vw)	3580(sb)	$\nu_1 \nu(\text{OH})$ [monomer]

See the footnotes of table 1 for notations and symbols used in this table.

been followed for numbering the fundamental frequencies, in which the vibrations from ν_1 to ν_{35} are of a' type and from ν_{36} to ν_{51} of a'' type.

4.1 C-H stretching modes

From the group theoretical considerations, seven C-H stretching [$\nu(\text{CH})$] frequencies are expected in the monosubstituted naphthalenes, and all these usually occur in the range from 3000 to 3100 cm^{-1} . In the present study, similar results have been observed for the α - and β -naphthols; however, in deuterated β -naphthol only three C-H stretching frequencies were found. Since, this region is comparatively free from complicating features, the assignments of $\nu(\text{CH})$ vibrations are straightforward.

Table 3. Vibrational frequencies and their assignments for deuterated β -naphthol

Infrared frequencies (cm ⁻¹)			Assignments
KBr pellet	Nujol mull	CH ₂ Cl ₂	
1	2	3	4
—	250(ew)		ν_{50} ϕ (CC)
—	284(vw)		ν_{49} ϕ (CC)
—	290(vw)		ν_{48} γ (C-OD)
—	320(vw) }		?
340(ew)	332(vw) }		
350(ewb)	350(vwb)		ν_{35} α (CCC)
372(vw)	371(vw)		?
383(vw)	381(vw)		$\nu_9 - \nu_{21}$
398(vw)	395(vw)		?
423(w)	420(msb)		ν_{47} ϕ (CC)
441(ms)	440(ms)		ν_{46} ϕ (CC)
468(sh)	469(sh)		ν_{45} ϕ (CC)
479(vs)	478(vs)		ν_{34} α (CCC)
520(msb)	520(vwb)		ν_{33} β (C-OD)
532(sh)	533(vw)		ν_{32} α (CCC)
565(msd)	{ 550(vwb) 565(vw)		ν_{44} γ (OD)
583(msd)	577(vw)		ν_{43} ϕ (CC)
620(s)	620(s)		ν_{31} α (CCC)
634(ms)	631(sh)	—	?
712(ms)	715(vw)	715(wb)	ν_{42} γ (CH)
738(vs)	737(vs)	735(w)	ν_{41} γ (CH)
749(s)	747(vw)	752(w)	ν_{40} γ (CH)
763(ms)	760(ew)	764(w)	ν_{30} ν (CC) [breathing]
770(sh)	777(ew)	774(w)	$\nu_{33} + \nu_{60}$
810(vsb)	807(s)	807(vs)	ν_{29} α (CCC)
840(vs)	838(s)	838(ms)	ν_{39} γ (CH)
848(sh)	843(sh)	856(vw)	$2\nu_{47}$
874(s)	872(ms)	871(vw)	ν_{38} α (CCC)
900(s)	900(ms)	907(w)	$\nu_{34} + \nu_{47}$
941(sh)	941(vw)	936(w)	ν_{36} γ (CH)
953(vs)	953(ms)	950(vw)	ν_{37} γ (CH)
975(ew)	970(vw)	972(w)	ν_{36} γ (CH)
988(ew)	—	983(ms)	$\nu_{33} + \nu_{45}$
1010(ms)	1008(vw)	1005(ms)	ν_{27} α (CCC)
1023(ewb)	1028(vwb)	1035(ms)	ν_{26} ν (CC)
1082(vw)	—	1082(ew)	$\nu_{31} + \nu_{45}$
1098(vw)	—	1094(ew)	$\nu_{31} + \nu_{34}$
1112(s)	1110(vw)	1115(ms)	ν_{25} β (CH)
1134(s)	1130(vw)	1140(ms)	ν_{24} β (CH)
1146(sh)	1150(w)	—	$\nu_{31} + \nu_{32}$
1168(vs)	1170(ms)	1172(s)	ν_{23} β (CH)
1211(vsb)	1211(ms)	1212(ms)	ν_{22} β (CH)
1240(vsd)	1239(ms)	1238(ms)	ν_{21} β (CH)
1258(sh)	1254(ms)	1250(vwd)	ν_{20} β (CH)
1270(vs)	1270(msb)	1263(vwd)	ν_{19} ν (C-OD)
1284(vs)	1284(ms)	1275(vwb)	ν_{18} β (OD)
1317(ms)	—	1321(ew)	$\nu_{30} + \nu_{44}$
1345(sh)	1340(sh)	1342(sh)	ν_{17} ν (CC)
1359(s)	1360(sh)	1357(ms)	ν_{16} ν (CC)

Table 3. (Continued)

