

$\pi^* \leftarrow \pi$ electronic transition in hydroxy-benzonitriles. I. Ortho-hydroxybenzonitrile

S RAM*, J S YADAV and H D BIST*

Department of Physics, Banaras Hindu University, Varanasi 221 005, India

* Department of Physics, Indian Institute of Technology, Kanpur 208 016, India

MS received 5 August 1983

Abstract. The longest wavelength $\pi^* \leftarrow \pi$ electronic band system of ortho-hydroxybenzonitrile vapour through the absorption technique has been reported for the first time. Assuming a planar molecular geometry in both the electronic states, the molecule is classified into a C_s point group, and the present spectrum is attributed to ${}^1A' \leftarrow {}^1A'$ type corresponding to electric dipole forbidden transition ${}^1B_{2u} \leftarrow {}^1A_{1g}$ (260 nm band system) of benzene. The most intense band at 33914 cm^{-1} has been assigned as the 0, 0 band, and the other vibronic bands have been interpreted in terms of the excited state and a few ground state fundamentals.

Keywords. Infrared spectrum; Raman spectrum; electronic absorption spectrum; vibronic analysis.

1. Introduction

The vapour phase electronic spectra of benzonitrile (Hirt and Howe 1948; Joshi 1955) and some of its mono-derivatives (Cooper 1953; Sen 1955; Singh 1962; Singh 1967) have been extensively investigated. However, the UV absorption and emission spectra of hydroxybenzonitriles in vapour phase have not yet been studied. Such spectral studies of similar molecules in the solution forms have been reported by McGlynn and his coworkers (Carsey *et al* 1979; Findley *et al* 1979). The infrared and Raman spectra of these molecules in the solid phase have already been reported earlier (Ram *et al* 1981). The present paper is a continuation of our vibrational and electronic spectroscopic studies of some mono-substituted benzonitriles and deals with the results of the vapour phase electronic absorption spectrum of ortho-hydroxybenzonitrile. All the vibronic transitions have been considered and assignments for the observed bands have been suggested.

2. Experimental details

Pure sample of ortho-hydroxybenzonitrile was of Fluka make and was used as such. The electronic absorption spectrum of the sample in vapour phase was photographed on a Hilger large quartz spectrograph. The absorption tube containing the sample was heated from 20 to 120°C by an electrical heating tape system. A high pressure DC xenon arc lamp of about 350 watt was employed for the continuous source of radiation. The following experimental conditions were found most suitable to record the spectrum on 400 ASA panchromatic films: slit width = 0.05 mm; cell length = 98 cm; temperature =

73°C; exposure time = 1 minute, and a vapour pressure of about 10^{-2} torr. The sharp and intense bands were measured on a Russian comparator with a least count of 10^{-3} mm, whereas the weak and diffuse bands were measured from the enlarged positive prints. The accuracy of measurements is estimated to be $\pm 2 \text{ cm}^{-1}$ in sharp and strong bands and $\pm 5 \text{ cm}^{-1}$ or even more in very weak and diffuse bands.

3. Description of observed spectrum

The positive print of the 0, 0 band region in the electronic absorption spectrum of ortho-hydroxybenzointrile is reproduced in figure 1. Some characteristic features of this spectrum may be summarized as follows:

(i) The vibronic structure shows the presence of a single band system $\bar{A}^1 A' \leftarrow \bar{X}^1 A'$ lying in the spectral region 270–310 nm. Most of the bands are sharp and red-degraded, but some on the lower wavelength side are broad and diffuse. In a few cases, bands show a width of about 10 cm^{-1} and do not form any head. Their frequencies are, therefore, not very accurately determined. Further, with increase of vapour pressure and temperature, the intensity of hot bands on the longer wavelength side, usually, has been marked to increase.

(ii) The most intense band at 33914 cm^{-1} , which has been taken as the 0, 0 band in the present spectrum, is found to remain strong under all experimental conditions, *i.e.*, variation of temperature, pressure and the absorption cell length. Electronic transition energy corresponding to this band in the vapour phase is almost the same (within $\pm 0.05 \text{ eV}$) as those reported in solution forms using different polar and non-polar solvents (Ram 1982). Further, the introduction of a hydroxyl group in place of a hydrogen atom at ortho position in benzonitrile reduces the transition energy by about 2600 cm^{-1} .

(iii) The origin band (0, 0 band) is accompanied with several sequence bands on the longer wavelength side; among which those arising from the vibrational modes ν_{25} and ν_{36} are the important ones (see table 2).

4. Vibronic analyses and discussion

The molecular geometry of benzonitrile (Hirt and Howe 1948) in the ground and the first excited singlet electronic state is planar. If the substituent group –OH is assumed to be point mass, as has been done by previous workers (Carsey *et al* 1979; Findley *et al* 1979), the molecule ortho-hydroxybenzointrile would belong to C_s symmetry. Under this symmetry classification, the 36 normal modes of vibration of this molecule may be written as $25a' + 11a''$. Both a' (planar) and a'' (non-planar) types of vibrations are infrared and Raman-active.

