Measurement of the Rotational Constant of the Benzene Molecule from the Structure of the $\nu_7+\nu_{16}$ Near Infrared Vibration Band

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The rotational structure of the $\nu_7+\nu_{16}$ vibrational band of benzene has been investigated. The rotational constant derived from the measurements is

$$B''=0.18975\pm0.00015\ \text{cm}^{-1}.$$

The present knowledge of the bond lengths in the benzene molecule is primarily based on the rotational constant measurements of different isotopic molecules by Stoicheff [1, 2] using pure rotational Raman spectrum. The structure of this molecule has also been investigated using X-ray and electron diffraction cf. Cox et al. [3] and Karle [4], but with somewhat less accurate results. The C–H bondlength has also been evaluated from the NMR spectra of different isotopic species of crystalline benzene [5]. Lord and McCubbin [6] have obtained the B'' constant from the rotation-vibration band ν_{11} near 670 cm^{-1}. Callomon et al. [7] analyzed the rotational structure of the electronic spectrum around 2700 Å. While the use of the infrared method has been very limited, it seemed worthwhile to try further a measurement of this kind. According to the thorough work of Brodersen and Langseth [8] the only possible parallel band in the near infrared region proved to be $\nu_7+\nu_{16}$ at 3455 cm^{-1}.

The band was studied using a high resolution grating spectrometer [9]. The path length was 3 metres and the vapour was almost saturated at room temperature. Under these conditions the Q branch appeared as a very strong peak but the absorption in the P and R branches still remained low. The absorption of water vapour caused disturbances at some points thus making it impossible to measure many of the lines. In some places the structure of the band was not well resolved. This may be due to the unresolved K structure or it may be caused by some other overlapping band. Altogether about 70 rotational lines were measured and all of them from several recordings. The observed wavenumbers are given in Table 1. The lines were fitted to a second order polynomial. The mean difference between the observed wavenumbers and those from the polynomial was 0.03 cm^{-1}. The fit led to the following results:

$$\nu_0=3455.24\ \text{cm}^{-1},$$
$$B''=0.18975\ \text{cm}^{-1},$$
$$B'-B''=-3.7\cdot10^{-4}\ \text{cm}^{-1}.$$

In Fig. 1 is given a plot of $\Delta F_2''-0.70\ (J+\frac{1}{2})$ versus $J+\frac{1}{2}$. The slope of the line gives the same value for B'' as that mentioned above. The accuracy of this constant can be estimated to be $\pm15\cdot10^{-5}\ \text{cm}^{-1}$.

J	$R(J)$	$P(J)$	J	$R(J)$	$P(J)$
6	3457.88		30	3466.61	
7	58.26		31		3443.18
8			32	67.30	
9	59.01	3451.78	33	67.66	
10	59.38	51.41	34	67.99	41.87
11	59.77	51.08	35	68.37	41.46
12	60.16	50.68	36	68.72	41.15
13	60.47	50.29	37	69.09	40.67
14	60.87	49.89	38	69.44	40.27
15			39	69.79	39.86
16	61.57		40	70.12	39.44
17	61.95	48.68	41	70.48	39.03
18	62.32		42		38.63
19		47.92	43		38.24
20	63.03	47.56	44		37.84
21	63.41		45		37.45
22	63.80		46	72.26	37.02
23	64.16	46.37	47	72.64	36.59
24		45.96	48	73.00	36.20
25		45.57	49		35.77
26	65.17	45.16	50	73.68	35.39
27			51	74.03	35.00
28			52	74.34	34.60
29		44.00	53		34.16
			54		33.72

Table 1. Observed freqencies (cm^{-1} in vacuum) in the $\nu_7+\nu_{16}$ band of benzene.

The result obtained is in good agreement with $0.18960\pm0.00005\ \text{cm}^{-1}$ of Stoicheff [1] and with $0.18975\pm0.00015\ \text{cm}^{-1}$ of Lord and McCubbin [6].

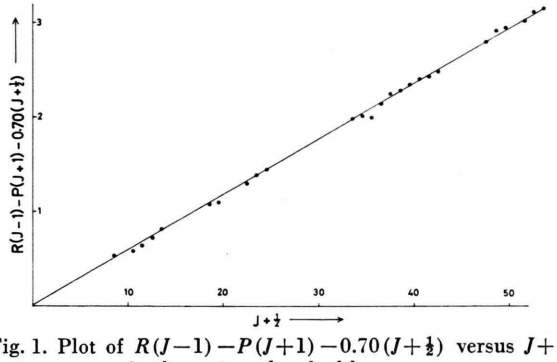

Fig. 1. Plot of $R(J-1)-P(J+1)-0.70\,(J+\frac{1}{2})$ versus $J+\frac{1}{2}$ in the $\nu_7+\nu_{16}$ band of benzene.

Because of the low absorption in P and R branches the accuracy of the measurements was not high enough to allow the derivation of the centrifugal distortion constant D_J. According to Stoicheff [1] this constant is very small ($2.2\cdot10^{-8}\ \text{cm}^{-1}$).

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