Emission Spectrum of Antimony Nitride

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In a discharge through a mixture of nitrogen and antimony vapor a new band system has been found with the molecule SbN as carrier. The vibrational analysis yields the following formula for the heads

$$\nu = 34465 + [830.7(v'+\tfrac{1}{2}) - 6.0(v'+\tfrac{1}{2})^2] - [942.0(v''+\tfrac{1}{2}) - 5.6(v''+\tfrac{1}{2})^2].$$

A comparison is made with other molecules of the fifth group.

INTRODUCTION

UNTIL 1933, spectroscopic knowledge of diatomic molecules formed by combination of atoms of the fifth group of the periodic table was limited to molecules of like atoms. In 1933 Herzberg[1] and collaborators were able to prove spectroscopically the existence of a mixed molecule of this group, namely PN, and further succeeded in obtaining the vibrational analysis of the band system discovered and the rotational analysis of several of its bands. Independently of this work, Ghosh and Datta[2] in 1933 also published an account of the spectroscopic detection of PN. This work on mixed molecules of the fifth group was followed by a publication in 1934 by Spinks[3] on a band system having AsN as carrier. It seemed logical to assume that experimental conditions similar to those used by the above experimenters should prove favorable for the production of the diatomic molecule SbN. In the following an account of this work is given.[4]

EXPERIMENTAL

The experimental set-up was very similar to that used by Herzberg and Spinks. A discharge was run through a mixture of nitrogen and antimony and later through a mixture of hydrogen and antimony. For the excitation of the discharge a quartz tube, 57 cm in length and 9 mm internal diameter was used. To confine the discharge, an inner tube of six mm diameter was inserted into the outer tube. The ends of the former were slightly turned inward to prevent the molten metal from falling into the electrodes. A quartz window sealed on to one end of the tube was separated 15 cm from the nearer electrode to prevent fogging. The electrodes were cylinders of pure aluminum fitted tightly into Pyrex tubes sealed to the main discharge tube and hanging vertically. These electrodes were water cooled. Nitrogen from a tank was stored in a two-liter flask and from here was led into the discharge tube, the set-up being such that it could be admitted either continuously or intermittently. For the experiments performed with hydrogen, the hydrogen was admitted through a palladium tube. The antimony was "analytical reagent," granular form (Mallinckrodt).

The discharge was maintained by a transformer rated at 3 kw and 2200 volts. Secondary resistances varying from 300 to 2500 ohms placed in oil were inserted into the circuit.

Photographs were taken both with the Hilger E3 and E1 spectrographs. Eastman spectroscopic plates OI, OII and OIII were used. For obtaining spectrograms the following procedure was adopted. After taking plates with the discharge through nitrogen alone for orientation, the metal was placed in the tube and melted while the tube was being exhausted. Nitrogen was then admitted and the discharge started in nitrogen. All these plates showed only the nitrogen bands and NO bands. The latter were finally removed by frequent heating and pumping of the tube. The tube was then heated with an air-oxygen flame while the discharge was running. When

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[1] J. Curry, L. Herzberg and G. Herzberg, Zeits. f. Physik **86**, 348 (1933).

[2] P. N. Ghosh and A. C. Datta, Zeits. f. Physik **87**, 500 (1934).

[3] J. W. T. Spinks, Zeits. f. Physik **88**, 511 (1934).

[4] A preliminary note was published in Phys. Rev. **53**, 495 (1938).

FIG. 1. Emission bands of SbN.

this was done a bright blue glow appeared. It was further noted that if more nitrogen was admitted when the tube had a bluish glow, the blue was replaced by a yellow color; also that the nitrogen was rapidly eaten up and had to be replaced during the exposure. This, as well as the appearance of a dark gray deposit in the tube, is taken as an indication of the formation of SbN.[5] Running the discharge in antimony and nitrogen under the conditions indicated above, new bands which were attributed to the molecule SbN were obtained. As a further check of this assignment, exposures were later made running the discharge in hydrogen and antimony. In order to be free from contamination by SbN a new discharge tube was used in these experiments. No SbN bands were observed as long as nitrogen was absent, but they appeared after admitting nitrogen. The discharge was then run in hydrogen once more with the result that the new bands could be noticed on the first few plates together with traces of nitrogen bands. When the nitrogen was completely eliminated, the SbN bands still persisted, although considerably diminished. This is probably due to residues of deposited SbN on the walls. The bands were finally removed by continued heating and running of the discharge. This final absence of SbN bands is not due to the distillation of Sb out of the tube as considerable amounts remained when all operations were completed. The color of the discharge with hydrogen in the tube was a brilliant orange yellow when the antimony was heated.

