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THE VISIBLE ABSORPTION SPECTRUM OF THE SnS MOLECULE

R. YAMDAGNI AND M. M. JOSHI

DEPARTMENT OF PHYSICS, UNIVERSITY OF ALLAHABAD, ALLAHABAD, INDIA

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Plate IV

ABSTRACT. The visible spectrum of the diatomic tin sulphide molecule was known to consist of only one system in the region λ λ 4700-4180. However, on the basis of results obtained by the rotational analysis, Douglas, Howe and Morton (1961) have concluded that more than one excited electronic state should be present in this region. The authors therefore, reinvestigated the visible absorption spectrum of SnS and in fact two systems B←X and C←X, lying in the region λ λ 5050-4000, have been recognised. The vibrational analyses seem to be in conformity with the rotational work Following expressions explain the proposed classifications·

$$V\leftarrow X, \nu = 22756.6+325.0(v'+\tfrac{1}{2})-2.50(v'+\tfrac{1}{2})^2-487.7(v''+\tfrac{1}{2})+1.34(v''+\tfrac{1}{2})^2.$$

$$C\leftarrow X, \nu = 23613.7+324.0(v'+\tfrac{1}{2})-1.00(v'+\tfrac{1}{2})^2-487.7(v''+\tfrac{1}{2})+1.34(v''+\tfrac{1}{2})^2$$

Perturbations have been observed in $v'=2$ level of the B system and in $v'=1$ level of the C system. Fragments of a third system D have also been recorded.

INTRODUCTION

The spectrum of the diatomic tin sulphide molecule was for the first time described by Butkow and Tachassowenny (1934). They proposed two system viz. λλ3799-3277 and λλ3764-2580. Rochester (1935) extended these two systems considerably and also recognised the new visible system *A* lying in the region λλ4700-4180. Shawan (1935) working simultaneously but independently proposed a different analysis for the above system. The rotational analysis of the (0, 0) and the (1, 0) bands of this system was also performed by Shawhan (1936). While Sharma (1945) studied the far ultraviolet system, Barrow and coworkers (1953) investigated the Schumann region also. Hari Mohan (1957) has reported the existence of a new but weak system in the region λλ26900-2490. Recently Douglas, Howe and Morton (1961) have studied the rotational structure of some prominent bands observed in the visible region. These workers have found that out of the four bands, analysed in the region, one did not contain the *Q* branch. This evidently led them to conclude that certainly more than one excited electonic states are involved in these transitions and the various vibrational analyses proposed by the low resolution work were incorrect. However they did not suggest any fresh vibrational analysis for this region. It was with an object to obtain more information regarding the visible systems and the electronic states involved, that the present investigation was undertaken.

EXPERIMENTAL

The vacuum graphite furnace, described earlier by H. Mohan and K. Majumdar (1961), was used for obtaining the absorption spectrum. A mixture of pure tin and sulphur was placed in a 15 cm. long graphite tube of 1 cm. internal diameter. Temperatures of about 1400°C were best suited for the strong development of bands. In order to avoid rapid diffusion of the vapours, from the experimental graphite tube, nitrogen gas was filled inside the furnace chamber at a pressure of 55 cm of mercury. A 500 watt ribbon filament lamp served as the source of continuum. Jilger E492 large quartz spectrograph was used for photographing the spectrum on Ilford R40 rapid process panchromatic plates. Exposures ranging from two to ten minutes were found enough to record the bands.

RESULTS

Wavelengths of the band heads along with the visual estimates of their intensities, wavenumbers and the vibrational assignments are given in tables I and II. Table III includes the bands forming two progression (a) and (b) with differences of ground state vibrational frequency. Unassigned bands have been listed in Table IV. Equations for representing the band heads are :

B System, (λλ5050–4270)

$$\nu = 22756.6+325.0(v'+\tfrac{1}{2})-2.50(v'+\tfrac{1}{2})^2-487.7(v''+\tfrac{1}{2})+1.34(v''+\tfrac{1}{2})^2 \quad \ldots \quad (1)$$

