

Estimation of rotational temperature of the source emitting the spectrum of PbO molecule

A B DARJI, T M PATEL, M B SURESHKUMAR, N R SHAH and P M SHAH
Physics Department, M.S. University of Baroda, Baroda 390 002, India

MS received 3 May 1993; revised 31 August 1993

Abstract. The (1, 0), (0, 1) and (0, 2) bands of $D \rightarrow X$ system of lead monoxide have been excited in RF discharge source and photographed in the seventh order of a 2-meter PGS. Intensity records of the rotational lines have been obtained. Rotational constants and the intensity measurements of Q and P branch lines of the above three bands and J numbering are used to calculate the effective rotational temperature of the source emitting the spectrum of ^{208}Pb ^{16}O molecule.

Keywords. Rotational temperature; molecular spectrum; lead monoxide.

PACS No. 33.20

1. Introduction

The spectrum of lead monoxide extending from 6750 to 1700 Å has been extensively studied by earlier workers [1–14] in various degrees of details. They have recorded the spectrum in absorption as well as in flame, d.c. arc, microwave discharge and high frequency discharge. The vibrational analyses of various band systems and rotational analyses of large number of bands have been reported by employing moderate to high dispersions. Rotational constants of X , A , B , C , C' D and E states of the molecule are known. Ram *et al* [14] have reported the rotational analysis of (1, 0) and (1, 1) bands of $B \rightarrow X$ system and (0, 1) and (0, 2) bands of $D \rightarrow X$ system. They have observed several perturbations in the rotational levels associated with $v' = 1$ level of B state and $v' = 0$ level of D state. They have also calculated rotational constants using perturbing rotational levels. The work reported so far on the spectrum of PbO molecule has been well reported by Ram *et al* [14]. Though the study of this molecule is extensive it has been found that there is no report on the intensity measurements of vibrational bands and rotational lines. No one has employed intensity measurements to study the vibrational and rotational temperatures of the molecule. This study makes first attempt to calculate the rotational temperature of PbO molecule. Rotational structure well resolved up to almost the origin of (1, 0), (0, 1) and (0, 2) bands exhibiting sharp rotational lines have been obtained. The rotational analysis of (1, 0) band has also been reported here for the first time. By studying the intensity profiles of the above bands and employing the J numbering and rotational constants, the rotational temperature of the source has been calculated.

2. Experimental

The spectrum of lead monoxide has been excited in RF discharge source. A pure sample of lead oxide (BDH) is taken in a quartz tube of 25 cm long and 8 mm dia. The characteristic sky blue discharge was established by employing high frequency oscillator giving an output power of 125 W at 10–15 MHz. External heating by a burner was necessary to maintain the stable conditions of the discharge in the tube which was continuously evacuated by a high vacuum pump (10^{-3} mm of Hg). A strong emission in the blue-green region was seen to develop in intensity. The (1, 0), (0, 1) and (0, 2) bands of $D \rightarrow X$ system at 3264 Å, 3401 Å and 3485 Å respectively were photographed in a 2 m plane grating spectrograph (Carl-Zeiss) providing a dispersion of about 0.7 Å/mm in the seventh order of the plane grating blazed at 10500 Å, having 651 grooves per mm. It offers a resolution of about 2×10^5 . A pre-disperser (Carl-Zeiss) in the order-sorter mode has been used to avoid the overlapping of orders. Exposures for about 10 h were found satisfactory to photograph the rotational structure with sufficient intensity using the fine slit of 20 μ and Kodak T-Max and ORWO WU-3 spectral plates. The plates were measured on Abbe comparator (Carl-Zeiss). The error of measurements is within $\pm 0.05 \text{ cm}^{-1}$ for unblended and sharp lines. Atomic lines of lead present in the spectrum served as internal standards. Intensity measurements were made by recording the intensity distribution amongst the rotational lines of the (1, 0), (0, 1) and (0, 2) bands using a microdensitometer coupled with X–Y potentiometric recorder (Carl-Zeiss). The densitometer was calibrated for a temperature of T K using a standard continuous source of light. It was also calibrated for the spectral sensitivity of emulsion of the photographic plates. It has been found that the spectral sensitivity of the emulsion remains almost constant over a small extent of the rotational structure of a particular band. Then the area under the intensity peak of a rotational line is measured by using a planimeter having an accuracy better than 10^{-4} cm^2 . Thus the relative intensity measurements of rotational lines are made and average values for each line are employed to calculate the rotational temperature.

