

LETTERS TO THE EDITOR

ROTATIONAL ANALYSIS OF THE $A^2\Pi_0 - X^1\Sigma$ SYSTEM OF InI MOLECULE

The spectrum of Indium monoiodide in the region $\lambda\lambda$ 3848–4293 Å was studied at low dispersion by Wehrli¹ (1934) and Wehrli and E. Miescher² (1934). Barrett and Mandel³ (1958) studied the spectrum of InI molecule in the microwave region in absorption and obtained the rotational constants for the ground state of the molecule. The present work was undertaken to study the exact nature of the excited state involved in the emission of $A \rightarrow X$ band system of the molecule and to determine the rotational constants of the excited state. Rotational analysis of (0, 0), (0, 1) and (1, 0) bands of the $A \rightarrow X$ system has been

carried out and results obtained are reported here.

The spectrum of Indium monoiodide was excited in a high frequency discharge by keeping pure Indium metal in the presence of iodine vapours in a conventional type of a quartz discharge tube. The spectrum was photographed on Ilford N-40 plates in the seventh order of a two meter plane grating spectrograph (Carl-Zeiss) at a resolution of about 3×10^5 and a reciprocal dispersion of 0.35 Å/mm. Exposure time of about five hours for a slit-width of 15 microns was adequate to record the spectra of sufficient intensity. Measurements were made on Abbe Comparator using iron-arc standards.

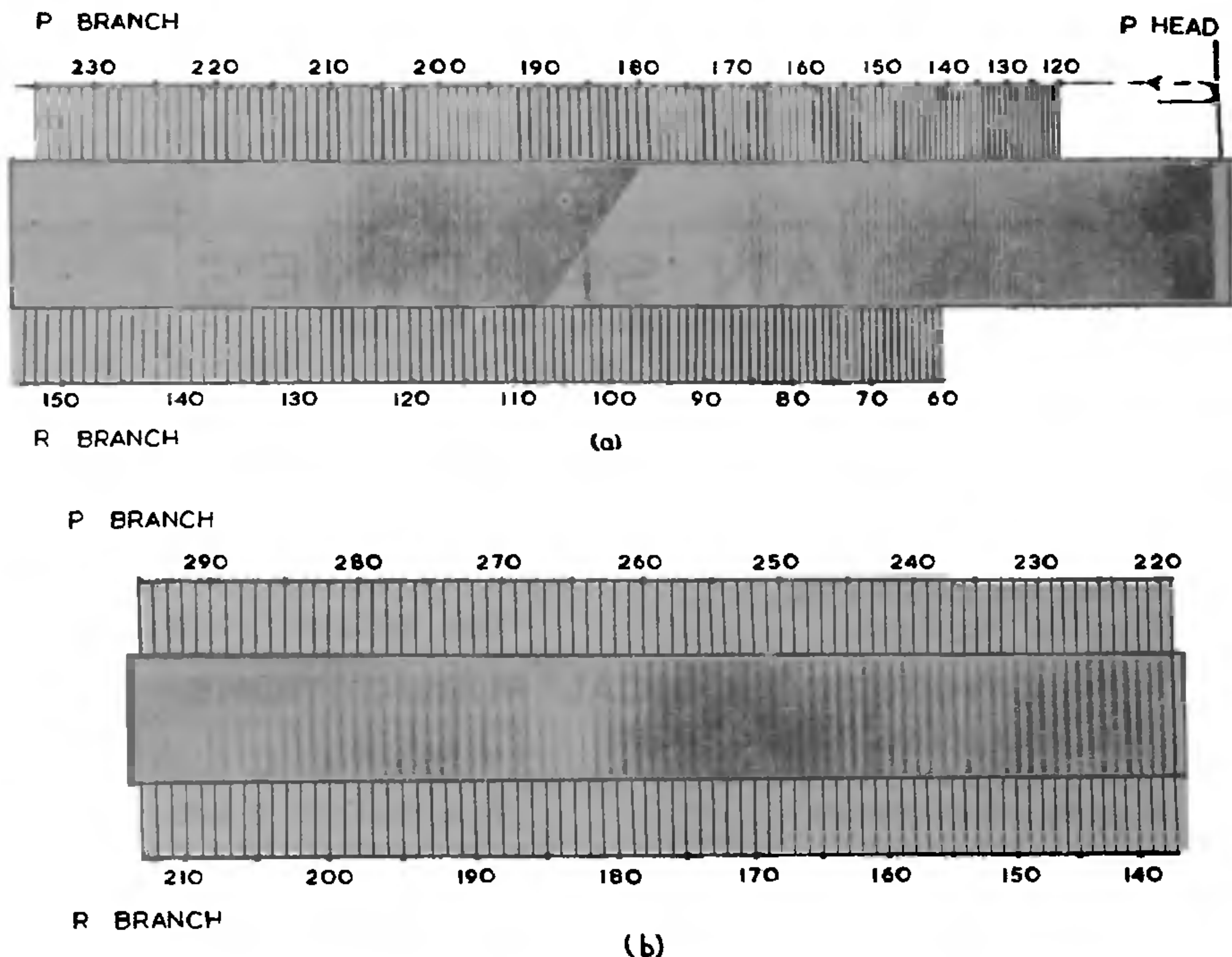


FIG. 1.

