

(iii) There is a finite heat of mixing of the two components which rises to a maximum at an intermediate concentration. This is accompanied with a contraction in volume which reaches a maximum at an intermediate concentration.

These observations indicate a complex formation in these systems. Storey<sup>1</sup> qualitatively explained, the excess in sound absorption in the aqueous solutions of ethyl alcohol, by assuming that association of different molecules are present in the solutions and that the equilibrium among them is altered by temperature changes associated with sound wave. The absorption parameter  $a/f^2$  in such a system would reach a maximum when the proportions of the constituents are more favourable for a complex formation. In the two systems studied here, the intermolecular association complex can be formed by way of hydrogen bonding between protons of O-Chlorophenol and lone pair electrons of the Picoline molecules.

A comparison of the experimental results of this study with the theoretical values obtained by the use of Barfield and Schneider model<sup>2</sup> is shown in Figs. 1 and 2. It can be seen that, though the calculated curves satisfactorily reproduce the shape of the measured absorption curves, the Peaks are shifted to lower concentration of O-Chlorophenol. The lack of perfect agreement between the theoretical and experimental absorption curves might be due to the inadequacy of the simple two-state model assumed by Barfield and Schneider, which does not take into account the difference in the number of protons and donor atoms available for hydrogen bonding between the two liquids forming hydrogen bonding complex. The theoretical model for complex formation as suggested by Andreae *et al.*<sup>3</sup>, could not be tested for the present study, because of the lack of absorption data at high frequencies extending into the relaxation region.

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### ROTATIONAL ANALYSIS OF 0, 0 BAND OF B-X SYSTEM OF CuBr MOLECULE

THE spectrum of CuBr molecule has been investigated by several workers<sup>1-3</sup>. It consists of four band systems viz., A-X, B-X, C-X and D-X extending in the region 5000-3700 Å. Out of these four band systems only C-X system has been studied at a high dispersion and rotational constants have been reported. The C system has been assigned on electronic transition  ${}^1\Sigma^+ - {}^1\Sigma^+$ . The present note deals with the rotational analysis of B-X system of the molecule.

The spectrum of CuBr molecule was excited in a high frequency discharge (10-15 MHz) having an output of 125 W. Specpure sample of copper bromide was kept in a conventional type of quartz discharge tube and the blue colour of discharge was maintained by intermittent external heating. The 0, 0 band of the system was photographed in the sixth order of a 2 meter plane grating spectrograph at a reciprocal dispersion of 0.6 Å/mm. Spectrum was recorded on WU3 plates. Measurements were made on an Abbe Comparator against iron arc standards.

Out of all the bands photographed only the 0, 0 band was free from overlapping and could be utilized for carrying out the rotational analysis. Rotational isotope effect for <sup>79</sup>Br and <sup>81</sup>Br was clearly observed at high J values. Three branches, viz., P, Q, R for each isotope of Bromine could be picked up. The J numbering of rotational lines and their analysis has been carried out by the method suggested by Yougner and Winans<sup>4</sup>. The analysis revealed a  $\Lambda$ -type doubling in the upper state  ${}^1\pi$ .  $\Lambda$ -type doubling constant  $q$  has been calculated by the method of combination defect. The doubling of rotational lines in some branches of 0, 0 band has been attributed to the isotope effect of Bromine. The appearance of structure observed in the band (a part of photometric record given in Fig. 1) shows five to six components, indicating overlapping of different branches. This overlapping persists even upto high J values. Presence of two isotopes thus provides a useful check on the present analysis, i.e., observed  $B_0^1/B_0 = \rho^2$  (0.9929) agrees with calculated value  $\rho^2 = 0.9889$ . The results are given in Table I.

TABLE I

State	$B_0$ cm <sup>-1</sup>	$D_0 \times 10^6$ cm <sup>-1</sup>	$q$ cm <sup>-1</sup>	$r_0$ Å
B ${}^1\pi$	$B_0 - 0.0992$	6.57	$1.8 \times 10^{-4}$	2.093
X ${}^1\Sigma$	$B_0 - 0.1058$	6.25	..	..

