

THE BAND SPECTRUM OF CADMIUM CHLORIDE

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(PLATE IX)

ABSTRACT. The spectrum of CdCl as excited by a H. F. oscillator is investigated from the red down to $\lambda 1850$. The Cornich system between $\lambda\lambda 2240-2181$ has been extended, altogether 19 bands being recorded. These are arranged into four v' progressions which enabled the determination of the vibrational constants chiefly of the upper state. The constants are

$$\begin{array}{lll} \omega' = 2040 & & A'\omega' = 7.5 \\ \nu_e = 45398.2 & & \\ \omega'' = 330.9 & & A''\omega'' = 1.0 \end{array}$$

The peculiar appearance of the bands is interpreted as due to the predissociation in the upper state at some high rotational level of $v' = 2$.

There is no evidence, in emission, of the bands recorded by Walter and Barratt in absorption in the region $\lambda\lambda 3181-3018$. A new emission system is observed in the visible region consisting of 23 red-degraded bands from $1800\text{\AA}-4000\text{\AA}$, some of these bands indicated a rotational structure even under small dispersion.

INTRODUCTION

Wieland (1929) was the first to investigate the band spectrum of cadmium chloride in the course of his extensive study of the halides of zinc, cadmium and mercury, as excited by a high frequency oscillator. While the halides of mercury were found to give several systems, Wieland reported a comparatively fewer systems for the halides of zinc and cadmium. For cadmium chloride he had only mentioned the existence of two groups of bands, (1) between $\lambda 6400-3300$ which are diffuse and red degraded; (2) an overlapping group between $\lambda 3400-3300$ which are sharp and violet degraded. Walter and Barratt (1929) photographed the absorption spectra associated with Zn, Cd and Hg, in the near ultra-violet and reported three groups of bands which might possibly be ascribed to Cd+Cl, (1) $\lambda 3181$ to $\lambda 3135$ (2) $\lambda 3101$ to $\lambda 3077$ (3) $\lambda 3074$ to 3018 ; altogether twenty seven band heads were measured. The data were in agreement with the earlier observation by Mohler and Moore (1927). Oeser (1935) made a more systematic work, specially on the absorption and fluorescence spectra of the halides of zinc and cadmium, and confirmed the assignment of bands in the region 3181\AA to 3018\AA to the cadmium chloride molecule. He also gave measurements of twelve absorption bands in the far ultra-violet between $\lambda 2163-\lambda 1774$. The wavenumber

interval between these bands was shown to increase successively from 850 cm^{-1} to about 1000 cm^{-1} . Cornell (1938) got the ultra-violet band spectra of the chlorides of zinc, cadmium and mercury, excited by a high frequency power oscillator. In CdCl, he reported a brief system consisting of seven red degraded bands between $\lambda_{2240}-\lambda_{2185}$ and arranged them into two progressions with $v'=0$ and $v'=1$. The constants for the lower state were estimated as $\omega''_1 = 330.5 \text{ cm}^{-1}$ and $v''_1 \omega''_1 = 1.2 \text{ cm}^{-1}$, but those for the upper state could not be calculated as no bands were observed involving $v' > 1$. Isotopic components were measured for the (0, 1) and (1, 2) bands and shown to occur in the expected positions. In an attempt to systematise the band systems of zinc, cadmium and mercury halides, Howell (1943) arranged the Walter and Barratt's three groups of bands of cadmium chloride ($\lambda\lambda_{3181}-3080$) into a doublet system represented by the transition ${}^2\Pi \rightarrow {}^2\Sigma$ with a ${}^2\Pi$ interval of 1115 cm^{-1} which is in agreement with the predicted value of 1140 cm^{-1} . The constants for the lower ${}^2\Sigma$ state of this system are in fair agreement with those of the lower state of the Cornell system.

Summarising our present knowledge of the band spectrum of the CdCl molecule, the following systems may be stated to have been definitely established:

	Region	Transition	Occurrence
1. Cornell System	$\lambda\lambda_{2240}-2181$	${}^2\Sigma \rightarrow {}^2\Sigma$	in emission only
2. Howell System	$\lambda\lambda_{3181}-3083$	${}^2\Pi \rightarrow {}^2\Sigma$	in absorption only

In the course of a series of investigations on the spectra of the halides of Group II-*b* elements, Zn, Cd, and Hg, the emission spectrum of cadmium chloride was studied by the author from the visible region down to $\lambda 1850$, as a result of which the Cornell system, mentioned above, could be much extended. Also the visible bands, the existence of which was just reported by Wieland, could be photographed and measured. The purpose of the present paper is to record these observations.

