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Rotational Constants of SnS

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Rotational constants of SnS in its lowest state and one excited state have been determined from the (0,0) and (1,0) bands of the visible system. Empirical formulae were used to determine the combination differences. The constants determined are $B'=0.140$ cm^{-1} and $r_e'=2.18$A for the upper state of the visible system and $B''=0.157$ cm^{-1} and $r_e''=2.01$A for the lowest state of the molecule.

OUR knowledge of the molecular constants of the metallic sulphides is confined to the vibrational constants of MgS,[1] GeS,[2] PbS[3] and SnS.[4, 5] Recent interest[6, 7, 8] in theoretical relationships between the molecular constants of similar molecules makes additional data on the metallic sulphides desirable, and in particular, data on the heavier sulphide molecules. The relatively simple structures of the (0,0)† and (1,0)† bands in the visible SnS system indicated that rotational constants of this molecule might be determined in spite of the complex isotopic composition of Sn.

EXPERIMENTAL

The spectrograms used for the analysis were taken in the first order of a 21-ft. concave grating in a Paschen-Runge mount. This grating is ruled with 30,000 lines to the inch and gives a dispersion of 1.25A/mm in the first order. The SnS was introduced into an iron tube approximately 80 cm long and 1 cm in internal diameter, which was heated to about 1000°C in two nichrome-wound Hoskins furnaces placed end to end. A five-hundred watt projection lamp provided the continuous radiation that was passed through the iron tube containing the SnS vapor. Fe comparison lines were added to the spectrograms by replacing the lamp with an iron arc.

RESULTS

The lines of the (1,0) band are sharp near the tail of the band because of cancelation of the vibrational and rotational isotope displacements and appear increasingly diffuse toward the head. The lines of the (0,0) band are sharp toward the head, but become increasingly diffuse and finally blend together at a considerable distance from the head because of the combined vibrational and rotational displacements. The other bands of the system are made hopelessly complex by the overlapping of the patterns corresponding to the five abundant and six less abundant tin isotopes.

The lines of the (1,0) band, whose head is at 23,899.3 cm^{-1}, clearly separate into two branches of approximately equal intensity near the tail of the band. Nearer the head the lines of the two branches are practically coincident and, because of their diffuseness, in most cases cannot be separated. In this part of the band the centers of the blended lines were measured. The lines of the P branch are represented within the errors indicated in Fig. 1(a) by the formula:

$$\nu=23,879.70-0.998m-0.0169m^2. \qquad (1)$$

The lines of the R branch in this band differ by the amounts shown in Fig. 1(b) from the values calculated from the formula:

$$\nu=23,879.70-1.011m-0.0166m^2. \qquad (2)$$

The lines of the two branches are practically coincident over the portion of the (0,0) band

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† Rochester, reference 4, using moderate dispersion, assigned an additional v'' progression to this system which would make these bands (1,0) and (2,0), respectively. Measurements from high dispersion plates show that Rochester's v'' values for bands in this progression should be increased by one. Hence the progression cannot belong to this system. Moreover, the system origin corresponding to his assignment is inconsistent with the isotope structure observed at high dispersion. The first constant of the formula used to calculate heads in this system appears incorrectly in our paper.[5] It should be 23,591.81.