3. Results and discussion

(a) Rotational analysis of (1, 0) band of $D \rightarrow X$ system

The (1, 0) band of $D \rightarrow X$ system at 3264 Å of PbO molecule reproduced in figure 1(a) and (b) as seen on negative exhibits a fine rotational structure well resolved up to the origin comprising of R , Q and P branches of which R is head forming. The branch lines are correctly picked up using the intensity records. The rotational analysis was performed using the standard method of Herzberg [15] and by plotting the graphs of $\Delta_1 F(J)/J + 1$ and $\Delta_2 F(J)/J + \frac{1}{2}$ against $(J + 1)^2$ and $(J + \frac{1}{2})^2$ respectively. The criterion for the correctness of J numbering suggested by Younger and Winans [16] was employed. Thus the rotational constants B'_1 , D'_1 and B''_0 and D''_0 were derived from the graphical plots. The constants were also computed by using least squares fit up to the confidence level of 95%. The accuracy of the constants was further checked by employing iterations in J numbering and B'_1 and D'_1 values so as to converge the differences of observed and calculated line frequencies ($\nu_{\text{obs}} - \nu_{\text{cal}}$) to a minimum of within $\pm 0.1 \text{ cm}^{-1}$. The J numbering, vacuum wave-numbers of R , Q and P lines and combination differences are given in table 1. The rotational constants