Electronic spectral studies on benzonitrile and its mono-derivatives (Hirt and Howe 1948; Joshi 1955; Carsey *et al* 1979; Findley *et al* 1979) reveal that the longest wavelength $\pi^* \leftarrow \pi$ electronic band system in ortho-hydroxybenzointrile arises from a transition between the lowest excited singlet state S_1 and the ground state S_0 . The excited state S_1 results from a π to π^* electron promotion. In the notation of C_s symmetry, both the electronic states would be designated as $^1A'$, and the electronic

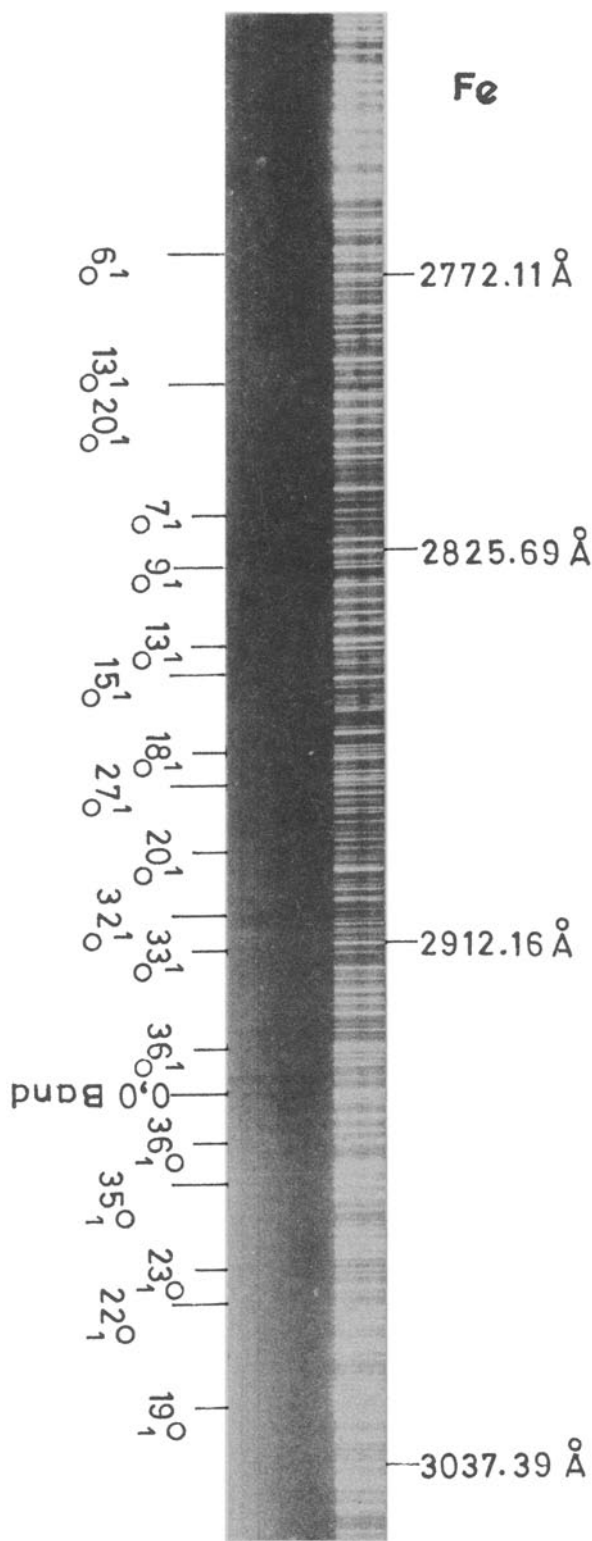


Figure 1. Longest wavelength $\pi^* \rightarrow \pi$ electronic transition in ortho-hydroxybenzonnitrile vapour.

transition ${}^1A' \leftarrow {}^1A'$ is allowed by both symmetry and spin-selection rules, with the transition moment lying in the plane of the molecule. This electronic transition corresponds to the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ (260 nm system) electric dipole forbidden transition in benzene and the ${}^1B_2 \leftarrow {}^1A_1$ (274 nm system) transition in benzonitrile. Though the reduction of molecular symmetry from D_{6h} in benzene to C_{2v} in benzonitrile makes this transition symmetry-allowed in the latter case, the spectrum also contains some characters of a forbidden transition because the carbon ring still retains a charge distribution with a largely D_{6h} symmetry. A similar admixture of allowed and forbidden character is also expected in the spectrum of hydroxybenzonitriles. As a consequence of the allowed nature of this transition, the 0, 0 band and the bands involving totally symmetric vibrations (a' symmetry) in any number of quanta should appear with strong intensity in the spectrum. On the other hand, non-totally symmetric vibrations (a'' symmetry) would give rise to very weak bands with the transition moments perpendicular to the molecular plane. However, a vibronic band involving two non-totally symmetric vibrations may appear with appreciable intensity as a sequence or combination band.

