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VIBRATIONAL QUANTUM ANALYSIS AND ISOTOPE EFFECT FOR THE LEAD OXIDE BAND SPECTRA[*]

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Abstract

Each strong line ($Pb^{206}O$) in the band spectrum emitted by a uranium lead arc in air is represented by three lines ($Pb^{208,\ 207,\ 206}O$ with relative intensities in agreement with Aston) in the band spectrum from an ordinary lead arc. The first and second orders of a 21 ft. Rowland grating were used to make this comparison. The observed separations between corresponding band lines of isotopic molecules are in good agreement with the theory of the isotope effect in band spectra with PbO as the emitter.

New measurements of the wave-lengths of the band heads were made from moderate dispersion spectrograms of the ordinary lead arc in air. The bands in the near ultra-violet form a new system[**]

$$\nu=30{,}197.0+[530.6\,(v'+\tfrac{1}{2})-1.05\,(v'+\tfrac{1}{2})^2]-[722.3(v''+\tfrac{1}{2})-3.73(v''+\tfrac{1}{2})^2].$$

Three other systems in the visible have been discussed already by Mecke. Evidence in favor of combining two of these systems (C and B) into one is presented. All of the band systems have a common lower state.

Introduction

THE lead arc in air gives a fairly bright band spectrum consisting of a large number of heads all degrading towards longer wave-lengths. The same spectrum appears with compounds of lead subjected to a variety of conditions of excitation, and consequently there has been a great deal of speculation concerning the identity of the emitter.[1] Using low and moderate dispersion, Eder and Valenta[2] photographed the bands excited upon the introduction of lead chloride into an oxygen illuminating gas flame. They gave wave-length measurements of the heads to four figures, and believed that lead oxide was the emitter. Using the same method of excitation, Lamprecht[3] photographed the visible region at moderate dispersion, and in addition the yellow green region at high dispersion, failing however to resolve the fine structure completely.

Grebe and Konen[4] photographed the spectrum of a carbon arc containing ordinary lead chloride at high dispersion, and repeated using uranium lead

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[*] Paper presented at the Annual Meeting of the A. P. S., New York City, Dec. 28, 1928 (cf. Phys. Rev. **33,** 285 (1929)).

[†] This work was done at Ryerson Physical Laboratory of the University of Chicago.

[**] The symbol v is used in this work for the vibrational quantum number.

[1] H. Kayser, Handbuch der Spektroscopie, VI 256.

[2] J. M. Eder und E. Valenta, Atlas Typischer Spektren **17,** Wien, new printing 1924.

[3] H. Lamprecht, Zeits. f. Wiss. Phot. **33,** 10, 16 (1911).

[4] L. Grebe und H. Konen, Phys. Zeits. **22,** 546 (1921).

chloride. They limited themselves to a narrow region in the blue and found that the isotope effect was evident only as a slight wave-length shift and difference in the degree of sharpness of the band spectrum lines compared.

The first part of the present work deals with the vibrational quantum analysis of the lead oxide bands. New measurements of the wave-lengths of the band heads, believed to be more accurate than existing data, are used for most of this analysis. The isotope effect served to guide this part of the work.

In the second part the observed isotope effects will be discussed in detail, and it will be shown that the comparison of the single lines from uranium lead ($Pb^{206}O$) with the corresponding lines in the triplets $Pb^{208,\ 207,\ 206}O$ from ordinary lead is in quantitative agreement with the fact that ordinary lead contains isotopes 208, 207, 206.[5] This comparison furnishes a direct test of the theory of the isotope effect in band spectra.

While this work was in progress, and after preliminary reports on the isotope effect had been issued,[6] a short paper by Mecke[7] appeared dealing with his independent work based on Lamprecht's data, leading to a vibrational quantum analysis. These data are not quite complete since Lamprecht gives no measurements of the bands in the red and near ultra-violet. Further details of Mecke's work will be taken up later.

EXPERIMENTAL PROCEDURE

Measurements were made from moderate dispersion spectrograms of the ordinary lead arc in air. In addition comparisons and measurements were made from high dispersion spectrograms in the study of the band structure and isotope effect, and these spectra were taken first with an ordinary lead arc and then with a uranium lead arc. The uranium lead used originated in Belgian Congo ores, and had an atomic weight of 206.1.

The arc electrodes were copper rods $\frac{1}{2}''$ in diameter. A bead of a molten alloy of copper and lead was formed on both the upper $(-)$ and lower $(+)$ electrodes while the arc was in progress by melting pure thin copper wire and lead filings. With the proper proportions of lead and copper in each of the two beads, the arc had a blue color and emitted the lead oxide bands in a satisfactory manner. Fresh lead filings were added at intervals of several hours to prevent the appearance of the green tinge denoting strong emission of the copper spectrum. Copper lines were present on the spectrograms but did not interfere seriously with the work. The red copper oxide bands, generally recorded in a few minutes when the copper arc itself is used, were weak or entirely absent. The current carried was three amperes supplied at 220 volts with a suitable series resistance.

