

CHAPTER - V

ROTATIONAL TEMPERATURE OF PbO MOLECULE

1. MEASUREMENT OF SPECTRAL INTENSITY

INTRODUCTION

Besides wavelength determination another aspect of prime importance is the intensity of a spectral line of a band. These two aspects shed light on various molecular processes. Intensity measurements are related to the population of the excited levels which are given by Maxwell-Boltzmann

distribution. Few other concepts like the Franck-Condon factors, band strengths, variation of an electronic transition moment etc. are also related to the intensities of the bands. The variation of the intensity of the lines in a rotation-vibration band as a function of J is given essentially by the thermal distribution of the rotational levels.

The intensity distribution resembles closely the distribution of the rotational levels. The total intensity of the band remain constant as long as the temperature is not so high that the number of molecules in the lower vibrational level is appreciably reduced.

The intensity distribution in a band can be used for determining the temperature of the source of emission or absorption. From the position of the maximum intensity of a line or a band, the temperature of the source can be determined. More accurate and reliable values are obtained when the whole intensity distribution is studied.

VARIOUS METHODS OF INTENSITY MEASUREMENT

There are four principle means by which

intensity can be determined.

- (1) Absorption of radiation by blackened surface of a radiometric device, where in the heating effect of radiant energy is used to obtain the signal.
- (2) The photoelectric device can be used to measure the radiation where photoelectric current produced by radiation is taken as a measure of the intensity.
- (3) The radiation is allowed to affect the photographic plate or film for a particular time period. The density of the silver deposit produced in the emulsion on development can be made to measure total radiation.
- (4) The eyeball fits : This type of visual measurement is less reliable as the exact quantitative measurements are difficult to judge. Moreover, eye is sensitive only to a narrow band of wavelengths. It is most sensitive to the green-yellow region of the electro-magnetic spectrum.

PHOTOGRAPHIC PHOTOMETRY

Of all these methods, photographic photometry is preferred to other methods. Harrison et al. (1948) have suggested six parameters which serve as the criteria for intensity measurement for a particular range and for any particular experimental set up. These parameters are (i) Wavelength range, (ii) Sensitivity, (iii) Linearity, (iv) Neutrality, (v) Cumulative property and (vi) Panoramic property.

The photographic photometry is used in the wavelength range $\lambda\lambda$ 10-12000 Å and has high sensitivity. The linearity is poor in this method which indicates that the curve relating the photographic response to the radiant energy is not a straight line. The parameter neutrality is the measure of the photographic response for the radiation of different wavelengths. If these responses vary appreciably for different wavelengths, then neutrality is low or poor. The cumulative property and the panoramic property are possessed by photographic emulsions. The former is the ability of the emulsion to respond to light of exceedingly low

intensity by prolongation of exposure time. Panoramic property means that the photographic emulsion can simultaneously register different beams of radiation on different part of the plate or film.

Photographic photometry is a sensitive method having good cumulative property and excellent panoramic property. But the advantages outweigh the disadvantages and there are methods to account for nonlinearity.. In the present work photographic photometry has been used to measure the intensities.

OPTICAL DENSITY AND ITS CORRELATION WITH INTENSITY

A photographic record of a spectral line is produced when the affected photographic emulsion is developed. The blackening is produced due to affected silver halide grains. The degree of blackening or optical density d is defined by the relation $d = \log I_0 - \log I$; where I_0 is the intensity of a beam before transmission through an image and I is the intensity of a beam after transmission. Besides the intensity of radiation, other factors which control optical density are wavelength of radiation, exposure time, age and processing of the plate.

In order to study the calibration of an emulsion, one must have the characteristic curve or Hurter-Driffield diagram in which the plate is exposed to a spectrum of constant intensity source for equal time of exposures through series of neutral filters. In the absence of neutral filters, a regular variation in the slit width also can be used. From this characteristic curve the intensity of a spectral line can be read by determining the blackening due to it.

RELATIONSHIP BETWEEN DENSITY AND SLIT WIDTH

Let E_λ be the spectral energy of the source at wavelength λ . Radiant energy passing through slit width J in time interval t is given by $E_\lambda Jt$. The optical density d is now given as

$$d_\lambda = K E_\lambda J t \left(\frac{d\lambda}{dl} \right) \quad \text{.....(62)}$$

where K is the constant determined by the last two factors influencing the density, $d\lambda/dl$ is the linear reciprocal dispersion or plate factor of the spectrograph used. For a given λ , d_λ is function of J only when t is maintained constant. A plot of d_λ against J , therefore, is equivalent to the Hurter-Driffield curve.