In accordance with the group theory and Franck–Condon principle, the strongest band on the longer wavelength side, at 33914 cm^{-1} has been identified as the 0, 0 band. This band remains the strongest band even for the smallest absorption cell length and the lowest vapour pressure employed in our experiment and thus support the above assignment of the 0, 0 band. The vibronic bands observed in the absorption spectrum of ortho-hydroxybenzonitrile have been analysed using the infrared and Raman spectra of this molecule. The assignment of the ground state fundamental frequencies and their magnitudes as obtained from the vibrational spectra (IR and Raman) are summarized in table 1. The main vibronic bands and their assignments are given in table 2. The notation K_j^i (used in this table stands for a vibronic band which involves i quanta of the K th fundamental vibration in the excited state and j quanta of the same vibration in the lower electronic state). Vibrational numbering is made according to the scheme proposed by Mulliken (1955) in which the vibrations: ν_1 to ν_{25} are planar (a') and those from ν_{26} to ν_{36} are non-planar (a'').

4.1 C-C stretching modes

The strong absorption bands at 35339 and 35461 cm^{-1} as observed through electronic absorption spectrum of ortho-hydroxybenzonitrile vapour involve the excited state frequencies 1425 and 1547 cm^{-1} , respectively. The higher excitations of these frequencies do not seem to occur in the spectrum, but both give rise to considerably strong combination bands with other prominent fundamental bands. In agreement with the previous studies on some disubstituted benzenes (Srivastava and Singh 1972), both these bands have been correlated with C–C stretching modes $8b$ and $19b$ (Wilson's notation) of benzene in the excited state. Corresponding hot bands (ground state frequencies) are not observed in the electronic absorption spectrum, as the spectrum does not extend upto this region in the longer wavelength side, but appear strongly in the infrared spectrum and with poor (or zero) intensity in the Raman spectrum having the magnitudes 1507 and 1607 cm^{-1} (see table 1).

Table 1. Ground state vibrational (infrared and Raman) frequencies of ortho-hydroxybenzotrile in solid phase.

Vibrational mode	Frequencies (cm ⁻¹)		Assignment
	Raman	Infrared	
ν_1	—	3400 (sh)	ν (OH) Dimer
	—	3258 (vsb)	ν (OH) Polymer
ν_2	—	3120 (sh)	ν (CH); (20a)
ν_3	—	3087 (sh)	ν (CH); (2)
ν_4	3065 (ew)	3070 (sh)	ν (CH); (20b)
ν_5	—	3024 (sh)	ν (CH); (7b)
ν_6	2232 (vs)	2236 (vs)	ν (C \equiv N)
ν_7	1604 (w)	1607 (vs)	ν (CC); (8b)
ν_8	—	1572 (sh)	ν (CC); (8a)
ν_9	—	1507 (s)	ν (CC); (19b)
ν_{10}	—	1460 (vs)	ν (CC); (19a)
ν_{11}	—	1370 (vs)	ν (CC); (14)
ν_{12}	1305 (ew)	1307 (vs)	β (CH); (3)
ν_{13}	—	1270 (s)	ν (C—OH); (7a)
ν_{14}	1239 (vw)	1241 (s)	β (OH)
ν_{15}	1180 (vw)	1185 (ms)	ν (C—C'N); (13)
ν_{16}	1160 (vw)	1162 (s)	β (CH) (9a)
ν_{17}	—	1105 (s)	β (CH); (18a)
ν_{18}	1031 (ms)	1036 (ms)	β (CH); (18b)
ν_{19}	841 (ew)	850 (s)	β (CCC); (12)
ν_{20}	728 (ms)	735 (s)	Ring breathing (1)
ν_{21}	—	605 (ms)	β (CCC); (6a)
ν_{22}	565 (w)	573 (ms)	β (C \equiv N)
ν_{23}	468 (vw)	473 (vwd)	β (CCC); (6b)
ν_{24}	393 (ew)	398 (vw)	β (C—OH); (9b)
ν_{25}	176 (ew)	181 (s)	β (C—C'N); (15)
ν_{26}	—	989 (w)	γ (CH); (5)
ν_{27}	—	952 (ms)	γ (CH); (17b)
ν_{28}	—	861 (sh)	γ (CH); (17a)
ν_{29}	—	771 (vs)	γ (CH); (11)
ν_{30}	—	689 (s)	ϕ (CC); (4)
ν_{31}	—	657 (ms)	γ (OH)
ν_{32}	—	501 (s)	ϕ (CC); (16a)
ν_{33}	415 (ew)	415 (vw)	ϕ (CC); (16b)
ν_{34}	363 (ew)	369 (ew)	γ (C—OH); (10a)
ν_{35}	250 (ew)	251 (w)	γ (C \equiv N)
ν_{36}	158 (ew)	156 (vw)	γ (C—C'N); (10b)

* For detailed description, see Ram (1982) and Varsanyi (1974).

