The Spectrum of Tin Hydride at High Pressure

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(Received January 3, 1939)

SnH spectra produced in a d.c. arc in hydrogen at 5 atmospheres pressure are described. Two red-degrading bands in the violet with first heads at 4054A and 4447A together are a $(0,0)^2\Delta\rightarrow{}^2\Pi$ transition with a sharp cut-off at $K'=17$. For the $^2\Pi$ state $B_0=5.31$, $r_0=1.822$A, $A=2182.70$ and $p_0=0.991$. For the $^2\Delta$ state $B_0=4.91$, $r_0=1.848$A, $A=-1.75$ and $\gamma_0=+0.694$. Some details of another band system in the red with principal head at 6095A are given.

AS in the case of the lead arc in hydrogen at several atmospheres pressure,[1] a high pressure tin arc in hydrogen yields new band spectra originating in the diatomic metal hydride molecule. In fact, an arc between tin electrodes in hydrogen at about 5 cm of Hg pressure produces no molecular spectra at all. But with the hydrogen gas at 5 atmospheres pressure we have photographed red-degrading bands in the violet at 4054A and 4447A which together constitute the SnH analog of the $^2\Delta\rightarrow{}^2\Pi$ CH band at 4300A and the SiH band at 4140A.[2] In addition, some bands which are undoubtedly SnH occur in the visible red with principal head at 6095A.

The experimental procedure was much the same as that of the previous investigation.[1] Because of the higher boiling point of tin, both the gas pressure and current were increased (5 atmospheres and 1 ampere, respectively) in order to vaporize a sufficient amount of the metal. Good spectrograms of the violet bands were obtained in the second order of the 21-foot grating, average dispersion 2.47A per mm, in four hours, but double this exposure time failed to yield a complete registration of the band system in the red. Still longer times of exposure and current strength are not possible owing to the intensity of the ever-present continuum arising from the high ion density in the source. If this continuous spectrum is too intense the weaker band lines are obliterated.

The effectiveness of the high gas pressure in producing these SnH spectra probably lies in the more nearly thermodynamic equilibrium then existing among all the possible states of the molecule. Thus the population of the excited states, ordinarily depleted by predissociation into neighboring repulsion states, is maintained at a sufficiently high level. Frequently, however, the probability of the radiationless transitions to repulsion states may be very large, the predissociation may be of the "induced" type, or there may be a complete lack of stable levels. In any of these cases the high pressure would not produce discrete spectra. For example, we find that the $^2\Delta\rightarrow{}^2\Pi$ SnH band produced at 5 atmospheres pressure is sharply cut off at $K'=17$, while the levels of the upper $^2\Sigma$ state of the red PbH spectrum are similarly cut off at a point about $\frac{1}{3}$ volt above $J=0$, $v=0$. Work in this laboratory with an Sb arc at this same high pressure, as well as at reduced pressure of hydrogen, has failed to produce any SbH spectrum.

THE $^2\Delta\rightarrow{}^2\Pi$ SnH BANDS

The violet spectrum of SnH consists of just the two isolated bands with first heads at 4054A and 4447A. Subsidiary stronger heads lie at 4071A and 4466A, respectively, and both bands are only some 90A long. Preliminary analysis showed the shorter wave-length band to have twelve branches while the longer wave-length band has but six. This fact, together with the magnitude of the interval between the bands and the knowledge of expected transition types for SnH indicated that the two constitute the 0,0 band of a $^2\Delta\rightarrow{}^2\Pi$ system. Since the $^2\Pi$ is practically pure case *a*, the levels of the $^2\Pi_{1\frac{1}{2}}$ component should have negligible Λ-doubling while those of the $^2\Pi_{\frac{1}{2}}$ component should have large Λ-doubling. And since the Λ-doubling of Δ-states is always negligible, the $^2\Delta\rightarrow{}^2\Pi_{1\frac{1}{2}}$ sub-band would be expected to

[1] W. W. Watson, Phys. Rev. **54**, 1068 (1938).
[2] C. V. Jackson, Proc. Roy. Soc. **126**, 373 (1930); R. S. Mulliken, Phys. Rev. **37**, 733 (1931).

display but six branches for moderately low J values. The $^2\Delta\rightarrow{}^2\Pi_{\frac{1}{2}}$ sub-band, on the other hand, should have the full complement of twelve branches, with satellite branches about as intense as the main branches. This reasoning indicates at once that the $^2\Pi$ state is regular.

