JUNE 1, 1934 PHYSICAL REVIEW VOLUME 45

A New Band System of Tin Oxide

F. W. Loomis and T. F. Watson, *University of Illinois*

(Received April 4, 1934)

A new band system of SnO with origin at 36,803 cm^{-1} has been observed in an arc at reduced pressures. The lower state of this system is identical with that of the known A and B systems. The upper state is new and has a vibrational frequency, $\omega_e=497.8\ \text{cm}^{-1}$. The complexity of the isotope effect prevents rotational analysis.

In the course of an investigation conducted with another object, a new band system of tin monoxide has been observed in the region from 2400 to 3100A. Some 100 bands of SnO in the region 3070 to 4800A have previously been observed in various flame and arc sources at or near atmospheric pressure and have been assigned by Mahanti[1] and Connelly[2] to one fairly extended band system (A) and two somewhat dubious ones (B and C).

The light source in the present investigation was a tin arc operated in oxygen at reduced pressures. With this source the intensities of all bands were considerably enhanced, and in particular the new ones were developed to the point where they could be photographed in 40 hours in the second order of a 30,000 line/inch grating. The electrodes were of hollow copper containing metallic tin, the upper electrode being so constructed that molten tin dropped through a small hole and kept a supply of fresh tin on the lower electrode. The optimum pressure for the production of the new bands seemed to be about 2 to 6 cm of mercury. The bands were photographed with a Hilger E-2 quartz spectrograph, a 3-meter quartz prism spectrograph and in the first and second orders of a 30,000 line per inch 21-foot grating in a Paschen mounting.

Because of the complex isotopic structure of tin, it is hard to measure the heads accurately, particularly those remote from the origin of the system. The frequencies of most of the measured band heads, including all the strong ones, can be expressed within the accuracy of measurement by the formula

$$\nu=36{,}803+\{497.8(v'+1/2)-2.56(v'+1/2)^2\}-\{821.9(v''+1/2)-3.6(v''+1/2)^2\}. \quad (1)$$

In this equation the term in v'' is identical with those of Mahanti's and Connelly's A and B systems, which indicates that the lower level in all three systems is the same.

Table I gives the frequencies and roughly estimated intensities of all measured bands of the new system, together with quantum numbers and differences between the observed frequencies and those calculated from Eq. (1) for bands which have been assigned. In Table II the intensities are entered as a function of v' and v'', showing that the locus of maximum intensity is a wide open Franck-Condon curve such as is to be expected from the great difference between the vibrational spacings in Eq. (1).

Tin, according to Aston,[3] consists of eleven isotopes, whose atomic weights and relative abundances (given in parentheses in percents) are as follows:

112 (1.07) 114 (0.74) 115 (0.44) 116 (14.19) 117 (9.81)
118 (21.48) 119 (11.02) 120 (27.04) 121 (2.96) 122 (5.03)
124 (6.19)

Hence each line in the spectrum should be split by the isotope effect into eleven lines, of which about five should be prominent. The isotopic displacement is approximately equal to $(\rho-1)(\nu_v+2\nu_r)$, in the usual notation, and the

---

[1] Mahanti, Zeits. f. Physik **68**, 114 (1931).

[2] Connelly, Proc. Phys. Soc. **45**, 780 (1933).

[3] Aston, *Mass Spectra and Isotopes*, p. 237 (1933).

TABLE I. *Frequencies and intensities of the new band system.*

Intensity	v'	v''	Frequency	Observed −Computed Frequency
0	13	1	41827	−5
0	10	0	41334	−4
0	13	2	41022	−3
1	9	0	40889	−2
2	8	0	40439	0
0	11	2	40160	−3
0	9	1	40071	−5
2	7	0	39993	+11
3	6	0	39525	+5
0	11	3	39353	−4
0	7	1	39159	−9
3	5	0	39052	−1
1			38868	
0	8	2	38809	−8
1			38788	
1	6	1	38703	−3
4	4	0	38585	+4
5	5	1	38241	+2
5	3	0	38108	+4
2			38068	
0	8	3	38011	−6
6	4	1	37768	+2
6	2	0	37610	−12
6	3	1	37291	+2
0	1	0	37142	+8
2	6	3	37106	+8
0	11	6	37001	+2
1	4	2	36964	+5
2			36838	
7	2	1	36795	−12
0	0	0	36648	+8
1	5	3	36628	−3
0	10	6	36551	−6
6	3	2	36484	+2
0	13	8	36331	0
4	1	1	36315	−3
3			36215	
1	4	3	36164	+5
6	2	2	35994	−5
3			35868	
3	0	1	35832	+6
1	3	3	35683	+2
1	8	6	35652	−7
0	13	9	35581	+7
2			35562	
8	1	2	35516	+4
2			35300	
2			35258	
0	12	9	35144	+2
1	5	5	35045	−7
4	0	2	35022	+3
2			34947	
1		4	34890	+2
4	6	6	34743	+3
6	1	3	34707	−4
3	4	5	34582	+2
1	7	7	34425	−6
8	0	3	34216	−2
5	3	5	34108	+6
1	6	7	33966	−3
6	1	4	33915	−3
1	9	9	33823	−5
2			33720	
4	2	5	33619	−1
0	11	10	33517	+3
2	5	7	33507	+5
8	0	4	33430	+5
2	3	6	33332	+8
1			33182	
2	1	5	33144	+11
0			33102	
0	10	10	33068	0
0	7	9	32908	−1
2	4	7	33032	+4
6	2	6	32846	+5
0	5	8	32744	+7
3	0	5	32637	−2
0	6	9	32442	−5
1	1	6	32360	+6

bands are degraded sharply to the red, that is, ν_r is essentially negative. Hence the isotope effect should be zero where $\nu_v=-2\nu_r$, i.e., at points halfway between the origin of the band system and the origin of any band which lies to the short-wave side of the system origin. Although the complexity of the isotope effect in tin renders the rotational analysis practically impossible, the effect can be seen to be qualitatively in accord with these considerations. For instance, near 2680A, which is halfway between the system origin and the origin of the (4,1) band, the band lines are fairly sharp and single, and branches can be followed for some distance. In bands a little further from the origin the lines become diffuse; further on they are split into about five lines; and further still the isotope splitting becomes so large that it overlaps the successive rotational lines and the whole spectrum becomes hopelessly complex. Since the isotope splitting vanishes in the expected region, and where observable is of the right order of magnitude, it can be taken as confirmation of the general vibrational arrangement of the system, and of the assumed carrier. This is also true of the *A* system.

TABLE II. *Intensities as functions of v′ and v″.*

v'' v'	0	1	2	3	4	5	6	7	8	9	10
0	0	3	4	8	8	3					
1	0	4	8	6	6	2	1				
2	6	7	6	–	–	4	6				
3	5	6	6	1	1	5	2				
4	4	6	1	1		3		2	0		
5	3	5		1	1			2		0	
6	3	1		2			4	1		0	
7	2	0						1			
8	2		0	0			1				
9	1	0								1	
10	0										0
11			0	0			0				0
12										0	
13		0	0							0	