A NEW BAND SYSTEM OF INDIUM IODIDE MOLECULE IN THE REGION λλ 3490-3604 Å

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ABSTRACT

The spectrum of Indium iodide molecule in the region λλ 3490–3604 Å has been excited in a high frequency discharge (10–15MHz) for the first time. It has been recorded at a reciprocal dispersion of 3·55 Å/mm on a 2 meter Carl Zeiss plane grating spectrograph. The vibrational analysis has been carried out for 19 bands and the following quantum equation satisfactorily represents Q heads of the bands.

$$\nu_Q = 28011\cdot73 + 191\cdot9\,(v' + \tfrac{1}{2}) - 0\cdot8\,(v'' + \tfrac{1}{2})^2 - 148\cdot0\,(v' + \tfrac{1}{2}) + 1\cdot3\,(v'' + \tfrac{1}{2})^2 .$$

The bands have been designated as belohging to $D \rightarrow B\,(^3\Pi)$ system.

INTRODUCTION

THE spectrum of Indium iodide molecule was studied earlier at low dispersion by M. Wehrli[1] and M. Wehrli and E. Miescher[2]. It consists of three band systems A–X, B–X and C–X. The bands in the region λλ 3948–4293Å were observed[1,2] in emission as well as in absorption and were analysed as two subsystems, *viz.*, $A^3\Pi_0 \rightleftarrows X^1\Sigma^+$ and $B^3\Pi_1 \rightleftarrows X_1\Sigma$. The salient feature of double shading of the bands was noticed for some of the bands in this region. The bands in the region λλ 2800–3200 Å were observed[2] to be weak in intensity and lying over a continuum at 3180 Å. An electronic transition of the type $C^1\Pi \leftarrow X^1\Sigma^+$ was assinged to them. In an attempt to study A–X and B–X systems of InI molecule at higher dispersion, a new band system in the region λλ 3490–3604 Å has been obtained. The paper describes the vibrational analysis of this system.

EXPERIMENTAL

The spectrum of InI molecule was excited in a high frequency discharge using 150 W oscillator working in a frequency range 10–15 MH_z. Pure indium metal was placed in a conventional type of a quartz discharge tube and a free flow of idoine vapour was allowed. The colour of the discharge was bright blue in which the bands were found to develop better. The spectrum was photographed in the 2nd order on a 2 meter plane grating spectrograph (Carl–Zeiss) at a reciprocal dispersion of 3·55 Å/mm. Exposure time of about 45 minutes was sufficient to record the spectrum of satisfactory intensity on Ilford N–30 plates. The measurements of the band heads were carried out against iron arc standard lines on an Abbe comparator. The observed band heads in the region λλ 3490Å–3604Å were at 3603·20Å (v', v'' = 0, 2), 3596·40 (1, 3), 3589·80 (2, 4), 3584·76 (0, 1), 3578.60 (1, 2), 3572·22 (2, 3), 3566·14 (0, 0), 3560·47 (1, 1), 3554·64 (2, 2), 3548·59 (3, 3), 3542·24 (1, 0), 3536·83 (2, 1), 3530·98 (3, 2), 3525·30 (4, 3), 3518·70 (2, 0), 3513·71 (3, 1), 3508·11 (4, 2), 3495·89 (3, 0) 3490·80 (4, 1). The difference between the calculated and observed (vac.) wavenumbers $\triangle\nu$ was between + 2·9 and − 3 1 cm^{-1}.

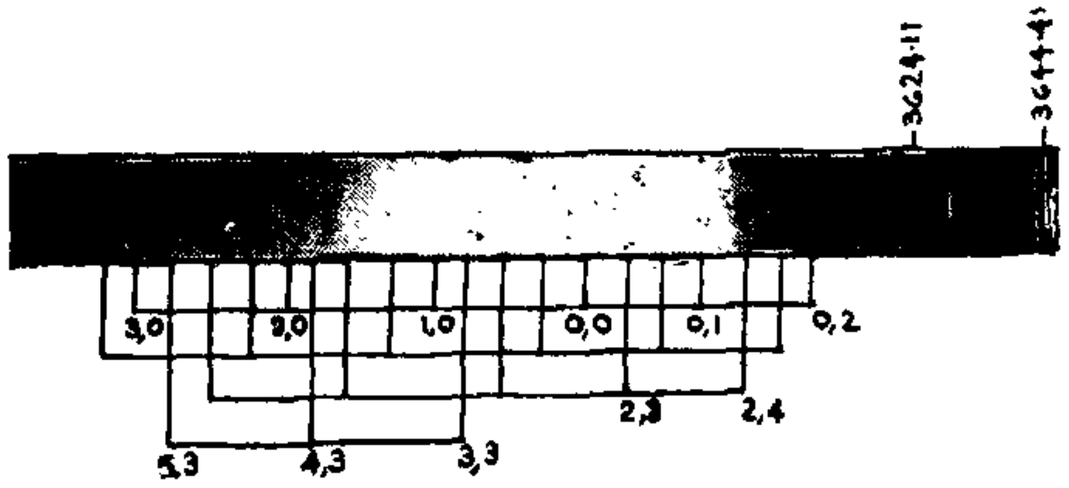

FIG. 1. Grating spectrogram of $D \rightarrow B\,(^3\Pi)$ system of InI molecule (λλ 3490–3600 Å).