EXPERIMENTAL

The spectrum of cadmium chloride is excited in a Pyrex tube with external electrodes by means of a H. F. oscillator described by the author (Ramasastry, 1947). Strong heating with an etna burner was found necessary between and beyond the electrodes. No trace of N_2 or NO bands is observed when fresh crystalline salt is heated in the tube though the OH bands are invariably present (Plate X-*a*). But, if fused salt is reheated N_2 and NO bands do predominate (Plate X-*b*).

The dispersing instruments employed are the Hilger constant deviation, small and medium-quartz spectrographs. Ilford Selo-Chrome plates, sensitised with mobil oil (Ramasastry and Rao, 1947), are used to record the spectrum in the ultraviolet,

TABLE I

Wavelength	Int.	Wavenumber (Author)	Wavenumber (Cornell)	Classification	Obs.-Cal.
2191.85	4	45609.3	45609.9	1,0	-2.8
2196.15	2	45519.0	...	2,1	+1.8
2201.80	1	45403.2	...	3,2	-6.0
2205.05	10	45366.8	45363.4	0,0	+3.7
2207.40	8	45287.4	45282.9	1,1	+4.2
2212.07	2	45190.5	...	2,2	+0.3
2217.50	1	45081.8	...	3,3	-2.5
2219.90	6	45033.7	45033.9	0,1	-0.5
2223.55	5	44959.4	44959.3	1,2	+1.2
2228.05	2	44868.3	..	2,3	+1.0
2233.36	1	44761.3	..	3,1	-0.1
2236.07	4	44706.8	44708.0	0,2	-0.4
2239.90	5	44630.2	44632.8	1,3	-1.1
2243.90	1	44541.6	...	2,4	-0.8
2249.20	0	44440.8	...	3,5	+6.2
2252.45	1	44282.5	...	0,3	+0.2
2256.30	2	44306.1	...	1,4	-3.1
2260.80	0	44217.2	...	2,5	-4.3
2272.75	0	43985.0	...	1,5	-2.5

TABLE II

...	0	1	2	3	4	5
0	10	6	4	1		
1	4	8	5	5	2	0
2		2	2	2	1	0
3			1	1	1	1

TABLE III *

(v', v'')	ν	Obs. shift	Calc. shift
0, 1)	45033.7	7.5	7.6
1, 2)	44959.4	0.1	9.4
(0, 2)	44706.8	15.0	14.3
1, 3)	44630.2	15.0	17.1

RESULTS

Cornell System.—As many as 19 bands are measured in this system, reproduced in Plate X(a) obtained with Hilger small quartz instrument of

* The large difference in the (1, 3) band may be due to overlapping by NO bands.

dispersion $14\text{\AA}/\text{mm}$ at λ_{2200} . The wavelength, intensity, wavenumber data and classification of the bands are given in Table I together with Cornell's values. The spectrum taken with the larger Hilger instrument (Plate X-b), clearly showed the isotopic components of $(0, 2)$, $(1; 3)$ bands, in addition to those of $(0, 1)$ and $(1, 2)$ measured by Cornell.

Table II gives the vibrational analysis of the bands (each band is represented by its intensity) which is an extension of the Cornell's scheme.

The new data enabled the determination of the vibrational constants of the upper state as well, which could not be obtained by Cornell. The constants are:

$$\begin{array}{ll} \omega_e' = 261.0 & x_e' \omega_e' = 7.5 \\ \nu_e = 45398.2 & \\ \omega_e'' = 330.9 & x_e'' \omega_e'' = 1.0 \end{array}$$

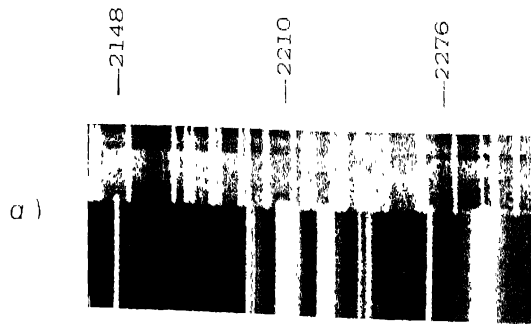
Table III gives the observed and calculated isotope shifts for the different bands. The agreement confirms the vibrational assignments.

