

TABLE IV. Lines reported in the palladium I spectrum.

WAVE-LENGTH	TRANSITION	STRUCTURE	WAVE-LENGTH	TRANSITION	STRUCTURE
3894.18	$5s^1D_2 - 5p^3D_3^0$	Single	3433.44	$5s^1D_2 - 5p^1P_1^0$	Single
3799.16	$5s^3D_2 - 5p^3P_2^0$	"	3421.24	$5s^3D_2 - 5p^3D_2^0$	"
3718.91	$5s^3D_1 - 5p^3P_2^0$	Broadened	3404.60	$5s^3D_2 - 5p^3F_4^0$	Broadened
3690.34	$5s^1D_2 - 5p^3F_2^0$	Single	3373.02	$5s^3D_2 - 5p^3D_3^0$	Single
3634.70	$5s^3D_3 - 5p^3P_2^0$	Broadened	3302.15	$5s^3D_1 - 5p^3D_1^0$	"
3609.56 -	$5s^3D_2 - 5p^3F_2^0$	Single	3287.26	$5s^3D_3 - 5p^3D_2^0$	"
3571.16	$5s^3D_1 - 5p^3P_2^0$	"	3258.78	$5s^3D_1 - 5p^1D_2^0$	"
3553.10	$5s^1D_2 - 5p^1F_2^0$	"	3251.64	$5s^3D_1 - 5p^1P_1^0$	"
3516.95	$5s^3D_2 - 5p^3P_1^0$	"	3242.71	$5s^3D_3 - 5p^3D_3^0$	Broadened
3489.79	$5s^1D_2 - 5p^3D_1^0$	"	3114.05	$5s^3D_2 - 5p^1F_3^0$	Single
3481.17	$5s^3D_1 - 5p^3F_2^0$	"	3065.31	$5s^3D_2 - 5p^3D_1^0$	"
3460.76	$5s^3D_3 - 5p^3F_3^0$	"	3027.92	$5s^3D_2 - 5p^1D_2^0$	"
3441.40	$5s^1D_2 - 5p^1D_2^0$	"	2763.08	$a^1S_0 - 5p^3P_1^0$	"

the iron lines were excited when the current was large. One might expect that such lines would be sharper when excited in the Schuler tube than when excited in the ordinary arc. We photographed and examined about 190 of them, but found no structure. The half-breadth of two of

the stronger unreversed lines was about 0.11 cm^{-1} , which, if the broadening is due to the Doppler effect, would correspond to a temperature of about 1200°C .

This research was financed in part by a grant from the National Research Council.

SEPTEMBER 1, 1938

PHYSICAL REVIEW

VOLUME 54

Ultraviolet Band Spectra of HgCl, CdCl, and ZnCl*

S. D. CORNELL

Sloane Physics Laboratory, Yale University, New Haven, Connecticut

(Received June 29, 1938)

The spectra of the chlorides of mercury, cadmium, and zinc, excited in a high frequency discharge, are examined at high dispersion in the region 3200–2000A. Vibrational analyses of several systems are presented. Included is a discussion of the electronic configurations involved in the systems analyzed.

INTRODUCTION

THE most extensive spectroscopic work on the halides of mercury, cadmium, and zinc appears to be that of Wieland^{1,2} in which he explored the wave-length region between 7000A and 2200A. This work was done in emission, a Geissler tube discharge serving as source, and at a relatively low dispersion, 10A per millimeter at best. A number of band systems were found; those of interest to the present discussion are as follows: for mercury chloride, a system between 2650A and 2400A, degraded to the violet, ascribed to HgCl, and a system from 2900A to 2700A, likewise degraded to the violet, but

ascribed to HgCl₂; for cadmium chloride, nothing in the region of the present investigation; for zinc chloride, a system between 3100A and 2900A, degraded to the violet, and tentatively ascribed to ZnCl, although the author expresses some doubt concerning its true origin.

Of these systems, only the shorter wave-length one of HgCl appears well developed and for this system Wieland presents an extensive vibrational analysis. Detailed analyses are made for none of the other systems, although in a later paper³ Wieland mentions the "poorly established" fundamental frequency of 290 cm^{-1} for the 2900A–2700A system.

