# Band Spectrum of Pb₂ in Absorption and Emission

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A band system has been observed when light is absorbed by lead vapor heated to about 1400°C. The same band system has also been found in emission. Some ninety band heads have been located between the wavelengths of 4600 and 5200A. The bands are degraded toward the red. The vibrational analysis has been made but the complexity of the isotope effect has prevented a rotational analysis.

Within the error of observation the heads are represented by the formula:

$$\nu = 19{,}570.8 + 159.22(v' + \tfrac{1}{2}) - 0.882(v' + \tfrac{1}{2})^2$$
$$+ 0.00518(v' + \tfrac{1}{2})^3 - 256.5(v'' + \tfrac{1}{2}) + 2.96(v'' + \tfrac{1}{2})^2.$$

Fairly conclusive evidence is presented for the ascription of this band system to the molecule Pb₂.

## INTRODUCTION

SINCE band spectra cannot originate from single atoms, the presence of band spectra in metallic vapors is evidence for the formation of molecules of like or unlike metallic atoms. The alkali metal vapors which have been investigated from this point of view have shown extensive band spectra which may be ascribed to molecules formed from two like alkali atoms. In the case of lithium,[1, 2, 3, 4] sodium,[5, 6, 7] and potassium,[8, 9, 10] partial vibrational and rotational analyses are available. Partial vibrational analyses of several band systems of diatomic caesium[11, 12] and rubidium[12] have been made. Similar investigations carried out on the vapors of the metals of the second group[13, 14, 15, 16] have revealed bands which have been attributed to diatomic molecules but no vibrational analyses have been obtained. A study of the band spectra of metals of the fifth group shows that these metals also form diatomic molecules in the vapor state. In the case of phosphorus[17, 18] both vibrational and rotational analyses have been made. Only vibrational constants are known for arsenic,[19, 20] antimony[21] and bismuth.[21, 22]

Since it is of interest to extend this type of investigation to metals occurring in other groups of the periodic table, it was decided to investigate lead vapor in order to determine whether or not molecules of this element exist in the vapor state.

## EXPERIMENTAL

Chemically pure lead was introduced into a graphite tube about 50 cm long and 2 cm in internal diameter. This tube, which was heated by means of a Hoskins electric furnace operated at 25 volts a.c. and 400 amperes, was open to air at atmospheric pressure. The temperature was maintained at about 1400°C. The carbon vapor from the interior of the graphite tube served as a reducing agent and thus decreased the rate of oxidation of the lead vapor. A five-hundred watt projection lamp or an under-water spark with magnesium electrodes provided a source of continuous radiation. When the background used in obtaining the absorption spectrum was removed the bands could be photographed in emission from the hot vapor.

The spectrum, which showed bands between 4600 and 5200A, was photographed both in absorption and emission with a Hilger E-1

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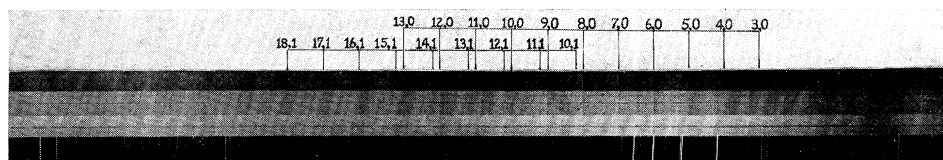[22] G. M. Almy and F. M. Sparks, Phys. Rev. **44**, 365 (1933).

FIG. 1. Band spectrum of Pb₂ in absorption between 4600 and 5200A with iron comparison spectrum.

quartz spectrograph and with a large two-prism glass spectrograph giving a dispersion of 6 to 13A/mm in the region of the spectrum used. It was also photographed in absorption in the second order of a Littrow mounted concave grating having a radius of curvature of 10 feet and giving a dispersion of 2.7A/mm. The time of exposure ranged from 30 seconds on the E-1 spectrograph to 30 minutes on the concave grating.

