The Absorption Spectra of CdF and SnCl

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(Received May 21, 1942)

Cadmium fluoride, vaporized in an electric furnace, shows no absorption in the region λλ1950–7000 at temperatures below 1350°C, but above this temperature a band system of CdF appears at λλ2716–2924. Strong continuous absorption is observed at higher temperatures. The spectrum of SnCl is photographed in absorption for the first time. The spectrum consists of the two band systems observed in emission, a new system in the farther ultraviolet, and two continua. Its similarity to the absorption spectrum of the homologous molecule SnF is discussed.

I. CdF

PEARSE and Gaydon have shown[1] that the only spectrum previously attributed to CdF was actually due to the presence of CaF as an impurity. They have listed six other bands between λ2819 and λ3005 as possibly due to CdF inasmuch as they could not be traced to any known impurity, but have hesitated to attribute them definitely to this molecule because of their weakness and general behavior. Since those investigations were carried out in arc emission, it was thought that an attempt to observe the spectrum in absorption might give less ambiguous results.

The absorbing vapor was produced by heating a small amount (∼10 g) of CdF_2 in a carbon-tube furnace previously described.[2] The spectral region λλ1950–7000 was surveyed under low dispersion and regions showing band structure were photographed in the first order of the 30,000 lines-per-inch, 21-foot concave grating with average dispersion of 1.3A/mm. The experimental technique has been fully described in a previous article.[3]

At the lower furnace temperatures no bands were observed but at about 1350°C some narrow regions of absorption around λ2800 appeared. With the vapor at 1600° the bands were quite strong (Fig. 1), but at higher temperatures continuous absorption, coming in from shorter wave-lengths, began to cover up the region. High dispersion spectrograms revealed six bands shaded to the red and spaced almost equally,

their intensities decreasing from band to band in the direction of shorter wave-lengths. Although the first two bands of longest wave-length are the strongest of the system, they have very diffuse heads. The third has a fairly definite head while those of the fourth, fifth, and sixth are of increasing sharpness. Each of the third, fourth, and fifth bands has a weak satellite associated with the strong head. A narrow continuum with its maximum at λ2824 and a group of three closely spaced heads apparently not belonging to the principal system constitute the remaining features of the spectrum. Measured wave-lengths of the heads and the corresponding wave numbers in vacuum are given in Table I together with an assignment of probable values for $v' - v''$. The individual quantum numbers cannot be assigned with certainty because only a single progression is observed, the higher members of each sequence being covered by the first member. The values of $v' - v''$ in Table I are the most probable when one considers the great likelihood of a v' progression in absorption, despite the fact that the trend of
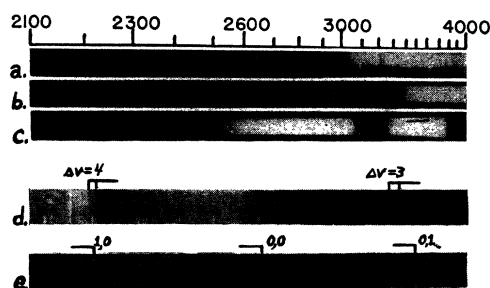

Fig. 1. Low dispersion absorption spectra of (a) CdF, (b) SnCl with the vapor density high, (c) SnCl with the vapor density low. High dispersion spectrograms of (d) part of the CdF band system and (e) the lower energy component of the $C^2\Pi$, $X^2\Pi$ system of SnCl.

[1] R. W. B. Pearse and A. G. Gaydon, Proc. Roy. Soc. 50, 711 (1938).
[2] F. A. Jenkins and G. D. Rochester, Phys. Rev. 52, 1135 (1937).
[3] C. A. Fowler, Jr., Phys. Rev. 59, 645 (1941).

TABLE I. Band heads of CdF.

