Molecular Spectrum of Cadmium Vapor

S. Winston Cram, *University of Wisconsin*

The fluorescence and discharge spectra between 1900A and 5000A of Cd vapor were observed when the vapor was excited under various conditions. The observations include: emission of band spectra between 2212 and 2288 in both spectra, the process of excitation of some of the fluorescence spectrum, and a general summary of the Cd band spectra. Potential energy-nuclear separation curves for the Cd molecule are concluded from these observations and from the results to be presented in another paper.

THE band spectrum of Cd has been observed under a wide variety of conditions. It has not been possible to determine the molecular constants of Cd by the usual method of band analysis because none of the bands observed show rotational structure. The only way in which information concerning these constants has been obtained is through comparison of different types of spectra and through changes of intensity with variation in experimental conditions.

Previous observation on absorption, fluorescence and discharge spectra are summarized in Table I.

The limits of the bands change somewhat with change in vapor pressure—in this table the spectra listed are for a vapor pressure of approximately 80 mm of Hg unless otherwise stated.

The present work was undertaken to extend the observations on the band spectrum of Cd with the purpose of obtaining more information concerning the properties of the Cd molecule.

Experimental Procedure

The experimental arrangement is given by Fig. 1. The quartz tube AB was set in two adjoining furnaces allowing control of both temperature and pressure in the portion A. The vapor could be excited either by the light from a spark or by a low voltage Tesla coil through external electrodes. Condensed sparks between terminals of Cu, Zn or Al served as light sources. When the vapor was excited with light from a spark, the short wave-length limit and the intensity could be controlled by use of filters and mesh screens, respectively. The filters were thin pieces of Pyrex glass. The mesh screen used had a transmission coefficient of 25 percent. The
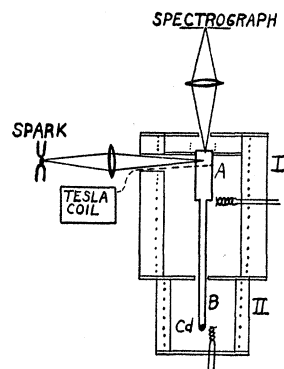

Fig. 1.

resulting emission from either type of excitation (fluorescence or discharge) was analyzed with a quartz spectrograph.

Exposures made with the tube cold showed that the intensity of scattered light was negligible.

Each tube (eight different ones were used) was prepared by evacuating and baking at 800°C for 32 hours and at 1000°C for eight hours. Cd was then distilled into the tube and it was sealed off. Five different samples of Cd were used. Tl was added to one sample and CdO to another to determine the effect of these impurities. The purest sample was electrolytic Cd which had been distilled five times in a vacuum. Unless otherwise stated, all exposures were taken at a temperature of 600°C (80 mm vapor pressure) in furnace II and about 650°C in furnace I.

Eastman Speedway and Process plates were used both with and without an oil coating. Exposures for fluorescence pictures varied from 15 minutes to eight hours. Electrodeless discharge exposures varied from one to 30 minutes.

TABLE I. *Previous observations of absorption, fluorescence and discharge spectra of Cd.*

Band Spectra of Cd

Absorption	Wave-lengths in exciting light	Fluorescence Bands observed	Discharge
a. 2125[1] a narrow band extending 1990–2150, maximum 2110–2140, faint from 1990–2110.	a. Below 2125	a. 2125[1] a narrow band extending 2110–2140.	a. 2125[7] a narrow band extending 2110–2140 with maximum at 2124.
b. 2212[2] a narrow band broadens toward long wave-lengths at high pressure.	b.	b.	b.*
c. 2288[2] a broad band extending 2212–3050 at high pressures. Flutings[3] between 2590–2825.	c. Below 3000	c. 2288[4] a broad band extending 2260–3050. Flutings 2700–3050.	c. 2288[7] continuous band extending 2191–3050 (pressure not given).
d. 3178[2] a narrow band at high pressures.	d. Below 3178	d. 3178[5] a narrow band.	d. 3178[7] a narrow band.
e. 3261[2] resonance line with band overlying it.	e. Below 3261 2600–3261	e. 3261[4] resonance line with band overlying it. 3261 appears with weak intensity.	e. 3261[7] resonance line with band over lying it.
	f. Below 3000	f. 4000[6] broad band extending 3800–5000.	f. 4058[7] a broad band extending 4058–5400.

