

Intensity distribution in the bands of the $B1 \rightarrow X^1\Sigma^+$ system of PbO

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Abstract. Relative intensities of a few bands of the $B1 \rightarrow X^1\Sigma^+$ system of PbO have been measured by the technique of heterochromatic photographic photometry. The Franck-Condon factors and r -centroids have been computed by the more reliable numerical integration procedure, using a suitable potential. The effective vibrational temperature of the source is found to be 3836 K.

Keywords. Integrated intensities; Franck-Condon factors; r -centroids; effective vibrational temperature; PbO(B—X) band system.

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1. Introduction

Studies on intensity distribution in the spectra of many diatomic molecules which are of interest in astrophysics, combustion physics and allied subjects are important for an understanding of the physicochemical conditions of the emitting sources. However, only the peak intensity data are available for the band system ($B1 \rightarrow X^1\Sigma^+$) of PbO (Dube *et al* 1970). The integrated intensities are preferred for intensity study of the molecular spectra as these represent the total as well as true intensity of the bands (Rajamanickam 1985).

In the present study, the relative integrated intensities of a few bands of the $B1 \rightarrow X^1\Sigma^+$ system of PbO have been measured by the technique of heterochromatic photographic photometry and interpreted using the computed Franck-Condon factors and r -centroids to arrive at the effective vibrational temperature of the source. The procedure adopted in the present study for the measurement of integrated intensities and its interpretation have been discussed in detail elsewhere (Bagare and Sreedhara Murthy 1982; Rajamanickam 1985, 1987, 1988).

2. Experimental

A vertical copper arc of length 8 cm and diameter 8 mm run with a stabilized d.c. source was used to excite the bands. The arc was maintained steady at 225 V and 1 A current, using a power supply unit (AIMIL, India). Pure lead metal was placed on the flat-topped lower electrode. On striking the arc, the lead melts to form a globule and burns steadily. In the bluish white flame of the arc, PbO bands are well developed.

The bluish white flame of the arc was focussed on the slit of a quartz spectrograph (Q-24; Carl-Zeiss, West Germany). However, a few intense Cu-lines were recorded. They are not overlapping the PbO bands. A slit width of about 0.01 mm was used. The dispersion of the spectrograph ranged from 31.5 to 58 Å/mm in the region of study. The neutral filter was a platinum-on-quartz step weakener with 4, 6, 10, 16, 40 and 100% transmission. It was employed to impress the continuous spectrum of the standard lamp and to obtain the desired sensitivity on the photographic emulsion at various wavelengths. The lamp was calibrated at the National Physical Laboratory, New Delhi, had a colour temperature of 2040 K with 2.5 A current through the filament, and was operated with a stabilized d.c. power supply unit (Universal Electronics Ltd, India).

The bands and calibration marks were photographed on Fortepan 34 film. The exposed films were developed at 18°C. A Jarrell-Ash microdensitometer with an Omni-Scribe recorder was used to obtain band profiles and densities of calibration marks at the required wavelengths. Figure 1 illustrates the spectrum of the (B—X) bands of PbO with the calibration marks. A portion of the densitometer tracing of PbO (B—X) bands is shown in figure 2.

3. Integrated intensities

A Seidel function (Kaiser 1941) calibration curve was constructed at the band head for each band. The background intensity was estimated by drawing a line across the base of the band system (Dean 1960) and was subtracted from that of the band profile (Pierce and Nachtrieb 1941). The procedure of Hébert and Tyte (1964) was followed to extrapolate intensity profiles in the overlapped regions. The area under the intensity profile is multiplied by the appropriate spectral-energy (E_λ) to obtain the integrated band intensity.

After assigning a value of 100 for the most intense band (2, 0), other band intensities were properly scaled. The integrated intensities ($I_{v',v''}$) of the (1, 0), (2, 0), (3, 0) and (4, 0) bands of PbO (B—X) are listed in table 1 with band-head wavelengths (Bloomenthal 1930), $\lambda_{v',v''}$. The listed results are averages for six measurements. Self-absorption effects were negligibly small. The standard errors of the intensities vary from 3 to 9%. Integrated intensities were determined only for bands with uniform background for which proper background corrections are possible. The weak bands such as (0, 0) were not analysed.

Dube *et al* (1970) reported the peak intensities of 9 bands. In the present study, some of these bands had varying background as shown in figure 3 and therefore they are discarded.