For comparison spectrum the iron lines originating from a Pfund arc were used. The wave-lengths were computed from Hartmann's formula.

RESULTS

Plates taken of a mixture of antimony and nitrogen under the favorable experimental conditions described above showed a system of bands degraded to the red in the region 3200–2900A. An enlargement of part of a typical plate taken with the Hilger E1 is given in Fig. 1. It is evident from the plate that only the regions which are free from nitrogen bands can be examined in the search for new bands. In Table I are listed the bands measured. Column one gives a rough visual estimate of the intensity of the bands. Column two and three list the wave-lengths and wave numbers. The bands in the wave number region 34,000 to 33,000 cm^{-1} show structure. In some of the bands double heads are obvious. This is represented in Table I as R and Q, which refer to the rotational branches. On the plates the band at 34,409 cm^{-1} is the most intense. It also shows fine structure. The bands in the 32,000 cm^{-1} region show considerable background of nitrogen fine structure. In the 31,000 cm^{-1} region a comparison with the plates taken with nitrogen alone indicates that the fine structure of nitrogen is in some places replaced in the SbN plates by narrow diffuse bands. Overlapping and diffuseness made accurate measurements of the bands impossible. The errors vary from 1 to about 6 cm^{-1}. It also cannot be excluded definitely that some of the bands in the 31,000 cm^{-1} region have been erroneously attributed to SbN. Besides the bands in Table I additional very faint bands have been found. They are best developed on a plate taken with the blue glow maintained continuously and without admitting nitrogen as frequently as in the other exposures. These bands are attributed to the molecule Sb_2. They are listed in Table II.

DISCUSSION OF RESULTS

In attempting to identify the carrier of the observed spectrum, there are obviously two possibilities, namely the SbN and the Sb_2 molecules. It seems plausible to disregard as carrier any molecule that might be present as an impurity since the only atomic lines present

[5] There is evidence that antimony nitride has been obtained chemically in an impure state, J. W. Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longmans, Green and Co., 1928), VIII, p. 124.

were mercury, iron and antimony. Further since the electrodes and glass system were torched and pumped for hours as a preliminary preparation for the experiment and the antimony was melted while pumping, adsorbed gases, particularly oxygen, were removed. (The disappearance of the oxygen was evidenced by the disappearance of the NO bands.) From a comparison of the band system reported here and a system of the Sb_2 molecule observed by Naudé[6] and Nakamura and Shidei[7] in absorption it was found that the wave numbers of the two systems show great similarity; nevertheless this similarity is regarded as coincidental for the following reasons: (1) the failure of these bands to appear with hydrogen as carrier gas as already described, (2) the similarity concerns only frequencies but not intensity and structure of the two systems, (3) a comparison of the AsN bands reported by Spinks and of As_2 reported by Almy and Kinzer[8] shows also a number of similarities in the frequencies. In addition to (2) should be mentioned that the (0,0) band of the SbN scheme which coincides with Naudé's (11,0) band is not only the most intense band observed on all plates but under suitable conditions shows fine structure, whereas for such a heavy molecule as Sb_2 the resolution of fine structure can hardly be expected with a Hilger E1.

TABLE I. *Heads of* SbN *bands. v st=very strong, st=strong, m=medium, w=weak, vw=very weak.*

Intensity	Wave-Lengths (A)	Wave Numbers (cm^{-1})	v′	v″
w	2837.9	35,227	1	0
vw	2856.9	34,993	3	2
m	2904.3	34,422 *R*	0	0
v st	2905.3	34,409 *Q*		
m	2912.0	34,309 *R*	1	1
st	2914.8	34,297 *Q*		
m	2824.1	34,189	2	2
m	2985.7	33,485 *R*	0	1
v st	2986.2	33,476 *Q*		
st	2995.3	33,378	1	2
st	2996.1	33,367		
st	3004.5	33,274	2	3
st	3005.8	33,259		
m	3015.5	33,152	3	4
m	3052.8	32,747	7	8
m	3054.1	32,733		
m	3062.3	32,646	8	9
m	3166.1	31,575	1	4
m	3172.4	31,513		
w	3174.4	31,492	2	5
w	3182.7	31,411	3	6
vw	3190.8	31,331	4	7
vw	3193.2	31,307		
w	3198.7	31,254	5	8
w	3207.6	31,167	6	9
w	3214.7	31,098		
vw	3216.4	31,082	7	10
w	3225.0	30,999	8	11