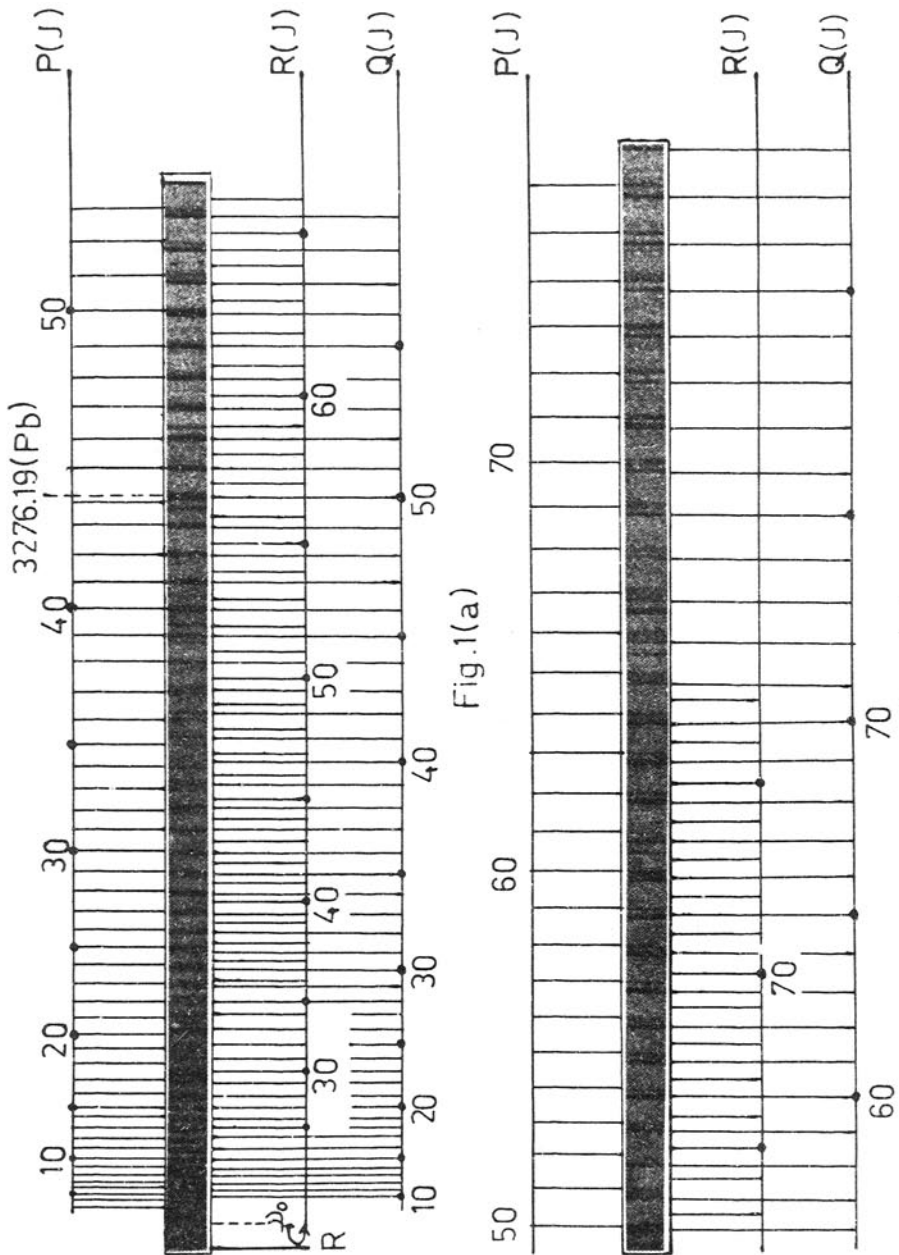


Figure 1. Rotational structure of (1, 0) band of $D \rightarrow X$ system of $^{208}\text{Pb } ^{16}\text{O}$ molecule at $0.7088 \text{ \AA}/\text{mm}$.

Table 1. J assignments, vacuum wavenumbers and combination differences of $D \rightarrow X$ system of $^{208}\text{Pb}^{16}\text{O}$.

J	$Q(J)$ cm^{-1}	$P(J)$ cm^{-1}	$R(J)$ cm^{-1}	$\Delta_2 F'(J)$ cm^{-1}	$\Delta_2 F''(J)$ cm^{-1}
4		30620.19			
5		619.24			
6		618.20			
7		617.08			
8		615.88			
9		614.59			
10	30618.51	30613.22	30624.34	11.12	12.89
11	617.58	611.76	623.94	12.18	14.12
12	616.57	610.22	623.46	13.24	15.35
13	615.48	608.59	622.89	14.30	16.58
14	614.29	606.88	622.24	15.36	17.80
15	613.03	605.09	621.50	16.41	19.03
16	611.68	603.21	620.68	17.47	20.26
17	610.24	601.24	619.77	18.53	21.48
18	608.73	599.20	618.78	19.58	22.70
19	607.12	597.07	617.71	20.64	23.93
20	605.44	594.85	616.55	21.70	25.16
21	603.66	692.55	615.30	22.75	26.39
22	601.80	590.16	613.98	23.82	27.61
23	599.86	587.69	612.56	24.87	28.84
24	597.84	585.14	611.06	25.92	31.15
25	595.16	581.41	608.40	26.99	32.44
26	593.12	578.62	606.83	28.21	32.50
27	590.87	575.90	605.16	29.26	33.80
28	588.57	573.03	603.48	30.45	35.03
29	586.28	570.13	601.75	31.62	36.26
30	584.09	567.22	599.76	32.54	37.49
31	584.41	564.26	597.80	33.54	38.72
32	578.87	561.04	595.42	34.38	39.96
33	575.80	557.84	593.12	35.28	41.28
34	572.93	554.14	590.87	36.73	42.49
35	570.13	550.63	588.28	37.65	43.65
36	566.92	547.22	585.59	38.37	44.91
37	563.66	543.37	582.68	39.31	46.14
38	560.19	539.45	579.95	40.50	47.35
39	556.84	535.33	577.12	41.79	48.58
40	553.39	531.37	574.25	42.88	49.82
41	549.87	527.30	571.29	43.99	51.05
42	546.32	523.20	568.24	45.04	52.29
43	542.73	519.00	565.08	46.08	53.52
44	539.00	514.22	561.83	47.11	54.75
45	535.00	510.33	558.45	48.12	55.97
46	531.11	505.86	555.08	49.22	57.21
47	527.10	501.24	551.58	50.34	58.44
48	523.00	496.64	547.93	51.29	59.67
49	518.80	491.91	544.35	52.44	60.90
50	514.47	487.03	540.55	53.52	62.12

(Continued)

Estimation of rotational temperature

Table 1. (Continued)