Spectrograms were taken with the Hilger Littrow-mounted El prism spectrograph, having a dispersion with the glass optical system of approximately 21A/mm at 6500A to 6A/mm at 4400A, and with the quartz system of 14A/mm at 4200A to 5.8A/mm at 3200A. The resolution of the structure

[5] F. W. Aston, Nature **120**, 224 (1927).

[6] S. Bloomenthal, Phys. Rev. **33**, 285 (1929). Science **69**, 229, 676 (1929).

[7] R. Mecke, Die Naturwissenschaften **17**, 122 (1929).

lines is incomplete and the heads are single and fairly sharp except where overlapping is great. Exposure of one hour sufficed with the El.

The high dispersion work was done in the first and second orders of the six inch 21 ft. Rowland concave grating having about 14,500 lines per inch and set up in a Rowland mounting. The dispersion in the first order is about 2.63A/mm. The exposure time was usually in excess of 15 hours. Fine grained plates were used in most of the photographic work. Iron lines were placed on the plates before and after exposure. Shifts due to temperature changes were minimized by an efficient system of temperature control consisting of thermostat, fan and heating unit with a mercury current break actuated by a sensitive relay circuit.

Reductions of the measurements of the moderate dispersion plates were made using the Hartmann[8] formula and an automatic Monroe calculating machine. The residuals were small, generally of the order of 0.02A. The formula was applied to only about 200A of the plates at any one time. Kayser's "Schwingungszahlen" served to convert the corrected measurements to vacuum wave-numbers. The iron line wave-lengths selected by the International Astronomical Union served as standards[9] in most of the reductions.

VIBRATIONAL QUANTUM ANALYSIS

In making the assignment of v values the new data on band head wave-lengths, which are believed to be better than the older data, were used. These were supplemented, however, where necessary by older values. This assignment is in agreement with the observed isotope effects (to be described later) using half integral values for the vibrational quantum number following Mulliken,[10] who first found them necessary in the analysis of the BO band spectra. The suggestions of Birge[11] proved useful in evaluating the constants in the empirical frequency equations by means of a consideration of the first and second differences of the wave-numbers in the usual two dimensional matrix diagram.

Assuming that the head is close to the band origin, where the change in rotational energy is approximately zero, one employs the following formula for the frequency of a band head

$$\nu=\nu^0+\omega_e'(v'+\tfrac{1}{2})-x'\omega_e'(v'+\tfrac{1}{2})^2+\omega_e''(v''+\tfrac{1}{2})-x''\omega_e''(v''+\tfrac{1}{2})^2$$

where ω_e is the frequency of vibration for infinitesimal amplitude and v is the vibration quantum number which takes integral values 0, 1, 2..... Primes (′) and double primes (″) refer, respectively, to the quantity indicated in the upper and lower electronic states.

Mecke assigned the bands in the wave-length region covered by Lamprecht's data to three systems *A*, *B* and *C*. The bands of the *C* system were extremely weak on the plates taken by the writer, and hence no measure-

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[8] A. Hartmann, Astrophys. J. **8**, 218 (1898).

[9] H. Kayser, Op. Cit. VII 405.

[10] R. S. Mulliken, Phys. Rev. **25**, 259 (1925).

[11] R. T. Birge. Nat. Res. Council Bulletin 57, **11**, 123 (1926).

ments were made on such heads. The writer has found an additional system *D* in the region 3209—3594A which was not photographed by Lamprecht. The band head data and vibrational quantum assignments for the *A*, *B* and *D* systems are given in Tables I, II and III.

The data apply to band heads. In the case of PbO the origin of each band as shown by the results of the following paper lies close to the head. *I* is the relative photographic intensity of the band as a whole, λ the wave-length in air in international Angstroms and ν the vacuum wave-number. *O-C* is the difference between the observed wave-number and the value calculated from the proper empirical formulas given below. Under remarks brackets [ ] denote masking by a band of higher frequency whose v values are enclosed. In some cases of masking it was not possible to secure the measurement of a head and the value of the wave-number calculated from the appropriate empirical formula is given in brackets. In such instances the relative intensity estimate was made from the plate enlargement, although the head was not measured. In cases where a measured wave-number value is classified in two systems, evidence justifying this has been found in extensive overlapping of the fine structure examined at high dispersion. The wave-number data for systems *A*, *B* and *D* are from new measurements.

