

FLAME EMISSION SPECTRUM OF SnO MOLECULE IN THE VISIBLE REGION

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(Plate 2 and 3)

ABSTRACT. The emission from the flame containing tin halides or metallic tin has been investigated in the visible region. One hundred and thirteen bands have been photographed in the region $\lambda\lambda$ 6480-3500 and have been attributed to the diatomic oxide SnO. Most of these bands have been arranged into three systems—A, B and C, whose lower level has been identified to be the ground state. It has been found that Mahanti's systems B and C do not exist separately but are in fact parts of the present system C \rightarrow X. Vibrational schemes have been drawn according to the following expressions:

$$A \rightarrow X, \nu = 19073.8 + 453.0(v' + \frac{1}{2}) - 4.00(v' + \frac{1}{2})^2 - 822.4(v'' + \frac{1}{2}) + 3.73(v'' + \frac{1}{2})^2.$$

$$B \rightarrow X, \nu = 24312.8 + 595.0(v' + \frac{1}{2}) - 3.90(v' + \frac{1}{2})^2 - 0.25(v' + \frac{1}{2})^3 - 822.4(v'' + \frac{1}{2}) + 3.73(v'' + \frac{1}{2})^2.$$

$$C \rightarrow X, \nu = 25448.5 + 561.0(v' + \frac{1}{2}) - 1.20(v' + \frac{1}{2})^2 - 0.16(v' + \frac{1}{2})^3 - 822.4(v'' + \frac{1}{2}) + 3.73(v'' + \frac{1}{2})^2.$$

The $v'' = 2$ level has been found to be perturbed in both the systems B and C. Some bands have also been added to the already known system D.

INTRODUCTION

While studying the emission spectrum of the oxy-coal-gas flame containing tin sulphide or tin chloride, Eder and Valenta (1924) for the first time reported the presence of all marked red degraded bands which extended through the blue and the near ultraviolet regions. Later on, these bands are also recorded in the arc spectrum of metallic tin on carbon poles by Mahanti (1931), who attributed them to the diatomic molecule SnO. Mahanti arranged these bands in three systems and termed them as A, B and C. The system A occurring in the region $\lambda\lambda$ 4490-3200 was the most intense one and all the principal bands fitted into it. System B and C were, however, weak and fragmentary. Connelly (1933) photographed the emission and absorption spectrum of SnO in $\lambda\lambda$ 4660-3070 region, and furnished an extended and revised vibrational scheme for Mahanti's A system which he designated as D \rightleftharpoons X. Connelly, however, questioned the separate existence of the B and C systems while, Pearse and Gaydon (1941) have referred their vibrational analyses as uncertain. The ultraviolet absorption was studied in emission by Loomis and Watson (1934); in absorption by Sharma (1944); and an extensive study of this region was also made by Eisler and Barrow (1949). Barrow and Rowlinson (1954) studied the absorption in the Schumann region. Jevons (1938) removed certain anomalies in the values of the anharmonic coefficients by proposing

a new expression for Connolly's D system. The rotational analysis of the (1, 0), (0,0) and (0, 1) bands of the D system was performed by Lagerquist, Nilsson and Wigartz (1959) and according to them the system corresponds to $^1\pi-^1\Sigma$ transition. It is evident from the foregoing that while the spectroscopic constants for the D system are well established, and fairly reliable information is available for the ultraviolet and Schumann region, no satisfactory data for the visible region, on the longer wavelength side of $\lambda 4660$ region, exist. Whatever little information we possess is insufficient to draw any definite conclusions. On the other hand several well marked band systems, stretching almost through the entire visible region are known to exist for the PbO molecule; Mecke (1929); Bloomenthal (1930); Shawhan and Morgan (1935); Howell (1936); and Barrow, Deutsch and Travis (1961). Similar band systems for SnO molecule can therefore be reasonably expected. The aim of the present communication is to report the fresh results obtained by the authors in the $\lambda 6480-3200$ region of the flame spectrum of the SnO molecule.