Line Spectra of Cd

Wave-lengths in exciting light	Fluorescence Lines observed	* 2212[8] a narrow band (pressure 0.1 mm) probably due to impurity.
a. 1850–2125	a. Sharp triplet[9, 10] $(5^3P_1 - 6^3S_1)$ Diffuse triplet $(5^3P_1 - 5^3D_{123})$	
b. 2300–3050	b. Some lines of the exciting source re-emitted by the vapor.[9]	

[1] Jabłonski, Zeits. f. Physik **45**, 878 (1927).
[2] Mohler and Moore, J.O.S.A. **15**, 74 (1927).
[3] Jabłonski, Bull. de l'Acad. Pol. d. Sc. et d. L. **10A**, 163 (1928).
[4] Van der Lingen, Zeits. f. Physik **6**, 403 (1921).
[5] Mrozowski, Zeits. f. Physik **62**, 311 (1930).
[6] Kapuscinski, Nature **116**, 170 (1925).

[7] Hamada, Phil. Mag. **12**, 50 (1931).
[8] Robertson, Phil. Mag. **14**, 795 (1932).
[9] Kapuscinski, Zeits. f. Physik **41**, 214 (1927).
[10] Miss Kalinowska, Comptes Rendus **196**, 168 (1933), observed that this triplet was excited by a single absorption process at high vapor pressures.

RESULTS

Fluorescence

(a) When the vapor was excited by the total radiation from a Cu spark all the fluorescence bands and lines described in Table I were observed.

To determine the wave-lengths effective in exciting different lines and bands the wave-length and the intensity in the exciting light were varied.

With light of wave-length greater than 1990A from a Cu spark as source, the intensity of the 2125 band relative to the 2288 band was the same as with the total radiation from the Cu spark as source. The intensity of the sharp triplet was reduced to about 1/100, and the diffuse triplet could not be observed.

With light of wave-length greater than 1930 from an Al spark as source the 2125 band was too weak to be observed and the intensity of both the sharp and the diffuse triplet relative to the 2288 band was reduced to about 1/5 that with the total radiation from the Al spark as source.

Following a method used by Wood,[11] the amount of emitted radiation from the tube was reduced by placing the mesh screen first between the spark and the cell and then between the cell and the spectrograph. Equal intensity for the two cases indicated that the initial level for the transition was excited by a single absorption process. If the first case appears with 1/4 the intensity of that of the other case, a two-fold absorption process is indicated. The results distinctly showed the initial levels of the 2125 band and the sharp triplet to be populated primarily by a single stage absorption, and those of the diffuse triplet by a two-stage process. This agrees with Miss Kalinowska's[10] results for the sharp triplet.

(b) & (c) The Van der Lingen[4] fluorescence band (2288–3050) was found to extend from 2212–3050 (Fig. 2) with a broad reversed portion at 2288. The 2212–2288 part of the band was much weaker than the remainder of the band.

It was also found that lines from the exciting light of wave-lengths between 2212–2288 were re-

[11] Wood, Phil. Mag. **6**, 352 (1928).

3261   2288 2212 2125

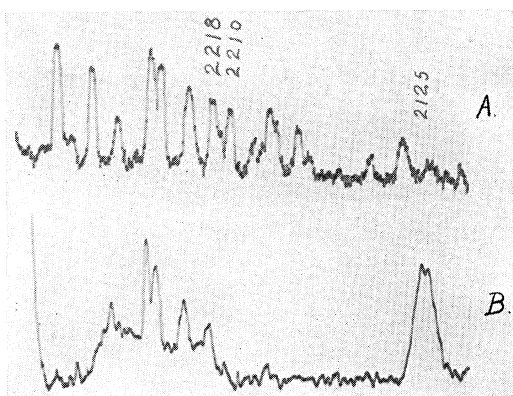FIG. 2. Cd fluorescence excited with Cu spark.

FIG. 3. Microphotometer curves: (A) Cu spark (B) Cd fluorescence.