When the suitable v' and v'' values are inserted, the following formulas give the wave-number of a classified band head to within a small difference from the measured value.

For heads in system *A*

$$\nu=19{,}863.3+\left[451.7(v'+\tfrac{1}{2})-3.33(v'+\tfrac{1}{2})^2\right]-\left[722.3(v''-\tfrac{1}{2})-3.73(v''+\tfrac{1}{2})^2\right]$$

For heads in system *B*

$$\nu=22{,}289.8+\left[496.3(v'+\tfrac{1}{2})-2.33(v'+\tfrac{1}{2})^2\right]-\left[722.3(v''+\tfrac{1}{2})-3.73(v''+\tfrac{1}{2})^2\right]$$

For heads in system *D*

$$\nu=30{,}197.0+\left[530.6(v'+\tfrac{1}{2})-1.05(v'+\tfrac{1}{2})^2\right]-\left[722.3(v''+\tfrac{1}{2})-3.73(v''+\tfrac{1}{2})^2\right]$$

Because of the fact that the isotope effect is unresolved at moderate dispersion, the constants given in these formulas are but approximations.

It is evident from inspection of these equations that all three systems have a common final state, which is probably the normal state of the PbO molecule. The systems *A*, *B* and D arise then from transitions from 2.5, 2.8, and 3.7 volt electronic levels, respectively, to this common lower state.

Mecke's equations based on Lamprecht's data are

$$(A)\quad \nu=19{,}877+\left[445(v'+\tfrac{1}{2})-1(v'+\tfrac{1}{2})^2\right]-\left[722(v''+\tfrac{1}{2})-3.5(v''+\tfrac{1}{2})^2\right]$$

$$(B)\quad \nu=22{,}293+\left[498(v'+\tfrac{1}{2})-1.4(v'+\tfrac{1}{2})^2\right]-\left[722(v''+\tfrac{1}{2})-3.5(v''+\tfrac{1}{2})^2\right]$$

$$(C)\quad \nu=24{,}875+\left[537(v'+\tfrac{1}{2})-15(v'+\tfrac{1}{2})^2\right]-\left[722(v''+\tfrac{1}{2})-3.5(v''+\tfrac{1}{2})^2\right]$$

System *D* is missing from Mecke's analysis since Lamprecht failed to secure wave-number data below 3740A. Although the new equations of *A* and *B* are similar numerically to Mecke's, the writer believes that his equations

TABLE I. *The A bands. New data and vibrational quantum analysis.*

System *A*

v' \ v''	0	1	2	3	4	5	6	7	8
0	1	2	6	6	6	4	3	1	
1	1	3	3	1	1	2	5	2	
2	2	2	1	2	3	2	1	3	2
3	1	1	1	1	0	1	2	1	3

System *B*[a]

v' \ v''	0	1	2	3	4	5	6	7
0	3	4	3	3	3	3	2	1
1	4	4	2	[A]	[A]	[A]	[A]	
2	4	3		1	2			[A]
3	4	2	2	1				
4	3							
5	2							
6	1	2						
7	1	2						
8		2	2					

System *D*

v' \ v''	0	1	2	3	4
0	1	5	6		
1	2	2			1
2	2			1	

[a] The intensity data of Table I for system *B* comes from Lamprecht's data. [A] denotes masking by *A* heads. These superposed bands are unusually strong in some cases.

v'	v''	I	λHd. (I.A)	ν(cm^{-1})	O-C (cm^{-1})	Remarks
0	7	1	6720.32	14,876.2	−4.3	
2	8	2	6620.23	15,101.1	− .1	
1	7	2	6524.25	15,323.2	−2.3	
3	8	3	6433.63	15,539.0	6.2	
0	6	3	6427.73	15,553.3	2.6	
2	7	333	6342.01	15,763.5	− .4	
1	6	5	6250.75	15,993.4	−2.3	
3	7	1		[16,195.6]		[0,5]
0	5	4	6160.52	16,227.9	− .4	
2	6	1d		[16,434.1]		
1	5	2		[16,673.3*]		[Pb 6002.0]
3	6	2		[16,865.8]		[0,4]
0	4	6	5910.74	16,913.7	.3	
2	5	2	5842.13	17,112.3	.6	
1	4	1d		[17,358.4]		[0,3]
3	5	1		[17,543.5]		[0,3]
0	3	6	5677.78	17,607.6	1.7	
2	4	3	5617.65	17,796.1	− .7	
1	3	1		[18,050.9]		[0,2]
3	4	0		[18,228.5]		[0,2]
0	2	6d	5459.38	18,312.0	6.2	also 2,7 B
2	3	2	5407.18	18,468.8	− .5	also 1,6 B
1	2	3	5331.11	18,752.6	1.7	
3	3	1		[18,921.1]		[0,1]
0	1	2	5258.26	19,012.4	− .9	
2	2	1	5211.98	19,181.2	8.1	
1	1	3	5138.18	19,457.4	−1.0	
3	2	1	5093.19	19,628.6	7.6	
0	0	1	5068.78	19,723.1	−5.0	
2	1	2	5024.21	19,898.1	−1.4	
1	0	1		[20,233.1]		[0,2 B]
3	1	1	4916.62	20,333.5	−5.1	
2	0	2	4850.12	20,612.1	− .6	
3	0	1	4747.81	21,047.7	−3.4	