EXPERIMENTAL

The flame apparatus, described in figure 1 was used as the source of emission. A solution of pure stannic chloride, sucked through *T*, was fed into the burner

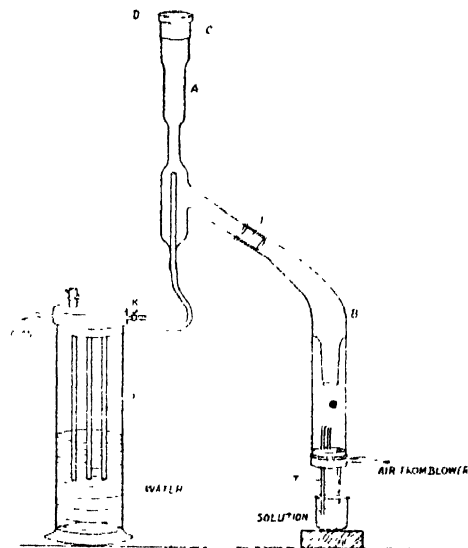


Fig. 1.

A, in the form of a fine spray obtained by blowing air under pressure. The pressure of the gas was controlled with the mechanism S and it was let into the burner through the cock K. The mixture gave a blue bright flame with a faint yellow centre which appeared occasionally. The intensity of the light source could be increased with the concentration of the solution. The spectrum of the flame obtained in this manner was photographed on Hilger E612 glass and Hilger E492 quartz spectrographs. Investigations were also made by feeding stannous

chloride, stannic bromide, stannic oxide and tin metal powder. Exactly similar bands lying in the region $\lambda\lambda 6480-3200$ were recorded in each case. The brightest emission was obtained either by putting the tin metal powder over the porcelain disc *D*, fitted at the top of the apparatus, or by feeding the stannous bromide solution. However, the intensity of the flame emission was found to be markedly different in different regions. While with the glass spectrograph, bands in the different regions could be photographed in two to four hours, prolonged exposures were needed to record them with the quartz spectrograph. Spectrograms were obtained by using Ilford R40 rapid process panchromatic and N40 process plates. Copper, iron d.c. arcs and neon discharge tube were used as source of comparison standards in different regions.

R E S U L T S

The flame emission described above and attributed to SnO has yielded a large number of bands in the region $\lambda\lambda 6480-3200$ stretching practically without a break. Out of these bands, 86 have been recorded for the first time while the rest include the prominent SnO bands reported by Connelly and others in this region. Almost all of the new bands have been arranged into three systems *A*, *B* and *C*, different from those of Mahanti, seven new bands have been added to the system *D* and the remaining few are left unclassified.

System A ($\lambda\lambda 6480-5250$)

This system consists of 19 entirely new bands. Most of these are sharp and only a few are somewhat diffuse. The system can be satisfactorily represented by the following expression :

$$\nu = 19073.8 + 453.0(v' + \frac{1}{2}) - 4.00(v' + \frac{1}{2})^2 - 822.4(v'' + \frac{1}{2}) + 3.73(v'' + \frac{1}{2})^2 \quad \dots (1)$$

The wavelengths of bands, their wavenumber equivalents in vacuum, together with the visual estimates of intensity on a scale of 10, and vibrational assignments for the system have been incorporated in Table I. It is to be noted that the intensity measurements are on a scale of 10 taking all the three systems together. Diffuse bands with uncertain measurements are marked as *d*. The bands (1,3) and (3,4) are presumably masked by the broadening of the yellow doublet of sodium occurring as an impurity. Figure 2, (plate 2A) reproduces the spectrogram.

System B ($\lambda\lambda 5840-3930$)

Thirty three bands have been incorporated in this system. They include twenty eight entirely new bands, while 5 unclassified bands reported by Connelly have also been accounted for. The proposed system is entirely different from the one suggested by Mahanti. Equation (2) explains the vibrational analysis within limits of experimental error :

$$\nu = 24312.8 + 595.0(v' + \frac{1}{2}) - 3.90(v' + \frac{1}{2})^2 - 0.25(v' + \frac{1}{2})^3 - 822.4(v'' + \frac{1}{2}) + 3.73(v'' + \frac{1}{2})^2 \quad \dots (2)$$

It is to be noted that the system in general is weak and the level $v' = 2$ is found to be perturbed by about 9 cm^{-1} . Like Table I, Table II explains the data for $B \rightarrow X$ system. Spectrogram is reproduced in figures 3 and 4, (plate 2).