Walter and Barratt,⁴ working in absorption, at very low dispersion, list ten heads between 3000A

* Part of a dissertation presented to the faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

¹ K. Wieland, *Helv. Phys. Acta* **2**, 46 (1929).

² K. Wieland, *Helv. Phys. Acta* **2**, 77 (1929).

³ K. Wieland, *Zeits. f. Physik* **77**, 157 (1932).

⁴ J. M. Walter and S. Barratt, *Proc. Roy. Soc.* **122**, 201 (1929).

and 2900A which they attribute to "Zn+Cl." Nothing further is done with this system, but it is probably part of the system observed by Wieland in this region. In addition, a system between 3180A and 3018A ascribed to a chloride of cadmium is mentioned, but no further work was done on it.

More recently, Oeser⁵ has reported this same 3180A to 3018A system as due to CdCl₂, and has mentioned the absence of absorption and fluorescence spectra of ZnCl₂ in both visible and ultraviolet regions.

In the present work the spectra of the chlorides of mercury, cadmium, and zinc have been investigated in the ultraviolet between about 3200A and 2000A. We have the advantages of very high dispersion.

EXPERIMENTAL

The spectra were excited by means of a high frequency power oscillator, of the tuned grid, tuned plate type described by Sloan, Thornton, and Jenkins.⁶ The discharge tube was of vitreous silica, 12 inches in length and of $\frac{1}{2}$ inch bore, with external electrodes. Tapers were ground on the ends of the tube, one to receive the pump line, the other to receive a 5-inch glass tube of $1\frac{1}{4}$ inch diameter, narrowed at one end to fit the discharge tube, and ground flat at the other end to carry a quartz window. The tapered joints between discharge tube and glass fittings were waxed and water cooled.

In each case, the bichloride of maximum obtainable commercial purity was used. A small quantity of it was dried out in an evaporating dish and introduced into the discharge tube, which was then pumped out. It was found that in general favorable discharge conditions could be maintained by keeping a Meeker burner constantly playing on the tube, and pumping on the system continuously with a Hyvac pump.

The aluminized 30,000 lines per inch 21-foot grating in an Eagle mounting was used, which gave a dispersion of 1.27A per millimeter in the first order. Exposure times were of the order of two hours, and during this time replenishment of the material in the discharge tube was in general

necessary only once. Iron and copper arc lines were used for comparison purposes. Eastman type II-O plates were used throughout, sensitized with the usual ultraviolet sensitizer for wavelengths shorter than 2350A.

One exposure was made with zinc metal alone; for this purpose small strips of zinc were placed along the discharge tube, and the above technique then employed. Several exposures were made with the normal incidence 10-foot vacuum spectrograph on mercury chloride in the vacuum region. For these exposures, a metal cap with a hole carrying a small fluorite window was waxed over the slit-tube of the spectrograph, and the glass fitting of one end of the discharge tube was in turn waxed onto this metal cap. Ilford Q-plates were used in this region, and again exposures of roughly two hours were made.

For mercury chloride, the two systems reported by Wieland¹ were photographed at the present high dispersion, and remeasured. Wieland did little with the 2900–2700A system, which will be discussed below. A single brief CdCl system was found between 2240A and 2185A. For ZnCl a fragmentary system was photographed, at 2980–2905A. This evidently corresponds to the observations of Walter and Barratt.⁴ Another emission region between 2095A and 2075A was observed.

Impurity spectra, in particular those of OH and N₂, were present on most of the plates. These came about as a result of the often troublesome property of a high frequency discharge which causes excitation of the spectra of vapors present at very low pressures. These impurities, however, in general caused little trouble, and extended efforts to eliminate them were not made. In the case of the longer wavelength ZnCl system, the entire region is overlaid by the $\Delta v = -2$ sequence of the second positive system of N₂, but these impurity lines were easily compared with those on a plate showing N₂ alone, and eliminated.