J	$Q(J)$ cm^{-1}	$P(J)$ cm^{-1}	$R(J)$ cm^{-1}	$\Delta_2 F'(J)$ cm^{-1}	$\Delta_2 F''(J)$ cm^{-1}
51	510.33	482.23	536.88	54.65	63.29
52	505.86	477.26	532.99	55.73	64.57
53	501.54	472.31	529.13	56.82	65.78
54	496.99	467.21	525.15	57.94	67.04
55	492.33	462.09	521.12	59.03	68.27
56	487.53	456.88	516.85	59.97	69.52
57	482.98	451.60	512.54	60.94	70.77
58	478.04	446.13	508.24	62.11	71.90
59	473.20	440.64	503.78	63.14	72.99
60	468.06	435.25	499.18	63.93	74.14
61	463.22	429.64	494.75	65.11	75.41
62	457.95	423.77	490.12	66.35	76.72
63	452.61	418.03	485.15	67.12	77.89
64	447.28	412.23	480.52	68.29	79.04
65	441.78	406.11	475.55	69.44	80.30
66	436.40	400.22	470.56	70.34	81.56
67	430.77	393.99	465.58	71.59	82.78
68	425.26	387.78	460.35	72.57	84.00
69	419.45	381.58	455.25	73.67	85.17
70	413.58	375.18	450.02	74.84	86.32
71	407.68	368.93	444.48	75.55	87.70
72	401.56	362.32	438.90	76.58	88.73
73	395.46	355.75	433.22	77.47	90.01
74	389.32	348.89	427.35	78.46	91.26
75	382.98	341.96	421.56	79.60	92.36
76	376.45	334.99	415.89	80.90	93.56
77	370.20	328.00	410.12	82.12	94.74
78	363.70	321.15	—	—	—
79	357.08	314.13	—	—	—
80	350.32	—	—	—	—
81	343.53	—	—	—	—
82	336.66	—	—	—	—
83	329.57	—	—	—	—

obtained from the present analysis of (1, 0) band are given in table 2. The electronic transition giving rise to the emission of $D \rightarrow X$ system is considered to be $1 \rightarrow 0^+$ both belonging to Hund's case (c) as rightly ascribed by Ram *et al* [14]. However, well resolved extremely sharp lines do not show perturbation of any rotational levels as observed in (0, 2) and (0, 1) band structures. The exposures were so adjusted that the rotational isotopic shifts due to ^{206}Pb and ^{207}Pb are not observed. Thus the constants are evaluated for the molecule $^{208}\text{Pb} \ ^{16}\text{O}$.

(b) *Estimation of rotational temperature of PbO molecule*

Intensity distribution in the rotational structure of (1, 0), (0, 1) and (0, 2) bands together with rotational constants and J numbering has been employed to calculate the rotational temperature of the molecule. The area under the intensity profile of a

Table 2.

(i) Rotational constants of $D \rightarrow X$ system of $^{208}\text{Pb } ^{16}\text{O}$ molecule.			
State	Constant	Values	Values reported by Ram et al [14]
D1	B'_1	= 0.26487 cm^{-1}	—
	D'_1	= $2.81 \times 10^{-7} \text{cm}^{-1}$	—
	r'_1	= 2.069 Å	
	I'_1	= $105.64 \times 10^{-40} \text{g cm}^2$	
$X0^+$	B''_0	= 0.30703 cm^{-1}	0.3063 cm^{-1}
	D''_0	= $2.34 \times 10^{-7} \text{cm}^{-1}$	$2.27 \times 10^{-7} \text{cm}^{-1}$
	r''_0	= 1.922 Å	—
	I''_0	= $91.13 \times 10^{-40} \text{g cm}^2$	—
Band Origin	ν_0	= 30623.15 cm^{-1}	—
(ii) Effective rotational temperature of the source emitting the spectrum of PbO molecule			
Band	Branch	Rotational temperature (K)	
(1, 0)	Q	4897	
	P	4605	
(0, 1)	Q	5085	
	P	4591	
(0, 2)	Q	4668	
	P	4585	
Effective rotational temperature $T = 4738.5 (\pm 126.3) \text{K}$			

rotational line is measured by taking the base line corresponding to the background intensity of the emulsion. A standard source of continuous emission spectrum is used for a calibration of temperature T K as well as emulsion. It is assumed that these two parameters remain constant over the small extent of the rotational structure.