System C ($\lambda\lambda 5010-3700$)

The proposed system C, consisting of 41 bands, is well developed and quite intense. Besides eighteen new bands, it includes 15 prominent bands of Mahanti's B and C systems and 8 of Connelly's unclassified bands as well. Compared with systems A and B the sequences are better marked in this case. The level $v' = 2$ is found to be perturbed by about 12 cm^{-1} .

Within the limits of experimental error the following expression explains the vibrational scheme for system C^2 :

$$\nu = 25448.5 + 561.0(v' + \frac{1}{2}) - 1.20(v' + \frac{1}{2})^2 + 0.16(v' + \frac{1}{2})^3 - 822.4(v'' + \frac{1}{2}) + 3.73(v'' + \frac{1}{2})^2 \quad \dots (3)$$

Figures 5 and 6 in plate 3 display the bands of the system, and Table II describes the relevant data about it. Bands marked with (+) were reported by Connelly as unclassified.

Table IV indicates the new bands added to the system D , while the bands left unclassified have been entered in table V.

TABLE I

λ_{atr} in A	Int.	ν_{vac} Obs.	in cm^{-1} calc.	Classification
6479.8	4	15428	15422	(3,6)
6456.3	1	15485	15486	(5,7)
6378.6	4	15673	15674	(0,4)
6335.8	3	15779	15771	(2,5) d
6309.8	1	15844	15843	(4,6)
6202.2	3	16119	16119	(1,4)
6172.6	4	16196	16200	(3,5)
6069.9	6	16470	16467	(0,3)
6039.5	2	16553	16556	(2,4)
6015.2	1	16620	16621	(4,5)
5789.6	8	17268	17267	(0,2)
5643.9	5	17713	17712	(1,2)
5612.5	0	17812	17819	(5,4) d
5532.4	3	18071	18074	(0,1)
5399.8	2	18514	18519	(1,1)
5371.5	2	18612	18612	(5,3)
5292.0	1	18891	18889	(0,0)
5276.5	0	18947	18956	(2,1) d
5256.5	1	19019	19017	(6,3)

d-Diffuse, measurement uncertain.

TABLE II

λ_{atr} in A	Int.	ν_{vac}		Classification
		Obs.	in cm^{-1} Calc.	
5838.1	1	27124	17133	(0,9) d
5590.0	3	17884	17884	(0,8)
5409.5	1	18481	18475	(1,8)
5360.1	3	18651	18651	(0,7)
5302.0	5	18856	18861	(3,9)
5250.4	0	19041	19051	(2,8) p
5196.8	0	19237	19238	(1,7)
5148.0	6	19420	19421	(0,6)
5096.3	3	19617	19616	(3,8)
5047.9	2	19805	19814	(2,7) p
4949.7	3	20198	20199	(0,5)
4904.7	1	20382	20379	(3,7)
4859.3	0	20573	20584	(2,6) p
4810.9	2	20780	20785	(1,5)
4763.9	5	20985	20984	(0,4)
4727.5	1	21147	21149	(3,6)
4681.0	1	21352	21362	(2,5) p,d
4634.6	3	21571	21570	(1,4) +
4590.7	5	21777	21777	(0,3) +
4557.4	0	21936	21926	(3,5) d
4470.5	4	22363	22363	(1,3)
4428.3	4	22576	22577	(0,2) +
4360.2	1	22928	22939	(2,3) p
4316.0	1	23163	23163	(1,2)
4297.3	0	23264	23263	(4,4)
4275.8	0	23381	23384	(0,1) AM
4253.4	2	23504	23504	(3,3)
4212.3	2	23733	23739	(2,2) p
4112.9	3	24307	24304	(2,2) BM +
4074.3	0	24537	24547	(2,1) p
4022.0	1	24856	24856	(4,2)
3942.9	0	25355	25362	(2,0) p
3936.5	1	25396	25393	(5,2) CM +

d —Diffuse, measurement uncertain.

p —Perturbation.