FIG. 1 (a) and (b). Rotational structure of (0, 0) band $A \rightarrow X$ system of InI molecule taken at a dispersion of 0.35 Å/mm.

In the A - X system of InI molecule, (0, 0), (0, 1) and (1, 0) bands degraded to violet were analysed. These bands reveal the presence of single P and R branches of which P is the head forming branch (Fig. 1). The rotational analysis has been carried out by standard methods (Herzberg⁴, 1955 and Younger and Winans⁵, 1960). Analysis of (0, 1) band at 4072.7 Å was carried out by comparing the combination relations for the common upper and lower state respectively of (0, 0) band at 4098.5 Å. The rotational constants for the three bands of A → X system obtained in the present work are given below:

Physics Department,
M.S. University of Baroda,
Baroda,
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A. B. DARJI,
S. P. VAIDYA**.

** Present Address: Physics Department, S.V.P. Regional Engineering College, Surat.

1. Wehrli, M., *Helv. Phys. Acta*, 1934, 7, 611,
2. — and Miescher, L., *Ibid.*, 1934, 7, 298.
3. Barrett, A. H. and Mandel, M., *Phys. Rev.*, 1958, 109, 1572.

Band	ν cm ⁻¹	B' cm ⁻¹	B'' cm ⁻¹	D' cm ⁻¹	D'' cm ⁻¹
(1, 0)	24548.535	0.0374 ₂	0.0368 ₁	0.12 × 10 ⁻⁷	0.087 × 10 ⁻⁷
(0, 0)	24393.853	0.0377 ₂	0.0368 ₂	0.087 × 10 ⁻⁷	0.075 × 10 ⁻⁷
(0, 1)	24216.705	0.0376 ₁	0.0364 ₁	0.1 × 10 ⁻⁷	0.06 × 10 ⁻⁷

Molecular constants of InI molecule obtained from the present analysis are given below along with the microwave data.

State	B _e cm ⁻¹	r _e Å	ΔG ₃ cm ⁻¹	a _e cm ⁻¹
A ³ Π ₀	0.0376 ₂	2.710 ₂	155.7 ₂	0.6 × 10 ⁻⁴
X ¹ Σ ⁺	0.0362 ₂	2.770 ₁	176.1 ₂	1.3 × 10 ⁻⁴
	*0.0368	*2.754	—	1.04 × 10 ⁻⁴

The ground state configuration of Indium moniodide molecule can be written as $zo^2 y\sigma^2 w\pi^4 x\sigma^2$ analogous to those of halides of the same group (InCl, InBr, InF) giving rise to ¹Σ⁺ ground state. The excited electron configuration is $zo^2 y\sigma^2 w\pi^4 x\sigma\pi$ which gives rise to ¹Π or ³Π state. ¹Π—¹Σ⁺ transition is attributed to C → X system which is analogous to those of similar molecules. However ¹Π state is repulsive in the case of InI molecule which gives a continuum at 3180 Å. The ³Π state belongs to Hund's case (a) due to its large coupling constant (648.9 cm⁻¹). Hence ³Π₀, ³Π₁ and ³Π₂ states are analogous to ¹Σ, ¹Π and ¹Δ states respectively. ³Π₂ → X¹Σ⁺ transition is a forbidden one whereas ³Π₁ → ¹Σ⁺ has been ascribed to the B → X system. Hence ³Π₀ → ¹Σ⁺ transition may be attributed to the A - X system of InI molecule. The appearance of single P and R branches in case of (0, 0), (0, 1) and (1, 0) bands confirms this assignment.

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*Microwave data (1958).

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COPPER COMPLEXES OF PHTHALHYDRAZIDE-5-AZO-2-NAPHTHOL

Our previous work on metal chelates of o-hydroxyazo compounds¹ led us to a tridentate ligand, phthalhydrazide-5-azo-2-naphthol, which unlike the bidentate o-hydroxyazo compounds, forms stable metal chelates with a variety of metal ions. Complexes of this tridentate ligand with Copper (II), wherein the fourth co-ordination position of the metal ion is occupied by ammonia or a heterocyclic base (pyridine or α, β or γ-picoline) have been characterised.

Experimental

Phthalhydrazide-5-azo-2-naphthol was prepared as follows: 3-Nitrophthalic anhydride was treated with hydrazine sulphate in presence of sodium acetate. The resulting 5-nitrophthalhydrazide was reduced with ammonium sulphide to yield pale yellow 5-aminophthalhydrazide (luminol) in 90% yield². This was diazotised and coupled with β-naphthol when phthalhydrazide-5-azo-2-naphthol³ resulted in 70% yield. Recrystallised from ethyl alcohol m.p. 305–307° C.

The copper complex containing ammonia was prepared as follows: Copper(II) chloride dihydrate (0.85 g; 0.005 mole), dissolved in the minimum amount of water, was added with stirring to a