The intensities of the rotational lines of rotation-vibration bands in emission is given by

$$I_{em} = \frac{C_{em} \nu^4}{Q_r} (J' + J'' + 1) \exp\left[\frac{-B'_v J'(J' + 1)hc}{KT}\right], \quad (1)$$

where C_{em} is a constant depending upon the change of dipole moment and the total number of molecules in the initial vibrational level ν and Q_r is the rotational state sum. From (1), one obtains immediately

$$\ln \frac{I_{em}}{J' + J'' + 1} = A - \frac{B'_v J'(J' + 1)hc}{KT}, \quad (2)$$

where

$$A = \ln \frac{C_{em} \nu^4}{Q_r},$$

which may be taken as a constant for a small range of ν .

Estimation of rotational temperature

By plotting $\log(I_{em}/(J' + J'' + 1))$ against $J'(J' + 1)$ a straight line is obtained whose slope is $(B'_e hc/KT)$. Thus by measuring line intensities and using rotational constants and J numbering, the temperature of the source can be determined. Strictly speaking (1) holds for emission from a purely thermal excitation. However, it has been found experimentally that the intensity distribution in emission bands in electric discharges is of the same type. Further it is quite clear that the normal intensity distribution in electron discharges results under the situation that the angular momentum is not strongly altered in excitation by electron collision. Considering this we have calculated the rotational temperature of the source emitting the spectrum of lead monoxide molecule.

The well resolved single lines free from any overlapping are considered from Q and P branches of (1, 0), (0, 1) and (0, 2) bands. Area under the peak of each rotational line is measured using a planimeter and the average of area under the peak is used in the calculation. Considering the calibration of the standard source and spectral sensitivity of the emulsion over a small range of wavelength, it is assumed that intensity of rotational lines in emission is proportional to the area under the peak in the intensity records. Thus $\log I_{em}/(J' + J'' + 1)$ is plotted against $J'(J' + 1)$ for Q and P branch lines of (1, 0) band. Using the J numbering and rotational constant B'_1 obtained from the present analysis rotational temperature is calculated. Further the rotational temperature is also calculated using P and Q branches of (0, 2) and (0, 1) bands and rotational constants reported by Ram *et al* [14]. The constants obtained from the present study are given in table 2. The rotational temperature so obtained is an effective one. In electric discharge sometimes rotational intensity distribution deviates from the thermal distribution. Repeated exposures give the position of intensity maxima at the same J number of the rotational lines in the Q and P branches of the above bands. Thus it is believed that the effective rotational temperature obtained from the present study is fairly constant. It is proposed that high dispersion spectrum of PbO molecule existing in the interstellar space and distant stars giving emission be carried out. The band spectroscopic methods for determination of vibrational and rotational temperatures of the interstellar molecules still have interest.

Acknowledgement

Authors are thankful to Dr S H Behere, Marathwada University, Aurangabad for fruitful discussions on the rotational temperature.

References

- [1] J M Eder and E Valenta, *Atlas Typischer Spectrum* 17, 28 (1924)
- [2] H Lamprecht, *Z. Wiss. Phot* 33, 16 (1911)
- [3] L Grebe and H Konen, *Phys. Zeit.* 22, 546 (1921)
- [4] R Mecke, *Naturwissenschaften* 17, 122 (1929)
- [5] S Bloomenthal, *Phys. Rev.* 135, 34 (1930)
- [6] H G Howell, *Proc. R. Soc. (London)* A153, 683 (1936)
- [7] E E Vago and R F Barrow, *Proc. Phys. Soc.* 59, 449 (1947)
- [8] A Christy and S Bloomenthal, *Phys. Rev.* 35, 46 (1930)
- [9] R F Deutsch Barrow and D N Travis, *Nature (London)* 191, 374 (1961)
- [10] T Torring, *Z. Naturforsch.* A19, 426 (1964)
- [11] L Gero, *Z. Phys.* 93, 669 (1936)

- [12] R Schmid and L Gero, *Z. Phys.* **94**, 386 (1935)
- [13] I Kovaes, *Z. Phys.* **106**, 431 (1937)
- [14] R S Ram, J Singh and K N Upadhy, *Spectrosc. Lett.* **6**, 515 (1973)
- [15] G Herzberg, *Molecular spectra and molecular structure 1 spectra of diatomic molecules* (Van Nostrand, New York, 1950)
- [16] P Youngner and J G Winans, *J. Mol. Spectrosc. (USA)* **4**, 23 (1960)