+ —Observed by Connelly also.

AM, BM, CM—Bands of Mahanti's A, B and C systems.

TABLE III

λ_{air} in Å	Int.	ν_{vac} Obs.	in cm^{-1} Calc.	Classification
5009.2	1	19958	19959	(7,12)
4923.6	0	20305	20300	(5,10) d
4879.8	1	20487	20487	(4,9)
4833.5	2	20679	20683	(3, 8)
4783.1	1	20901	20888	(2,7) p
4749.7	0	21048	21048	(5,9)
4738.0	0	21100	21100	(1, 6)
4706.4	3	21242	21242	(4, 8)
4662.0	3	21444	21446	(3, 7)+
4623.6	0	21622	21612	(6, 9) d
4612.1	2	21676	21658	(2, 6) p, +
4569.5	2	21878	21878	(1, 5) C
4543.1	2	22005	22005	(4, 7)+
4522.6	2	22105	22104	(0, 4)+
4499.1	3	22220	22216	(3, 6)+
4452.5	7	22453	22436	(2, 5) p, CM
4411.6	7	22661	22663	(1, 4) C
4389.1	2	22777	22775	(4, 6) +
4366.1	4	22897	22896	(0, 3) BM
4347.9	1	22993	22994	(3, 5)
4302.2	6	23237	23221	(2, 4) p, CM
4262.3	9	23455	23455	(1, 3) C
4218.8	8	23697	23696	(0, 2) BM
4160.8	2	24027	24013	(2, 3) p, CM
4145.9	1	24113	24114	(5, 5)
4121.9	7	24254	24255	(1, 2) C
4107.7	2	24338	24338	(4, 4) d
4079.9	10	25404	24504	(0, 1) BM
4068.5	2	24572	24572	(3, 3)+
4026.9	3	24826	24813	(2, 2) p, CM
4014.3	1	24904	24899	(5, 4) d, BM

TABLE III (contd.)

λ_{atr} in Å	Int.	ν_{vac} Obs.	in cm^{-1} Calc.	Classification
3978.8	6	25126	25131	(4, 3) BM
3948.5	8	25319	25319	(0, 0) BM
3899.3	6	25638	25621	(2, 1) p
3863.5	9	25876	25878	(1, 0)
3855.4	2	25930	25931	(4, 2) d, BM
3818.8	5	26179	26179	(3, 1)
3779.9	4	26448	26436	(2, 0) p, +
3773.1	1	26496	26492	(5, 2)
3738.9	1	26738	26738	(4, 1)
3703.2	2	26996	26994	(3, 0)

d — Diffuse.

p — Perturbation.

+ — Observed by Connelly also.

BM, CM—Bands of Mahanti's B and C systems.

TABLE IV

λ_{atr} in Å	Int.	ν_{vac} Obs.	in cm^{-1} Calc.	Classification
4048.3	1	24695	24696	(4, 9)
3879.6	2	25769	25768	(5, 8)
3860.0	1	25994	25993	(6, 9)
3704.5	2	26986	26984	(4, 6)
3562.9	0	28059	28057	(6, 6)
3531.9	2	28305	28303	(5, 5)
3501.8	0	28549	28547	(4, 4)

TABLE V

λ_{atr} in A	Int.	ν_{atr} in A	Int.
5954.0	2	4463.1	1
5772.3	2	4139.2	0
5242.3	1	4056.4	1
5217.7	2	4039.6	0
5176.3	3	4005.3	1
4837.9	0	3762.3	0
4693.2	1		

DISCUSSION

The earlier work on the absorption spectrum of SnO molecule has established its ground state vibrational frequency to be 822.4 cm^{-1} , Herzberg (1950). A glance on the expressions (1), (2) and (3), pertaining to the systems A, B and C, immediately reveals that they involve a common lower electronic state with a vibrational frequency of 822.4 cm^{-1} . The new bands obtained in emission from the flame containing tin or tin compounds and arranged in the three systems referred to above, have therefore rightly been assigned to the diatomic oxide SnO.