HgCl

It was deemed of value to remeasure the 2650–2400A HgCl system, shown in Fig. 1(a), because of the greatly increased dispersion in the present work as compared with that of

⁵ E. Oeser, *Zeits. f. Physik* **95**, 699 (1935).

⁶ D. H. Sloan, R. L. Thornton, and F. A. Jenkins, *Rev. Sci. Inst.* **6**, 75 (1935).

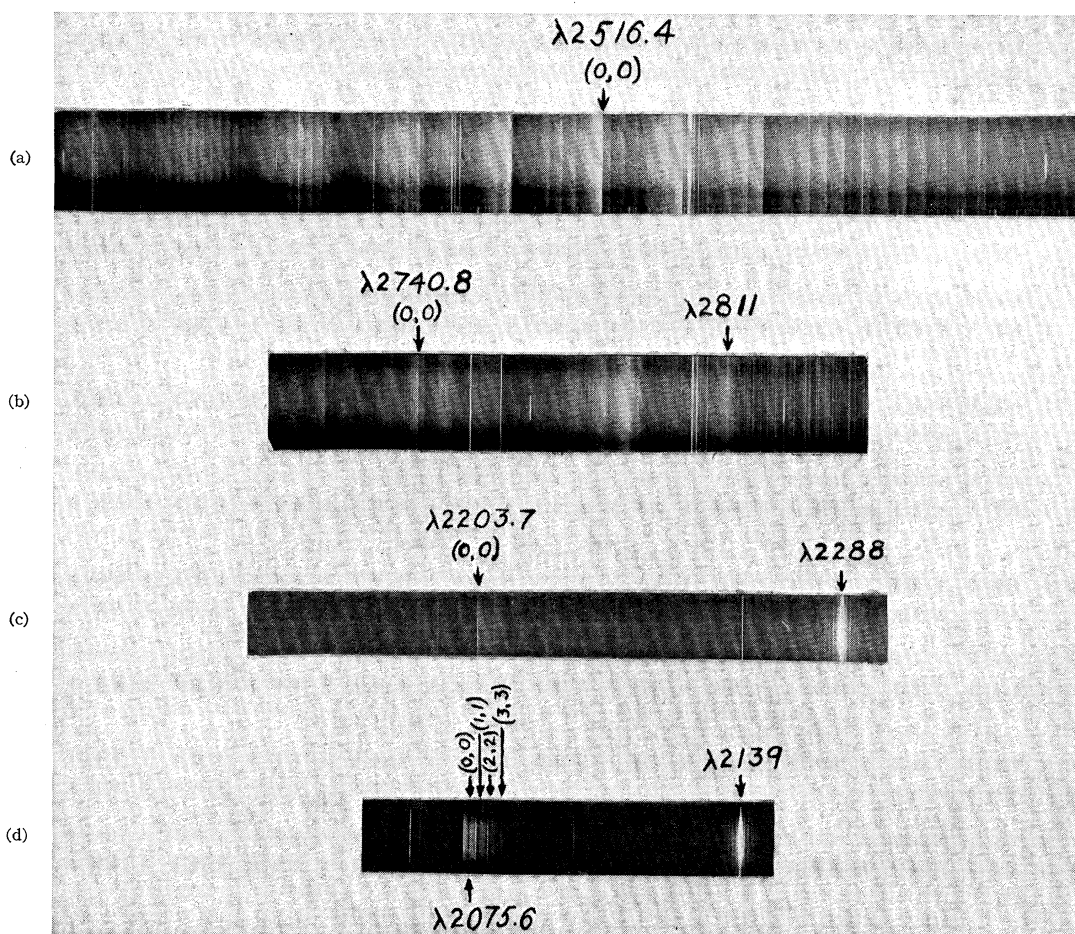


FIG. 1. (a) Mercury chloride system, 2650–2400Å. (b) Mercury chloride system, 2900–2700Å. The system starting at 2811Å is due to OH. (c) Cadmium chloride system, 2240–2185Å. The Cd resonance line is at 2288Å. (d) Zinc chloride system, $\Delta v=0$. The Zn resonance line is at 2139Å.