* Eder and Valenta give λ5998A ($\nu = 16,667.6$).

fit the new data better than Mecke's do the data of Lamprecht. Mecke assigned the three systems A, B and C to a $^3\pi \rightarrow {}^3\Sigma$ transition, but the fine structure analysis to be reported in a companion paper does not justify this designation. Furthermore it has been noticed that practically all the bands belonging to system C can be accounted for equally well as members of B.

TABLE II. *The B bands. New data and vibrational quantum analysis.*

v'	v''	I	λ Hd. (I.A)	ν(cm^{-1})	O-C (cm^{-1})	Remarks
0	7	1	5770.01	17,326.2	−3.3	
0	6	1	5553.83	18,000.6	− .9	
2	7	2	5459.38	18,312.0	4.1	also 0,2 A
1	6	2	5407.18	18,488.8	1.6	also 2,3 A
0	5	3	5353.82	18,673.1	−4.7	
1	5	0		[19,168.1]		[2,2 A]
0	4	6	5162.31	19,365.8	3.3	
1	4	0		[19,853.2]		[0,3]
0	3	6	4983.79	20,051.4	3.6	
2	4	1	4916.80	20,341.0	− .3	
1	3	0		[20,545.7]		[2,0 A]
0	2	6	4816.90	20,754.5	.5	
2	3	1	4753.55	21,031.1	2.3	
1	2	2	4706.43	21,241.6	4.1	
0	1	5	4657.98	21,462.5	− .2	
3	3	1	4647.49	21,511.1	4.2	
2	2	1		[21,733.4*]		[1,1]
1	1	6	4553.71	21,954.0	−1.0	
0	0	1	4509.23	22,170.5	6.7	
3	2	1	4499.99	22,216.1	− .7	
2	1	1	4454.80	22,441.4	− .7	
1	0	5	4410.38	22,667.4	.5	
3	1	0		[22,922.7†]		[2,0]
2	0	4	4317.06	23,157.4	−1.8	
3	0	4	4229.01	23,639.6	−2.0	
4	0	2	4145.93	24,113.3	1.5	

* Lamprecht gives λ4597.9 (ν=21,743) (doubtful)
† Lamprecht gives λ4358.3 (ν=22,938)

It has been remarked previously that the bands of system C in the region from 4280A to 3740A were not sufficiently strong to be measured on the plates taken by the writer. On the other hand, Lamprecht's data do not extend beyond 3740A where the heads of the D system occur. Thus the older data in this region cannot be corrected to conform to the measurements made by the writer. Employing, therefore, Lamprecht's data for all the heads of

TABLE III. *The D bands. New data and vibrational quantum analysis.*

v'	v''	I	λ Hd. (I.A)	ν(cm^{-1})	O-C (cm^{-1})	Remarks
1	4	1	3594.16	27,815.0	− .3	
0	2	6	3485.68	28,680.6	1.1	
2	3	1	3442.76	29,038.2	4.6	
0	1	5	3401.92	29,386.9	0	
1	1	2	3341.83	29,915.2	.1	
0	0	1	3320.68	30,105.7	3.7	
1	0	2	3264.36	30,625.1	−4.9	
2	0	2	3209.21	31,151.3	−4.5	

the bands in this region an equation for the B system is found including practically all of the heads of system C.[12] The equation is

$$\nu = 22{,}292 + [495.7(v'+\tfrac{1}{2}) - 2.05(v'+\tfrac{1}{2})^2] - [722.3(v''+\tfrac{1}{2}) - 3.73(v''+\tfrac{1}{2})^2]$$

The observed minus calculated values obtained from this equation are well within the experimental error of the measurements given by Lamprecht. It is obvious that this equation differs but little from the equation for the B system based upon the new data. However, until new data are obtained one may reasonably assume that thus far only three systems are known to be present in the spectrum of PbO, namely A, B, and D.