Note—

- (i) The notations ν , β and γ denote bond stretching, in-plane bending and out-of-plane bending, respectively. ϕ (CC) refers to the non-planar torsional vibrations of the carbon skeleton, and C' refers to carbon atom of the nitrile group.
- (ii) The symbols written inside the small brackets against the vibrational frequencies denote the relative intensities of the corresponding bands, and details of these are 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; wb = weak and broad; wd = weak and diffuse; vw = very weak; ew = extremely weak

Table 2. Wavenumbers and assignments of the principal band groups in the longest wavelength $\pi^* \leftarrow \pi$ electronic absorption spectrum of ortho-hydroxybenzotrile vapour.

Wavenumber (cm^{-1})	Separation		Relative		Wavenumber		Separation		Relative	
	from 0,0 band (cm^{-1})	band (cm^{-1})	intensity	intensity	1	2	from 0,0 band (cm^{-1})	band (cm^{-1})	intensity	Assignments
1	2	3	4	1	2	3	4			
32584	-1320	w	27 ₁ ⁰ 24 ₁ ⁰	296	-618	msd	33 ₁ ⁰ 25 ₁ ⁰ 36 ₁ ¹			
612	-1302	ms		322	-592	ms	33 ₁ ⁰ 25 ₁ ⁰			
654	-1260	ms	13 ₀ ⁰	356	-558	sb	22 ₀ ⁰			
701	-1213	ms	18 ₁ ⁰ 25 ₁ ⁰	376	-538	ms	32 ₁ ⁰ 25 ₁ ¹			
734	-1180	ms	15 ₁ ⁰	413	-501	ms	32 ₁ ⁰			
755	-1159	ms		430	-484	s	23 ₁ ⁰ 33 ₁ ¹			
793	-1121	w	22 ₂ ⁰	448	-466	ms	23 ₁ ⁰			
824	-1090	ms	19 ₁ ⁰ 35 ₁ ⁰	483	-431	msb	22 ₁ ⁰ 36 ₀ ⁰			
849	-1065	msb	22 ₁ ⁰ 32 ₁ ⁰	501	-413	w	33 ₁ ⁰			
878	-1036	ms	18 ₁ ⁰	524	-390	msb	24 ₁ ⁰			
909	-1005	ms	32 ₂ ⁰	548	-366	s				
932	-982	w	20 ₁ ⁰ 35 ₁ ⁰	560	-354	wd	25 ₂ ⁰			
967	-947	w	27 ₁ ⁰	579	-335	ms	35 ₁ ⁰ 27 ₁ ¹			
998	-916	wb		595	-319	msb	23 ₁ ⁰ 25 ₀ ⁰			
33044	-870	s	19 ₁ ⁰ 33 ₁ ¹	612	-302	ms	36 ₂ ⁰			
069	-845	msb	19 ₁ ⁰	629	-285	ms	27 ₁ ⁰ 20 ₁ ⁰			
104	-810	ms	27 ₀ ⁰ 25 ₀ ⁰	641	-273	vw	25 ₀ ⁰ 27 ₁ ¹			
121	-793	ms	22 ₁ ⁰ 35 ₁ ⁰	672	-242	ms	35 ₁ ⁰			
154	-760	w	20 ₁ ⁰ 36 ₁ ¹	688	-226	w				
33184	-730	ms	20 ₁ ⁰	699	-215	w	25 ₂ ¹			
227	-687	msb		716	-198	wd	25 ₁ ⁰ 33 ₁ ¹			
274	-640	ms	23 ₁ ⁰ 25 ₁ ⁰	33736	-178	ms	25 ₁ ⁰ 36 ₁ ¹			

Table 2. (Contd.)

1	2	3	4	1	2	3	4
747	-167	vw		095	181	ms	
763	-151	sb	36 ⁰	106	192	s	25 ⁰ 27 ¹
776	-138	vw		115	201	ms	36 ⁰ 25 ¹
809	-105	ms	27 ¹ 33 ¹	155	241	vsb	36 ⁰
822	-92	vsb	27 ¹	178	264	s	35 ⁰
836	-78	vw	25 ²	198	284	ms	25 ⁰
856	-58	ms	36 ²	233	319	ms	
867	-47	s	36 ¹ 33 ¹	245	331	s	24 ⁰
876	-38	ms	25 ¹ 33 ²	282	368	ms	36 ⁰
886	-28	ms	36 ¹	311	397	vsb	33 ⁰
896	-18	s	33 ¹	366	452	msd	23 ⁰
904	-10	vw		380	466	s	18 ¹ 35 ⁰
914	00	vsb	0,0 Band	399	485	vsb	32 ⁰
923	9	vw	33 ¹ 24 ⁰	453	539	s	22 ⁰
940	26	ms	35 ¹	478	564	ms	20 ⁰ 27 ¹
952	38	s	22 ⁰ 32 ⁰	538	624	ms	21 ⁰ 33 ²
962	48	vs	25 ⁰ 27 ¹	557	643	s	20 ⁰ 33 ¹
984	70	msd	32 ⁰ 23 ⁰	577	663	vs	20 ⁰
995	81	ms	35 ⁰ 25 ⁰	609	695	wd	
34007	93	sb	36 ²	627	713	es	18 ⁰ 35 ⁰
018	104	w	25 ²	656	742	sb	
029	115	ms	35 ¹ 36 ⁰	34692	778	ms	18 ⁰ 25 ¹
038	124	vs	36 ⁰	710	796	sb	33 ⁰
34045	131	ms		733	819	ms	19 ⁰
056	142	s	25 ⁰	750	836	ms	27 ⁰ 33 ¹
074	160	vs	20 ⁰ 32 ⁰	767	853	vsb	27 ⁰

Table 2. (Contd.)