C System, (λλ4660–4000)

$$\nu = 23613.7+324.0(v'+\tfrac{1}{2})-1.00(v'+\tfrac{1}{2})^2-487.7(v''+\tfrac{1}{2})+1.34(v''+\tfrac{1}{2})^2 \quad \ldots \quad (2)$$

The $v' = 2$ level of the B system was found to be perturbed by about 50 cm^{-1}. Perturbations of the order of 40 cm^{-1} were also observed in the $v' = 1$ level of the C system. The spectrum has reproduced in figure 1,

TABLE I

λ air in A	Int.	ν vac	in cm^{-1}	Analysis	
		Obs.	Calc.	Authors	Rochester
5048 0	0	19804	19805	(0,6)	
4969.5	1	20117	20125	(1,6)	×
4928.3	2	20285	20277	(0,5)	
4879.3	0	20489	20440	(2,6) p	×
4855.0	3	20592	20597	(1,5)	×
4816.8	1	20755	20751	(0,4)	
4769.4	1	20961	20912	(2,5) p	×

TABLE I (*contd.*)

λ air in A	Int	ν van Obs.	in cm^{-1} Calc.	Analysis Authors	Rochester
4745.0	3	21069	21071	(1,4)	×
4708.9	0	21230	21228	(0,3)	(0,4)
4663.1	0	21439	21386	(2,4) p	×
4639.6	1	21548	21548	(1,3)	×
4605.5	3	21707	21708	(0,2)	(0,3)
4537.8	2	22031	22028	(1,2)	×
4505.3	6	22190	22190	(0,1)	(0,2)
4408.9	4	22675	22675	(0,0)*	(0,1)
4369.0	1	22882	22825	(2,1)p	
4320.3	0	23140	23135	(3,1)	
4279.7	1	23360	23310	(2,0)p	

p — Perturbed.
* — Rotational analysis performed by Douglas and Coworkers and classified as (*y, o*).
× — Bands also observed by Rochester and fitted in progressions.

TABLE II

λ air in A	Int.	ν vac Obs.	in cm^{-1} Calc.	Analysis Authors	Rohhester
4650.9	1	21495	21456	(1,5)p	(1,5)
4549.4	1	21975	21930	(1,4)p	(1,4)
4526.5	3	22086	22085	(0,3)	(0,3)
4494.0	0	22246	22250	(2,4)	
4453.7	6	22447	22407	(1,3)p	(1,3)
4430.5	7	22565	22565	(0,2)	(0,2)
4398.9	2	22727	22727	(2,3)U	
4360.5	2	22927	22887	(1,2)p	(1,2)
4337.8	9	23047	23047	(0,1)*	(0,1)
4306.3	1	23215	23207	(2,2)	
4248.6	10	23531	23532	(0,0)*	(0,0)
4221.3	2	23683	23689	(2,1)U	
4183.8	10	23895	23854	(1,0)p*	(1,0)
4165.6	2	24000	24007	(3,1)U	
4135.4	4	24175	24174	(2,0)U	
4114.8	1	24296	24297	(7,3)U	
4109.3	3	24328	24323	(4,1)U	
4082.6	4	24487	24492	(3,0)U	
4063.1	1	24605	24605	(8,3)U	
4057.8	3	24637	24637	(5,1)	
4035.2	0	24775	24777	(7,2)	
4029.9	2	24808	24808	(4,0)U	
4018.2	1	24913	24911	(9,3)	

p — Perturbed
* — Rotational analysis performed by Douglas and coworkers and classified as (x, 1), (x, 0) and (w, 0).
U — Bands left unclassified by Rochester.