It is quite evident from the reproductions of the spectrograms that the main feature of the visible spectrum of SnO is the presence of mutually overlapping systems. While systems A and B are weak, C appears to be fairly strong. The systems B and C exhibit perturbations and it is to be noted that the $v' = 2$ level is perturbed in both of them. The upper state vibrational frequencies of these systems are 453.0 cm^{-1} for A, 595.0 cm^{-1} for B and 561.0 cm^{-1} for C, respectively. Their comparison with the ground state vibrational frequency indicates that the Condon parabola for the system A is expected to be more wide than those for B and C and the intensity distribution of the system A demonstrates that it is indeed so. It is of interest to compare the results obtained by the authors with those of Mahanti (1931) and Connelly (1933). Mahanti proposed the formulae for the band heads, which he arranged in three different systems :

System A ($\lambda\lambda 4490-3200$)

$$\nu = 29630.5 + 586.0(v' + \frac{1}{2}) - 6.0(v' + \frac{1}{2})^2 - 824.0(v'' + \frac{1}{2}) + 4.0(v'' + \frac{1}{2})^2 \quad \dots (4)$$

System B ($\lambda\lambda 4525-3850$)

$$\nu = 25418.6 + 637.0(v' + \frac{1}{2}) - 8.0(v' + \frac{1}{2})^2 - 824.0(v'' + \frac{1}{2}) + 4.0(v'' + \frac{1}{2})^2 \quad \dots (5)$$

System C ($\lambda\lambda 4570-3930$)

$$\nu = 24370.4 + 582.0(v' + \frac{1}{2}) - 4.0(v' + \frac{1}{2})^2 - 813.5(v'' + \frac{1}{2}) + 5.5(v'' + \frac{1}{2})^2 \quad \dots (6)$$