1	2	3	4
1373(s)	1371(s)	1370(sh)	$\nu_{15} \nu(\text{CC})$
1401(vs)	1400(ms)	1383(ms)	$\nu_{14} \nu(\text{CC})$
1434(sh)	1433(sh)	1432(w)	$2\nu_{42}$
1451(sh)	1455(sh)	1452(sh)	$\nu_{41} + \nu_{42}$ [Reson.]
1462(vs)	1463(vs)	1460(s)	$\nu_{13} \beta(\text{CH})$
1503(s)	1506(ms)	1500(s)	$\nu_{12} \nu(\text{CC})$
1567(sh)	1570(msd)	1564(sh)	$\nu_{39} + \nu_{41}$ [Reson.]
1580(vs)	1580(msd)	1573(sh)	$\nu_{11} \nu(\text{CC})$
1596(vs)	1594(ms)	1594(vs)	$\nu_{10} \nu(\text{CC})$
1613(sh)	1612(sh)	1613(sh)	$\nu_{15} + \nu_{50}$
1621(vs)	1623(ms)	1620(vs)	$\nu_9 \nu(\text{CC})$
1635(sh)	1634(sh)	1644(ew)	$\nu_{29} + \nu_{39}$
1810(ew)	—	1805(ew)	$\nu_{15} + \nu_{46}$
1823(ew)	—	1823(ew)	$\nu_{11} + \nu_{50}$
1834(ew)	—	—	$\nu_{10} + \nu_{50}$
1950(ew)	—	1945(ewd)	$2\nu_{36}$
2000(ew)	—	—	$2\nu_{27}$
2285(ew)	2280(vwd)	2270(vw)	$2\nu_{24}$
2340(ewb)	2350(wd)	—	$2\nu_{23}$
2415(vwb)	2420(msb)	—	$\nu_8 \nu(\text{O-D})$ [polymer]
2440(vwd)	2450(msb)	—	$\nu_9 \nu(\text{OD})$ [dimer] ?
2505 (vw)	2505(vw)	2520(vwd)	$2\nu_{20}$
2600(ew)	—	—	$\nu_9 + \nu_{39}$
—	—	2645(sb)	$\nu_8 \nu(\text{OD})$ [monomer]
2840(vw)	—	—	$\nu_9 + \nu_{22}$
2865(vw)	—	—	$\nu_9 + \nu_{21}$
2900(ms)	—	—	$\nu_8 + \nu_{50}$
2935(ms)	—	2935(w)	$2\nu_{13}$
3010(ms)	3010(ms)	3010(w)	$\nu_7 \nu(\text{CH})$
3030(sd)	3030(ms)	3040(msd)	$\nu_6 \nu(\text{CH})$
3060(sd)	3060(ms)	3070(msd)	$\nu_3 \nu(\text{CH})$
3120(s)	3120(w)	3120(vw)	$\nu_8 + \nu_{34}$
3290(vsb)	3290(msb)	—	$\nu(\text{OH})$ [Polymer]
3510(msb)	—	—	$\nu_8 + \nu_{38}$
—	—	3580(ms)	$\nu(\text{OH})$ [monomer]

See the footnotes of table 1 for notations and symbols used in this table.

4.2 Carbon-carbon stretching modes

Out of the ten carbon-carbon stretching modes, $\nu(\text{CC})$, the first eight higher magnitude vibrations in naphthols are expected to appear between 1350–1630 cm^{-1} . These modes have been observed with strong (or medium strong) intensities, except a few cases where they have appeared as weak or the shoulder type bands. Because of the same symmetry (a') and nearly equal magnitudes, the $\nu(\text{CC})$ modes are expected to couple with the $\nu(\text{C-OH})$ [or $\nu(\text{C-OD})$] and $\beta(\text{OH})$ [or $\beta(\text{OD})$] vibrations. In the present vibrational analysis, frequencies assigned to the $\nu(\text{CC})$ vibrations do not show an appreciable change (except being intensified due to the reduction of molecular symmetry from D_{2h} to C_s) on substitution as compared to their values in

naphthalene; and thus it reveals that the above type of mixing of modes does not take place in naphthols.

