THE NORMAL FREQUENCIES OF VIBRATION OF BENZENE COMPOUNDS IN THE ULTRAVIOLET ABSORPTION.

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Received February 8th, 1936. Published April 28th, 1936.

Introduction. Although some investigations have been made on the ultraviolet absorption spectra of benzene and its derivatives in vapour state, little progress has however been made in this direction, since these results rest always on an assumption, that (0.0)-band is the most intense, applying the intensity distribution of Frank-Condon principle to vibration bands in excited state. However, certain spectroscopic data (Raman and infrared) may be identified with the normal frequencies of vibration, by which the abovementioned assumption may be proved experimentally, provided that (1.0)-bands on the ultraviolet absorption are known. Unfortunately these data are not yet obtained for reason of complications of bands and the feeble intensity, the band of wave number 500 cm.^{-1} at room temperature being less intense than (0.0)-band by an amount of 10% from calculation by Maxwell-Boltzmann's energy distribution law. Author's attempts have however been made with considerable success, obviating this difficulty by purification of the sample, and by comparison of a number of plates which were taken in good experimental conditions.

This paper contains the results of the spectroscopic investigation of vapour of the following mono-substituted substances: toluene, chlorobenzene, bromobenzene, phenol, aniline, benzaldehyde, and benzonitrile.

Experimental. The samples, supplied as "purest" by Kahlbaum, were repurified by several fractional distillations under reduced pressure until the distillation temperature became constant with accuracy higher than ±0.05°C. The absorption vessels were cylindrical glass tubes 15–60 cm. long with quartz windows cemented on. The apparatus, in which the sample was cooled with liquid air, was first evacuated by an oil pump, and then by opening a cock it was filled with vapour of the sample to a suitable pressure which was measured by a mercury manometer. A water-cooled hydrogen discharge tube constructed to have a powerful intensity was employed as a source of the ultraviolet radiation. An exposure of 30 minutes or of one hour was found sufficient, the slit-width being 0.02 mm. The spectra were photographed on a Hilger E_2 and also on E_1 spectrograph. The iron arc was used as comparison.

Results. In Table 1–7, the experimental data are given with the wave number shifts⁽¹⁾ in Raman. The figures in brackets give the relative intensities of the spectra, d indicating diffuse band.

Discussion of these results will be given in another place.

Table 1. Toluene ($C_6H_5CH_3$)

Wave length in air (Å)	Wave number in vacuo (cm.$^{-1}$)	Frequency separation	Wave number shifts in Raman
27274–43 (d)	36654–96	781	786 (4)
27126–45	36854	623	622 (2)
27048–66	36960–36	517	520 (2)
26915	37143	334	333 (2)
26675	37477–60	0	

Table 2. Chlorobenzene (C_6H_5Cl)

27501	36353	701	704 (8)
27437	36436	618	615 (6)
27286	36638	416	418 (8)
26980	37054	0	

Table 3. Bromobenzene (C_6H_5Br)

27519	36328	668	670
27472	36390	606	608
27253	36682	315	314
27231	36712	285	—
27187	36771	226	—
27021	36996	0	

Table 4. Phenol (C_6H_5OH)

28134	35534	820	813 (3b)
27962	35752	604	614
27903	35828	528	526 (2)
27671	36128	228	235 (2)
27498	36356	0	

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(1) Kohlrausch, "Der Smekal-Raman-Effekt," 1931.

Table 5. Aniline ($C_6H_5NH_2$)

Wave length in air (Å)	Wave number in vacuo (cm.$^{-1}$)	Frequency separation	Wave number shifts in Raman
30292	33002	1032	1028 (5)
30255	33043	991	993 (10)
30100	33213	821	813 (5b)
29838	33505	529	530 (3)
29742	33613	421	—
29575	33803	231	233 (3)
29374	34034	0	

Table 6. Benzaldehyde (C_6H_5CHO)

29242	34187	1007	1001 (8)
29122	34328	866	827 (3)
29030	34437	757	752 (0)
28940	34544	650	648 (1)
28911	34579	615	615 (3)
28747-85 (d)	34776-30	418-464	439 (4)
28588-601 (d)	34970-54	224-240	239 (1b)
28478	35105	89	
28406	35194	0	

Table 7. Benzonitrile (C_6H_5CN)

28155 (d)	35507	1009	998 (5)
27846	35901	616	619 (1)
27793	35970	547	545 (1)
27758 (d)	36015	501	—
27726 (d)	36057	459	460 (1/2)
27377	36516	0	