Photographs of the spectrum taken through the hot graphite tube without the lead vapor in it, showed no bands in this region. Tin, which might be expected to occur as an impurity in the lead, was introduced into the tube without the lead, but only the band spectrum of tin oxide was developed. It was, however, found possible to observe the band heads associated with lead vapor when the graphite tube was replaced by an iron tube. In this case the temperature at which the bands first appear is somewhat lower—at about 1300°C. At this temperature the iron is near its melting point. The rate of oxidation of the iron is large and the lead probably oxidizes less rapidly than in the carbon tube so that the concentration of lead vapor is higher than it would be if the lead were heated to the same temperature in a graphite tube. Hence sufficient vapor is present to develop the bands at a lower temperature. The iron tube, when heated without the lead in it, did not show this band system either in absorption or emission.

Lead vapor rapidly attacks quartz and alundum tubes so that the choice of tubes that can be used at these temperatures is quite limited.

An iron arc was used as a standard of wavelengths and the bands on the several plates were measured by means of a Geneva Society comparator which could be read to ±0.001 mm. However, the diffuseness of the heads does not permit settings to be made to this accuracy.

## RESULTS

Some ninety band heads in all were measured. These bands lie between 4600A and 5200A and degrade to the red. They therefore occur in the same region of the spectrum as the $A$ and $B$ systems of PbO which extend from 4145A to 6720A. Fig. 1 shows this band system with iron comparison spectrum as photographed on the glass spectrograph. The wave numbers of the band heads which have been measured are recorded in Table I, together with their vibrational quantum numbers and estimated intensities. These heads are represented within the observational error by the formula:

TABLE I. *Band heads of Pb₂.*

| $I$ | $v'$ | $v''$ | $\nu_{obs.}$ | $\nu_{obs.} - \nu_{calc.}$ | $I$ | $v'$ | $v''$ | $\nu_{obs.}$ | $\nu_{obs.} - \nu_{calc.}$ |
|---|---|---|---|---|---|---|---|---|---|
| 2 | 2 | 2 | 19337.5 | -3.2 | 0 | 12 | 2 | 20806.5 | -4.3 |
| 0 | 7 | 5 | 19396.8 | 0.4 | 2 | 19 | 6 | 20838.6 | 1.8 |
| 0 | 1 | 1 | 19430.6 | 1.0 | 8 | 9 | 0 | 20881.0 | 0.2 |
| 0 | 12 | 8 | 19466.5 | -0.6 | 5 | 11 | 1 | 20911.8 | -2.3 |
| 0 | 11 | 7 | 19533.5 | -2.4 | 6 | 10 | 0 | 21023.8 | -0.2 |
| 0 | 14 | 9 | 19536.1 | -4.3 | 6 | 12 | 1 | 21054.7 | 0.7 |
| 7 | 10 | 6 | 19612.7 | 3.4 | 0 | 14 | 2 | 21084.9 | -2.4 |
| 0 | 7 | 4 | 19622.2 | -1.3 | 0 | 16 | 3 | 21116.3 | -3.6 |
| 1 | 4 | 2 | 19646.6 | -0.6 | 5 | 11 | 0 | 21165.1 | -0.6 |
| 0 | 15 | 9 | 19675.1 | -1.6 | 7 | 13 | 1 | 21194.9 | 0.6 |
| 0 | 9 | 5 | 19691.0 | 3.9 | 0 | 15 | 2 | 21224.1 | 0.5 |
| 0 | 6 | 3 | 19708.1 | -0.4 | 5 | 12 | 0 | 21305.2 | -0.8 |
| 0 | 3 | 1 | 19738.4 | -1.0 | 7 | 14 | 1 | 21333.0 | 1.1 |
| 7 | 8 | 4 | 19769.5 | 0.1 | 1 | 16 | 2 | 21359.5 | 0.9 |
| 0 | 13 | 7 | 19815.8 | 0.6 | 0 | 18 | 3 | 21387.2 | 0.0 |
| 6 | 15 | 8 | 19878.5 | -1.4 | 3 | 13 | 0 | 21442.2 | -2.7 |
| 0 | 4 | 1 | 19893.4 | 1.6 | 5 | 15 | 1 | 21467.8 | -0.4 |
| 0 | 17 | 9 | 19944.0 | -1.5 | 3 | 17 | 2 | 21495.2 | 2.9 |
| 4 | 11 | 5 | 19967.3 | -4.7 | 1 | 19 | 3 | 21515.0 | -3.5 |
| 3 | 3 | 0 | 19988.2 | -1.8 | 1 | 23 | 5 | 21571.8 | -0.9 |
| 7 | 13 | 6 | 20032.9 | 2.7 | 3 | 16 | 1 | 21605.1 | 1.9 |
| 0 | 15 | 7 | 20090.5 | 1.4 | 4 | 18 | 2 | 21627.4 | 2.5 |
| 0 | 7 | 2 | 20094.2 | -0.6 | 1 | 20 | 3 | 21648.6 | -0.1 |
| 6 | 4 | 0 | 20143.0 | 0.6 | 0 | 22 | 4 | 21671.2 | -0.5 |
| 0 | 14 | 6 | 20170.1 | 2.3 | 3 | 17 | 2 | 21734.1 | -0.9 |
| 0 | 16 | 7 | 20226.5 | 2.4 | 3 | 19 | 2 | 21755.3 | -0.9 |
| 0 | 8 | 2 | 20240.4 | -0.6 | 1 | 21 | 3 | 21776.6 | -1.2 |
| 8 | 5 | 0 | 20294.0 | 1.0 | 1 | 23 | 4 | 21796.0 | -3.6 |
| 1 | 15 | 6 | 20306.1 | 2.0 | 1 | 18 | 1 | 21865.7 | -3.7 |
| 3 | 20 | 9 | 20334.8 | -4.8 | 1 | 20 | 2 | 21886.1 | -0.3 |
| 3 | 7 | 1 | 20340.6 | 0.8 | 2 | 22 | 3 | 21906.9 | 1.4 |
| 0 | 17 | 7 | 20356.7 | -1.1 | 1 | 24 | 4 | 21923.0 | -1.4 |
| 10 | 6 | 0 | 20443.4 | 1.0 | 0 | 26 | 5 | 21946.3 | 0.0 |
| 1 | 13 | 4 | 20480.9 | 2.8 | 1 | 28 | 6 | 21973.9 | 3.6 |
| 1 | 8 | 1 | 20486.0 | 0.4 | 0 | 30 | 7 | 21995.6 | 1.2 |
| 0 | 10 | 2 | 20532.2 | 3.5 | 1 | 21 | 2 | 22015.7 | 0.2 |
| 10 | 7 | 0 | 20591.3 | 1.2 | 1 | 23 | 3 | 22029.1 | -4.3 |
| 2 | 16 | 5 | 20661.8 | 1.7 | 1 | 25 | 4 | 22053.9 | 4.6 |
| 0 | 11 | 2 | 20669.9 | -0.5 | 0 | 27 | 5 | 22068.1 | -1.2 |
| 0 | 13 | 3 | 20711.8 | 0.9 | 0 | 31 | 7 | 22119.0 | 2.7 |
| 10 | 8 | 0 | 20736.8 | 0.6 | 1 | 22 | 2 | 22140.6 | -2.7 |
| 0 | 15 | 4 | 20756.4 | -4.4 | 1 | 24 | 3 | 22161.2 | 2.9 |
| 0 | 10 | 1 | 20771.9 | -1.3 | 0 | 26 | 4 | 22175.9 | 2.7 |
| | | | | | 0 | 28 | 5 | 22192.7 | 1.4 |

$$\nu = 19{,}570.8 + 159.22(v' + \tfrac{1}{2})$$
$$-0.882(v' + \tfrac{1}{2})^2 + 0.00518(v' + \tfrac{1}{2})^3$$
$$-256.5(v'' + \tfrac{1}{2}) + 2.96(v'' + \tfrac{1}{2})^2.$$