The last two lower energy $\nu(\text{CC})$ vibrations ν_{26} and ν_{30} have the frequencies 1025 and 763 cm^{-1} in naphthalene. It should be noted that in naphthalene both modes are inactive in the infrared spectrum (a_g symmetry), but are prominent in the Raman spectrum. The mode ν_{26} , although occurs out of the familiar $\nu(\text{CC})$ region, also does not seem greatly affected in the substituted naphthalenes (Michaelian and Ziegler 1973) and thus has been assigned at 1045, 1040 and 1030 cm^{-1} in α -naphthol, β -naphthol and deuterated β -naphthol, respectively. Remaining $\nu(\text{CC})$ vibration ν_{30} is usually referred to as a 'ring breathing' mode, and its assignment in substituted naphthalenes is still a subject of controversy. The ring breathing frequency appears strongly in the Raman spectrum whereas its intensity in the infrared is relatively small even for substituted naphthalenes. A band of 710 cm^{-1} appears very strongly in the Raman spectrum and with strong (or medium strong) intensity in the infrared spectrum of α -naphthol. The corresponding band for the normal and the deuterated β -naphthols is observed at about 765 cm^{-1} and shows relatively strong intensity in the Raman spectrum. The bands now observed have been proposed for the ring breathing vibration and this agrees with the results obtained with substituted naphthalenes (Sharma *et al* 1977). Considerably large reduction in the magnitude of the 'ring breathing' mode in α -substituted naphthalenes is in conformity with the theoretical calculations of Luther (1948). This fact is further supported by the high resolution electronic absorption spectra of similar compounds in the vapour phase (Pandey 1982), where the corresponding ground and excited-state frequencies appear prominently in fundamentals, overtones and combinations.

4.3 C-H deformation modes

There are eight C-H in-plane [$\beta(\text{CH})$] and out-of-plane [$\gamma(\text{CH})$] bending modes in naphthalene, and these lie at approximately 1100–1450 cm^{-1} and 700–1000 cm^{-1} , respectively. In mono-substitution, one in-plane (1135 cm^{-1} , b_{3u}) and one out-of-plane (950 cm^{-1} , b_{2g}) bending vibrations become C-X (X = substituent group) deformation modes and would be discussed separately, while the remaining vibrations retain the pure $\beta(\text{CH})$ and $\gamma(\text{CH})$ characters. The frequencies of both types of hydrogen deformation modes are not affected too much (shifts upto 15 cm^{-1} have been noted) by a substitution of OH (or OD) group for one hydrogen atom either at α - or β -position in naphthalene. However, the modes ν_{25} [$\beta(\text{CH})$] in α -naphthol, and ν_{39} and ν_{41} [$\gamma(\text{CH})$] in the normal and deuterated β -naphthols are associated with relatively large frequency shift (of about 35 cm^{-1}).

4.4 C-X stretching and deformation modes

In phenols (Ram 1982), the C-OH stretching frequency generally falls at 1200–1300 cm^{-1} with relatively strong intensity in the infrared spectrum, and is believed to interact with in-plane O-H bending vibration. Recently, Singh and Rai (1980) have assigned this mode at ~ 1250 cm^{-1} in some substituted phenols. On the basis of these assignments, the bands observed at ~ 1280 , ~ 1275 and ~ 1265 cm^{-1} in α -naphthol, β -naphthol and deuterated β -naphthol, respectively, have been assigned to the C-OH (C-OD) valence vibration. The COH deformation modes in substituted

naphthalenes are highly sensitive to the substitution and, usually, appear in the spectral region 250–600 cm^{-1} with very small intensity in both the Raman as well as the infrared spectrum. Vibrational frequencies and tentative assignments of these modes are given in tables 1 to 3.

4.5 CCC angle deformation modes

The in-plane angle deformation frequencies, α (CCC), are sometimes modified and become X-sensitive in the substituted naphthalenes, provided the substitution is made at a carbon atom involved directly in the angle bend. The frequency of the vibration is not expected to change appreciably if the substitution occurs elsewhere on the carbon skeleton. The α (CCC) vibrations, in naphthalenes, occur at sufficiently low frequencies (below 1000 cm^{-1}); the interaction with the ν (C-X) mode or the internal modes of the substituent group (frequencies above 1200 cm^{-1}) is not expected.

The frequencies observed at 480, 790 cm^{-1} in the α -naphthol, and at 480, 800 cm^{-1} in the normal and deuterated β -naphthols, appear prominently in the infrared spectrum and with weak (or zero) intensity in the Raman spectrum. Both these frequencies are assigned to the in-plane skeletal distortion modes b_{1g} (506 cm^{-1}) and b_{2u} (810 cm^{-1}) of naphthalene, and are numbered as ν_{34} and ν_{29} . The other α (CCC) mode which shows relatively large frequency reduction (about 60 cm^{-1}) as compared to its value in naphthalene (938 cm^{-1} , b_{1g}), is assigned as the ν_{28} mode, and it has the frequency 880, 870 and 870 cm^{-1} in the α -naphthol, β -naphthol and β -naphthol-OD. All these features support the X-sensitivity of the corresponding modes. The remaining four α (CCC) modes are observed with medium and weak intensities in the infrared as well as the Raman spectrum (except a few ones which show zero intensity in the Raman spectrum), and have nearly the same frequencies as those in naphthalene.

