For the longitudinal vibrations x_1, x_2 and x_3 represent the displacements from equilibrium of the hydrogen, nitrogen, and carbon atoms, respectively. Then

$$q = x_3 - x_1; \quad z = x_2 - x_3;$$

and

$$m_1\ddot{x}_1 + m_2\ddot{x}_2 + m_3\ddot{x}_3 = 0.$$

In this case the kinetic energy is $T = \frac{1}{2}m_1\dot{x}_1^2 + \frac{1}{2}m_2\dot{x}_2^2 + \frac{1}{2}m_3\dot{x}_3^2$ or in terms of $\dot{q}$ and $\dot{z}$, $T = \frac{1}{2}\mu_q\dot{q}^2 + \frac{1}{2}\mu_z\dot{z}^2 + \frac{1}{2}\cdot 2\mu_{qz}\dot{q}\dot{z}$ where

$$\mu_q = \frac{m_1(m_2 + m_3)}{S}; \quad \mu_z = \frac{m_2(m_1 + m_3)}{S}; \quad \mu_{qz} = \frac{m_1 m_2}{S}$$

and $S = m_1 + m_2 + m_3$, the total mass of the molecule. The potential energy is subject to the geometric symmetry of the molecule. It may be written $V = \frac{1}{2}(k_{11}q^2 + k_{22}r^2 + 2k_{13}qz + k_{33}z^2)$. The secular determinant of the normal coordinate transformation factors into a linear and a quadratic expression, and yields the following set of equations,

$$\lambda_1 + \lambda_3 = \frac{\mu_q k_{33} + \mu_z k_{11} - 2\mu_{qz}k_{13}}{\mu_q\mu_z - \mu_{qz}^2},$$

$$\lambda_1\lambda_3 = \frac{k_{11}k_{33} - k_{13}^2}{\mu_q\mu_z - \mu_{qz}^2},$$

$$\lambda_2 = k_{22}/\mu_r.$$

In normal coordinates the kinetic and potential energies assume the forms

$$T = \frac{1}{2}(\dot{Q}^2 + \dot{R}^2 + \dot{Z}^2), \quad V = \frac{1}{2}(\lambda_1 Q^2 + \lambda_2 R^2 + \lambda_3 Z^2).$$

The normal vibrations expressed in wave numbers are $\nu_i = (1/2\pi c)(\lambda_i)^{\frac{1}{2}}$. The constant k_{22} may be computed from ω_2 of HCN and DCN and is nearly the same for both as would be expected. Using the fundamentals ω_1 and ω_3 of HCN and the fundamental ω_3' of DCN the unobserved fundamental ω_1' of DCN can be calculated as well as the other three constants k_{11}, k_{13} and k_{33}. There are two sets of constants because the equations are quadratic. These are

$k_{22} = 0.8071\times10^5$		$k_{22} = \ 0.8071\times10^5$	dynes/cm
$k_{11} = 5.6987$ "	Or	$k_{11} = \ 5.6981$ "	
$k_{13} = 6.443$ "		$k_{13} = -0.30491$ "	
$k_{33} = 25.34$ "		$k_{33} = \ 18.065$ "	

k_{13} represents the interaction between the extreme atoms, and should be small. Hence the second set is the more plausible.

The observed and calculated values of the wave numbers for the fundamental bands of HCN and DCN are as follows:

Observed wave numbers	Calculated wave numbers
$\omega_1 = 2089.0$ cm^{-1}	$\omega_1 = 2089.6$ cm^{-1}
$\omega_2 = \ 712.1$	$\omega_2 = \ 712.8$
$\omega_3 = 3312.9$	$\omega_3 = 3312.3$
$\omega_1^1 = \ —$	$\omega_1^1 = 1896.7$
$\omega_2^1 = \ 569.1$	$\omega_2^1 = \ 568.6$
$\omega_3^1 = 2630.0$	$\omega_3^1 = 2629.5.$

Absorption Spectrum of Tin Sulphide

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The absorption spectrum of tin sulphide between 3200A and 4600A has been photographed at moderate dispersion and between 4000A and 4600A at high dispersion. The system in the near ultraviolet may be represented by the formula:

$$\nu = 28{,}336.2 + 332.77(v'+\tfrac{1}{2}) - 1.42(v'+\tfrac{1}{2})^2 \\ - 488.25(v''+\tfrac{1}{2}) + 1.47(v''+\tfrac{1}{2})^2.$$

This formula is not in agreement with that given by

Butkow and Tschassowenny who seem to have incorrectly assigned the system origin. A new system has been located in the visible which is limited by predissociation to two v'' progressions. These bands are given by the formula:

$$\nu = 23{,}287.67 + 367.5(v'+\tfrac{1}{2}) - 488.25(v''+\tfrac{1}{2}) + 1.47(v''+\tfrac{1}{2})^2.$$

The observed isotope structure of the strong bands in this system confirms their vibrational assignment.