Wieland.¹ The *P* and *Q* heads were easily resolvable throughout the system, which was not the case in Wieland's work, and hence far more accurate settings on the *Q* heads could be made than were before possible. The new vibrational constants calculated for the 2650–2400Å HgCl system are as follows:

For HgCl³⁵

$$\begin{aligned}\omega_e'' &= 293.4 \text{ cm}^{-1}, & x_e''\omega_e'' &= 1.82 \text{ cm}^{-1}, \\ \omega_e' &= 341.8 \text{ cm}^{-1}, & x_e'\omega_e' &= 1.87 \text{ cm}^{-1}, \\ \nu_e &= 39703.5 \text{ cm}^{-1}.\end{aligned}$$

For HgCl³⁷

$$\begin{aligned}\omega_e'' &= 283.9 \text{ cm}^{-1}, & x_e''\omega_e'' &= 1.53 \text{ cm}^{-1}, \\ \omega_e' &= 333.4 \text{ cm}^{-1}, & x_e'\omega_e' &= 1.60 \text{ cm}^{-1}.\end{aligned}$$

The system is very well developed and entirely normal in appearance except for a striking intensity anomaly of some sort which causes the (1, 1) band to be missing, even on a heavily exposed plate. This anomaly is puzzling, for it cannot be attributed to a perturbation of either level involved, inasmuch as no similar anomaly is observed in the remainder of either the $v'=1$ or the $v''=1$ progression. While the chlorine isotope effect is readily observable, and provides a valuable check on the vibrational analysis, the mercury isotope effect remains beyond the available resolving power, and manifests itself only in the broad and diffuse appearance of bands far from the system origin.

Figure 1(b) shows the 2900–2700Å system,

TABLE I. Mercury chloride system, 2900–2700A.

v'	v''	0	1	2	3	4	5	6	7	8
0		36475.3	36197.1	35920.2	35644.5					
1		36761.8	36482.7		35925.7	35653.5				
2			36767.2	36488.8			35663.7			
3				36772.2	36496.5			35674.7		
4					36780.3	36506.0			35687.0	
5						36789.0	36515.6			
6							36797.1	36524.6		
7								36804.8	36533.4	
8									36813.5	36542.5

attributed by Wieland to HgCl_2 . That a system thus appearing in both a Geissler tube discharge and a high frequency discharge can be due to a triatomic molecule seems most improbable, in view of the highly disruptive nature of such spectroscopic sources. The system is therefore ascribed here to HgCl and discussed on this basis. An outstanding feature of the system is the presence of two well developed sequences, as can be clearly seen from the figure. These are apparently sequences of Q heads, and the weaker P heads are clearly visible, forming brief similar sequences. It is at first tempting to interpret these P heads as isotope heads, inasmuch as their spacing from the main Q heads is closely what one expects for the $\text{HgCl}^{35}-\text{HgCl}^{37}$ shift in successive sequences. However, on this basis, the calculated position of the system origin is near the extreme red limit of the system itself, and consequently the P head interpretation has been adopted. The longer wave-length of the two clearly distinguished sequences is the better developed, and is taken as the main diagonal of the vibrational array given in Table I. The vibrational constants are as follows:

$$\begin{aligned}\omega_e'' &= 279.7 \text{ cm}^{-1}, & x_e''\omega_e'' &= 0.6 \text{ cm}^{-1}, \\ \omega_e' &= 285.1 \text{ cm}^{-1}, & x_e'\omega_e' &= 0.4 \text{ cm}^{-1}, \\ \nu_e &= 36472.5 \text{ cm}^{-1}.\end{aligned}$$

The Condon parabola is very narrow; its development is limited to a region very close to the main diagonal, as has been found in the case of other chloride systems which have the fundamental frequencies of the two states nearly equal. Furthermore, this near equality explains the broad, headless appearance of many of the bands, a characteristic which renders measurement difficult. Unfortunately, the entire long

wave-length side of the system is very poorly developed; it would be of interest to photograph this in absorption if possible, to see what change in appearance is brought about. The fact that no chlorine isotope shift is observed is explained by the circumstance that the expected shift is in each case very nearly the same as the sequence spacing of the main bands, and because of the broad nature of these bands, resolution of the isotope bands is impossible. Beyond the short wave-length limit of each of the two principal sequences there are evidences of further bands showing similar spacings, which do not appear to belong to this system. A possible interpretation of these as part of a fragmentary system spaced about 80 cm^{-1} from the main system will be given below.