Assignments of all the measured lines based on the usual combination relations are given in Table I. A rather large number of multiple assignments in the head-forming ${}^RQ_{21}$, R_1, Q_2 and ${}^QR_{12}$ branches is necessitated in part by the pressure broadening of all lines. Because of this line breadth we list the wave numbers to just one decimal place. The satellite branches are practically as intense as the main branches, and in all branches there is a sharp drop in intensity as the last $K'=17$ is approached.

The various molecular constants are assembled in Table II. It is highly probable that this band is the 0,0 transition of the $^2\Delta\rightarrow{}^2\Pi$ system. For the $^2\Pi$ state, in view of the case a relation $B^*=B(1\pm 2B/A)$, we may take the mean of the $B_1{}^*$ and $B_2{}^*$ values, 5.31, as the correct value of B_0. The magnitude of the constant $A=2182.7$ cm^{-1} of the $\Lambda\Sigma$ interaction is to be compared with the intervals 1692 and 1736 in the ground ^3P state of SnI. In a $^2\Delta\rightarrow{}^2\Pi$ transition the separations of the pairs of lines such as ${}^SR_{21c}(J)$ and ${}^SR_{21d}(J)$ measure directly the widths of the Λ-doubling. The case a relation that for the $^2\Pi_{\frac{1}{2}}$ terms $\Delta\nu_{dc}=\pm p(J+\frac{1}{2})$ is obeyed since no departure from a linear increase in the doubling with J is noted. The large size of the observed $p_0=0.99$ is not surprising since the A is so large

TABLE I. *Quantum assignments in the* $^2\Delta\rightarrow{}^2\Pi$ SnH *band. d denotes fused lines.*

$J''+\frac{1}{2}$	P_{1dc}	P_{1cd}	Q_{1c}	Q_{1d}	R_{1dc}	R_{1cd}	${}^QP_{21c}$	${}^QP_{21d}$	${}^RQ_{21dc}$
1									
2									24544.8*d*
3							24516.5*d*	24520.5*d*	47.0*d*
4							10.3*d*		49.1*d*
5			24502.1		24552.0*d*	24556.4*d*	01.4	06.9*d*	49.3*d*
6			493.1		52.0*d*	58.3*d*	490.4*d*	496.8	49.1*d*
7	24424.3	24431.3	83.0	24490.4*d*	52.0*d*	58.3*d*	79.9*d*	86.8	47.0*d*
8	03.6	10.7*d*	72.1	79.9*d*	50.0*d*	58.3*d*	67.9	75.8	44.8*d*
9	382.0	391.0	60.3	69.2	47.0*d*	56.4*d*	55.0	64.0	41.8*d*
10	59.8*d*	69.9	47.2	57.2	44.3*d*	54.6*d*	41.2	51.1	36.8*d*
11	36.5*d*	47.2	33.1	43.9	38.8	49.1*d*	26.5	37.3	31.6
12	12.2	23.9	18.0	29.7	32.7	44.3	10.7	22.4	24.7*d*
13	286.6	299.5	01.6	14.2	24.7*d*	36.8*d*	393.5	06.1	16.5
14	60.0	73.6	383.7	397.3	16.5*d*	29.2*d*	75.2	388.7	06.9
15	32.1	46.8	63.5	78.8	05.0	20.5*d*	55.4	69.9	495.8
16	02.9	18.3	43.3	58.6			34.1	49.5	83.0*d*
17	171.7	188.3	20.5	36.5*d*	477.2*d*		12.2*d*	27.2	69.2*d*
18	39.1	56.4	295.4	12.2			286.6*d*	03.5	
19	03.9		68.8					277.5	