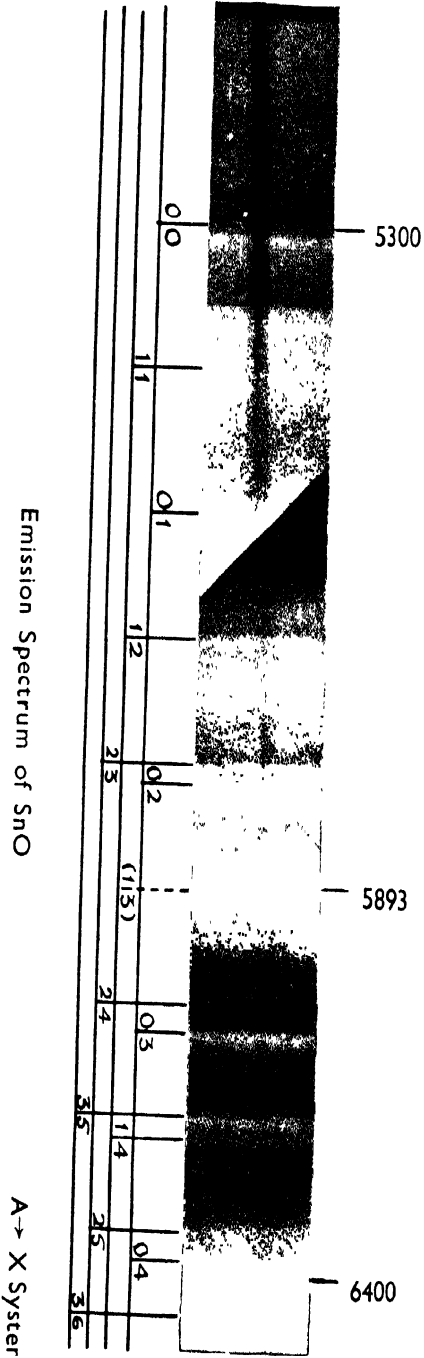


Fig 2

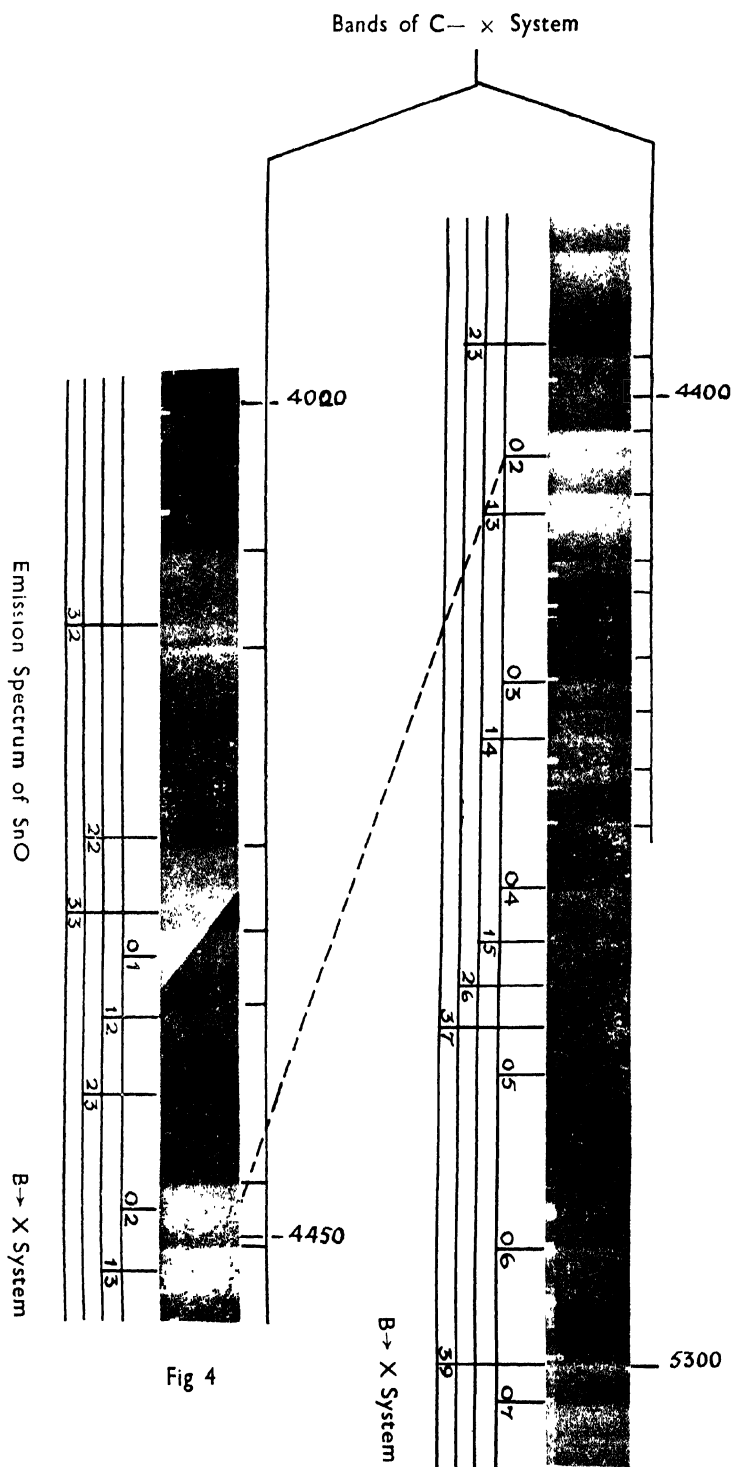