CdCl

Figure 1(c) shows the brief system between 2240 and 2185A, attributed to CdCl. The heads are sharply defined, but the unresolved rotational structure causes slight shading toward longer wave-length. Table II gives the vibrational array which appears best to fit the observed heads. Vibrational constants from this array are:

$$\begin{aligned}\omega_e'' &= 330.5 \text{ cm}^{-1}, & x_e''\omega_e'' &= 1.2 \text{ cm}^{-1}, \\ \Delta G'(\frac{1}{2}) &= 247.9 \text{ cm}^{-1}.\end{aligned}$$

Unfortunately no calculation of ω_e' or $x_e'\omega_e'$ is possible since no bands are observed involving v' greater than 1. This is in all probability ac-

TABLE II. Cadmium chloride system, 2240–2185A.

v'	v''	0	1	2	3
0		45363.4	45033.9	44708.0	
1		45609.9	45282.9	44956.3	44632.8

counted for by predissociation occurring in the upper state for vibrational levels of higher quantum numbers.

The chlorine isotope effect is observed in the case of the (0,1) and (1,2) bands; the separations of -7.6 cm^{-1} and -8.9 cm^{-1} respectively agree satisfactorily with the expected splittings of -7.0 cm^{-1} and -8.5 cm^{-1} . In the (1,0) band the isotope head is weak and lost in the impurity lines in this region; the isotope heads for the (0,2) and (1,3) bands are too weak to measure accurately, but can be observed in the expected positions.

ZnCl

The system between 2980 and 2905A is apparently that observed at low dispersion by Walter and Barratt.⁴ It consists of fairly strong heads appearing in groups, probably *Q* heads, with the heads of each group decreasing in intensity toward longer wave-length. A reproduction of the spectrogram is of little value because of the overlying $\Delta v = -2$ sequence of the second positive system of N_2 . Two very strong groups of heads are in all probability the $\Delta v = 0$ sequences of the two components of an electronic doublet, the doublet splitting being 383.5 cm^{-1} . Table III gives the two vibrational arrays for the doublet components. The vibrational constants are: For the shorter wave-length component,

$$\begin{aligned}\omega_e'' &= 391.0\text{ cm}^{-1}, & x_e''\omega_e'' &= 1.8\text{ cm}^{-1}, \\ \omega_e' &= 381.8\text{ cm}^{-1}, & x_e'\omega_e' &= 1.0\text{ cm}^{-1}, \\ \nu_e &= 33978.1\text{ cm}^{-1}.\end{aligned}$$

For the longer wave-length component,

$$\begin{aligned}\omega_e'' &= 390.0\text{ cm}^{-1}, & x_e''\omega_e'' &= 1.3\text{ cm}^{-1}, \\ \omega_e' &= 384.0\text{ cm}^{-1}, & x_e'\omega_e' &= 1.1\text{ cm}^{-1}, \\ \nu_e &= 33593.2.\end{aligned}$$

The chlorine isotope shift should again be observable, and several heads are observed in positions close to those calculated for ZnCl^{37} . Confusion of heads, however, is greatly increased by the happenstance of the near equality of the doublet splitting and the vibrational frequencies, and it appears impracticable to attempt to distinguish isotope heads from main heads and from N_2 lines.

Figure 1(d) shows the brief and unorthodox appearing ZnCl system which extends to longer

wave-lengths from 2074.4A. The most satisfactory interpretation of this seems to be as a $\Delta v = 0$ sequence; the flanking sequences are apparently too weak to observe on any of the plates obtained. In Figure 1(d) the arrows indicate the band origins measured. The first one, at 2075.6A, is shown by a null line gap, as are the second and third. Clearly, the *R* head is becoming progressively closer and closer to the origin, and the fourth band position is measured by setting on the head itself. Wave numbers of these four bands are as follows:

$$\begin{aligned}(0,0) &\rightarrow 48163.0\text{ cm}^{-1}, & (1,1) &\rightarrow 48111.0\text{ cm}^{-1}, \\ (2,2) &\rightarrow 48052.1\text{ cm}^{-1}, & (3,3) &\rightarrow 47986.8\text{ cm}^{-1}.\end{aligned}$$

The *P* branches in each case are cut off rather abruptly on the long wave-length side. This doubtless indicates a predissociation limit at a certain rotational energy.