TABLE III

		(485)		(485)		(461)		(980)		(453)		(943)		
(a)	24230		23745		23260		22799	——	21819		21366	——		00423
	(6)		(1)		(2)		(1)	(3)	(1)		(0)	(1)		(0)
		(500)											(464)	
(b)	24538		24033									21644		21180
	(2)		(1)									(0)		(0)

TABLE IV

λ air in Å	Int.	ν vac in cm⁻¹
5038.2	0	19843
5006.8	0	19967
4457.2	2	22429
4329.1	4	23093
4293.2	3	23286
4218.0	0	23701

DISCUSSION

The absorption spectrum lying in the region λλ5050—4000 and attributed to SnS molecule is quite complex and consists of two mutually overlapping systems B (λλ5050–4270) and C (λλ4660–4000) of which the former is somewhat weaker. It is interesting to compare the results obtained by the authors with those of earlier workers. The authors have been able to record 57 red degraded bands in this region. The systems B and C consist of 18 and 23 bands respectively, 11 appear to fall into progressions showing ground state intervals and the remaining five are unclassified. The vibrational scheme for SnS as drawn by Rochester (1935) consisted of only thirteen sharp and intense bands having only three v'' progressions. Besides reporting some unclassified bands, he also arranged a few progressions exhibiting the differences of the ground state vibrational frequency. Leaving aside four very faint ones, rest of the above bands have appeared on our plates. Shawhan (1935) had, however, classified only nine bands and failed to observe any vibrational quanta v′ greater than unity. He had mentioned the presence of certain unclassified heads most of which he had found to be due to the accidental grouping of rotation lines occuring in the complex structure resulting from overlapping of bands corresponding to the numerous isotopes of tin. It is curious to note that the vibrational assignments of these two workers were mutually inconsistent and while Rochester assigns the origin of band system to be at 23211 cm^{-1}, Shawhan reports the same at 23591 cm^{-1}. Although the simple consideration of the Franck Condon principle indicates that Shwhan's analysis is more

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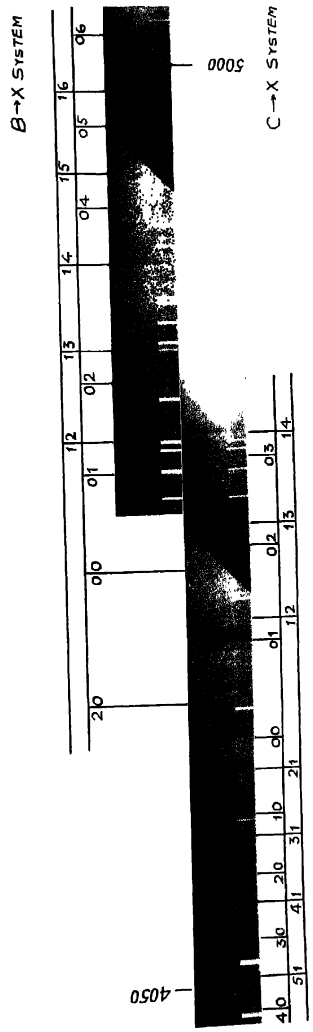

Figure 1 Absorption Spectrum of Sns

plausible, it is, however, unable to explain the 4 bands attributed to $v' = 0$ progression by Rochester.

The use of somewhat higher temperatures in the present investigation has resulted in the considerable extension of the visible region hitherto known as *A*, and it is now possible to explain most of the principal bands in terms of two systems, while fragments of a third one are also present.

System B ($\lambda\lambda$5050–4270)

The 487.7 cm^{-1} value of the ground state vibrational frequency of the SnS molecule is well established. The bands as explained by the equations (1) and (2) have therefore, rightly been attributed to SnS. Leaving aside the (3 1) band, all the bands attributed to the system B fall into three progressions viz. $v' = 0$, 1 and 2 Transitions involving $v' > 3$ are, however, found to be absent. The $v' = 0$ progression is well developed and self explanatory. Practically similar situation occurs for the $v' = 1$ progression. The agreement of the observed and the calculated band head data for these is also satisfactory. Further, the intensity distribution of the bands belonging to these progressions also appears to be reasonable. However, a somewhat different situation arises for the $v' = 2$ progression. The entire progression is poor in intensity and the observed and the calculated values exhibit a difference of about 50 cm^{-1} for each band This suggests that $v' = 2$ level might be perturbed by about 50 cm^{-1}. Though the (3, 1) band fits in quite well but more information involving higher v' values is required to make the assignments of $v' = 2$ progression unambigous. Attempts to include the progression elsewhere did not suceed and intensity considerations also indicate that its present assignment is quite plausible.