Now if I is the intensity of the line which has the optical density d_λ explained above, then by matching the density with a point on H-D curve, a curve can be constructed for the wavelength with the same exposure time. We can write

$$I = K E_\lambda J t \left(\frac{d\lambda}{dl} \right) \quad \dots\dots(63)$$

This equivalence is in accordance with the principles of photographic photometry. That is, the same optical densities are produced by radiant energies of equal intensities.

When relative intensities of two lines in the spectrum are required, we can write

$$\frac{I_1}{I_2} = \frac{\{E_{\lambda_1} J(d\lambda/dl)\}_1}{\{E_{\lambda_2} J(d\lambda/dl)\}_2} \quad \dots\dots(64)$$

In the above equation values of J are read from H-D curves constructed for wavelengths λ_1 and λ_2 respectively. This is the principle of heterochromatic photographic photometry.

SOURCE FOR CALIBRATING THE EMULSION

A source emitting continuous spectrum and

calibrated for a colour temperature T° Kelvin is usually employed. In terms of T° , the spectral energy at wavelength λ is given by the Planck's law for black body radiation. Accordingly,

$$E = C_1 \lambda^{-5} [\exp (C_2/kT) - 1]^{-1} \quad \dots\dots(65)$$

where $C_1 = 3.703 \times 10^{-5} \text{ erg cm}^2/\text{sec}$ and
 $C_2 = 1.433 \text{ cm Kelvin}$

INTEGRATED INTENSITIES

The intensities of various bands can be measured from the area under the band profiles which are plotted by using different neutral filters inserted between slit and source. It is shown below that area under the profile is a measure of integrated intensity of the band.

Consider that the intensity contour is divided into a number of narrow strips, each of infinitesimal width Δl . Assuming an average wavelength λ for the whole band, at each point on the profile, the intensity is proportional to $E_\lambda J \left(\frac{d\lambda}{dl} \right)$ and for a strip of width Δl which is

very small, the intensity vested in it is given as

$$\text{Intensity} \propto E_{\lambda} \left(\frac{d\lambda}{dl} \right) J \cdot \Delta l \quad \dots\dots(66)$$

In a spectrograph Δl is a function of plate factor; a large plate factor (smaller numerical value) gives rise to greater spread for the band at that wavelength and vice-versa. The extent through which a band spreads in the spectrum is therefore inversely related to the plate factor. This means that the actual band width is given by dividing the apparent width Δl by the corresponding plate factor. So above equation reduces to

$$\text{Intensity} \propto E_{\lambda} (J \cdot \Delta l) \quad \dots\dots(67)$$

The quantity $(J \cdot \Delta l)$ is the area of the narrow strip. Adding up the intensities associated with all such strips, the total or the integrated intensity of the band is obtained.

$$\text{Thus} \quad I_{\text{band}} = I_{v'v''} \propto E_{\lambda} J \cdot \Delta l \quad \dots\dots(68)$$

$$\text{or} \quad I_{v'v''} \propto E_{\lambda} (\text{Area under the profile}) \dots\dots(69)$$

When two bands are compared for the relative integrated intensity we have

$$\frac{(I_{\nu'\nu''})_1}{(I_{\nu'\nu''})_2} = \frac{(E \lambda_1 \cdot \text{Area})_1}{(E \lambda_2 \cdot \text{Area})_2}$$

This indicates that the intensity can be obtained from the measurement of the area of a band contour.

EXTRAPOLATION OF OVERLAPPED BANDS

The area of a band can be easily measured if the tail of the band extends up to zero on the distance axis but as observed in general this is not the case and usually certain amount of overlap of the neighbouring band is seen. To extrapolate the contours in such cases the procedure suggested by Hebert and Tyte (1964) is used. A slightly different method suggested by Murthy and Bagare (1980) is also sometimes useful.

MICRODENSITOMETER

Veb Carl Zeiss JENA model GII microdensitometer system coupled with potentiometric recorder G1B1 was employed to measure the density of band profiles in the spectra in the present course of work. The system

combines an accurate high speed photometer with a precision x-y coordinate scanning system to allow acquisition of density and position information from transparent films or plates of size up to 25 cm x 25 cm. Various speeds to run the plate stage as well as the paper on the recorder are available. High paper speed coupled with low plate stage speed is used to get the finer details of intensity and spacing of rotational lines.