$J''+\frac{1}{2}$	${}^RQ_{21cd}$	${}^SR_{21c}$	${}^SR_{21d}$	${}^OP_{12}$	P_2	${}^PQ_{12}$	Q_2	${}^QR_{12}$	R_2
1		24563.7	24564.8						
2	24547.0*d*	75.4	77.5				22376.2*d*	22376.2*d*	22407.1
3	50.0*d*	86.8	89.8			22350.7	80.4*d*	80.4*d*	19.7
4	52.7*d*	97.5	601.7	22312.8	22343.6*d*	43.6*d*	82.6*d*	83.2*d*	30.6
5	54.6*d*	607.4	12.3	295.5	34.3*d*	35.4	82.6*d*	85.1*d*	40.6
6	54.6*d*	16.3	22.3	77.1	24.2	26.3	82.6*d*	85.1*d*	49.9
7	54.6*d*	24.4	31.5*d*	57.3	12.8	16.2	80.4*d*	85.1*d*	57.5
8	52.7*d*	31.5*d*	39.3*d*	36.6	00.7	05.0*d*	77.4	83.2*d*	64.5
9	50.0*d*	37.3	46.0*d*	15.0	287.8	292.9	74.2	80.4*d*	70.3
10	47.0*d*	42.0	52.1	192.3	73.6	79.7	69.5	76.2	74.5
11	41.8*d*	46.0*d*	56.4	68.2	58.6	65.2	63.8*d*	70.8*d*	77.5*d*
12	36.8*d*	47.8*d*	59.6	43.5	42.1	49.5	55.9*d*	63.8*d*	79.1*d*
13	29.2	47.8*d*	60.9	17.8	24.4	32.4	47.2	55.9*d*	79.1*d*
14	20.5	47.8*d*	60.9		05.3	13.9	37.0	45.9	77.5*d*
15	10.3	44.1	58.7		184.9	193.8	25.1	34.3	73.7
16	498.5*d*	39.3*d*	54.7		62.8	71.8	11.3	20.5	68.2
17	84.2*d*				38.9	48.0	295.5*d*	05.0	
18					13.2	22.5			

and the existence of something like "pure precession" interaction with other states coming from the same electron configuration is probable.

There is some difficulty in the calculation of the constants of the terms of the $^2\Delta$-state. The combination differences show that the state is inverted with the spin doubling small in magnitude, and increasing roughly linearly with K at the lower K values but at a rapidly decreasing rate as the final $K'=17$ is approached. We therefore first apply the case b doublet separation relation[3] $\Delta f(K)=[A\Lambda^2/K(K+1)+\gamma](K+\frac{1}{2})$ to the spin doublet intervals for $K<12$. This yields mean values $A=-1.75$ for the LS coupling and $\gamma=+0.694$ for the SK coupling. Corrections $-2A(1/(K+2)-1/K)-\gamma$ and $+2A(1/(K+1)-1/(K-1))+\gamma$ are then applied to the $\Delta_2F_1'(J)$ and $\Delta_2F_2'(J)$ combination differences, respectively, after which the simple, strictly case b relations are used. This yields $B_0'=4.911$ and $D'=-5.0\times10^{-4}$. The rather sudden change in the rate of increase of the spin-doublet widths near the sharp cut-off points in the band branches could arise from the interaction with the neighboring electronic state.

TABLE II. *Constants of the energy terms for* SnH (*cm^{-1} units*).

CONSTANT	$^2\Pi$	$^2\Delta$
B_1*	5.293	
B_2*	5.331	
B_0	5.31	4.911
r_0	1.822A	1.848A
D_0	-1.94×10^{-4}	-5.0×10^{-4}
A	2182.70	-1.75
γ_0		$+0.694$
p_0	0.991	

[3] R. S. Mulliken, Rev. Mod. Phys. **2**, 60 (1930).

THE RED SnH SYSTEM

Study of the incomplete data on these bands leads to a few definite conclusions. They are not similar to the PbH bands[1] in this same spectral region. Whereas the latter possess four branches with very large second differences between successive lines in a branch, indicative of a large change in the moment of inertia of the molecule in the transition, these SnH bands have more than four branches and with small second differences. Associated with the strongest (Q) head at 6095A are subsidiary heads at 6022A and 6063A which seem to belong to $^SR_{21}$ and R branches, respectively. Since the R branch is considerably less intense than the P branch, the transition may be either $\Sigma\rightarrow\Pi$ or $\Pi\rightarrow\Delta$. A second weaker band is present with principal head at 6214A.

No combination differences common with those of the violet SnH bands can be found. Probable combinations that have been tabulated indicate $B''\sim5.5$, a reasonable value for SnH. But since there is apparently no electronic state common to these two band systems, we believe that the analysis should not be presented until it is more complete and checked by the comparison of internal combination differences. The difficulties in the obtaining of better experimental data have been already mentioned.