1	2	3	4	1	2	3	4
790	876	s		461	1547	s	7 ₀ ¹
816	902	ms	23 ₀ ²	483	1569	wd	9 ₀ ¹ 25 ₀ ¹
834	920	vs	18 ₀ ¹ 25 ₀ ¹	507	1593	ms	33 ₀ ⁴
854	940	ms	18 ₀ ¹ 33 ₀ ¹	531	1617	msd	18 ₀ ¹ 20 ₀ ¹ , 15 ₀ ¹ 13 ₀ ¹
868	954	es	18 ₀ ¹	553	1639	ms	19 ₀ ²
895	981	ms	15 ₀ ¹ 25 ₀ ¹	585	1671	ms	27 ₀ ¹ 19 ₀ ¹
910	996	vs	20 ₀ ¹ 24 ₀ ¹	598	1684	sb	7 ₀ ¹ 25 ₀ ¹ , 13 ₀ ¹ 23 ₀ ¹
935	1021	ms		620	1706	msd	27 ₀ ²
978	1064	msb	9 ₀ ¹ 25 ₀ ²	657	1743	msb	18 ₀ ¹ 33 ₀ ²
996	1082	ms	19 ₀ ¹ 35 ₀ ¹	692	1778	w	18 ₀ ¹ 19 ₀ ¹
35023	1109	ms		722	1808	s	27 ₀ ¹ 18 ₀ ¹
038	1124	s	15 ₀ ¹ 25 ₀ ¹	740	1826	ms	15 ₀ ¹ 20 ₀ ¹
053	1139	msd	13 ₀ ¹ 27 ₀ ¹	751	1837	s	7 ₀ ¹ 25 ₀ ^{2?}
077	1163	s	15 ₀ ¹	799	1885	vsb	13 ₀ ¹ 20 ₀ ¹
103	1189	msd	33 ₀ ¹	818	1904	ms	18 ₀ ¹
144	1230	vsb	13 ₀ ¹	898	1984	wd	33 ₀ ² 20 ₀ ³
159	1245	sb	9 ₀ ¹ 25 ₀ ¹	35938	2024	msb	15 ₀ ¹ 18 ₀ ¹
198	1284	wd	18 ₀ ¹ 24 ₀ ¹	998	2084	msb	13 ₀ ¹ 27 ₀ ¹
241	1327	s	20 ₀ ¹	36026	2112	msd	15 ₀ ¹ 18 ₀ ¹
35265	1351	s	18 ₀ ¹ 33 ₀ ¹	057	2143	msb	18 ₀ ¹ 33 ₀ ¹
283	1369	vs	13 ₀ ¹ 25 ₀ ¹	093	2179	w	13 ₀ ¹ 18 ₀ ¹
310	1396	ms	27 ₀ ¹ 22 ₀ ¹	112	2198	sb	6 ₀ ¹
339	1425	vs	9 ₀ ¹	148	2234	vwd	18 ₀ ² 24 ₀ ¹
385	1471	sb		201	2287	w	
394	1480	ms	19 ₀ ¹ 20 ₀ ¹	224	2310	ms	18 ₀ ² 33 ₀ ¹
432	1518	ms	13 ₀ ¹ 25 ₀ ¹	238	2324	ms	15 ₀ ¹

Table 2. (Contd.)

1	2	3	4	1	2	3	4
251	2337	ms	6 ₀ ¹ 25 ₀ ¹ , 7 ₀ ¹ 33 ₀ ¹	854	2940	wb	13 ₀ ¹ 27 ₀ ¹
273	2359	s	7 ₀ ¹ 17 ₀ ¹	902	2988	msb	6 ₀ ¹ 33 ₀ ¹
308	2394	msd	13 ₀ ¹ 15 ₀ ¹	965	3051	vw	6 ₀ ¹ 27 ₀ ¹
354	2440	sb		37013	3099	ew	7 ₀ ¹
367	2453	ew	19 ₀ ³	071	3157	wd	6 ₀ ¹ 18 ₀ ¹
374	2460	ms	13 ₀ ¹	195	3281	w	13 ₀ ¹ 19 ₀ ¹
453	2539	vw	18 ₀ ¹ 33 ₀ ¹	221	3307	msb	13 ₀ ¹ 27 ₀ ¹
474	2560	w	27 ₀ ³	281	3367	ms	6 ₀ ¹ 15 ₀ ¹
505	2591	ms	6 ₀ ¹ 33 ₀ ¹	326	3412	ew	27 ₀ ⁴
550	2636	msb		345	3431	ms	6 ₀ ¹ 13 ₀ ¹
563	2649	ew	20 ₀ ¹ 6 ₀ ¹ 23 ₀ ¹	408	3494	ew	15 ₀ ¹
574	2660	ms	27 ₀ ² 18 ₀ ¹	477	3563	msd	13 ₀ ¹ 15 ₀ ¹
650	2736	w	6 ₀ ¹ 22 ₀ ¹	535	3621	ms	6 ₀ ¹ 9 ₀ ¹
36745	2831	ms		604	3690	vw	13 ₀ ³
772	2858	vw/	18 ₀ ³	658	3744	ms	6 ₀ ¹ 7 ₀ ¹
779	2865	sb	6 ₀ ¹ 20 ₀ ¹				