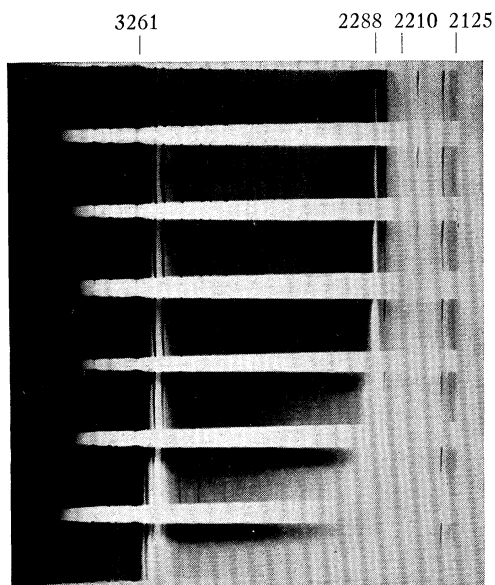3261   2288 2210 2125

FIG. 4. Electrodeless discharge spectrum of Cd (1) 25 mm, (5) 125 mm, (7) 350 mm.

emitted by the Cd vapor in the same manner as previously found[9] for lines between 2300–3050. In Fig. 3 A and B are microphotometer records of the source and the fluorescence, respectively. The fluorescence showed a continuous band from 2212 to 2288 with five re-emitted Cu lines (2218,

2229, 2243, 2247, 2264) superimposed. If the lines were due to scattered light, the strong Cu lines between 2218 and 2125 should have appeared along with these five. The short wave-length limit for re-emission must fall between 2218 and 2210, since the 2210 Cu line does not appear. The short wave-length limit for the fluorescence band is about 2212.

Forty flutings were observed between 2560 and the long wave-length end of the 2288 band. These agreed within the error of measurement with the absorption flutings between 2590 and 2825 measured by Jabłonski[3] and Mohler and Moore,[2] and the fluorescence flutings between 2627 and 3050 measured by Kapuscinski.[12]

Discharge spectra

(a) When the Cd vapor was excited by the Tesla coil, all the discharge bands described in Table I were observed except Robertson's[8] 2212 band.

Fig. 4 shows discharge spectra at different vapor pressures of Cd. At high pressures the 2125 band is reversed at the wave-length of maximum intensity for lower pressures (2124). This shows that the emission maximum coincides with the absorption maximum.

(b) & (c) At low pressures the 2288 band extends from 3070 to a sharp edge at 2210, and at high pressures the limits are 3070 and about 2300 as shown by Fig. 4. At high pressures the part from 2300–2210 is absorbed by the Cd vapor.

The 2288 band showed only six of the series of 40 flutings observed in fluorescence. These six coincide with the six fluorescence flutings between 2780 and 2870. Another set of flutings of smaller separation, originally found by Hamada, extending from 2890–3070 appeared with more intensity than the 2780–2870 flutings. However the intensity of the 2890–3070 flutings relative to that of the 2780–2870 flutings does not appreciably change with pressure.

The observation of only six of the 40 fluorescence flutings may be due to the superposition of the 2890–3070 series and the Cd arc lines on the 2288 band.

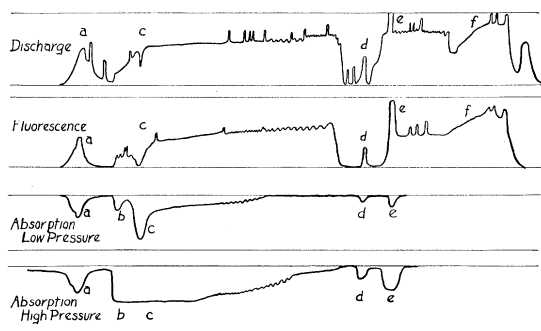[12] Kapuscinski, Bull. de l'Acad. Pol. d. Sc. et d. L. **10A**, 1 (1927).

FIG. 5. Graphic description of Cd band spectra.