TABLE IV. *Unidentified heads in the lead oxide band Spectrum.*[h]

λ Hd. (I.A)	ν(cm^{-1})	I	Investigators	Remarks
6680	14,966	2[g]	Eder and Valenta	also 6677.77 (1) S.B
6476	15,437	2	Eder and Valenta	also 6475.78 (1) S.B
6288	15,899	1	Eder and Valenta	b
6210	16,099	2	Eder and Velanta	b
6021	16,604	1	Eder and Valenta	b
5858	17,066	1	Eder and Valenta	d
4784.9	20,893	2	Lamprecht	b
4694	21,289	1	Eder and Valenta	c 4692.94 (1) S.B.
4632	21,583	2	Eder and Valenta	d
4619	21,644	1	Eder and Valenta	d
4369.4	22,880	1	Lamprecht	e
4281.2	23,351	1	Lamprecht	b
4156.3	24,053	2	Lamprecht	b
4036.2	24,769	2	Lamprecht	b
3950.6	25,306	1	Lamprecht	e
3878.3	25,777	1	Lamprecht	e
3839.6	26,037	1	Lamprecht	e
3804.9	26,275	1	Lamprecht	f 3810.61 (1) S. B.
3771.8	26,505	1	Lamprecht	e
3748	26,673	1	Eder and Valenta	d
3736.3	26,757		Lamprecht	e
3557	28,106	1	Eder and Valenta	f 3554.43 (1) S.B.

[a] Observed also by Lamprecht but not by S. B.
[b] Observed also by Eder and Valenta but not by S. B.
[c] Observed also by S. B. but not by Lamprecht.
[d] Observed by neither Lamprecht nor S. B.
[e] Observed by neither Eder and Valenta nor S. B.
[f] Observed also by both Eder and Valenta and by S. B.
[g] The relative intensity estimates for Eder and Valenta's data were made by the writer from an examination of the PbO spectra in the Atlas.
[h] These unidentified heads cannot be accounted for even if Mecke's system C is included with the other three systems. Many of these heads represent, no doubt, the superposition of a number of lines.

Table I illustrates the experimental intenstity data. Comparison with the Franck-Condon theory is postponed until a fine structure analysis yields further data concerning the molecular constants of PbO.

BAND STRUCTURE AND ISOTOPE EFFECT

Under high dispersion each band consists apparently only of a P and R branch, which run coincident near the head of each band. Because of the fine

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[12] The heads not included in B are 4281.2A, 4156.3A and 4036.2A.

scale of the band structure and overlapping of series, it is difficult to make accurate measurements of the wave-lengths of the individual lines. The bands in the red, yellow and green, photographed already at high dispersion with the uranium lead arc as source, appear to offer the best possibilities for a fine structure analysis. Such an analysis has been made already for some of the bands, and the results are given in a subsequent paper in collaboration with Dr. A. Christy.

The expression for the separation in wave-numbers between the corresponding band spectrum lines of two isotopic diatomic molecules[13] is

$$\nu_2-\nu_1=(\rho-1)\left[(v'+\tfrac{1}{2})w_{e1}'-(v''+\tfrac{1}{2})w_{e1}''\right] \\ -(\rho^2-1)\left[(v'+\tfrac{1}{2})^2x_1'w_{e1}'-(v''+\tfrac{1}{2})^2x_1''w_{e1}''\right]-(\rho^2-1)(\nu_1-\nu_{Hd})$$

where $\rho=(\mu_1/\mu_2)^{1/2}$ and $\mu_1=m_1m/m_1+m$, $\mu_2=m_2m/m_2+m$ m_1 and m_2 are the masses of the isotopic atoms and m is the mass of the common kind of atom in the molecules m_1m and m_2m. Subscript 1 refers to the constant for the more abundant and subscript 2 to that for the less abundant molecule. In our case m_1 is the mass of Pb^{208}, and m_2 the mass of Pb^{207}. For convenience one can make the following abbreviations.

$$\Omega=(\rho-1)\left[(v'+\tfrac{1}{2})w_e'-(v''+\tfrac{1}{2})w_e''\right]$$

$$o=-(\rho^2-1)\left[(v'+\tfrac{1}{2})^2x'w_e'-(v''+\tfrac{1}{2})^2x''w_e''\right]$$

$$\tau=(\rho^2-1)(\nu-\nu_{Hd}).$$

The subscript 1 is dropped above since the isotope effect is unresolved at moderate dispersion.