DISCUSSION

Because of the proximity of the origin of the shorter wave-length HgCl system to the 2537A intersystem combination line of Hg , the transitions involved in the two cases must in all probability bear a close relationship to one another. It can be inferred, then, that the lower

TABLE III. Zinc chloride electronic doublet system, 2980-2905A.

v'	v''	0	1	2
0	0	33973.7	33586.9	
1	0	34354.3	33966.1	33581.3
2	0		34343.3	33960.1
0	1	33590.2		
1	1	33971.9	33584.2	
2	1	34350.7	33963.7	33579.2
3	1		34341.1	33955.9

state of the HgCl system is formed from a 1S ground state Hg atom plus a $^2P_{3/2}$ ground state Cl atom, and is probably a $^2\Sigma$ state, the ground state of the HgCl molecule. The upper state involved is undoubtedly formed from a 3P_1 excited Hg atom plus a 2P ground state Cl atom, and is a $^2\Pi$ upper state (accounting for the occurrence of *Q* branches) if the electronic coupling is of the case *a* type. It appears entirely possible that the upper state may represent a

situation tending markedly toward case *c*, as has been discussed by Mulliken⁷ for HgH, and by Howell⁸ for TlF, and if so, then the upper state is to be designated by its Ω value alone, and accordingly is probably a $\frac{1}{2}$ or $\frac{3}{2}$ state. The other component of the expected electronic doublet is not present, in all likelihood because of predissociation.

The longer wave-length HgCl system cannot involve the same $^2\Sigma$ lower state as that mentioned above, because of the different ω_e'' observed. However, another $^2\Sigma$ state is to be expected from the 1S Hg atom plus a $^2P_{1/2}$ Cl atom, and this is assumed to be the lower state of this system, inasmuch as configuration theory indicates that the Π states possible from $^1S+^2P$ combinations are in this case of little or no stability. The upper state is probably formed from a 3P_0 Hg atom plus a 2P ground state Cl atom, and is again in case *c* notation, a $\frac{1}{2}$ or $\frac{3}{2}$ molecular level. The fragmentary system mentioned above, 80 cm^{-1} further toward shorter wave-lengths, may be assumed to involve the same $^2\Sigma$ ground state, and an upper $\frac{3}{2}$ state which is considerably less stable than the $\frac{1}{2}$ state which may be taken as the upper level of the main 2900–2700A system.

The CdCl system, showing no electronic doublet characteristics, probably represents a

$^2\Sigma-^2\Sigma$ transition. Proximity of this system to the Cd resonance line at 2288A suggests that the lower $^2\Sigma$ arises from a 1S ground state Cd atom plus a 2P ground state Cl atom, while the upper state derives from a 1P Cd atom plus a 2P ground state Cl atom.

The ZnCl system, 2980–2905A, is fairly close to the 3076A $^3P_1-^1S$ combination line of Zn, and shows characteristics of an electronic doublet. It can, then, be assigned to a $^2\Pi-^2\Sigma$ transition; the $^2\Pi$ arising from a 3P_1 excited Zn atom plus a 2P ground state Cl atom, and the $^2\Sigma$ coming from the $^1S+^2P$ combination exactly analogous to that observed in HgCl and CdCl.

The shorter wave-length sequence at 2075A is not far from the 2139A resonance line of Zn, and, because it shows only *P* and *R* branches, may therefore be considered to arise in the $^2\Sigma-^2\Sigma$ transition analogous to that observed in CdCl.

An attempt was made to find a HgCl system of shorter wave-length than the 1850A resonance line of Hg, similar to the systems found for CdCl and ZnCl, but exposures of several hours' duration failed to bring out any such system.