4. Franck-Condon factors and r -centroids

The square of the overlap integral is termed as the Franck-Condon (FC) factor (Bates 1952),

$$q_{v',v''} = \left[\int \psi_{v'} \psi_{v''} dr \right]^2 \quad (1)$$

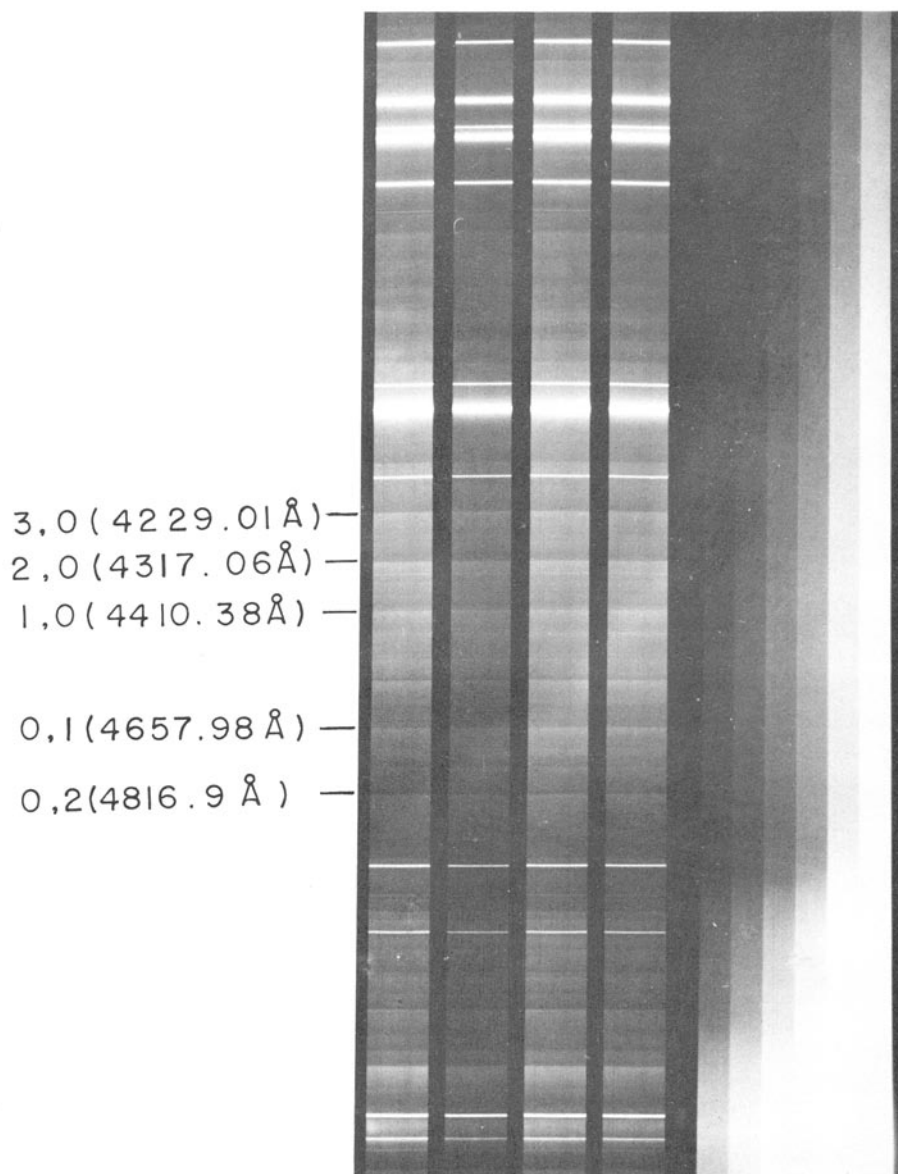


Figure 1. $PbO(B-X)$ band spectrum and calibration marks.

where $\psi_{v'}$ and $\psi_{v''}$ are the vibrational wave functions for the upper and lower states respectively. The r -centroid is defined as

$$\bar{r}_{v'v''} = \frac{\int \psi_{v'} r \psi_{v''} dr}{\int \psi_{v'} \psi_{v''} dr} \quad (2)$$

It is found that the Morse (1929) function represents the potential energy curves for the electronic states of B- and X- of PbO quite adequately since Rydberg-Klein-Rees turning points are nearly coincident with the Morse ones. Morse wave functions