$$\nu_2-\nu_1=\Omega+O+\tau\,.$$

Neglecting the rotational contribution τ and also the term O, the approximate magnitude of the (vibrational) isotope effect can be calculated simply by the relation

$$\nu_2-\nu_1=(\rho-1)(\nu-\nu^0)$$

where ν^0 is the wave-number of the band system origin. ρ for PbO is $[(208\times16)(207+16)/(208+16)\ (207\times16)]^{1/2}=1.000173$. This is approximately equal to $[(207\times16)(206+16)/(207+16)\ (206\times16)]^{1/2}$. Hence in the A system where $\nu^0=19{,}863.3$ and ν for the head of the 0,5 band is 16,227.9, then $\nu_2-\nu_1=-0.63$ cm^{-1}. This is close to the observed value $-0.68\ \pm0.05$ determined by direct comparison of the lines $Pb^{206}O$ from uranium lead with the lines $Pb^{208,\,207,\,206}$ O from ordinary lead. If Pb_2 were the emitter, then

$$\rho=[(208\times207)(207+207)/(208+207)(207\times207)]^{1/2}=1.0015,$$

and the isotope separation $\nu_2-\nu_1$ for the 0,5A band ought to be about 5.5 wave-numbers, almost nine times as large as the value actually observed.

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[13] R. S. Mulliken, Phys. Rev. **25,** 119 (1925) and F. W. Loomis, Nat. Res. Council Bulletin 57, **11,** 123 (1926). The last term in this formula is only an approximation.

Figure 1 illustrates the isotope effect observed near the head of the λ5677.78A (0,3*A*) band. The upper microphotometer record was secured from a spectrogram taken with uranium lead of atomic weight 206.1 in the arc. Below is the record of the same region on a spectrogram taken with ordinary lead (atomic weight 207.2) in the arc. A Moll microphotometer, which records automatically was used. The central reference line is a lead arc line of wave-length 5692.329A which probably shows a small atomic isotopic effect. The light vertical lines serve to identify the corresponding lines in the two spectra, namely $Pb^{206}O$. The lines $Pb^{208}O$ and $Pb^{207}O$ are apparently absent from the upper trace. Isotope 208 is the most abundant in ordinary lead, and hence $Pb^{208}O$ gives the strongest lines. Aston gives 208 (7), 207 (3), and 206 (4) as the composition of ordinary lead, and the results of this investigation are in agreement with these relative abundancies. The wave-lengths of the series lines are given in the lower part of the figure.

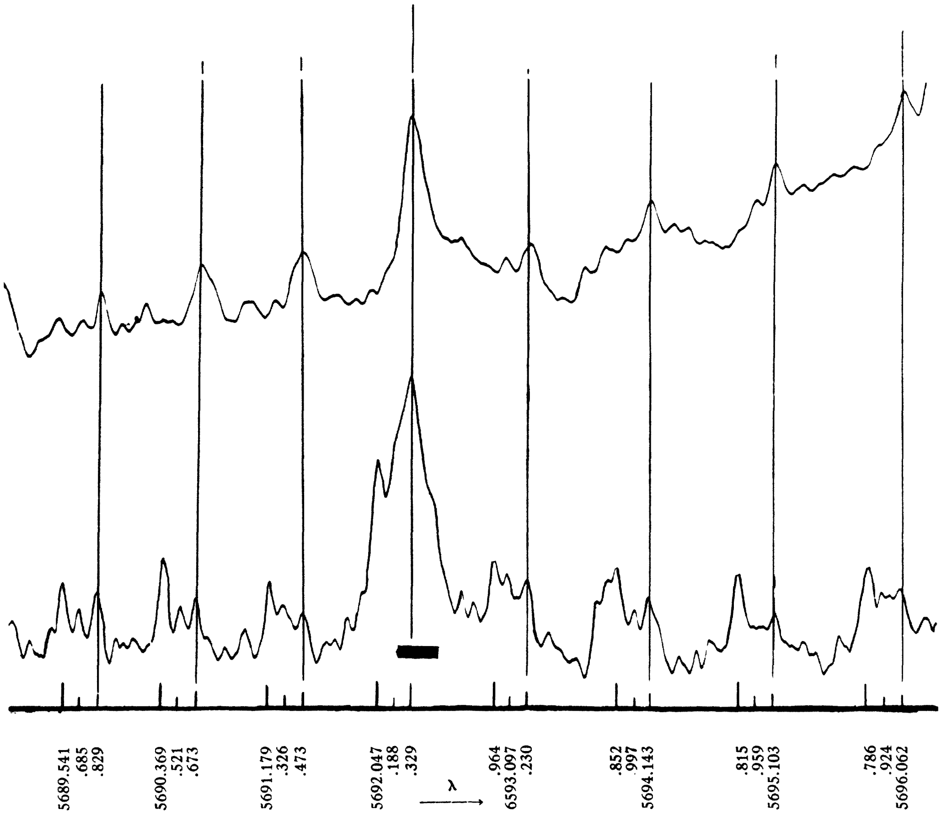

Fig. 1. Isotope effect in the λ5677.78 (0,3 *A*) band of PbO. Above, $Pb^{206}O$ from uranium lead. Below, $Pb^{208,\ 207,\ 206}O$ from ordinary lead. Isotopic displacement −0.428 wave-numbers.

