MICROWAVE SPECTRUM OF PENTAFLUOROBENZENE

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ABSTRACT

The microwave spectrum of pentafluorobenzene has been measured in the frequency region 12.5 to 18.00 KMHz. The spectrum is analysed on the basis of rigid asymmetric rotor theory. The rotational constants obtained are \( A = 1471.963 \) MHz, \( B = 1026.278 \) MHz, \( C = 604.693 \) MHz and the asymmetry parameter \( \kappa = -0.0278 \). The inertial defect is \( \Delta = I_x - I_y - I_z = -0.014 \text{amu Å}^2 \). The bond distances are \( d_{cc} = 1.328 \text{Å} \) and \( d_{ch} = 1.089 \text{Å} \), assuming \( d_{cc} = 1.395 \text{Å} \).

INTRODUCTION

The present work on pentafluorobenzene is in continuation of the studies of the substituted pentafluorobenzene compounds undertaken in this laboratory. The molecule pentafluorobenzene is assumed to be planar. Using the values for \( d_{cc} \) and \( d_{cr} \) reported for pentafluorobenzenitrile and hexafluorobenzene and assuming \( d_{ch} = 1.084 \text{Å} \), an expected rotational spectrum

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Fig. 1. Pentafluorobenzene.
was generated using computer programme written by Dr. L. Pierce.* It was found as expected that the axis of intermediate moment of inertia, along which the dipole moment lies, coincides with the C-H bond. Therefore only $b$ type transitions are permitted with the selection rules $\Delta K_1 = \pm 1$ and $\Delta K_1 = \pm 1$. Pentafluorobenzene has a rich spectrum. There are lines every 5 to 10 MHz in $K$ band region (18–26 GHz) and as such the investigation was undertaken in the $KU$ band (12.5–18 GHz) even where there are numerous lines. The spectrum showed strong $Q$ lines of high $J$ but $R$ lines were comparatively weak and could not be resolved by Stark effect. So Stark effect was of no help in the assignment of the spectrum. The analysis was therefore carried out by the identification of $Q$ lines as starting point and later completing it by finding $R$ lines.

**EXPERIMENTAL**

A conventional 100 KHz Stark modulated microwave spectrometer was used for the investigation of this molecule. The compound pentafluorobenzene was obtained from Imperial Smelting Corporation and was used without further purification. The measurements were all made at dry ice temperature and the pressure in most of the cases was maintained below 10 microns. As reported in the earlier paper,¹ the frequency measurements were made by comparing the Klystron frequency with the harmonics of a James Knights JKTO-43 10-MHz crystal Oscillator. Frequencies of the lines were determined by superimposing a frequency marker directly upon the absorption maxima on the oscilloscope. The frequencies of the absorption lines were determined by sweeping both from lower to higher frequencies and from higher to lower frequencies. The values obtained are the averages of these two values; the reproducibility is within a MHz in most cases. The observed spectra consisted of many lines which are narrower than those of pentafluorobenzonitrile. Excepting a few which were insensitive, the lines exhibited quadratic Stark effect—both regular and inverted.

**ANALYSIS**

Assuming a regular hexagonal structure for the carbon ring and with $d_{cc} = 1.394$ Å, $d_{cf} = 1.328$ Å and $d_{ch} = 1.084$ Å, the spectrum was generated. The programme written by Dr. Pierce was used with slight altera-

* This programme was kindly provided to us by Dr. C. Thomas of Harvard University, 12 Oxford Street, Cambridge 38, Massachusetts, U.S.A.