Table 3. Ground and excited state fundamental frequencies observed in the electronic absorption spectrum of ortho-hydroxybenzotrile vapour.

Mode of vibration*	Ground state frequencies (cm ⁻¹)	Excited state frequencies (cm ⁻¹)	Assignments
ν_{36}	151 (sb)	124 (vs)	γ (C-C'N)
ν_{25}	178 (ms)	142 (s)	β (C-CN)
ν_{35}	242 (ms)	264 (s)	γ (C' \equiv N)
ν_{24}	390 (msb)	331 (s)	β (C-OH)
ν_{33}	413 (w)	397 (vsb)	ϕ (CC)
ν_{23}	466 (ms)	452 (msd)	β (CCC)
ν_{32}	501 (ms)	485 (vsb)	ϕ (CC)
ν_{22}	558 (sb)	539 (s)	β (C' \equiv N)
ν_{20}	730 (ms)	663 (vsj)	ν (CC)
ν_{19}	845 (msb)	819 (ms)	β (CCC)
ν_{27}	947 (w)	853 (vs)	γ (CH)
ν_{18}	1036 (ms)	954 (es)	β (CH)
ν_{15}	1180 (ms)	1163 (s)	ν (C-C'N)
ν_{13}	1260 (ms)	1230 (vs)	ν (C-OH)
ν_9	—	1425 (vs)	ν (CC)
ν_7	—	1547 (s)	ν (CC)
ν_6	—	2198 (sb)	ν (C' \equiv N)

* See table 1.

4.2 C-H deformation modes

Hydroxybenzotrile, being a disubstituted benzene (C_s symmetry), has in all eight C-H deformation modes of which four are C-H in-plane bending (ν_{12} , ν_{16} , ν_{17} and ν_{18}) and four C-H out-of-plane bending (ν_{26} , ν_{27} , ν_{28} and ν_{29}). The assignment of suitable magnitudes for all these C-H vibrations in the ground state of ortho-hydroxybenzotrile has been well established from the infrared and Raman spectral data, and the results so obtained are summarized in table 1. Correlation of all these bands with those observed in the vapour phase electronic absorption spectrum is not always possible because of the complicated vibronic structure. In the present investigation, we have been able to assign only one in-plane (ν_{18}) and one out-of-plane (ν_{27}) bending modes in both the electronic states (see table 3). Both the bands occur very strongly in the first excited singlet electronic state and show successively decreasing intensity for the higher excitations (upto three quanta of $\nu'_{18} = 954 \text{ cm}^{-1}$ and four quanta of $\nu'_{27} = 853 \text{ cm}^{-1}$ have been noted). In addition, these frequencies also appear in binary combinations with several other prominent fundamental bands in the excited state. The above two C-H deformation frequencies usually occur in all disubstituted benzenes (Ram *et al* 1981; Ram 1982) and show relatively large frequency decrease (about 100 cm^{-1}) in going from ground to the excited electronic state.

4.3 C-X modes

The C-X (X being substituent atom or group of atoms) modes comprise stretching and wagging (both planar and non-planar) motions of the substituent group, as a whole,

against the phenyl ring. For hydroxybenzotrile these are in total six and all [except γ (C–OH) vibration] have also been observed as hot bands in the vapour electronic absorption spectrum. The assignment of these bands in the ground state is mainly based on a comparison with the infrared and Raman frequencies of this molecule in the solid state, and those in the first excited singlet state on the ground of the magnitudes of these modes in the parent molecules (benzotrile and phenol) and some of their mono-derivatives (Tiwari 1966; Singh 1962; Ram 1982). The results so obtained are given in table 3. Some of the vibronic bands involving C–X in-plane (ν_{25}) and out-of-plane (ν_{36}) bendings are summarized in tables 4 and 5, under the Deslandre's scheme. These provide a natural explanation of the main sequence bands on the longer wavelength side of the 0, 0 band. Some bands included in this scheme are weak and diffuse, and hence whenever these bands are involved, the frequencies may differ from their actual values due to the error of measurement in the position of such bands. It is seen that the medium strong sequence bands at 33886 and 33876 cm^{-1} (sequence intervals 28 and 38 cm^{-1} , respectively) probably result from the vibrational modes ν_{36} and ν_{25} , respectively. Hirt and Howe (1948) have also observed a similar sequence interval of 40 cm^{-1} in the absorption spectrum of benzotrile and attributed it to the out-of-plane C–CN bending mode. Moreover, band contour shape and depolarization ratio of the corresponding fundamental band in the ground state (Green and Harrison 1976; and Kuwae and Machida 1979) indicates that it would belong to a totally symmetric species a' , rather than to a non-totally symmetric species a'' .