Figure 2 gives a similar comparison near the head of the λ6160.52A (0,5*A*) band. Just as in the case of the 0,3 band, the lines Pb^{206} O are on the long wave-length side of the lines $Pb^{207}O$. The *P* and *R* lines are coincident in the middle of the picture and begin to diverge both on the far left and far right side, causing the lines to become fuzzy. The single lines Pb^{206}O in the upper spectrum were secured with a heavy exposure in order to bring out weak lines of other isotopic molecules that might possibly be present. This was done in an attempt to satisfy Dr. C. S. Piggot's[14] wish for a reliable qualitative analysis of uranium lead from the Belgian Congo. Data of this nature are necessary in estimating the age of uranium minerals. It is evident from inspection of Fig. 2 that 206 is the principal isotope in the uranium lead sample used. This is to be expected from its atomic weight of 206.1.

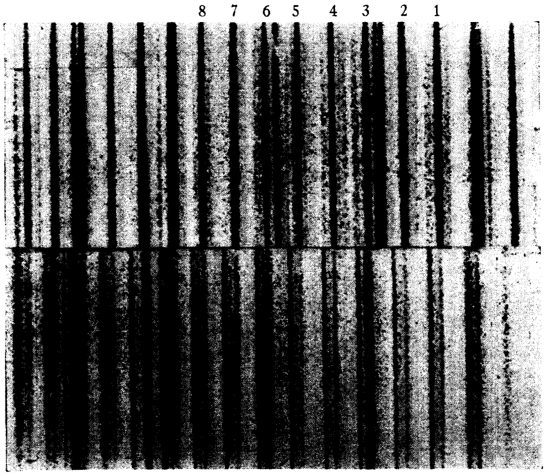

Fig. 2. Isotope effect in the λ6160.52A (0,5 *A*) band of PbO.

Table V gives the measured wave-lengths of the band lines examined in Fig. 2. The first order of the grating was used. The numbers above the lines Pb^{206}O in Fig. 2 correspond to those under "group" in Table V.

TABLE V. *Wave-lengths of lines in the 6160.52 A (0,5A) band.*

Group	Pb^{206}O	Pb^{207}O	Pb^{208}O
1	6204.916	6204.685	6204.434
2	3.327	3.077	2.800
3	1.717	1.461	1.174
4	0.117	6199.890	6199.653
5	6198.583	8.369	8.108
6	7.086	6.827	6.577
7	5.662	5.386	5.125
8	4.213	3.973	3.707

Figure 3 illustrates the isotope effect observed in one of the *D* system bands. The band lines in the upper half of the figure are the lines Pb^{206}O from uranium lead. These are shifted 0.036 ± 0.01A on an average approximately to longer wave-lengths with respect to the lower lines Pb$^{208, 207, 206}$O from

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[14] C. S. Piggot, Jour. Wash. Acad. of Sciences **18**, 10, 269 (1928).

ordinary lead, which are unresolved in this region. Table VI gives the wave-length data. These begin, reading from right to left, with the second line on the short wave-length side of the reference line in Fig. 4. It is to be noted that here the isotope effect is unresolved although the second order of the grating was used. This is in marked contrast to the effects observed in system *A*, but is in agreement with the shift calculated on the basis of the vibrational assignment for the *D* bands. The calculated shift is -0.271 cm^{-1} for Pb^{208}O as compared with Pb^{207}O while the value measured is -0.30 ± 0.08 cm^{-1}. The minus sign indicates that the lines from the molecules containing the lighter isotope are displaced towards lower frequencies with respect to the radiations from the molecules containing the heavier isotope.

Fig. 3. Isotope effect in the λ3485.68A (0,2 *D*) band of PbO. Upper spectrogram, uranium lead oxide. Lower spectrogram, ordinary lead oxide.

Table VI. *Wave-lengths of lines in the λ3485.68A (0,2D) band.*

Pb^{206}O	Pb$^{208,\,207,\,206}$O (unresolved)
(From uranium lead)	(From ordinary lead)
3490.106	3490.078
.372	.343
Fe 3490.577	Fe 3490.577
.632	.579
.922	.895
1.236	1.168
.501	.458
.807	.773
2.108	2.081
.443	.390

Table VII gives a comparison between the observed isotope effects and the values calculated as the sum $\Omega + O + \tau$.