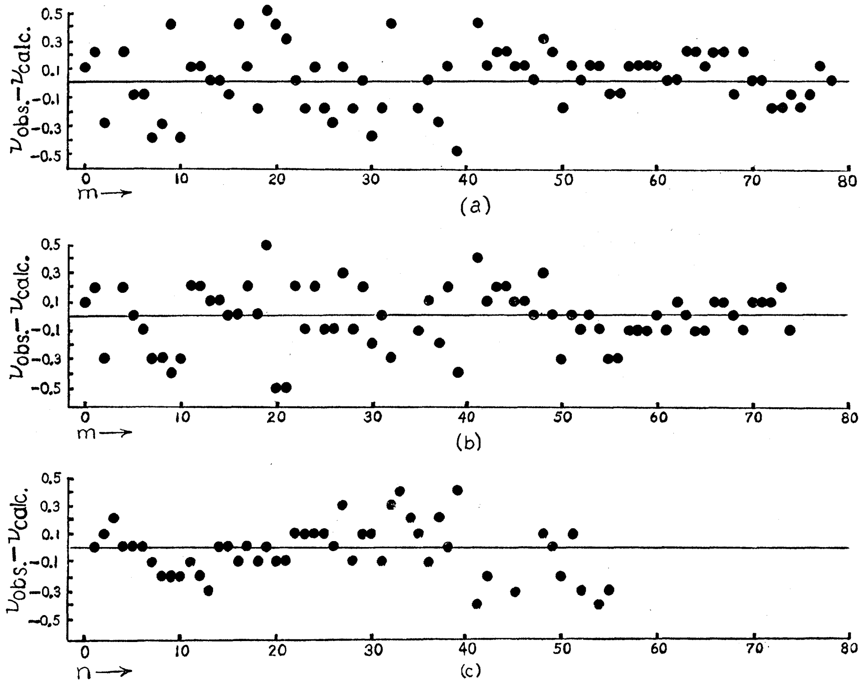

FIG. 1. (a) Differences between measured wave numbers of lines in P branch of (1,0) band and values calculated from (1). (b) Differences between measured wave numbers in R branch of (1,0) band and values calculated from (2). (c) Differences between measured centers of blended lines from P and R branches of (0,0) band and values calculated from (3).

where measurements may be made. Toward the head, which lies at 23,531.9 cm^{-1}, the lines appear quite sharp. The width of the blended lines at a greater distance from the head agrees with the calculated spread of lines arising from the more abundant tin isotopes. Fig. 1(c) gives the difference between the measured wave numbers of the centers of the blended lines and the values calculated from the formula:

$$\nu = 23{,}514.66 - 0.903n - 0.0185n^2. \qquad (3)$$

Since the most accurate measurements are obtained in different portions of the (1,0) and (0,0) bands the empirical series formulae were used to determine the combination differences.

From (1) and (2) the wave number difference

TABLE I. *Observed and calculated values of Δ_2F'' from the (1,0) and (0,0) bands.*

n	Δ_2F''calc.(1,0)	Δ_2F''obs.(1,0)	Δ_2F''calc.(0,0)	Δ_2F''obs.(0,0)
1	21.31		21.34	21.4
2	21.94		21.97	22.1
3	22.57		22.60	22.9
4	23.19		23.21	23.2
5	23.82		23.86	23.8
6	24.45		24.49	24.4
7	25.07	24.7	25.12	24.9
8	25.66	25.5	25.75	25.4
9	26.28	25.7	26.38	26.1
10	26.92	—	27.00	26.5
11	27.55	28.0	27.63	27.6
12	28.18	28.1	28.26	28.0
13	28.82	28.9	28.89	28.5
14	29.44	29.4	29.52	29.6
15	30.08	29.7	30.15	29.8
16	30.72	30.6	30.78	30.3
17	31.36	31.0	31.41	31.1
18	31.99	31.6	32.04	31.8
19	32.60	33.0	32.67	32.8
n	Δ_2F''calc.(1,0)	Δ_2F''obs.(1,0)	Δ_2F''calc.(0.0)	Δ_2F''obs.(0,0)
20	33.26	33.0	33.29	33.0
21	33.90	—	33.92	34.0
22	34.54	—	34.55	34.7
23	35.18	35.3	35.18	—
24	35.81	36.0	35.81	36.3
25	36.45	36.7	36.44	36.6
26	37.09	37.6	37.07	—
27	37.73	38.0	37.70	—
28	38.38	—	38.33	38.8
29	39.02	38.8	38.96	—
30	39.66	39.5	39.58	—
31	40.31	40.3	40.21	40.0
32	40.96	40.7	40.84	41.1
33	41.59	41.4	41.47	41.7
34	42.24	42.4	42.10	42.4
35	42.89	42.8	42.73	43.2
36	43.54	43.4	43.36	—
37	44.19	—	43.99	44.6
38	44.84	—	44.62	44.9

between a line in the R branch of the (1,0) band corresponding to $m=n-u$ and a line in the P branch of that band corresponding to $m=n-u+r$ is given by:

$$(0.998r+0.0169r^2+0.013u+0.0003u^2-0.0338ur)$$
$$(-0.013+0.0338r-0.0006u)n+0.0003n^2. \quad (4)$$