INTRODUCTION

OUR knowledge of the band spectra of the metallic sulphides seems quite meager when compared with the information available on the spectra of the oxides of the metals. This is perhaps in part due to the difficulties involved in obtaining spectra of sulphides in emission. Some progress has been made in several cases where it is possible to obtain absorption spectra. Wilhelm[1] has reported the spectrum of MgS and given its vibrational analysis. The absorption spectra of ZnS, CdS and HgS have been studied by Sen-Gupta.[2] He observed only regions of continuous absorption, which indicates that the potential curves of the excited states of these molecules either have shallow minima or none at all. Shapiro, Gibbs and Laubengayer[3] made a vibrational analysis of the absorption spectrum of GeS and identified heads due to four isotopes of germanium. Rochester and Howell[4] have given a rather complete vibrational analysis of the extensive absorption spectrum of PbS and indicate that the rotational analysis is in progress.

A short report on the vibrational analysis of the band spectrum of SnS in absorption has been published by Butkow and Tschassowenny.[5] They report only two band systems, one lying between 2580 and 3164A and the other between 3277 and 3799A. They give the band-head formula in each case without recording data on the bands observed. One would expect the spectrum of SnS to resemble that of PbS. The fact that the spectrum of PbS extends into the near infrared and includes at least five systems suggested that a further critical examination of the spectrum of SnS might reveal other systems lying farther toward the visible.

EXPERIMENTAL

Chemically pure tin sulphide (SnS) contained in a graphite tube about 50 cm long and 2 cm in internal diameter, open to the air at the ends, was heated by means of a Hoskins carbon resistance furnace operated at 25 volts a.c. and about 300 amperes. The temperature was varied between 800 and 1100°C. A five-hundred watt projection lamp provided a source of continuous radiation which was passed through the tin-sulphide vapor and then focused on the slit of the spectrograph.

The spectrum between 3200A and 4000A was photographed on an E-1 quartz spectrograph giving a dispersion of 6 to 12A/mm over this range. The times of exposure with this spectrograph ranged up to a half-hour. A Littrow mounted concave grating with a radius of curvature of ten feet, giving a dispersion of 5.6A/mm in the first order was used to photograph the region between 3400A and 4650A. In order properly to develop the bands near the red end of the spectrum it was necessary to increase the vapor pressure until the light on the slit appeared distinctly yellow. At a somewhat lower temperature the violet end of the spectrum could be photographed in about an hour.

For still higher dispersion between 4000A and 4650A this portion of the spectrum was photographed 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. This tube was heated to about 1000°C in two nichrome-wound Hoskins furnaces placed end to end. As in the previous case a five-hundred watt projection lamp provided the continuous radiation which was passed through the iron tube containing the SnS vapor.

RESULTS

Two band systems were observed, one in the ultraviolet extending from about 3250A to 4300A, and the other in the visible between approximately 4200A and 4600A. The system in the near ultraviolet probably includes the bands observed in this region by Butkow and Tschassowenny.[5] Their near ultraviolet system extended as far toward shorter wave-lengths but not as far to the red. The system in the visible does not seem to have been previously reported. It is confined to a few fairly strong bands degraded to the red as are all other bands in the spectrum.

[1] H. A. Wilhelm, Iowa State Coll. J. Sci. 6, 475 (1932).
[2] P. K. Sen-Gupta, Proc. Roy. Soc. A143, 438 (1934).
[3] C. V. Shapiro, R. C. Gibbs and A. W. Laubengayer, Phys. Rev. 40, 354 (1932).
[4] G. D. Rochester and H. G. Howell, Proc. Roy. Soc. A148, 157 (1935).
[5] K. Butkow and W. Tschassowenny, Zeits. f. Physik 90, 53 (1934).

The rotational structure of the stronger bands is resolved on the high dispersion plates.

A number of weak heads, scattered through the portion of the spectrum explored, were measured but could not be classified. Those falling in the region photographed on the 21-ft. grating were examined on the high dispersion plates. Most of them were found to be due to the accidental grouping of rotation lines occurring in the complex structure resulting from the overlapping of bands corresponding to the numerous isotopes of tin. The few unclassified heads that cannot be accounted for in this manner may belong to fragmentary systems. A number of unclassified heads[6] have also been observed in the spectrum of SnO.