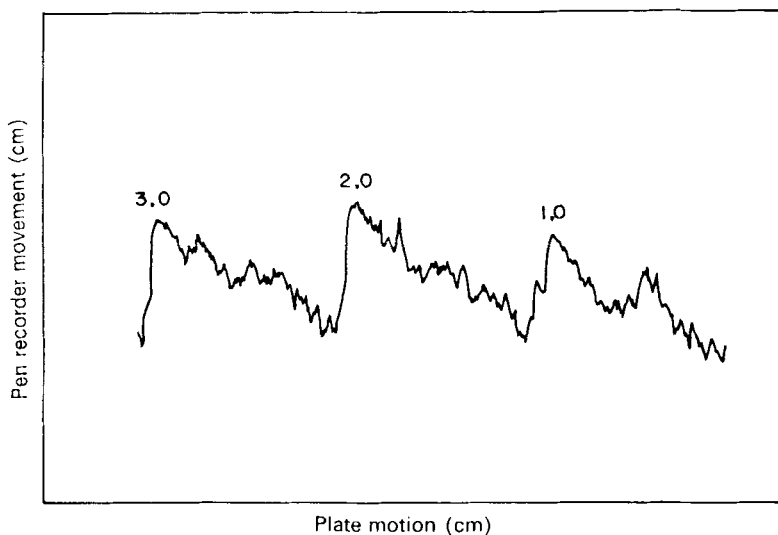


Figure 2. Portion of the microdensitometer tracing for PbO(B—X) band system.

Table 1. Measured relative integrated intensities ($I_{v',v''}$).

v', v''	$\lambda_{v',v''}$ (Å)	$I_{v',v''}$
1,0	4410.38	75.03
2,0	4317.06	100.00
3,0	4229.01	88.93
4,0	4145.93	61.04

were calculated using a TDC-316 computer at intervals of 0.005 \AA for $1.65 \leq r$, $\text{\AA} \leq 2.35$. The FC factors were computed by using Bates (1949) method of numerical integration according to the procedure provided by Tawde and Sreedhara Murthy (1959) and Rajamanickam (1988). Integrals in (1) and (2) for FC factors ($q_{v',v''}$) and r -centroids ($\bar{r}_{v',v''}$) were computed numerically and are listed in table 2. The r -centroids were computed by graphical and quadratic equation methods (Nicholls and Jarman 1956) and listed for comparison. The molecular constants reported by Howell (1936) and Barrow *et al* (1961) were used.

Dube *et al* (1970) reported Morse FC factors by approximate analytical integration method (Fraser and Jarman 1953) and r -centroids by quadratic equation method which are not safe (Jarman and Fraser 1953; James 1966). The reported $q_{v',v''}$ and $r_{v',v''}$ values by them are also given in table 2 for comparison. Even for the intense band (3,0), they have reported $q_{v',v''}$ to be 0.000015.

5. Vibrational temperature of the source

If the intensities of a sufficient number of bands cannot be measured, a determination of the vibrational temperature can still be obtained if the overlap integrals are

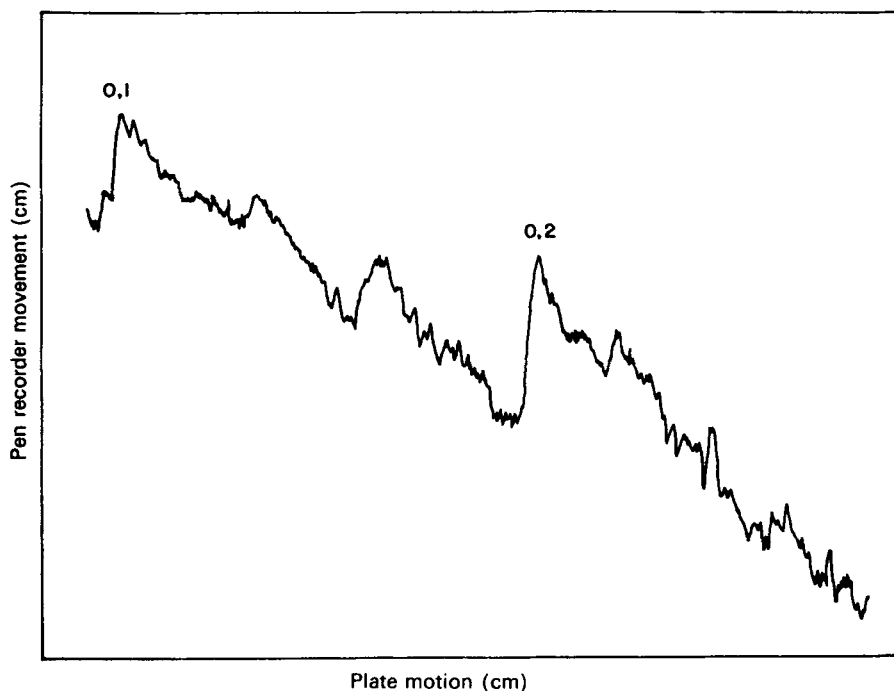


Figure 3. Portion of the microdensitometer tracing for PbO(B—X) bands with varying background.