System C ($\lambda\lambda$4660–4000)

It can be seen readily that the system C incorporates Shawhan's $v' = 0$ and $v' = 1$ progressions as such, but the level $v' = 1$ is found to be perturbed. The present vibrational assignment extends upto $v' = 9$ level which has enabled an improved determination of the upper state vibrational constants The general intensity distribution of the bands is found to be satisfactory and the intense bands lie on a well marked Condon parabola. However, the absence of the (1, 1) band requires some consideration and will be discussed a little later.

Douglas, Howe and Morton (1961) have studied the absorption and emission spectra of SnS in the visible region. They have reported ten absorption bands and designated seven of them as $(w, 0)$, $(x, 0)$, $(x, 1)$, $(x, 2)$, $(y, 0)$, $(y, 1)$ and $(y, 2)$ where the letters w, x and y are the vibrational levels in certain electronic state and the numbers 0, 1 and 2 are the vibrational levels of the ground state $(x'\Sigma^+)$ of the molecule. The rotational structure was measured and analysed for $(w, 0)$, $(x, 0)$, $(x, 1)$ and $(y, 0)$ bands. The $(x, 0)$, $(x, 1)$ and $(w, 0)$ bands are found to arise from a $\pi-\Sigma$ transition while the $(y, 0)$ band appeared to have arisen from a $\Sigma-\Sigma$ transition. This evidently leads to the existence of more than one excited electric state in the region. It is interesting to note that the $(y, 0)$, $(y, 1)$ and $(y, 2)$ bands have been identified as $B(0, 0)$, $B(0, 1)$ and $B(0, 2)$ bands and the $(x, 0)$, $(x, 1)$, $(x, 2)$ and $(w, 0)$ bands are identical with the $C(0, 0)$, $C(0, 1)$ $C(0, 2)$ and $C(1, 0)$ bands of the present classification. Thus the vibrational schemes proposed by the authors are in confirmity with the results of the rotational analysis.

Douglas and coworkers (1961) have remarked that while the band $(w, 1)$ was expected to be quite strong, actually no trace of such a band was found. The absence of the $(w, 1)$ band has been explained by them on the following lines The upper state rotational levels are found to be strongly perturbed, the perturbation increasing with higher J values. Perturbed strong branches were also found to overlap the $(w, 0)$ band. Thus the effect could reasonably be attributed to the rotational perturbations. It can be seen readily that the C(1, 1) band would be identical with the $(w, 1)$ band. The absence of the C(1, 1) band is therefore explained. In view of the above, it appears that the assignments of the present B and C systems are correct and in all probability they arise from the $\Sigma-\Sigma$ and $\pi-\Sigma$ trnsitions respectively.

Progressions and unclassified bands

Table III reveals that 11 bands can be grouped into two progressions a and b exhibiting the ground state differences. It can also be noted that the vertical differences of the order of 300 cm^{-1} are present. It is quite likely that these progressions may from the part of a third system with v_0 at 24230 cm^{-1} and upper state vibrational frequency in the vicinity of 300 cm^{-1}. However, no definite scheme can be suggested with this meagre data. The remaining 6 bands could not be classified.

It is needless to mention that the visible spectra of SnS and PbS molecules are quite similar in appearance and are characterised by overlapping progressions.

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REFERENCES

Barrow, R. F., Drummond, G., and Rowlinson, H. C., 1953, *Proc. Phys. Soc.* **A66**, 885.

Butkow, K., and Tschassowenny, W., 1934, *Zeit. f. Phys.* **90**, 53.

Douglas, A. E., Howe, L. L., and Morton, J. R., 1961, *J. Mol. Spect.* **7**, 161.

Mohan, H., 1957, *D. Phil Thesis*, University of Allahabad.

Rochester, G. D., 1935, *Proc. Roy. Soc.* **A150**, 668.

Sharma, D., 1945, *Proc. Nat. Acad. Sci. India* **A14**, 217.

Shawhan, E. N., 1935, *Phys. Rev.* **48**, 521.

1936, *Phys. Rev.* **40**, 810.