Near ultraviolet system

Table I gives the wave numbers of the heads in the near ultraviolet system, together with their estimated intensities, the values of v' and v'' and the departures of the observed wave numbers from those calculated from the formula:

$$\nu = 28{,}336.2 + 332.77(v'+\tfrac{1}{2}) - 1.42(v'+\tfrac{1}{2})^2 \\ -488.25(v''+\tfrac{1}{2}) + 1.47(v''+\tfrac{1}{2})^2.$$

At a temperature of about 1000°C this system is characterized by strong v' and v'' progressions which allow the values of v' and v'' to be assigned with confidence. At lower temperatures the bands

TABLE I. *Bands observed in near ultraviolet system.*

I	v'	v''	$\nu_{obs.}$	$\nu_{obs.}-\nu_{calc.}$	I	v'	v''	$\nu_{obs.}$	$\nu_{obs.}-\nu_{calc.}$
0	1	10	23865.5	−2.1	2	4	3	27637.3	−0.3
2	1	9	24329.0	+2.5	10	0	1	27773.1	−0.1
0	3	10	24520.6	+1.6	4	3	3	27791.8	−0.9
0	2	9	24650.1	−2.5	1	5	4	27957.8	+1.6
0	1	8	24788.3	0.0	10	1	1	28102.9	−0.2
1	0	7	24923.6	+0.5	4	0	0	28259.1	+0.6
0	3	9	24975.2	−2.6	4	3	2	28271.4	−0.9
1	2	8	25115.2	−0.2	8	2	1	28430.2	0.0
3	1	7	25253.8	+0.8	0	10	6	28559.7	−2.5
1	4	9	25296.3	−2.9	8	1	0	28589.2	+0.8
5	0	6	25391.5	+0.8	6	4	2	28594.3	+0.8
6	1	6	25720.5	−0.2	1	3	1	28753.4	−1.1
7	0	5	25862.8	+0.5	7	2	0	28915.8	+0.3
4	1	5	26190.7	−0.6	1	4	1	29075.2	−0.7
8	0	4	26337.5	+0.6	6	3	0	29239.5	−0.3
3	3	6	26369.4	−2.6	2	5	1	29393.4	−1.0
1	2	5	26517.7	−0.7	1	10	4	29504.5	−1.8
0	5	7	26548.5	−2.8	5	4	0	29560.5	−0.7
10	0	3	26811.0	−0.1	2	9	3	29677.7	−0.8
3	3	5	26845.6	−1.5	5	6	1	29710.3	+0.1
4	2	4	26989.2	−1.5	1	8	2	29852.0	+1.3
0	1	3	27139.8	−1.5	5	5	0	29880.1	+0.3
1	4	5	27167.3	+2.7	3	7	1	30022.1	−1.0
10	0	2	27291.7	+0.9	1	9	2	30159.8	+1.8
2	3	4	27315.7	−0.5	3	6	0	30195.5	0.0
5	2	3	27468.5	+0.1	2	8	1	30332.8	−0.3
5	1	2	27621.0	+0.2	1	7	0	30508.2	−0.2

[6] F. C. Connelly, Proc. Phys. Soc. **45**, 780 (1933).

TABLE II. *Intensity distribution in near ultraviolet system.*

v' \ v''	0	1	2	3	4	5	6	7	8	9	10
0	4	10	10	10	8	7	5	1			
1	10	10	5	0	4	6	3		0	2	0
2	10	8		5	4	1			1	0	0
3	10	1	4	4	2	3	3			0	0
4	8	1	6	2		1	1			1	
5	5	2		1				0			
6	3	5									
7	1	3									
8		2	1								
9			1	2							
10					1		0				

corresponding to the higher v'' values are noticeably weaker. Higher temperatures failed to reveal additional bands.

Watson and Loomis[7] found difficulty in measuring the heads of the bands in the far ultraviolet system of SnO because of the overlapping of bands corresponding to the five abundant and six less abundant isotopes of tin. The values of ρ for the various tin isotopes are larger for SnS than for SnO, but most of the bands in this system are so near the system origin that the heads corresponding to the several isotopes are nearly coincident and the observed heads are fairly sharp. Near the limits of the system the heads appear somewhat diffuse but the spreading is not sufficient to allow the individual isotope heads to be distinguished.

The intensity distribution of the bands in this system is shown in Table II. There is a rather open Condon parabola to be expected from the difference in the values of ω_e' and ω_e''. Inside this parabola, and separated from it by weaker bands, is another group of fairly strong bands. This effect[4] is quite marked in the A system of PbS.