Failure to observe progressions of these bands with $v' > 1$ led Cornell to suggest the occurrence of predissociation in the upper state for vibrational level of higher quantum numbers. In order to examine this feature clearly, the author has taken a number of exposures. Although there are bands involving higher quantum numbers, still the system exhibits a peculiar appearance. The heads, forming the progressions $v'=0$ and $v'=1$, are clearly red-degraded but the extent of shading off, i.e., the extent of rotational structure, diminishes very rapidly so that the bands with $v'=2$ are narrow and those with $v'=3$ are line-like and very faint. This might, in all probability, be accounted for by the occurrence of predissociation strongly in the upper state starting at 3 stage corresponding to some high rotational level associated with $v'=2$.

Howell System.—This system is not observed in emission by the author; Cornell made no mention of it. It was observed only in absorption. Howell analysed it as due to ${}^2\Pi - {}^2\Sigma$ electronic transition, on the analogy of the other halides of Hg, and Cd. The sharp and violet-degraded emission bands, briefly referred to by Wieland, could not be detected, even when special precaution was taken to avoid the OH bands in this region by keeping phosphorous pentoxide in a side bulb of the evacuated discharge tube for two days.

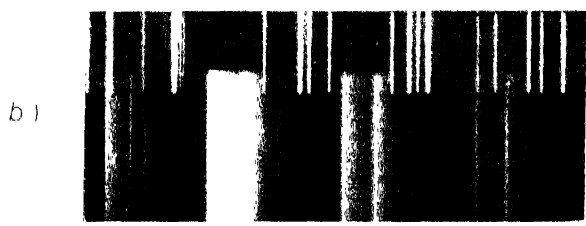
Visible Bands.—Examination of the spectrum in the visible region revealed another system between $\lambda_{4770} - \lambda_{4050}$ which does not appear to have been recorded by any of the previous investigators except Wieland, who made but a mere mention of it. About 23 bands are listed in all, of which only 14 could be measured from the constant deviation spectrograph, the rest being from pictures taken with small quartz instrument. Even under the small dispersion of the constant deviation the rotational structure of the more refrangible bands could be observed. Some are double headed probably due to the chlorine isotopes. Approximate measurements of the band heads are given in Table IV. The interval between alternate bands is only about

C_D C_L emission bands.



(0.1) —
(0.2) —
(1.0) —
(5.0) —
(10) —

—2210 —2225 —2244



(c)

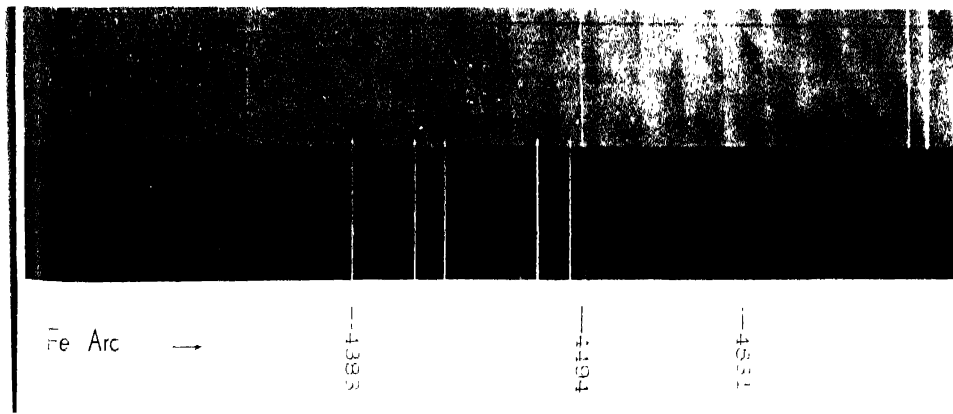


TABLE IV

Wavelength	Int.	Wavenumber	Wavelength	Int.	Wavenumber
4058	0	24636	4395.6	4	22744
4081	1	24497	4425.9	5	22588
4104	1	24360	4455.0	5	22440
4131	1	24200	4483.5	6	22298
4152	1	24078	4514.5	6	22145
4176	1	23940	4542.5	7	22008
4213	1	23729	4572.1	6	21866
4233	1	23617	4605.7	4	21706
4311.3	1	23188	4638.2	4	21554
4323.2	2	23125	4735.3	2	21112
4338.4	3	23044	4769.8	2	20959
4367.8	4	22888

300 cm, whereas the frequency of the ground state of the CdCl molecule is 330.9 cm. A second group of bands in the visible can also be clearly observed between $\lambda 6400 - \lambda 5400$ in a high dispersion spectrogram (15 Δ per mm.). There are altogether about fifteen bands; they are red degraded and diffuse but not measurable. Further work on these visible bands, chiefly to study their rotational structure, is in progress.

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