TABLE II. Sb_2 *band heads, wave-lengths and wave-numbers.*

λ(A)	ν(cm^{-1})	λ(A)	ν(cm^{-1})
2866.9	34,871	2900.2	34,470
2867.5	34,863	2914.2	34,204
2886.0	34,640	3005.1	33,267
2886.8	34,630	3048.9	32,789
2887.9	34,617	3058.2	32,689
2895.6	34,525		

Although thus the origin of the new bands seems established, it is quite likely that weak Sb_2 bands fall on top of some SbN bands thus adding to the diffuseness of the appearance. The presence of very faint Sb_2 bands is indicated by Table II, they were identified from comparison with Naudé's and Nakamura's results.

Considerations of intensity distribution, along with a comparison with the analysis of PN and AsN has led to the arrangement of the band heads into the quadratic scheme given in Table III. A difficulty arose in the decision as to which head should be used. It is obviously necessary in the case of the (0,0), (0,1) and (1,1) to take the second and stronger heads, but in the 33,000 region, the heads become less marked and in the region of lower wave numbers the distinction between them vanishes completely. The bands can be represented by the following formula

[6] S. M. Naudé, South African J. Sci. **32**, 103 (1935).

[7] G. Nakamura and T. Shidei, Jap. J. Phys. **10**, 11 (1935).

[8] G. M. Almy and G. D. Kinzer, Phys. Rev. **47**, 721 (1935).

TABLE III. *Deslandres table of* SbN *band heads.*

v′	v″=0	1	2	3	4	5	6	7	8	9	10	11
0	34,409 (0)	33,478 (0)	*m*	*m*								
1	35,227 (+0.7)	34,297 (0)	33,377 (+0.3)	*m*	31,575 (−3)							
2			34,189 (−5)	33,274 (+2)	*m*	31,492 (+0.4)						
3			34,993 (−14)	*m*	33,152 (+21)	*m*	31,411 (+1)					
4					*m*	*m*		31,331 (+0.4)				
5						*m*	*m*		31,254 (−6)			
6								*m*		31,167 (0)		
7									32,747 (+8)		31,082 (+2)	
8										32,646 (+3)		30,999 (+1)

which has been worked out from the values of the strongest and most accurately measured heads:

$$\nu = 34{,}409 + [824.7v' - 6.0v'^2] - [936.4v'' - 5.6v''^2].$$

In Table III the experimental values are given and directly beneath them their deviation from the figures computed from the formula. The letter *m* denotes regions where the corresponding bands are masked by nitrogen.

Since antimony has two isotopes, namely, 121 and 123, the abundance ratio of which is 56 to 44, the isotopic separation was computed for SbN. The greatest separation, namely in the 31,000 region, is of the order of 3 cm^{-1}. This could not be accurately resolved under our experimental conditions with the Hilger E1 and hence would appear only in the diffuseness of the bands.

The observed band system of SbN shows much similarity with those of PN and AsN with respect to the intensity distribution of the bands. In Table IV are listed the molecular constants of these three molecules and of the corresponding elemental molecules for comparison.[9] That the band system discussed is due to a $^1\Pi \rightarrow {}^1\Sigma$ transition is without doubt true for PN as Herzberg has shown from the rotational analysis. He has furthermore made it seem very plausible that the $^1\Sigma$ represents the normal state of the molecule. His conclusion has recently been confirmed by Moureu, Rosen and Wetroff[10] who obtained the PN bands in absorption. We have in all probability also $^1\Pi \rightarrow {}^1\Sigma$ transitions in the cases of AsN and SbN. Spinks has concluded this from the measurement of the fine structure of several AsN bands and the same is assumed here for the SbN bands. The shift of the band system towards longer waves when going to heavier nitrides is of the expected magnitude as is the decrease in frequencies. In analogy to PN it seems safe to assume that the ground state is involved also in the transitions of AsN and SbN. Values for the dissociation heats of the nitrides can only be given roughly. They all have been obtained by extrapolation according to the method of Birge and Sponer.[11] The best value is probably that of 6.3 volts for PN which has been discussed by Herzberg. The values for AsN and SbN are certainly too high and represent quite rough estimates, but give at least an idea of the order of magnitude. The whole comparison can be considered as further

[9] Most molecular constants have been taken from tables in H. Sponer, *Molekülspektren* (Julius Springer, Berlin, 1935), Vol. I, and G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice Hall, 1939).