There is no noticeable difference in the intensity distribution of the Pb₂ bands as observed in absorption and in emission. The system terminates abruptly at the red end with nearly all the strong bands included in two long $v'$ progressions and with no indication of corresponding $v''$ progressions. It is unfortunate that data are not available to make possible the construction of accurate potential curves and permit a quantitative examination of the processes involved. However, it seems likely that the absence of $v''$ progressions is due to a red edge occurring near the system origin. The existence of a red edge in the spectrum of Na₂ has been discussed by Loomis and Nile[23] and is to be expected in all cases where $\omega'' > \omega'$ while $D'' < D'$. For these bands $\omega''$ is 256.5 and $\omega'$ is 159.22. Plots of $\Delta G(v)$ against $G(v) - G(0)$ indicate that $D''$ is approximately 5000 cm⁻¹ and $D'$ about 20,000 cm. No explanation is offered for the apparently abnormal intensities of several bands near the red end of the spectrum. Similar anomalies have been observed in a number of cases, notably in the $A$ system of PbS.[24]

In the absence of the $v' = 0$ progression, the assignment of the values of $v'$ from the bands observed would be somewhat uncertain. The manner of locating the system origin will be discussed in connection with the isotope effect.

The heads near the red end of the system are quite sharp but become increasingly diffuse toward the violet end. Still farther to the violet are a number of headless bands, or possibly groups of very diffuse bands which appear both in emission and in absorption.

## IDENTIFICATION OF THE EMITTING MOLECULE

We believe this band system to arise from the diatomic lead molecule Pb₂ for the following reasons:

(1) This band system appeared only when lead was present in the carbon or iron tube. Hence it cannot be ascribed to any of the constituents out of which the tubes were made or to

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impurities in the tube. It therefore seems evident that lead is one of the atoms forming the diatomic molecule which gives rise to this band system.

(2) Since lead was heated in tubes open to the atmosphere so that lead oxide is formed, this band system might at first thought be ascribed to PbO. It does fall in the same region of the spectrum as lead oxide (PbO). That an assignment to any system of lead oxide is impossible is evident from the fact that for these bands $\omega_e'' = 255.6$, while for PbO $\omega_e'' = 722.5$. Moreover, when lead was heated in graphite tubes no known bands of the $A$ and $B$ systems of PbO were observed and, when lead oxide (PbO) was heated in an alundum tube, although the $A$ and $B$ systems appeared there was no trace of these bands.

(3) The fact that $\omega_e'' = 255.6$ for this system, while $\omega_e'' = 428.14$ for PbS indicates that the molecule is heavier than PbS so that an element with an atomic weight greater than that of sulfur must be assumed to have united with lead. This excludes the possibility that the molecule is formed by the union of lead with such lighter elements as carbon, nitrogen, oxygen, or silicon.

(4) Microphotometer traces were made of some of the spectrograms taken in the second order of the concave grating. Although the lines due to the different isotopes of lead are not resolved, it is possible from these traces to get some information which substantiates the selection of diatomic lead as the emitting molecule.

Lead is known to consist chiefly of three isotopes of masses 208, 207 and 206 with the relative abundances 7, 3, 4. The spectrum of Pb₂ should then consist of the overlapping spectra of the molecules Pb²⁰⁸ Pb²⁰⁸ (25), Pb²⁰⁸ Pb²⁰⁷ (21), Pb²⁰⁸ Pb²⁰⁶ (29), Pb²⁰⁷ Pb²⁰⁷ (5), Pb²⁰⁷ Pb²⁰⁶ (12), and Pb²⁰⁶ Pb²⁰⁶ (8) with the approximate per cent abundances indicated in parentheses. The displacements of the isotope lines from those of Pb²⁰⁸ Pb²⁰⁸ may be expressed by the usual approximation

$$\nu^i - \nu = (\rho - 1)\nu_v + 2(\rho - 1)\nu_r,$$

where $\rho$ has the values 1.0012, 1.0024, 1.0024, 1.0036 and 1.0048, respectively.

The heads should therefore be fivefold with increasing separation at greater distances from the system origin, but if the isotope heads were

obscured by overlapping fine structure the observed heads would merely appear increasingly diffuse. The extent of the diffuseness of these heads was determined by measuring the frequency differences of the positions of maximum and minimum absorption from microphotometer traces of the heads of the strong bands and found to be of the right order of magnitude. A plot of these differences against the frequencies of the heads indicates that the position of the sharpest heads and hence the location of the system origin, should be in the vicinity of 19,500 cm$^{-1}$.

