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Absorption Spectrum of Lead Oxide

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The spectrum of PbO has been photographed in absorption. A new system, designated as the *E* system, has been found. It is nearly coincident with the *D* system. A number of previously unclassified bands together with some new bands are assigned to a new system, replacing Mecke's *C* system. The *D* system has been extended and the new values require that $x_e\omega_e'$ be changed from 1.05 to 3.13. All three systems have the same lower level in common with the *A* and *B* systems.

Introduction

Eder and Valenta[1] photographed the band spectrum of lead oxide (PbO) and measured the wavelengths of the heads to four figures. Lamprecht[2] and Grebe and Konen,[3] using higher dispersion, repeated and extended the observations. Mecke[4] on the basis of Lamprecht's data gave a partial vibrational quantum analysis. Bloomenthal[5] made a new series of measurements of the wavelengths of these band heads on moderate dispersion spectrograms and revised and extended the vibrational analysis which had been given by Mecke. The fine-structure analysis of the bands in the *A* and *D* systems has been given by Christy and Bloomenthal.[6]

Since all observations on these bands seem to have been made in emission, it is of interest to study them in absorption in order if possible to extend them and improve the accuracy of the vibrational analysis.

Experimental

Chemically pure yellow lead oxide (PbO) was heated in an iron tube about 50 cm long and 2 cm in internal diameter. The tube was open at both ends so that the oxide was exposed to the air at atmospheric pressure. The tube containing the oxide was heated by means of a compressional ring Hoskins electric furnace operated at 25 volts a.c. and 400 amperes. The temperature of the tube and oxide was maintained at about 1200°C.

Light from an underwater spark with magnesium electrodes, arranged as used by Smith and Muskat,[7] was used as a source of continuous radiation in the ultraviolet. In the visible region of the spectrum continuous radiation was obtained from an ordinary incandescent lamp.

The spectrograms were taken with a Hilger Littrow mounted E-1 quartz spectrograph having a dispersion of about 5A/mm at 3100A and 14A/mm at 4200A. An iron arc provided a standard of wavelengths.

Results

To the *A* and *B* systems which were analyzed by Mecke[4] and by Bloomenthal[5] nothing has been added by this investigation. It may be of interest to state that we observed these systems in absorption and also in emission from the vapor of the lead oxide in the furnace. They are more completely developed in emission.

The *D* system, which was first observed by Bloomenthal,[5] is strongly developed in absorption, making an extension of the system possible. The positions of the heads of the bands of this system are shown in Table I, together with their vibrational quantum numbers. Those marked with an (*) have been previously observed by Bloomenthal.[5] The others are reported for the first time. The heads are represented within observational error by the formula

$$\nu=30{,}195.0+532.0(v'+1/2)-3.13(v'+1/2)^2 -722.5(v''+1/2)+3.75(v''+1/2)^2$$

which is essentially the same as that given by Bloomenthal[5] except that it is necessary to

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[1] Eder and Valenta, *Atlas Typischer Spectra.*

[2] Lamprecht, Zeits. f. wiss. Phot. **10**, 16, 33 (1911).

[3] Grebe and Konen, Physik. Zeits. **22**, 546 (1921).

[4] Mecke, Naturwiss. **17**, 122 (1929).

[5] Bloomenthal, Phys. Rev. **35**, 34 (1930).

[6] Christy and Bloomenthal, Phys. Rev. **35**, 46 (1930).

[7] Smith and Muskat, Phys. Rev. **29**, 663 (1927).