DISCUSSION AND RESULTS

The spectrogram in the region λλ 3490–3604 Å reveals Q heads and very weak P heads of the violet degraded bands. The Q heads of the observed bands were fitted in the following quantum equation:

$$\nu_Q = 28011\cdot73 + 191\cdot9\,(v' + \tfrac{1}{2}) - 0\cdot8\,(v'' + \tfrac{1}{2})^2 - 148\cdot0\,(v' + \tfrac{1}{2}) + 1\cdot3\,(v'' + \tfrac{1}{2})^2 .$$

The analysis reveals the lower state frequency as 148·0 cm^{-1} which is in close agreement with the vibrational frequency of the B-state of InI molecule (*viz.*, 146·7 cm^{-1}) obtained by the earlier workers[1,2]. This suggests that the lower state involved in the new band system is not the ground state of InI molecule having the vibrational frequency[1,2] 177·1 cm^{-1}. Further the upper state (D) frequency 191·9 cm^{-1} obtained from the present analysis does not agree with any of the experimentally known frequencies for InI molecule. Therefore the system may be ascribed to an electronic transition between two excited states.

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the lower state of which may be B ($^3\Pi$). The system D → B ($^3\Pi$) being not observed in absorption also indicates that the ground state X ($^1\Sigma^+$) is not involved in the electronic transition. The ν_e value for the present system indicates that the upper state (D) must lie in the region 53062·23 cm^{-1}. The nature of the upper state can be studied by rotational analysis only.

The newly observed system D→B ($^3\Pi$) of InI molecule is an addition to similar systems observed in case of monohalides of the same group reported by previous workers. In case of TlI molecule system E → $A^3\Pi_0$ was observed by A. Terenin[3] with maximum at 3475Å with the position of E state at $\nu_e = 54000\,cm^{-1}$. Analogous system D → $A^3\Pi_0$ was reported for TlBr molecule by H. G. Howell[4] with upper state D at $\nu_e = 54500\,cm^{-1}$. For TlCl molecule system D → $A^3\Pi_0$ in the region λλ 4180–4283 Å has been reported by P. T. Rao[5].

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SYNTHETIC AND STRUCTURAL STUDIES ON SOME MIXED LIGAND COMPLEXES OF MANGANESE(II)

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ABSTRACT

The present work deals with the study of mixed ligand complexes of manganese oxalate with nine ligands. The complexes are obtained by the action of manganese oxalate on the ligand in alcoholic solutions and have the general formulae $MnC_2O_4L\ H_2O$. Physicochemical properties such as magnetic susceptibility, electronic and infrared spectra, thermogravimetric analysis, etc., of these complexes have been investigated with a view to determine their structure. These complexes are polymeric in nature containing bidentate bridging oxalate groups and have octahedral symmetry.

INTRODUCTION

MIXED ligand complexes of divalent manganese containing hetero donor atoms have been studied by earlier workers,[1–3] in which primary ligands were halogens or pseudohalogens. The use of carboxylate as a primary ligand for the first row of the transition elements has also been described[4–6]. Though the thermal properties of 3*d* metals (including manganese^{2+}) oxalate mixed ligand complexes with hydrazine[7] have been reported, exhaustive work on manganese oxalate complexes is lacking. Further, it would be interesting to study the stereochemical and structural behaviour of such mixed ligand complexes. Thus the mixed complexes of manganese oxalate with amides and heterocyclic bases are described in this communication.

MATERIALS AND METHODS

The reagents used were AR in grade. The compounds were synthesised by suspending manganese oxalate ($MnC_2O_4 . 3H_2O$) in ethanol to which an excess of the ligand was added. The mixture was stirred and refluxed on a hot plate. The reaction required four to six days for completion and the compounds thus obtained were washed with alcohol and ether and dried in vacuum. In a few cases (DMF and DMSO), ethanol was replaced by methylcyanide as these medium of reaction. These compounds are almost insoluble in organic solvents.

Manganese and sulphur were estimated by the conventional methods[8] and nitrogen by micro analysis. Magnetic susceptibilities were measured at 30° C by Gouy's method using Hg [Co(SCN)$_4$] as the standard. I.R. spectra were taken, in nujol mulls; the electronic spectra were taken in solid phase with a Cary–14 model spectrophotometer.

RESULTS AND DISCUSSION

The analytical results and magnetic moments, given in Table I, show 1 : 1 stoichiometry and the formula can be written as $MnC_2O_4 . L . H_2O$. The magnetic moments of the complexes fall between 5·86–6·01 B.M. and indicate that these are spin-free octahedral complexes of manganese(II) having five unpaired electrons. However, in spite of repeated efforts,