Table 2. Franck-Condon factors ($q_{v'v''}$) and r -centroids ($\bar{r}_{v'v''}$).

v', v''	$q_{v'v''}$		$\bar{r}_{v'v''}(\text{\AA})$			
	Present* study	Dube <i>et al</i> (1970)	Numerical integration	Graphical	Quadratic	
					Present study	Dube <i>et al</i> (1970)
1,0	0.150	0.14216	1.970	1.971	1.981	1.972
2,0	0.215	0.20754	1.949	1.949	1.962	1.964
3,0	0.213	0.000015	1.928	1.928	1.945	1.948
4,0	0.164	0.07133	1.907	1.906	1.929	1.924

* Values used in the present investigation.

calculated for the measured bands (Herzberg 1950) using the following equation (Thorne 1974)

$$\ln \langle IE^{-4}/q \rangle_{v'v''} = \text{const.} \left\{ -\frac{hc}{kT} G(v') \right\} \quad (3)$$

where $E_{v'v''}$ ($= \lambda_{v'v''}^{-1}$) is the energy quantum, h , the Planck's constant, c , the velocity of light, k , the Boltzmann's constant, T , the effective vibrational temperature of the source emitting the band system and $G(v')$, the vibrational quantum of energy of the

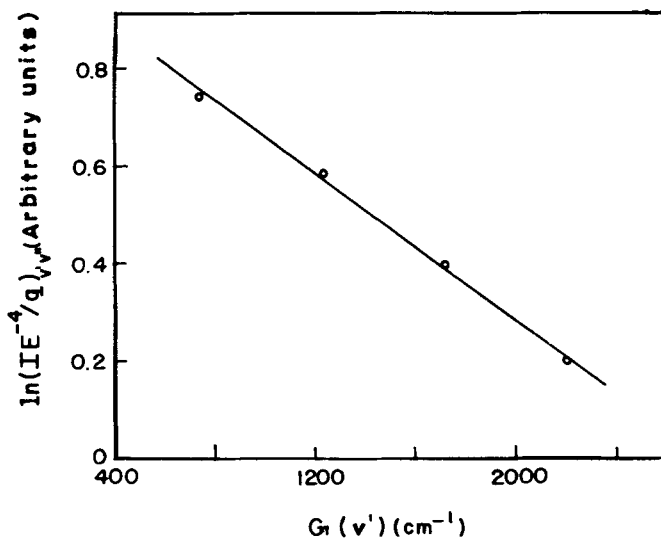


Figure 4. Plot of $\ln(IE^{-4}/q)_{v',v''}$ versus $G(v')$ for PbO(B—X) band system.

molecule in the level v' . Therefore by plotting $\ln(IE^{-4}/q)_{v',v''}$ against $G(v')$, a straight line is obtained whose slope is hc/kT from which T can be evaluated.

The integrated intensities of (1, 0), (2, 0), (3, 0) and (4, 0) bands only could be measured in the present study (Section 3). Therefore the effective vibrational temperature of the source for PbO(B—X) system is determined using (3). A similar situation arises in the case of YO(A—X) system (Bagare and Sreedhara Murthy 1982). The vibrational quanta $G(v')$ were calculated from the expression

$$G(v') = \omega'_e(v' + \frac{1}{2}) - \omega'_e x'_e(v' + \frac{1}{2})^2. \quad (4)$$

A graphical plot of $\ln(IE^{-4}/q)_{v',v''}$ versus $G(v')$ for PbO(B—X) system is shown in figure 4 and a straight line is fitted for the plot by the method of least-squares. From the slope, the effective vibrational temperature of 3836 K is obtained assuming the electronic transition moment as constant over the range of study. The least squares fitted straight line given in figure 4 has a standard deviation of 0.01. The effective vibrational temperature obtained for the source of PbO(B—X) band system is in the range of temperature as usually expected for d.c. arc.

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