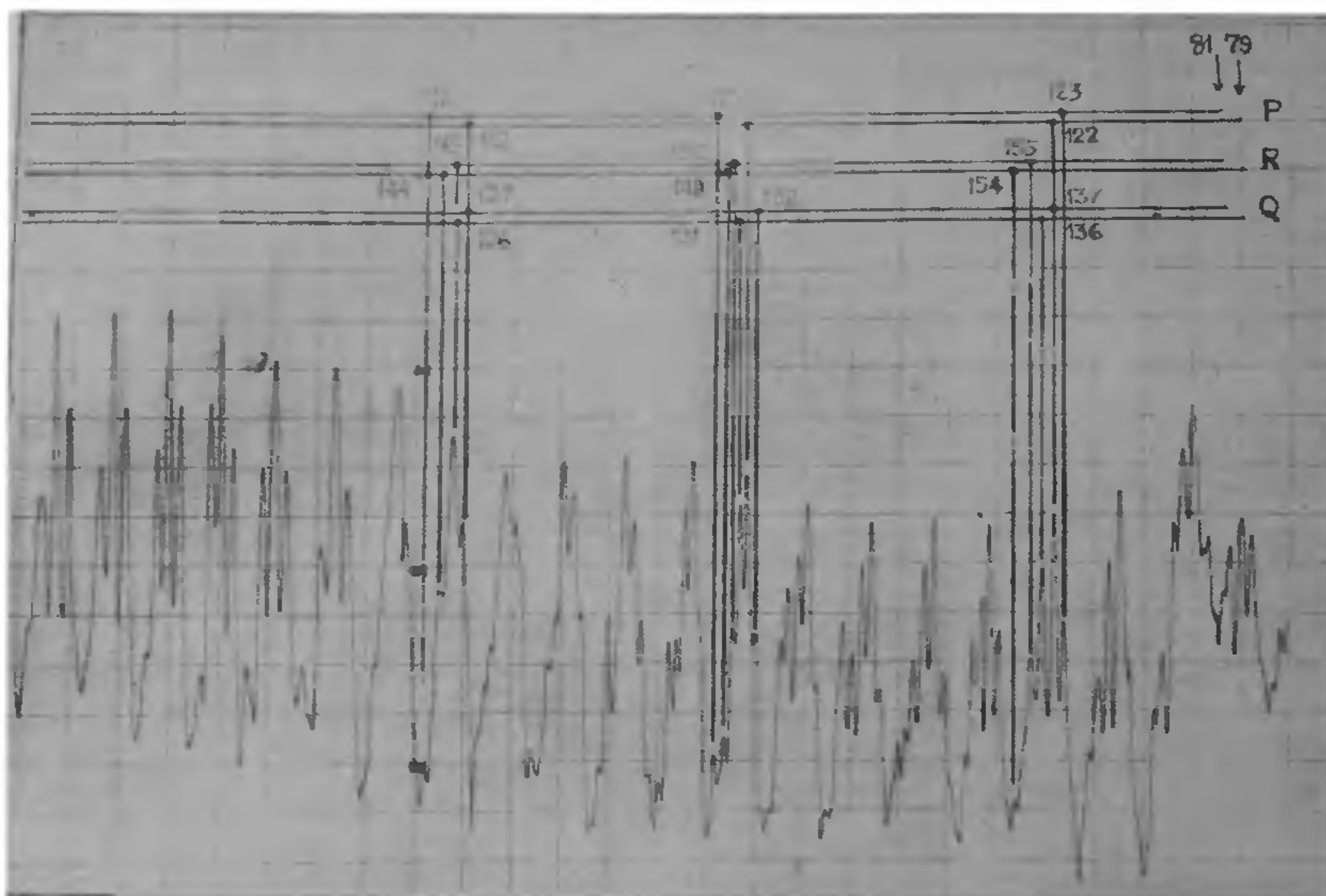


FIG. 1. Part of photometric record showing six components of CuBr 0,0 band.

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#### BOND-POLARIZABILITY DERIVATIVES OF SOME ORGANOMETALLIC COMPOUNDS

BOND and molecular polarizabilities as well as bond polarizability derivatives provide valuable information about the chemical bonds. On the basis of quantum mechanical models, several investigators developed a number of ways to compute the bond and molecular polarizabilities and bond polarizability derivatives for many ions, atoms and molecules. Among the different potential models, the delta function model of the chemical binding initiated by Frost<sup>1</sup>

and developed by Lippincott<sup>2</sup> is considered as most widely acceptable. Lippincott and Stutman<sup>3</sup> extended the semi-empirical delta-function model in the calculation of bond and molecular polarizabilities for various diatomic and polyatomic molecules and obtained good agreement between calculated and experimental values. In recent years, this model has been successfully applied by a number of workers to compute bond and molecular polarizabilities. Using delta-function model, Fontal and Spiro<sup>4</sup>, Lippincott and Nagarajan<sup>5</sup> and Long and Plane<sup>6</sup> have devised methods for calculating the bond polarizability derivatives. On account of the availability of Laser sources in Raman spectroscopy, a thorough study of the aforesaid data for different molecules is demanded. Therefore, the study has been extended for some organo-metallic compounds. The importance in undertaking such investigations is that firstly, bond polarizability derivatives obtained here would be much useful for interpretation of the results of (i) experimental refractive indices and (ii) experimental absolute Raman intensities and secondly to select the most suitable method out of the three. The molecules under present study have been taken from the references<sup>7-9</sup>.

The required data for such computations are the molecular structural data, electronegativities of the elements on Pauling scale, delta function strengths and atomic polarizabilities. The values are taken