Effect of purity

Effects due to impurities were determined by comparing the spectra of the different samples of Cd. Very small amounts of impurity did not materially affect the observations made at high vapor pressures. In the discharge it was observed that lines due to impurities and Cd arc lines which appeared at low Cd pressures became very weak in comparison to the intensities of the Cd bands at high Cd pressures.

There was no evidence of the band at 2212 reported by Robertson.[8] Since he observed this band at low pressures, in fact much lower than those at which any other Cd band spectra has been observed, it was very likely due to an impurity.

Since the 2890–3070 discharge flutings do not become weaker at high pressures they are probably due to Cd.

Fig. 5 is a chart giving the absorption, fluorescence, and discharge spectra of Cd as they have been observed.

DISCUSSION

Since we interpret the observed bands in terms of absorption and emission by Cd molecules, it is interesting to see what knowledge of the potential energy-nuclear separation curves can be gained from the data.

A calculation giving the general characteristics of the potential energy-nuclear separation curves for molecules of this type will be published elsewhere by Professor J. H. Van Vleck.[13] These characteristics determine the general shapes of

the curves concerned; the observed data were applied only to determine the relative position and magnitude of their maxima and minima. Fig. 6 gives the results of this application when due consideration is given the following general principles:

The Franck-Condon principle states that for all transitions the position and momentum of the nuclei are unchanged. Mulliken[14] has shown that the nuclear separation r_0 must be fairly small in stable molecules (i.e., large heat of dissociation D). It has been found empirically that for different states in one molecule the expression $\omega_0 r_0^2$ is approximately constant. If the intensity distribution in a band is the same in the absorption spectrum as it is in the emission spectrum, then r_0 of the initial state is equal to r_0 of the final state.

Kuhn's[15] recently determined value of D, as well as other previous evidence, shows that the minimum of curve b must be very shallow. The Van der Waal force associated with this curve varies as the inverse sixth power of the nuclear separation.

The $5^1S_0 + 5^1P_1$ level splits up into two components, b and c, at small values of r. The minima of these two components are at approximately the same r_0''. The broad 2288 band necessitates a very deep minimum in c (i.e., large D''), from this it follows that $r_0'' < r_0'$ and therefore $\omega_0'' > \omega_0'$. Thus the minimum of
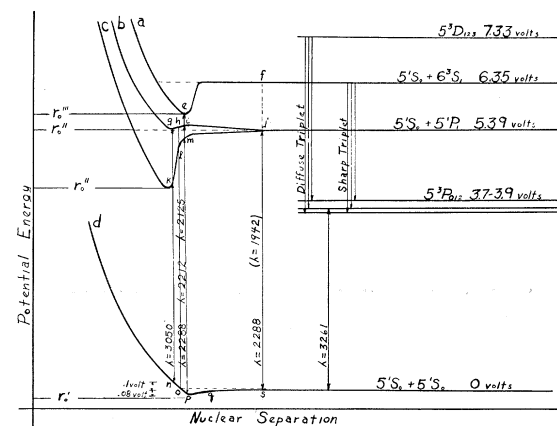

FIG. 6. Potential energy curves for the Cd molecule.

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[13] Van Vleck, a paper to be published soon.

[14] Mulliken, Phys. Rev. **32**, 186 (1928).
[15] Kuhn and Arrhenius, Zeits. f. Physik **82**, 716 (1933).

curve c must be as shown in Fig. 6. Such a conclusion allows an explanation of other observations if the life period of molecules in this state is too short for a Boltzmann distribution of molecules among the vibrational levels to form. For this would account for the fairly intense emission between 2288 and 3050, as well as the re-emission of line spectra in this region, corresponding to transitions from all the vibrational levels along $k\,l\,m$ to $n\,o\,p$. The large separation and the breadth of the fluorescence flutings in the 2288 band can be understood from the steep slope of $k\,l$ and the fact that $n\,o$ is an unquantized portion of curve d.

The re-emission of line spectra by the vapor can be explained as a resonance absorption and emission process between the unquantized portion of the initial state and some vibrational level in the final state (curves b or c). A short life period in the excited state would give sharper resonance, i.e., if short enough so that the population of an excited level cannot be reduced materially through a collision process.