4.6 Carbon-carbon torsion modes

The out-of-plane torsional modes of the carbon skeleton ϕ (CC) usually retain their magnitudes in substituted naphthalenes and show relatively poor intensities in both the Raman as well as the infrared spectrum. However, in a few cases, they depend slightly on the substitution. In the present study, the vibrational mode ν_{50} has been assigned for the infrared bands at 240, 240 and 250 cm^{-1} in the α -naphthol, β -naphthol and the deuterated β -naphthol, respectively; and provides a good example of the X-sensitive mode. In naphthalene, this vibration (213 cm^{-1} , a_g) is forbidden in the Raman and the infrared both. For the C_s point group, to which the present molecules belong this mode becomes allowed in the two types of spectra, though it is not observed in the Raman spectrum probably because of its very poor intensity.

4.7 Hydroxyl group modes and hydrogen bonding

The assignment of the three internal modes of the hydroxyl group is usually complicated because of the presence of strong hydrogen bonding. Puttnam (1960) has extensively studied the infrared bands of some substituted phenols in the region 3200–3600 cm^{-1} , and observed three distinct absorption bands in almost all the molecules undertaken. These bands were interpreted as due to the monomeric, dimeric and the polymeric O-H stretching frequencies.

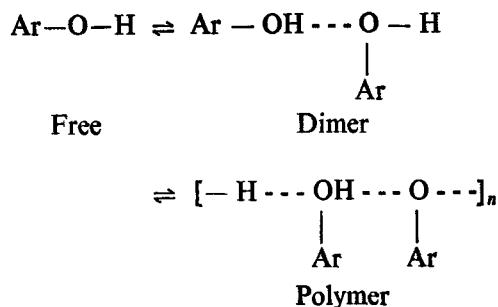
In the present study, we have also observed three distinct bands for all the three molecules in solution forms. However, a single broad and relatively strong asymmetric band (which seems to be composed of two or three different bands) was observed for each molecule in the condensed phase. The sharp infrared bands at 3550, 3580, and 2645 cm^{-1} for the α -naphthol, β -naphthol and the β -naphthol-OD, respectively, have been assigned to the $\nu(\text{OH})$ [$\nu(\text{OD})$] mode in the monomeric form. The corresponding bands in the associated forms (dimer and polymers) appear at slightly lower frequencies with relatively large band width and high intensity (see tables 1-3).

The OH in-plane bending mode has been assigned for the frequencies in the region from 1200 to 1300 cm^{-1} (Varsanyi 1974). In the present work, the infrared bands at 1305, 1285 and 1280 cm^{-1} have been assigned as the $\beta(\text{OH})$ and $\beta(\text{OD})$ bands. These bands are moderately strong in the infrared spectrum but show relatively poor intensity in the Raman spectrum. Similarly, the broad and diffuse bands of magnitude 619 and 550 cm^{-1} , in the infrared spectra of α -naphthol and deuterated β -naphthol, have been assigned to the $\gamma(\text{OH})$ and $\gamma(\text{OD})$ bands, respectively. The corresponding band is not observed in the solid phase infrared spectrum of β -naphthol, but it appears strongly in CH_2Cl_2 solution at 690 cm^{-1} .

5. Conclusion

The infrared and Raman spectra of α - and β - naphthols were obtained and all the 51 fundamental vibrations in each were assigned. For deuterated β -naphthol-OD, the infrared spectra (200-4000 cm^{-1}) were analysed in terms of 50 fundamental modes, one $\phi(\text{CC})$ torsion (which appears at ~ 170 cm^{-1} in the other two molecules) could not be observed since data below 200 cm^{-1} were not available. In the present vibrational analyses, the weak appearance of the Raman counterparts of the strong infrared frequencies in many cases and that of infrared counterparts for Raman frequencies in some cases along with the total absence of the Raman counterparts of some prominent infrared frequencies, suggest that the normal mode of vibration of the parent molecule naphthalene dominates the effect of substitution.

The results reported for the $\nu(\text{OH})$ and $\nu(\text{OD})$ vibrations are of particular interest in hydrogen bonding. The solid α - and β -naphthols exist only in the associated forms, and the shifted O-H stretching frequency is prominently due to this form. However, in the dilute solutions these molecules exist as an equilibrium mixture between the free naphthol and the dimeric and polymeric associated forms, the equilibrium lying to the right side:



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