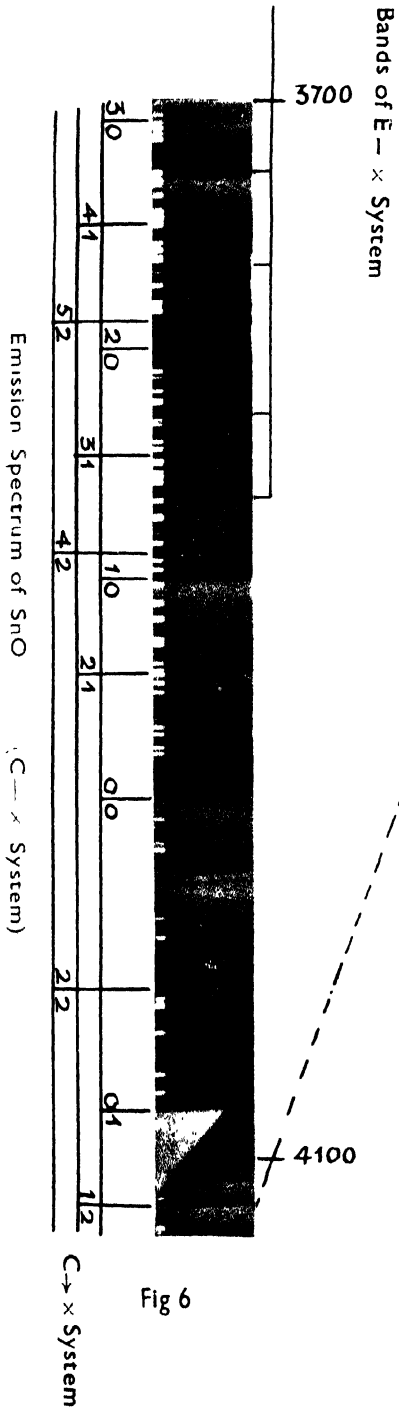
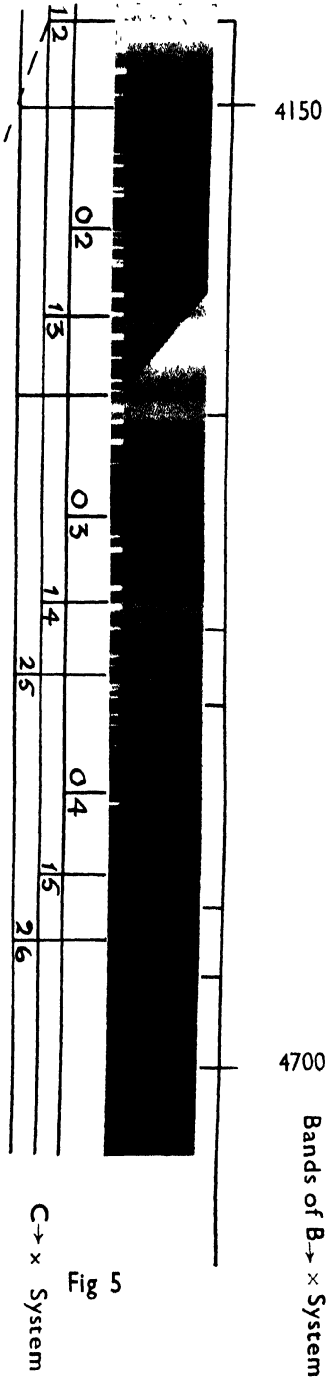