$v'-v''$	λ	ν	ΔG
0	2923.5 A	34196 cm^{-1}	
			509 cm^{-1}
1	2880.6	34705	
			514
2	2838.5	35219	
			522
3	2797.1	35741	
			529
4	2756.3	36270	
			535
5	2716.2	36805	
Satellite heads			
2	2837.2	35236	
			519
3	2796.0	35755	
			526
4	2755.5	36281	
Unclassified heads			
—	2788.2	35855	
			22
—	2786.5	35877	
			20
—	2784.9	35897	

the first differences indicates otherwise. Such a trend of the differences is possible, however, if the rotational and vibrational constants have certain, nearly equal values in the two electronic states involved in the transition.

A visual inspection shows that the over-all extent of each band is not large and that the rotational structure is unresolved except near the tail of the band, indicating a very small value for $B'-B''$, so that the band heads are formed at high J values and at considerable distances from the band origins. Furthermore, the distance between each band head and its origin will decrease rapidly with increasing v'. Therefore, although the first differences of the origin wave numbers will decrease with v', the first differences of the band heads may increase. Two features of the CdF bands support this assumption. The low (long wave-length) members of the progression whose heads should be formed at very high values of J show an almost headless nature, while the heads of the higher members are increasingly sharp. Furthermore, the third, fourth, and fifth bands possess satellite heads of increasing sharpness, which would not be expected in the lower members owing to the high J values at such

heads. The diffuseness and lack of resolution is increased by the approximate superposition of the many bands of each sequence, superimposed because of the near equality of ω_e' and ω_e''. It is evident from the foregoing that all of the $v'-v''$ might well have values less by one than those given in Table I.

The vibrational constants cannot be accurately determined because only one progression of heads is measurable. Moreover, the first differences are poor representations of the $\Delta G(v+\frac{1}{2})$ when B' and B'' are nearly equal. The data indicate that ω_e' and ω_e'' are almost equal and somewhat greater than 535 cm^{-1}. A comparison of the normal state vibration frequencies of CdCl (330.5 cm^{-1}), CdBr (230.0 cm^{-1}), and CdI (178.5 cm^{-1}) with those of the various alkaline earth halides[4] reveals strikingly similar trends, and predicts for CdF a vibration frequency of about 540 cm^{-1}. Such a comparison also predicts for ZnF a normal state vibration frequency of about 630 cm^{-1}, in close agreement with the 620 cm^{-1} reported by Rochester and Olsson.[5]

No other bands were observed between λ1950 and λ7000. It is to be noted that although they lie in the same general region, there is no correlation in wave-lengths or first differences between these bands and those of Pearse and Gaydon.

II. SnCl

The spectrum of SnCl has been observed only in emission where it shows two band systems, a $^2\Delta$, $^2\Pi$ system[6] at $\lambda\lambda$3486–3910 and a $^2\Sigma$, $^2\Pi$ system[7] in the region $\lambda\lambda$2830–3405. The $^2\Pi$ level, with doublet separation of 2360 cm^{-1}, is common to both systems and is assumed to be the normal state. The occurrence of a $^2\Pi$ lower state in the absorption spectrum of the SnF molecule[2] implies the same type of normal state for all of the halides of Si, Ge, Sn, and Pb.

This investigation was undertaken to test the possibility of observing any shorter wave-length band systems analogous to those of SnF by observing the spectrum in absorption.

[4] G. Herzberg, Molecular Spectra and Molecular Structure, I (Prentice-Hall, 1939), pp. 483–494.
[5] G. D. Rochester and E. Olsson, Zeits. f. Physik 114, 495 (1939).
[6] W. F. C. Ferguson, Phys. Rev. 32, 607 (1929).
[7] W. Jevons, Proc. Roy. Soc. A110, 365 (1926).

With furnace temperatures ranging from below the boiling point of $SnCl_2$ (605°C) to 1000°C a weak, general absorption due to $SnCl_2$ was observed, but only by superheating the vapor to higher temperatures did the bands and continua characteristic of SnCl become evident. At 1200°C the higher energy component of the $B^2\Sigma \leftarrow X^2\Pi$ system is of considerable intensity, but the lower energy component is hidden by a strong, sharply defined continuum covering the region $\lambda\lambda 3000$–3500. A second continuum extends from $\lambda 2500$ to the ultraviolet limit of observation at $\lambda 1950$. At these temperatures the salt was quickly vaporized, and the vapor density slowly decreased by diffusion from the carbon tube. The rate of this diffusion can be governed by regulating the temperature, and a series of low dispersion spectrograms showed that the continua decrease in extent as time goes on. At one stage the more refrangible component of the $A^2\Delta \leftarrow X^2\Pi$ system ($\lambda 3488$) could be observed under the edge of the weakening continuum. In the same manner the short wave-length continuum in retreating to the ultraviolet revealed a new band system at $\lambda\lambda 2250$–2450 consisting of a number of heads shaded to the ultraviolet (Fig. 1).