It is evident from the values of $\rho$ that the isotope lines will be evenly spaced with the separation $0.0012\nu_v + 0.0024\nu_r$, where $\nu_v$ is positive for all the strong bands and $\nu_r$ is essentially negative. Wherever this separation matches the spacing of the lines of a branch, the fine structure should exhibit a simplified appearance. Traces of the earlier members of the $v'' = 0$ progression show a region in each band consisting of regularly spaced maxima with weaker maxima between them. This agrees with the expected structure if

we interpret the stronger maxima as blends of the lines of Pb$^{208}$ Pb$^{208}$, Pb$^{208}$ Pb$^{206}$, Pb$^{207}$ Pb$^{207}$ and Pb$^{206}$ Pb$^{206}$ and the weaker maxima as due to the superimposed lines of Pb$^{208}$ Pb$^{207}$ and Pb$^{207}$ Pb$^{206}$. The average separation of the stronger maxima in the (4,0) band with head at 20,143 cm$^{-1}$ is 1.34 cm$^{-1}$. On the preceding interpretation this should be twice the spacing of the isotope lines. The center of the region where the maxima occur is about 50 cm$^{-1}$ from the head of the band. With $\nu_r = -50$ cm$^{-1}$, $\nu_v$ must be 658 cm$^{-1}$ corresponding to an origin at 19,485 cm$^{-1}$. Determinations of the origin made in this manner from the (5,0), (6,0) and (7,0) bands give 19,491, 19,532 and 19,595 cm$^{-1}$, respectively. These values agree with one another as well as can be expected. Hence all the available data on the isotope splitting are in accord with the conclusion that the emitting molecule is diatomic lead.

# The Four Vector Problem and Its Application to Energies and Intensities in Platinum-Like Spectra

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The theory of two-electron systems involves both the electrostatic interaction between the electrons and the magnetic interaction between the spin and orbital moments of each electron. The inclusion of this latter effect requires the knowledge of the matrix of $a_1 l_1 \cdot s_1 + a_2 l_2 \cdot s_2$. This matrix has been given by Johnson, who obtained it by the method of noncommutative vector algebra. An outline of an alternative method based on the correspondence principle is given here because of its simplicity.

Mack's data on the $5d^9 6s$ and $5d^9 6p$ configurations of Pt I, Au II, Hg III, Tl IV, Pb V and Bi VI are used to check the theory because they present a complete isoelectronic sequence in which the coupling is decidedly intermediate. We find it more convenient to use the secular determinants for the $jj$ rather than the Russell-Saunders system of representation as the starting point of our perturbation calculation. These secular equations contain five electrostatic and two magnetic parameters. One of the magnetic parameters, $a_1$, is determined from the triplet width in $5d^9 6s$. The other and the five electrostatic ones are determined from six relations between the observed intervals. The intervals computed from the secular equations by using these values of the parameters are then compared with the experimental intervals. The $5/2, 3/2|_4$ level was used as origin. The results are quite satisfactory. A second method in which the number of electrostatic parameters is decreased to three by the use of Shortley's theory of the electrostatic interaction of almost closed shells is also used. Here the agreement, though satisfactory, is not as good as that obtained by the first method. The $5d^9 6s$ configurations were considered by applying the well-known equations of Houston. These results make it possible to compute the intensities of lines in the transition array, $5d^9 6s - 5d^9 6p$. The intensities of $5d^{10} - 5d^9 6p$ are also found. Comparison with the observed intensities shows as good agreement as one can expect considering the difficulties under which the experimental values were determined.
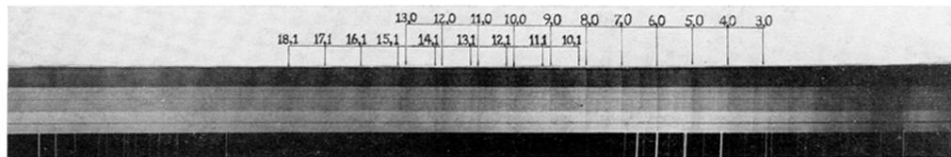
FIG. 1. Band spectrum of Pb₂ in absorption between 4600 and 5200A with iron comparison spectrum.