The maximum of curve b is apparently almost directly above p, with separation corresponding to a wave-length of 2212, since the short wave-length edge of the 2212–2288 band in emission coincides with the short wave-length edge of the 2212 band in absorption.

The behavior of the 2288 absorption band with increasing vapor-pressure[16] can perhaps be understood if $q\,s$ is quite long and flat for at low pressures the statistical number of quasi-molecules existing between q and s is greater than the number existing between o and p.

Curve a must have its minimum directly above that of curve d since the maximum of intensity of the 2125 band is at the same wave-length in both the absorption and the emission

spectra; that is r_0''' is about equal to r_0' and ω_0''' nearly equal to ω_0'.

At high vapor pressures the sharp triplet can be excited by a single absorption process if the excitation energy is 6.2 volts or greater. This fact indicates that the potential energy curve associated with the 6^3S_1 atomic energy level has a minimum at nuclear separations of approximately r_0'. So it is natural to associate curve $a\,e$ with the 6^3S_1 level,[17] particularly since it is the first atomic level above e. If the life period of the molecules in this state is long, one would expect transitions only from the lowest vibrational levels of e.

These curves differ somewhat from those suggested by Kuhn.[15] The van der Waal forces involved in curves b and c have been found[13] to vary as the inverse cube power of the nuclear separation, but the sign of this force is the opposite for the two curves involved. Thus the van der Waal force associated with curve b is repulsive instead of attractive as the Kuhn[15] curves suggest. The reasons for the other differences between these and Kuhn's curves follow from the observations presented.

Finkelnburg[18] showed curve b for Hg_2 as a pure repulsion curve. For Cd_2 it is necessary for it to have a minimum in order to account for the re-emission of lines between 2288 and 2212. From curves b and d the energy of dissociation of Cd must be less than $(pi-sj)$, i.e., (0.2 volts) the value given by Winans.[16]

In conclusion the writer wishes to express his thanks and appreciation to Professor J. G. Winans under whose direction this work was carried out, and to Professor J. H. Van Vleck for his helpful advice.

[16] Winans, Phil. Mag. 7, 555 (1929).

[17] There is, however, no positive proof that curve $a\,e$ is not associated with the 6^1S_0 atomic level.
[18] Finkelnburg, Phys. Zeits. 34, 529 (1933).

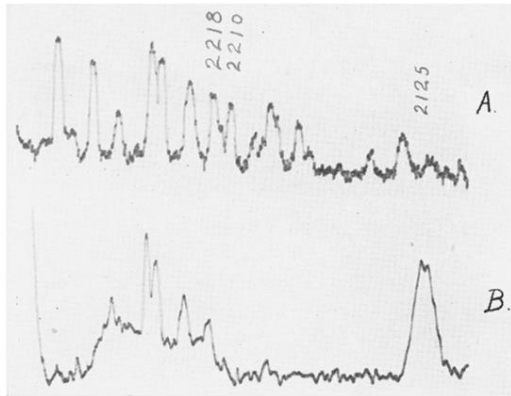Fig. 2. Cd fluorescence excited with Cu spark.

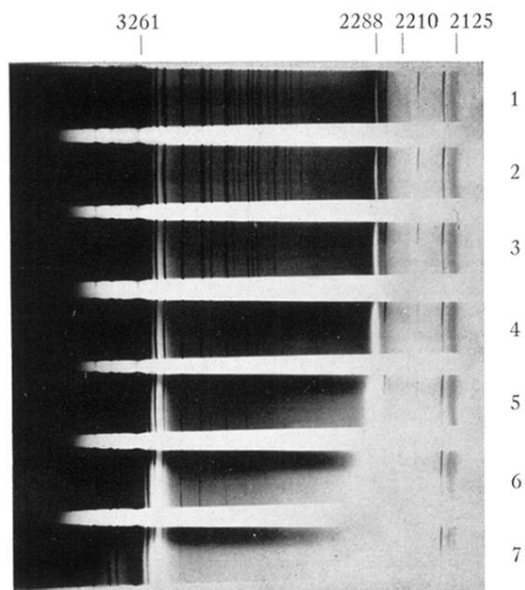Fig. 3. Microphotometer curves: (A) Cu spark (B) Cd fluorescence.

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