High dispersion plates of this system were taken with a furnace temperature of 1300°C and were exposed only during a predetermined 15-minute interval for which the vapor density was suitable for the bands to appear. The heads of the system fall readily into two groups, three faint bands at $\lambda\lambda 2436$, 2416, 2393 and six stronger ones between $\lambda 2249$ and $\lambda 2326$. These constitute the two components of a doublet system, the heads of the higher energy component being represented by the equation

$$\nu = 43656.1 + 392.8u' - 1.40u'^2 - 352.8u'' + 1.00u''^2.$$

TABLE II. Wave-lengths and intensities of the band heads of the $C \leftarrow X$ system of SnCl.

v', v''	λ	I	v', v''	λ	I
2,0	2248.86	8	0,1	2307.42	5
1,0	2268.62	10		2436.38	0
	2393.08	1	0,2	2326.16	2
0,0	2288.88	9	1,3	2323.80	3
	2415.67	1			

The observed wave-lengths and the estimated intensities are given in Table II.

A difference of 2292.2 cm^{-1} exists between the two 0,0 heads. Inasmuch as the $^2\Pi$ normal state has a separation of 2360.1 cm^{-1}, the new upper state must also be double, i.e., $^2\Pi$ or $^2\Delta$, since a $^2\Sigma$ upper level would produce two sub-bands whose separation equals the lower state interval. In both $^2\Pi$, $^2\Pi$ and $^2\Delta$, $^2\Pi$ transitions only two sub-bands are expected because of the selection rules, and the wave number difference must be the difference (or the sum) of the doublet separations of the two levels involved. Hence the new upper state is a doublet with a separation of 67.9 cm^{-1}. That the heads are apparently single implies that the upper state is $^2\Pi$, but this is not conclusive because of the low intensity of the bands.

The intensity ratio of the two sub-bands depends upon the temperature of the vapor and the splitting of the normal state if a Boltzmann distribution is assumed, and is given by $e^{-E/kT} = \frac{1}{9}$ for the temperature of 1300°C. This agrees well with a visual estimate of the 0,0 bands. Comparison of the intensities of the two sub-bands is very difficult, however, because of a rapid fall of background intensity toward shorter wave-lengths. This is an inherent characteristic of the H_2 continuum used as the source, and is here accentuated by a partially overlying absorption continuum.

The analogy between the electronic states of SnCl and SnF is quite obvious. Both possess $^2\Pi$ normal states. The $A^2\Delta$ and $B^2\Sigma$ states of SnCl correspond to the $B^2\Delta$ and $A^2\Sigma$ states, respectively, of SnF as pointed out by Jenkins and Rochester,[2] while the new state of SnCl is probably $^2\Pi$ corresponding to the $C^2\Pi$ state of the fluoride. Failure to observe the D state can be attributed to the strong overlying continuum. The two continua, because of their close association with the band systems, must be attributed to SnCl. They indicate the existence of the repulsive states E and F, and these, like the stable excited states, have somewhat smaller energies than their SnF analogues.
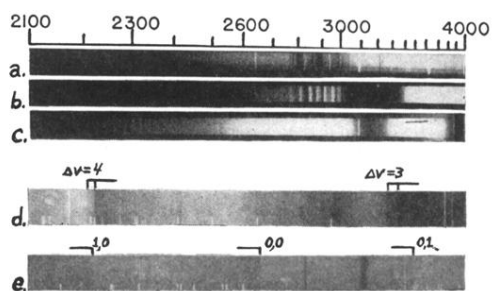
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