Comparison with earlier work. Butkow and Tschassowenny[5] gave the following formula for the bands between 3277A and 3799A:

$$\nu = 30{,}280.5 + 315.6(v'+\tfrac{1}{2}) - 0.59(v'+\tfrac{1}{2})^2 \\ -484.5(v''+\tfrac{1}{2}) + 0.50(v''+\tfrac{1}{2})^2.$$

This formula accounts for only a few of the strong bands observed in this region of the spectrum during this investigation. It may be that the lower temperatures used by these investigators, 600 to 840°C, were not sufficient to develop properly the bands near the red end of

[7] F. W. Loomis and T. F. Watson, Phys. Rev. **45**, 805 (1934).

the system, leading to an incorrect assignment of the system origin, which necessarily gives an incorrect value for ω_e'. The (0,0) band of the formula as given by Butkow and Tschassowenny with origin at 30,280.5 becomes the (6,0) band of the system proposed here with ν_e as 28,336.2. Their formula fits only bands which may be assigned values of v' equal to or greater than 6 in our formula.

Butkow and Tschassowenny represented the bands between 2580A and 3164A by the formula:

$$\nu = 34{,}868.3 + 288.3(v' + \tfrac{1}{2}) - 1.255(v' + \tfrac{1}{2})^2 \\ - 484.5(v'' + \tfrac{1}{2}) + 0.50(v'' + \tfrac{1}{2})^2.$$

At the temperatures used in this investigation SnS vapor is almost opaque to light in the far ultraviolet. No attempt was made to repeat their observations in this region.

Visible system

In the vicinity of 4300A there are three strong bands and six less intense, all degraded toward the red. These bands may be represented by the formula:

$$\nu = 23{,}287.67 + 367.5(v' + \tfrac{1}{2}) \\ - 488.25(v'' + \tfrac{1}{2}) + 1.47(v'' + \tfrac{1}{2})^2.$$

The vibrational assignments of the bands, estimated intensities, and differences between the observed and calculated wave numbers are given in Table III. No bands have been observed which

TABLE III. Bands in visible system.

v' \ v''	0	1	2	3	4	5
0	(10) 23531.89 (+0.09)	(10) 23046.51 (+0.02)	(6) 22563.78 (−0.34)	(1) 22084.34 (−0.35)		
1	(10) 23899.34 (+0.04)		(2) 22931.78 (+0.16)	(4) 22452.38 (+0.19)	(1) 21976.65 (−0.05)	(0) 21501.87 (−0.28)

seem to correspond to values of v' higher than 1. In view of the fact that the (0,2) band is fairly strong, this can be explained only by supposing that the potential curve of the upper state of this system is crossed by a repulsive state just beyond $v' = 1$. The conclusion that there is predissociation is supported by the fact that the rotational

structure of the (1,0) band seems to terminate abruptly about 200 cm^{-1} from the head.

The vibrational assignments of the three strong bands are qualitatively confirmed by the observed isotope structure. The lines of the (0,0) band are sharp and single near the head, but become broader and appear to split into several partially resolved components at a considerable distance from the head. On the other hand, the lines of the (1,0) band are rather diffuse near the head but become sharper toward the tail of the band. The structure of the (0,1) band is quite complex. The displacements of the lines of any isotopic molecule from those of the most abundant molecule may be expressed by the approximation,

$$\nu^i - \nu = (\rho - 1)\nu_v + 2(\rho - 1)\nu_r.$$

The value of $x_e'\omega_e'$ is not known but it is certainly small and the system origin must be in the vicinity of 23,580 cm^{-1}. Hence ν_v and ν_r have opposite signs for the (1,0) band and the same signs for the (0,0) and (0,1) bands. The lines of all isotopes should coincide because of the cancelation of the rotational and vibrational displacements at about 160 cm^{-1} from the head of the (1,0) band. This cancellation does not occur in the (0,0) and (0,1) bands. The lines of the (0,0) band are fairly sharp because of its proximity to the system origin but become broader at increasing distances from the head due to the combined rotational and vibrational displacements.

The rotational analysis of the bands in this system is in progress and will be the subject of a later report.

Grateful acknowledgment is made to Professor Alpheus W. Smith and Dr. R. V. Zumstein for their many helpful suggestions.

Note added in proof: While this paper was in the press Rochester (Proc. Roy. Soc. **A150**, 668 (1935)) also reported on the band spectrum of stannous sulphide. He assigns the origin of the visible system at 23,211.8 cm^{-1} whereas our analysis indicated that it is at about 23,580 cm^{-1}. Our data on these band heads taken from the high dispersion spectrograms are inconsistent with his assignment.