From (3), the wave number of a line in the R branch of the (0,0) band corresponding to n and a line in the P branch of that band corresponding to $n+s$ differ by:

$$(0.903s+0.0185s^2)+(0.0370s)n. \quad (5)$$

With $r=19$, $s=17$, $u=7$ and n as given in the first column of Table I, (4) and (5) represent the calculated combination differences listed in the second and fourth columns, respectively. No other set of integer values of r, s and u gives satisfactory agreement. The third and fifth columns of Table I list the corresponding differences between measured lines in the (1,0) and (0,0) bands, respectively. Observed values of Δ_2F'' have been omitted wherever one of the band lines involved is obscured by an atomic line or where blending makes the measurement too uncertain to have significance.

One-quarter of the difference of successive values of Δ_2F'' gives $B''=0.157$ cm^{-1}. Then $r_e''=2.01$A. The complex isotope structure of the other bands in the system prevents a direct check on the values of Δ_2F' but from the branch formulae of the (1,0) band, $B''-B'=0.017$ so that $B'=0.140$ cm^{-1} and $r_e'=2.18$A.* Allen and Longair[8] have noted that for the lighter molecules the product $\omega_e r_e^3\mu^{\frac{1}{2}}$ is approximately proportional to the number of completed shells in the molecule. For the ground state of SnS this product is 27.4×10^{-33} g$^{\frac{1}{2}}$ cm^2 while for the corresponding state of PBO it is 25.2×10^{-33} g$^{\frac{1}{2}}$ cm^2. This is somewhat better agreement than that obtained from the simpler Morse rule which gives $\omega_e r_e^3\mu^{\frac{1}{2}}=4.25\times10^{-21}$ cm^2 for SnS and 5.10×10^{-21} cm^2 for PbO.

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* From these considerations we may estimate very roughly the values of J for the lower levels of the lines measured. In Fig. 1(a), $J=m+21$; in Fig. 1(b), $J=m+38$; in Fig. 1(c), $J=n+16$ for the P branch and $J=n+31$ for the R branch. These numbers are probably in error by several units, but all by the same amount.

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The Diamagnetism of Some Organic Binary Mixtures at Different Temperatures

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Measurements of the magnetic susceptibilities of mixtures consisting of binary combinations of carbon tetrachloride, benzene and nitrobenzene, made with the improved manometric balance of Wills and Boeker over the range of temperatures from 10°C to 50°C, are described. The results for mixtures of benzene and nitrobenzene, each of which shows no variation of mass susceptibility with temperature, show that the principle of additivity of susceptibilities is valid within the limits of precision of measurement. For mixtures of either benzene or nitrobenzene with carbon tetrachloride, a systematic deviation from additivity is found. The deviations for both groups show a definite dependence upon both concentration and temperature.

Introduction

In a recent article, N. N. Pal[1] reported the results of his measurements on the dielectric polarization of mixtures of nitrobenzene and carbon tetrachloride, and also the results of similar measurements on mixtures of nitrobenzene and benzene. The measurements were made with various concentrations over a considerable temperature range. The practically nonpolar liquids, carbon tetrachloride and benzene, were considered as solvents for the highly polar nitrobenzene. The results showed apparently a notable dependence of the polarization of nitrobenzene upon both concentration and temperature, which was accounted for by the author in his theoretical discussion by assuming the association of the nitrobenzene molecules to depend upon both concentration and temperature.

Since changes in association are sometimes accompanied by changes in magnetic suscep-

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