Fig 4

Fig 3



It is to be noted that Mahanti's designation of various systems is not in conformity with the modern spectroscopic usage. The transitions corresponding to the above systems are shown at (a) in figure 7.

It is evident from Mahanti's classification that the systems A and B arise from the common lower level described by him as 'a', the lower level of the system C was called as X and none of the electronic states of this system were in common with those of A and B. As regards the ground state, Mahanti, on the basis of certain thermochemical considerations, decided in favour of X, a situation however not substantiated by any reliable spectroscopic evidence. Obviously the confirmation of this interpretation rested heavily on the absorption studies. Should the above genesis of the C system be correct, needless to say that it would be most natural to expect this transition in absorption.

Connelly, however succeeded in producing the SnO spectrum in absorption as well as in emission. Examination of the absorption spectrum obtained by Connelly revealed that only the bands of Mahanti's system A could be traced and those belonging to B and C systems of Mahanti were conspicuous by their absence. As already remarked, according to Mahanti's scheme of transitions, his system C must appear in absorption. Evidently, this fact is not observed by Connelly. It should further be noted that out of Mahanti's A and B systems, both of which involve the common lower state, if the former appears in absorption the latter should also appear. This situation is also not obtained by Connelly. It is therefore obvious that Mahanti's interpretation of facts is not in conformity with the absorption studies due to Connelly. It is to be noted that although Connelly observed a much larger number of bands than Mahanti did, but he arranged most of them into only one system which was termed as D in order to distinguish it from Mahanti's nomenclature. The system is well represented by the following expression due to Jevons (1938) :

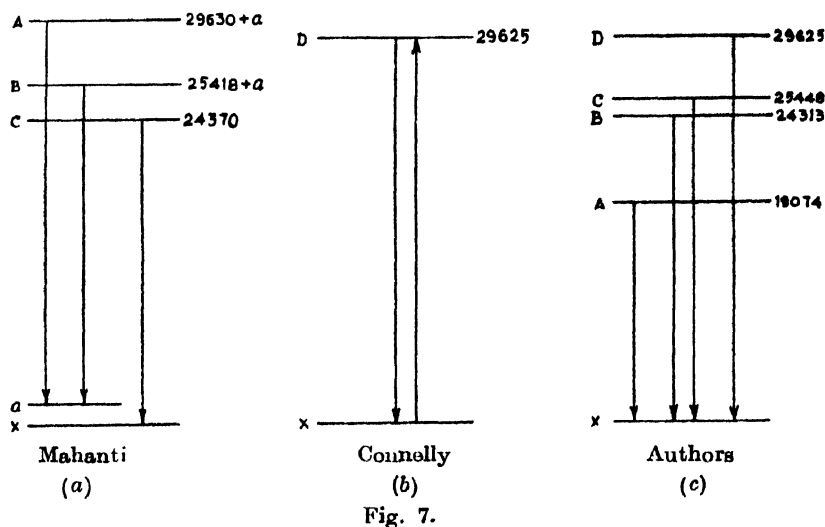
System D ($\lambda\lambda 4490-3070$)

$$\nu = 29624.9 + 582.6(v' + \frac{1}{2}) - 3.08(v' + \frac{1}{2})^2 - 0.135(v' + \frac{1}{2})^3 - 822.4(v'' + \frac{1}{2}) + 3.73(v'' + \frac{1}{2})^2 \quad \dots \quad (8)$$

Besides explaining a considerable number of new bands, the above expression also provides a satisfactory account of Mahanti's A system. The scheme of transitions suggested by Connelly is depicted as (b) in Fig. 7.

As regards Mahanti's B and C systems, although Connelly confirmed the presence of their principal bands in emission, yet he was doubtful about their existence as parts of two separate systems, and he also questioned their associations with the ground state of the molecule. To the best of our information these points have remained unresolved uptill now. However, due to the additional information furnished by the present investigations a better picture of the situation can now be presented.

The levels obtained by the authors have been displayed in part (c) of figure 7 where four transitions all terminating in the ground state have been observed.



The state designated as D is the same as observed by Connelly and in addition three more levels C, B and A have been discovered. It is to be remembered that Mahanti's level A corresponds to the present level D.

From Table III it can be observed that almost all the prominent progressions belonging to Mahanti's systems B and C have been satisfactorily incorporated in the present system C. Thus a single transition $C \rightarrow X$ accounts for both these systems and in fact they do not exist separately. Evidently, this is what Connelly had also suggested.

To complete the outline of the visible spectrum of SnO it will not be out of place to mention that Eisler and Barrow (1949) have referred to the unpublished work of Mrs. Richards who has observed the stronger bands of Mahanti's B and C systems in absorption. This significant observation confirms that the lower state of the present transition $C \rightarrow X$ has rightly been identified to be the ground state of the molecule and Connelly's apprehensions on this score were ill-founded. Thus all the major discrepancies in the interpretation of the visible spectrum of SnO appear to have been removed and the present work can be considered to offer a more rational explanation of experimental facts.

The unclassified bands in general are weak and do not form any progressions with consistent differences. Although their interpretation at the moment is not possible, chances for another system of SnO in the visible region can, however, not be ruled out.

A comparison of the information regarding the states of SnO molecule with those of the other heavy diatomic molecules, arising out of the combination of

IVb and VIB subgroups of the periodic table, will form the part of a separate communication.

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