THEORETICAL ASPECTS

The integrated intensity of a vibrational band (v', v'') may be written as

$$I_{v',v''} = D N_{v'} E_{v',v''}^4 R_e^2(\bar{r}_{v',v''}) q_{v',v''} \quad \dots\dots(70)$$

where D is a constant which depends on geometry of the experiment, $E_{v',v''} \propto \frac{1}{\lambda_{v',v''}}$ is energy of the (v', v'') band, $N_{v'}$ is the population in v' th level of the excited state, R_e is electronic transition moment which is a function of $\bar{r}_{v',v''}$ called \bar{r} -centroid and $q_{v',v''}$ is a Franck-Condon factor of that band.

The electronic transition moment $R_e(r)$ is a

measure of the change in electron charge configuration in a molecular transition defined as

$$R_e(r) = \int \psi_{e_l}' M \psi_{e_l}'' d\tau_{e_l} \quad \dots\dots(71)$$

ψ_{e_l}' and ψ_{e_l}'' are the wave functions due to electrons for the upper and lower states, M is dipole moment, $d\tau_{e_l}$ is the volume element of configuration space for the electrons.

Assuming thermal equilibrium and using Maxwell-Boltzmann distribution,

$$N_{v'} = N_0 \exp \left[- \frac{G(v') hc}{kT} \right] \quad \dots\dots(72)$$

$$\text{or } \frac{N_{v'}}{N_0} = \exp \left[- \frac{G(v') hc}{kT} \right] \quad \dots\dots(73)$$

N_0 is the number of molecules in the zeroth vibrational level, h is the Planck's constant, c is the velocity of light, k is the Boltzmann constant and T is the temperature in °Kelvin of the source emitting the band system. Using recent values of constants it is seen that hc/k is found to be 1.4388 cm deg. $G(v')$ is the vibrational quantum of energy in cm^{-1} , given by

$$G(v') = \omega_e'(v' + \frac{1}{2}) - \omega_e'x_e'(v' + \frac{1}{2})^2 \quad \dots\dots(74)$$

ω'_e and $\omega'_e x'_e$ are respectively harmonic and anharmonicity constants of the band system of a molecule.

The quantity $q_{v', v''}$ is called Franck-Condon factor. It is the square of overlap integral of vibrational wave functions.

$$q_{v', v''} = \left| \int \psi_{v'} \psi_{v''} dr \right|^2 \quad \dots\dots(75)$$

The Franck - Condon factor controls the intensity distribution from band to band in a system. The quantity $\bar{r}_{v', v''}$ is called r-centroid for the transition $v' \longleftrightarrow v''$ and defined as

$$\bar{r}_{v', v''} = \frac{\int \psi_{v'} r \psi_{v''} dr}{\int \psi_{v'} \psi_{v''} dr} \quad \dots\dots(76)$$

Another quantity of interest is band strength $P_{v', v''}$ defined as

$$P_{v', v''} = \text{Re}^2 (\bar{r}_{v', v''}) q_{v', v''} \quad \dots\dots(77)$$

The relative band strengths are given by

$$S_{v', v''} = P_{v', v''}/P_{00} \quad \dots\dots(78)$$

where P_{00} is a band strength of (0,0) band or a band of maximum intensity in that sequence.

VARIATION OF ELECTRONIC TRANSITION MOMENT

Equation (70) can be written as

$$(I/E^4 q)^{\frac{1}{2}}_{v', v''} = (D N_{v'})^{\frac{1}{2}} R_e(r_{v', v''}) \quad \dots(79)$$

where R_e is a function of $r_{v', v''}$ (i.e. r-centroid)

The left hand side is a quantity which can be calculated from measurements of intensity I , E^4 , i.e. $\frac{1}{\lambda^4}$ and Franck-Condon factor q of a band v', v'' .

A study of the relative variation of $R_e(r)$ along a v'' progression ($v' = \text{constant}$) is thus possible. Graphical plot of $(\frac{1}{E^4} q)_{v', v''}$ versus $r_{v', v''}$ should therefore give the trend of the graph of $R_e(r)$ with $r_{v', v''}$ for $v' = \text{constant}$ bands of the system, as $N_{v'}$ remains the same for a v'' progression. Naturally different vibrational levels in the excited state will have different $N_{v'}$, and therefore when large number of bands appear with different v', v''

values, it is necessary to bring all the curves of $R_e(\bar{r})$ versus r on to the same ordinate scale to arrive at the form of $R_e(\bar{r}_v, v'')$ for the whole band system. This rescaling procedure is described by Fraser (1954).