The author gratefully acknowledges the many suggestions and extensive assistance of Professor W. W. Watson, and likewise expresses his thanks to Professor F. A. Jenkins for interesting discussions of several of the points covered.

⁷ R. S. Mulliken, Phys. Rev. **36**, 1440 (1930).

⁸ H. G. Howell, Proc. Roy. Soc. **160**, 242 (1937).

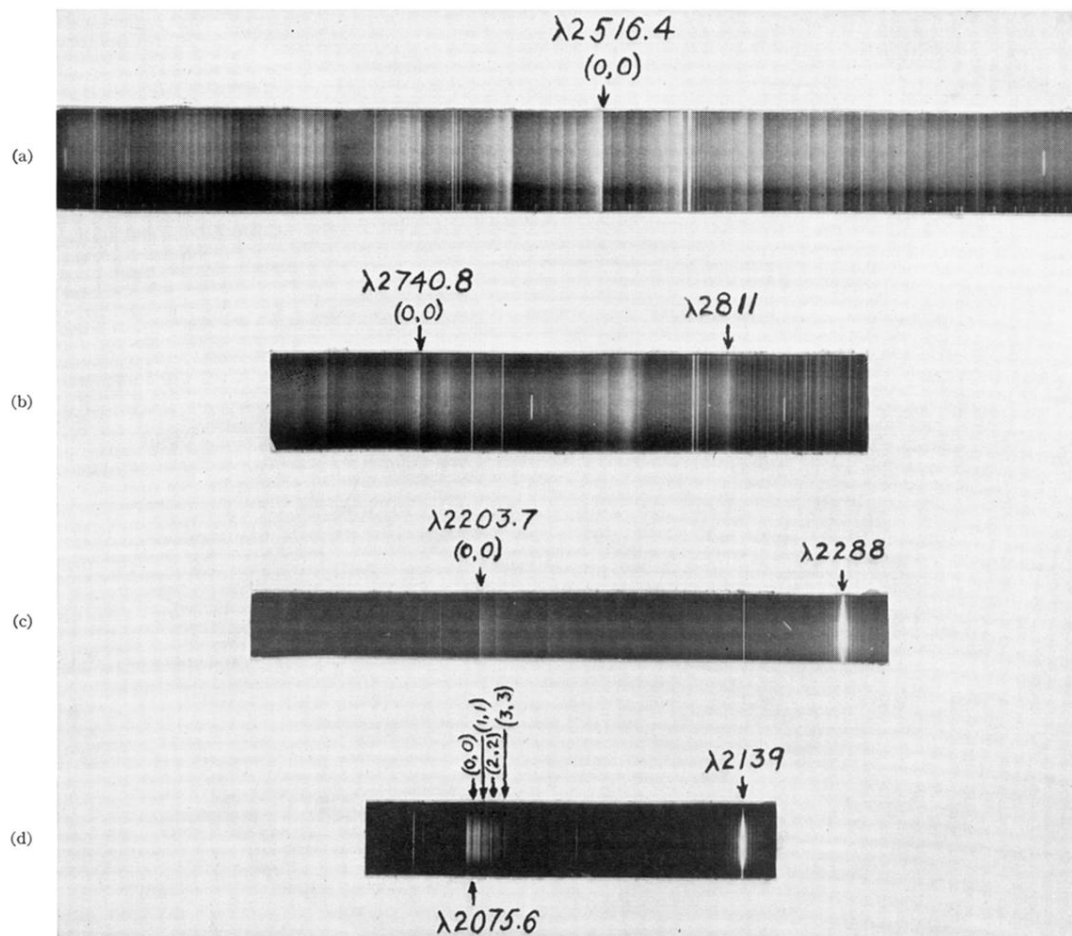


FIG. 1. (a) Mercury chloride system, 2650–2400Å. (b) Mercury chloride system, 2900–2700Å. The system starting at 2811Å is due to OH. (c) Cadmium chloride system, 2240–2185Å. The Cd resonance line is at 2288Å. (d) Zinc chloride system, $\Delta v=0$. The Zn resonance line is at 2139Å.