In the 0,3 band of system *A* the lines which we now recognize as $Pb^{208}O$ and $Pb^{206}O$ were measured by Lamprecht in 1911, who designated them as lines of series I and III in his tables of wave-lengths. The lines $Pb^{207}O$, which form the intermediate series, are missing from the data of Lamprecht, since he used lower dispersion and resolving power than did the writer.

TABLE VII. *Isotope effects observed by direct comparison of $Pb^{206}O$ from uranium lead with $Pb^{208,207,206}O$ from ordinary lead, and the values calculated as the sum $\Omega + o + \tau$.**

in Band	$\nu - \nu$Hd. (cm^{-1} approx.)	$\lambda_2 - \lambda_1$(I.A.) Observed	$\nu_2 - \nu_1$(cm^{-1})	Ω	*O* Calculated (cm^{-1})	τ	$\nu_2 - \nu_1$ (cm^{-1}) Calculated	Observers	Remarks
0,5*A*	− 78	0.255± .02	−0.68± .05	−0.648	+0.039	−0.027	−0.636	S. B.	Resolution into Triplets
0,3*A*	− 47	0.141± .02	−0.43± .06	−0.398	+0.016	−0.016	−0.398	S. B.	Resolution into Triplets
3,0*B*	−116	−0.055± .02	+0.31± .11	+0.238	−0.010	−0.040	+0.188	Grebe and Konen	Not Resolved
0,2*D*	− 36	0.036± .01	−0.30± .08	−0.267	+0.008	−0.012	−0.271	S. B.	Not Resolved

* The isotope effect calculated here is that of $Pb^{208}O$ and $Pb^{207}O$ and is approximately the same as that of $Pb^{206}O$ and $Pb^{207}O$ numerically.

Dr. R. S. Mulliken suggested this problem and gave a good deal of important advice in the course of this investigation. Consequently the writer takes this opportunity to thank him. To Drs. Gale, Compton, Harkins, Piggot, Hoag and Christy, the writer feels indebted for many helpful hints. The uranium lead of atomic weight 206.1 was a gift from the Wolcott Gibbs Memorial Laboratory of Harvard University, and the writer is indebted through Dr. Mulliken to Dr. L. P. Hall for making about 20 grams of pure material extracted from Belgian Congo uranium ores available.

When Dr. Mecke was informed of the present investigation, he very kindly agreed to leave further work on the fine structure analysis to the writer.

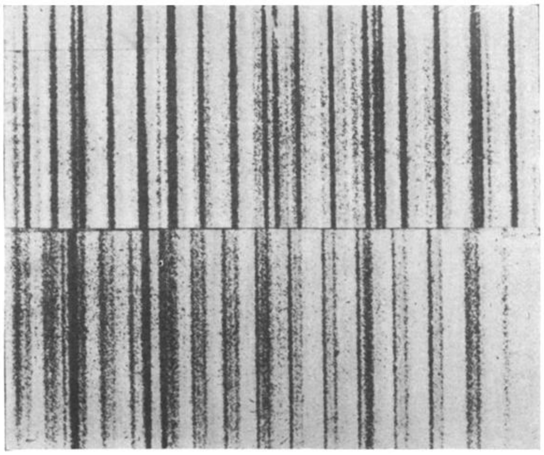

Fig. 2. Isotope effect in the λ6160.52A (0,5 *A*) band of PbO.

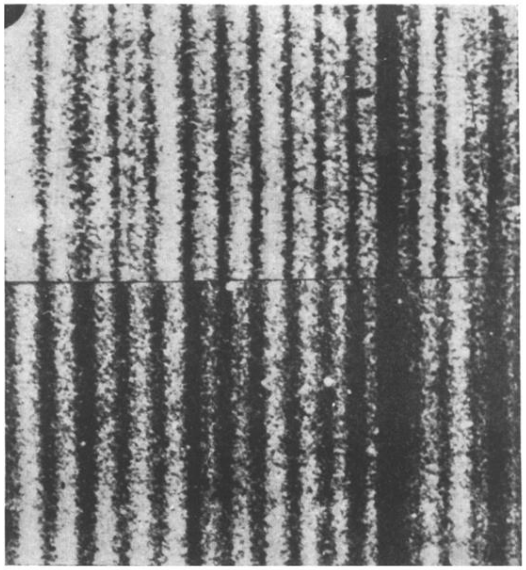

Fig. 3. Isotope effect in the λ3485.68A (0,2 *D*) band of PbO. Upper spectrogram, uranium lead oxide. Lower spectrogram, ordinary lead oxide.