If the curve is plotted between $R_e(\bar{r}_v, v'')$ and \bar{r}_v, v'' then a mathematical relation can be obtained which indicates the variation of $R_e(r_v, v'')$ versus \bar{r}_v, v'' . The smoothened values of $R_e(\bar{r}_v, v'')$ for r_v, v'' values are taken from graph and the substituted in equation (77) so as to get P_v, v'' .

EFFECTIVE VIBRATIONAL TEMPERATURE

Once we are familiar with the various terms defined in preceding section and their interrelationship, we can come to the calculation of vibrational temperature. There are two ways to calculate the vibrational temperature

- 1) assuming $R_e(r)$ as constant over the range of study and
- ii) taking into account variation of $R_e(r)$ with r .

ASSUMING $R_e(r)$ CONSTANT

Equation (70) can be written as

$$\sum_{v''} (I E^{-4})_{v', v''} = D N_{v'} \sum_{v''} R_e^2(\bar{r}_{v', v''}) q_{v', v''} \quad \dots\dots(80)$$

Summation is used because transition from an upper vibrational level v' can end on various v'' levels (v'' progression for same v'). If $D R_e^2(\bar{r}_{v', v''})$ is treated as some constant, say A , then equation (80) assumes the form

$$\sum_{v''} (I E^{-4})_{v', v''} = A N_{v'} \sum_{v''} q_{v', v''} \quad \dots\dots(81)$$

$q_{v' v'}$ is a Franck-Condon factor defined in equation (75). If the vibrational eigenfunctions ψ_v are properly normalised it can be shown from elementary properties of the system of orthogonal functions that the squares of overlap integrals summed up over all values of the vibration quantum number of the upper or the lower state, are equal to unity i.e.

$$\sum_{v'} (\int \psi_{v'} \psi_{v''} dr)^2 = 1 = \sum_{v''} (\int \psi_{v'} \psi_{v''} dr)^2 \dots(82)$$

Incorporating this sum in (81), we get

$$\sum_{v''} (I E^{-4})_{v', v''} \propto N_{v'} \quad \dots\dots(83)$$

$$\text{where } N_{v'} = N_0 \exp \left[- \frac{G(v') hc}{kT} \right] \quad \dots\dots(84)$$

The above equation yields

$$\ln \sum_{v''} (I E^{-4})_{v', v''} = \text{constant} - \frac{G(v') hc}{kT} \quad \dots\dots(85)$$

If intensities of only few bands are measured then the value of T can still be evaluated using relations (84) and (70). Thus

$$\ln \left(\frac{I E^{-4}}{q} \right)_{v', v''} = \text{constant} - \frac{G(v') hc}{kT} \quad \dots\dots(86)$$

A graph of L.H.S. versus $G(v)$ gives a straight line whose slope is $\frac{hc}{kT}$ from which T can be evaluated.

INCORPORATING THE VIBRATION OF $R_e(r)$

Using equations (77) and (78), eqn. (79) can be written as

$$\sum_{v''} (I E^{-4})_{v', v''} = D N_{v'} \sum_{v''} P_{v', v''} \quad \dots\dots(87)$$

$$= D N_{v'} P_{00} \sum_{v''} \left(\frac{P_{v' v''}}{P_{00}} \right) \quad \dots\dots(88)$$

$$\frac{\sum_{v''} (I E^{-4})_{v' v''}}{\sum_{v''} S_{v' v''}} = D N_{v'} P_{00} \quad \dots\dots(89)$$

Now applying the Maxwell-Boltzmann distribution and taking logarithm, we get

$$\ln \frac{\sum_{v''} (I E^{-4})_{v' v''}}{\sum_{v''} S_{v' v''}} = \text{constant} - \frac{G(v') hc}{kT} \quad \dots\dots(90)$$

T can now be evaluated as described in earlier section.

IMPORTANCE OF STUDYING EXPERIMENTAL MEASUREMENTS OF INTENSITY

One can calculate $R_e(r)$ theoretically as well, but it involves the play with complicated electronic wave functions. Nichollas (1956) has described few such methods which are outlined here.

LCAO and SCFMO procedures :

A fairly approximate method is to employ a linear combination of atomic orbitals (LCAO) with

the hybridization by Mullikan method (1933, 1935). This starts with the data of Slater (1931) on orbitals of atoms. By this method few observed forms of $R_e(r)$ were predicted by Nichollas (1956). But there are limitations to this approach. The other approach is less stringent approximation but extremely tedious in which a self consistent field molecular orbitals (SCFMO) method is used in the linear combinations of atomic orbital approximation.