4.4 Ring breathing and trigonal ring bending modes ν_{20} and ν_{19}

The ring breathing mode a_{1g} (992 cm^{-1}) of benzene does not appear in the infrared

Table 4*. Deslandre's scheme for the vibration mode ν_{25} of *ortho*-hydroxybenzotrile.

ν''/ν'	0		1		2	Mean
0	33914	142	34056	142	34198	~ 179
	178		180		180	
1	33736	140	33876	142	34018	~ 178
	176		177		182	
2	33560	139	33699	137	33836	
Mean		~ 140		~ 140		

* Entries in this table are in cm^{-1}

Table 5*. Deslandre's scheme for the vibration mode ν_{36} of *ortho*-hydroxybenzotrile.

ν''/ν'	0		1		2	Mean
0	33914	124	34038	117	34155	~ 150
	151		152		148	
1	33763	123	33886	121	34007	~ 151
	151		150		151	
2	33612	124	33736	120	33856	
Mean		~ 124		~ 119		

* Entries in this table are in cm^{-1} .

spectrum but occurs very strongly in the Raman spectrum, whereas its trigonal ring in-plane bending mode b_{1u} (1010 cm^{-1}) is inactive in both the spectra. In disubstituted benzenes (C_s symmetry) both are allowed in the infrared as well as the Raman spectrum. In the present study, the strong infrared bands at 735 and 850 cm^{-1} with relatively weak Raman counter parts at 728 and 841 cm^{-1} have been assigned for the ring breathing mode (ν_{20}) and trigonal ring bending mode (ν_{19}) of ortho-hydroxybenzonitrile. In the vapour phase electronic absorption spectrum these frequencies are identified as 730 and 845 cm^{-1} , where both show medium strong intensity. This assignment suggests that the above two modes in the ground state retain most of the forbidden characters of benzene even in disubstituted benzenes like hydroxybenzonitriles.

The modes ν'_{20} and ν'_{19} in the first excited singlet electronic state of most of the ortho-disubstituted benzenes (where both substituents are light) have the frequencies $650\text{--}750\text{ cm}^{-1}$ and $800\text{--}840\text{ cm}^{-1}$ (Singh 1962; Ram 1982), respectively. The cold bands at 34577 and 34733 cm^{-1} appear with strong and medium strong intensity in the electronic absorption spectrum of ortho-hydroxybenzonitrile, and involve the excited state frequencies 663 and 819 cm^{-1} , respectively. The higher quanta of excitations of these frequencies are noted upto four members long with successively decreasing intensity. These progression forming frequencies have also been marked to combine with several other intense fundamentals and their higher overtones. In agreement with previous studies (Ram *et al* 1981, 1982; Singh 1962), on similar molecules, the excited state frequencies 663 and 819 cm^{-1} have been proposed for the ν'_{20} and ν'_{19} modes in the first excited singlet electronic state of ortho-hydroxybenzonitrile vapour.

4.5 Ring deformation modes ν_{23} , ν_{32} and ν_{33}

The substituted benzenes are expected to show three distinct sets of in-plane and out-of-plane ring deformation modes, and under the assumption of C_s molecular symmetry, all the six are allowed in the infrared, Raman as well as the electronic spectrum. The reliable assignments for the ring deformation modes in the ground state of ortho-hydroxybenzonitrile have been made on the basis of infrared and Raman data (see table 1) recorded in the solid state. In the vapour absorption spectrum, only one in-plane (ν_{23}) and two out-of-plane (ν_{32} and ν_{33}) ring bending vibrations have been identified in both the electronic states. The ground state frequencies as observed from the vapour phase spectrum are almost the same as their values reported from infrared and Raman spectra (see tables 1 and 3) in the solid phase.

The electronic absorption bands at 34366 , 34399 and 34311 cm^{-1} involve the excited state frequencies 452 , 485 and 397 cm^{-1} , respectively. The former one has been noted to excite upto second quanta and the last one (*i.e.* 397 cm^{-1}) does seem to occur upto five members long with successively decreasing intensity (like ν'_{20} and ν'_{18}). No higher excitations are observed for the remaining frequency (*i.e.* 485 cm^{-1}), though it appears in combination with several fundamental frequencies in the either electronic state. These are correlated with the ground state frequencies 466 , 501 and 413 cm^{-1} which also appear in the vapour absorption spectrum, and therefore have been assigned to the modes ν'_{23} , ν'_{32} and ν'_{33} in the first excited singlet electronic state.