TABLE I. *Band heads in the D system.*

ν observed	v'	v''	$\nu_{\text{obs.}}-\nu_{\text{calc.}}$	ν observed	v'	v''	$\nu_{\text{obs.}}-\nu_{\text{calc.}}$
27287.7	0	4	−0.1	30234.0	3	2	−2.7
27811.3*	1	4	−2.2	30432.0	2	1	2.0
27979.3	0	3	0.0	30624.8*	1	0	−0.7
28314.3	6	7	1.5	30747.5	4	2	3.8
28480.9	5	6	−7.5	31036.0	6	3	−3.8
28679.4*	0	2	2.1	31102.5	9	5	−7.6
28843.9	3	4	0.7	31145.3*	2	0	0.3
29028.3*	2	3	3.8	31316.3	8	4	−2.1
29161.3	5	5	−8.6	31441.7	4	1	−8.5
29385.8*	0	1	1.0	31658.3	3	0	0.1
29725.2	2	2	1.7	32166.0	4	0	0.8
29909.8*	1	1	−0.7	32230.0	7	2	3.0
30100.8*	0	0	1.0	29857.0	5	4	3.1

* Reported by Bloomenthal.

raise the value of $x_e\omega_e'$ from 1.05 to 3.13 in order accurately to represent our data.

In addition to the *A*, *B* and *D* systems, a new system of bands has been observed. These bands, which are weaker than those of the *D* system, are degraded toward the red. The origin of the system is slightly farther toward the violet than that of the *D* system. The band heads of this system are represented by the formula:

$$\nu=30{,}899.0+425.8(v'+1/2)-1.48(v'+1/2)^2 \\ -722.5(v''+1/2)+3.75(v''+1/2)^2.$$

Table II gives a comparison of observed and calculated frequencies together with the assignment of vibrational quantum numbers. Additional bands of this system were observed which were either too weak to measure or were obscured by stronger bands of the *D* system.

TABLE II. *Band heads in the E system.*

ν observed	v'	v''	$\nu_{\text{obs.}}-\nu_{\text{calc.}}$	ν observed	v'	v''	$\nu_{\text{obs.}}-\nu_{\text{calc.}}$
27668.0	1	5	−5.6	30463.8	1	1	5.2
27932.8	0	4	−3.0	30585.7	3	2	−2.2
27979.3	5	7	−7.5	30752.3	0	0	1.5
28247.1	4	6	0.3	30887.3	2	1	8.8
28767.9	2	4	10.6	31172.8	1	0	−0.8
29193.9	3	4	−1.5	31232.6	8	4	1.4
29747.3	1	2	−3.8	31590.5	2	0	−3.5
29883.0	3	3	−4.9	31711.7	4	1	2.4
30037.2	0	1	1.4	31809.6	6	2	−9.1
30173.8	2	2	2.8	32425.0	4	0	−0.7

In the vicinity of λλ3600–4200 Lamprecht[2] reported a number of weak bands which have not been analyzed. Bloomenthal[5] states that the bands in this region were too weak to measure on his plates. These bands are fairly strong in absorption. It has been possible to measure them with an accuracy greater than that claimed by Lamprecht[2] and to add two additional bands not recorded by him. The heads of this system are represented by the formula

$$\nu=24{,}871.6+516.0(v'+1/2)-3.5(v'+1/2)^2 \\ -722.5(v''+1/2)+3.75(v''+1/2)^2.$$

The origin of this system lies between the origins of the *B* and *D* systems. It may therefore be referred to as the *C* system. It must not, however, be confused with the *C* system proposed by Mecke[4] although the origin is approximately the same. Bloomenthal[5] was able to include in his *B* system nearly all the bands originally attributed to Mecke's *C* system. The bands left out are included in the *C* system proposed here. The new values of the bands in this system are given in Table III. The bands in this table marked (*) were reported by Lamprecht[2] but not observed by us. Those marked (**) are reported for the first time.

TABLE III. *Band heads in the C system.*

ν observed	v'	v''	$\nu_{\text{obs.}}-\nu_{\text{calc.}}$	ν observed	v'	v''	$\nu_{\text{obs.}}-\nu_{\text{calc.}}$
23351*	0	2	5	25565.2	3	1	5.9
24052.6	0	1	−0.7	25780.8	2	0	1.5
24352.9	2	2	−3.9	26038.0	4	1	−9.3
24558*	1	1	−4	26278.9	3	0	4.6
24765.7	0	0	−2.6	26753.2	4	0	−9.1
25070.0	2	1	5.7	27244.8**	5	0	1.5
25278.2	1	0	0.9	27716.7**	6	0	−0.6

* Not observed by authors.
** Not previously reported.

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