[10] H. Moureu, B. Rosen and G. Wetroff, Comptes rendus **209**, 207 (1939).

[11] R. T. Birge and H. Sponer, Phys. Rev. **28**, 259 (1926).

TABLE IV. *Comparison of molecular constants for* PN, AsN, SbN *and corresponding elemental molecules.*

MOLECULE	TRANSITION	$\nu_{0,0}$	ω_0'	$\omega_0'x_0'$	ω_0''	$\omega_0''x_0''$	D VOLTS	SPECTRAL REGION IN A
N_2	$^1\Pi\rightarrow{}^1\Sigma$	68,956.6	1678.96	13.32	2345.16	14.45	7.35	1205–2500
P_2	$^1\Sigma\rightarrow{}^1\Sigma$	46,790.1	472.62	2.60	777.63	2.80	5.03	1900–3500
As_2	$^1\Sigma\rightarrow{}^1\Sigma$	40,261	~280		428.32	1.12	3.96	2100–3700
Sb_2	$^1\Sigma\rightarrow{}^1\Sigma$	32,027	~215		269.28	0.57	(3.7)	2840–3300
Bi_2	$^1\Sigma\rightarrow{}^1\Sigma$	36,446	146	0.5	173.3	0.41	3.3	2600–2900
PN	$^1\Pi\rightarrow{}^1\Sigma$	39,688.5	1095.87	7.22	1330.26	6.98	(6.3)	2375–2775
AsN	$^1\Pi\rightarrow{}^1\Sigma$	35,905.9	863.02	8.24	1062.60	5.36	(6.5)	2400–3100
SbN	$(^1\Pi\rightarrow{}^1\Sigma)$	34,409	824.7	6.0	936.4	5.6	(4.8)	2800–3200

evidence for the correctness of the analysis given for SbN.

A comparison of the nitrides with the corresponding elemental molecules seems of interest. In all these cases each of the two atoms which form the molecule has, besides closed shells, three p electrons which become responsible for the binding and form three bonding electron pairs. For all of them the normal state is a $^1\Sigma$, but the transition discussed here is a $^1\Pi\rightarrow{}^1\Sigma$ only for N_2, whereas it is a $^1\Sigma\rightarrow{}^1\Sigma$ for the heavier elemental molecules. A discontinuity is also observed when comparing the different molecular constants of N_2 with those of the succeeding molecules. This can be understood, however, as Herzberg[12] and Mulliken[13] have pointed out from the fact that N_2 approaches the "united atom," in this case Si, much more closely than P_2 or the succeeding heavier molecules approach the corresponding united atom.

The "rule of means" or a modified rule of means has been used[14] to calculate the vibrational frequency for the ground state of a compound molecule from the corresponding frequencies of the two elemental molecules whose atoms constitute the compound molecule. Whereas the relationship gives good results for the alkalis and their mixed molecules, the molecules of group six and their oxides, the halides and their mixed molecules, it does not hold for the nitrides of the fifth group. Howell and Clark took this failure as a possible indication that the band systems of the nitrides represent transitions between two excited states. That this possibility is now definitely ruled out for PN by the mentioned absorption experiments has already been pointed out by Moureu, Rosen and Wetroff. The same is most probably true for AsN and SbN. The poor fulfillment of Clark's rule for the nitrides of the fifth group may have something to do with the above-mentioned discontinuity in the molecular constants of N_2 and the succeeding molecules.

In conclusion, we wish to acknowledge the assistance of Dr. J. S. Kirby-Smith in taking some of the test experiments in hydrogen.

[12] G. Herzberg, Ann. d. Physik **15**, 677 (1932).
[13] R. S. Mulliken, Rev. Mod. Phys. **4**, 15 (1932).
[14] C. H. D. Clark, Trans. Faraday Soc. **31**, 1017 (1935); **33**, 1390 (1937); H. G. Howell, Nature **138**, 36, 290 (1936).

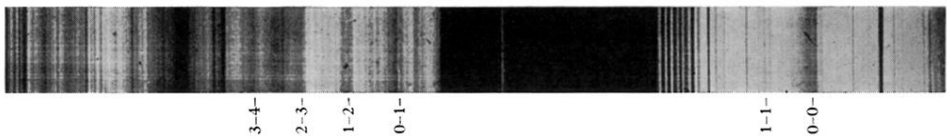

FIG. 1. Emission bands of SbN.