4.6 Nitrile group modes

Three internal vibrations concerned with the nitrile group of ortho-hydroxy-

benzotrile appear at 2232(2236), 565(573) and 250(251) cm^{-1} in the infrared (Raman) spectrum. The latter two frequencies have also been observed in the vapour absorption spectrum at 558 and 242 cm^{-1} on the longer wavelength side from the 0, 0 band.

The strong absorption band at 36112 cm^{-1} involves the excited frequency of 2198 cm^{-1} which could not be interpreted as the combination of two suitable lower magnitude fundamentals. It was therefore, considered to belong to a fundamental mode, namely the $\text{C}'\equiv\text{N}$ stretching ν'_6 . Padhye and Varadarajan (1962) and Singh (1962) in the electronic absorption spectrum of ortho-tolunitrile have assigned it at 2141 and 2137 cm^{-1} . Further, the fact that most of the ground and excited state fundamentals (taken in the present vibronic analysis) also fit in binary combination with this frequency, testifies to the fundamental character of this band. The remaining two $\text{C}'\equiv\text{N}$ group vibrations (ν_{22} and ν_{35}) in the excited state are identified as the intervals of 539 and 264 cm^{-1} . The remarkable point to be noted here is that the two planar vibrations (ν_6 and ν_{22}) of the nitrile group decrease in magnitude in going from ground to the first excited singlet electronic state S_1 , whereas the non-planar $\text{C}'\equiv\text{N}$ deformation mode ν_{35} seems to increase by 22 cm^{-1} , and it might be due to slight increase in the $\text{C}'\equiv\text{N}$ bond length in the S_1 state as compared to its ground state value.

5. Conclusions

If we can study a series of benzotriles through high resolution absorption technique, it may be possible to estimate their molecular geometry changes in going from ground to the excited electronic state. Unfortunately, no such spectrum is available to us, however, on the basis of changes in the fundamental frequencies (measured under medium resolution) discussed in the preceding sections, the following qualitative conclusions about the probable molecular geometry changes in ortho-hydroxybenzotrile have been attempted:

- (i) The $\text{C}'\equiv\text{N}$ bond increases in the S_1 electronic state as compared to its value in the ground state.
- (ii) The $\text{C}-\text{C}'\text{N}$ bond retains its single bond character even in the excited state S_1 .
- (iii) The carbon ring as well as the $\text{C}-\text{H}$ bonds expand in the S_1 state.

In view of these observations, the electronic charge distribution and the molecular geometry in the first excited singlet state S_1 do not seem to alter appreciably. However, the excitation of non-planar modes and their higher quanta with considerably large intensity in the excited state indicates that the molecule slightly deviates from the planar structure in the excited state S_1 as opposed to the ground state. Moreover, the longest wavelength $\pi^* \leftarrow \pi$ electronic transition (260 nm, shifted band system of benzene) in benzotrile is not perturbed (except a red shift of 2605 cm^{-1}) by the replacement of a hydrogen atom by a hydroxyl group.

References

- Carsey T P, Findley C L and McGlynn S P 1979 *J. Am. Chem. Soc.* **101** 4502
Cooper C D 1953 *J. Chem. Phys.* **21** 379
Findley G L, Carsey T P and McGlynn S P 1979 *J. Am. Chem. Soc.* **101** 4511
Green J H S and Harrison D J 1976 *Spectrochim. Acta* **A32** 1279
Hirt R C and Howe J P 1948 *J. Chem Phys.* **16** 480

- Joshi B D 1955-56 *J. Sci. Res. B.H.U.* **6** 266
- Kuwaie A and Machida K 1979 *Spectrochim. Acta* **A35** 841
- Mulliken R S 1955 *J. Chem. Phys.* **23** 1997
- Padhye M R and Varadarajan T S 1962 *J. Sci. Ind. Res.* **B21** 241
- Ram S 1982 *Vibrational and electronic spectra of the isomeric amino and hydroxybenzonitriles*, Ph.D. Thesis, Banaras Hindu University, Varanasi
- Ram S, Gupta B K and Yadav J S 1981 *Indian J. Pure Appl. Phys.* **19** 1110
- Ram S, Yadav J S and Upadhyay K N 1981 *Indian J. Pure Appl. Phys.* **19** 391
- Sen S K 1955 *Indian J. Phys.* **29** 561
- Singh P D 1967 *Spectroscopic studies of simple polyatomic and diatomic molecules*, Ph.D. Thesis, Gorakhpur Univ.
- Singh R N 1962 *Studies in the molecular spectra of isomeric tolunitriles, styrene and para-tolualdehyde*, Ph.D. Thesis, Banaras Hindu University, Varanasi
- Srivastava M P and Singh I S 1972 *Appl. Spectrosc.* **26** 278
- Tiwari S K 1966 *Spectroscopic studies of some polyatomic molecules*, Ph.D. Thesis, Banaras Hindu University, Varanasi
- Varsanyi G 1974 *Assignments for vibrational spectra of seven hundred benzene derivatives* (New York: Halsted Press) Vol. 1