The LCAO method was applied to the first and second positive band systems of N_2 by Fraser (1954). His results of $R_e(r)$ are in agreement with the experimental results of Nichollas and Turner (1954) for first positive system but differ for the second positive system of N_2 from the experimental results of Wallace and Nichollas (1954). The optimum degree of hybridization seems still a matter open for discussion.

The SCF approximation which Hartree (1928) developed for atoms has been extended to the LCAO approximation for molecular wavefunctions. Such studies are reported by Lennard and Jones (1929), Coulson-Moffitt-Roothan and others (see Slater). In this method the search is made using generalised

Schrodinger equation till the required self consistency is obtained.

Looking to the complications involved in above methods, the practical way to calculate $R_e(r)$ from the experimental measurement of intensities and theoretically evaluated quantities like F.C. factors and \bar{r} -centroids is preferred.

Originally Ornstein and Brinkman (1931) employed a method for band intensity measurement. Later there were many improvements by different workers like Johnson and Tawde (1932), Elliot (1934), Harrison (1934), Tawde and Patankar (1943), Tawde and Murthy (1960) and Prahalad et al. (1982).

ROTATIONAL TEMPERATURE

INTRODUCTION

Sufficiently resolved structure of a band permits the measurement of the intensity of rotational lines. These studies are of prime importance in diatomic molecular spectra because the rotational temperature calculated from these

measurements are often needed in the study of partition functions. In contrast to intensity distribution in a band system, a $(2J + 1)$ fold degeneracy comes into picture in the case of rotational structure.

THEORETICAL FORMULATION

As discussed earlier, the population in a vibrational level v is given by

$$N_v = N_o \exp \left\{ - \frac{hc}{kT} G(v) \right\} \quad \text{.....(91)}$$

whereas the population N_j in a rotational level J can be expressed as

$$N_j = (2J + 1) \exp \left\{ F(J) - \frac{hc}{kT} \right\} \quad \text{.....(92)}$$

or

$$N_j = (2J + 1) \exp \left\{ -BJ(J + 1) \frac{hc}{kT} \right\} \quad \text{.....(93)}$$

Now if Q_r represents the rotational state sum;

$$Q_r = 1 + 3e^{-2Bhc/kT} + 5e^{-6Bhc/kT} + \text{.....} \quad \text{.....(94)}$$

then,

$$N_j = \frac{N_o}{Q_r} (2J + 1) \exp \left\{ -BJ(J + 1) \frac{hc}{kT} \right\} \quad \text{.....(95)}$$

The intensity in emission is given as

$$I_{em} = \frac{C_{em}^4}{Q_r} \{ (J' + J'' + 1) \exp [- B'_v J' (J' + 1)] \} \quad \text{.....(96)}$$

C_{em} is a constant which depends on the change in dipole moment and the total number of molecules in the initial vibrational level.

Taking logarithms, expression (96) takes the form

$$\log \frac{I_{em}}{(J' + J'' + 1)} = A - \frac{B'_v J' (J' + 1) hc}{kT} \quad \text{.....(97)}$$

where $A = \log \left\{ \frac{C_{em}^4}{Q_r} \right\}$; B'_v is the rotational

constant for the vibrational level v' . The plot of L.H.S. versus $J' (J' + 1)$ gives a straight line, whose slope is $B'_v hc/kT$. Knowing all other quantities T can be evaluated.

ESTIMATION OF ROTATIONAL TEMPERATURE

On the basis of theoretical discussion of intensity, the estimation of rotational temperature of PbO molecule is discussed now in two parts.

In the first part, the rotational analysis of (1,0) band of $D \longrightarrow X$ system of PbO molecule has been described and in the second part the estimation of rotational temperature using the rotational constants of PbO molecule is presented.

PART I

ROTATIONAL ANALYSIS OF (1,0) BAND OF $D \longrightarrow X$ SYSTEM OF PbO MOLECULE

INTRODUCTION

The spectrum of lead monoxide extending from $\lambda\lambda$ 6750 Å to 1700 Å has been extensively studied by previous workers in various degree of details. They have recorded the spectrum in absorption as well as in gas, flame, d.c. arc, microwave discharge and high frequency discharge sources. The vibrational analysis of various band systems and rotational analysis 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. (1973) have reported the rotational analysis of (1,0) and (1,1) bands of $B \longrightarrow X$

system and (0,1) and (0,2) bands of $D \longrightarrow X$ system.

Ram et al.(1973) 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 nicely described by Ram et al.(1973).

We have obtained rotational structure well resolved upto almost the origin of (1,0), (0,1), and (0,2) bands exhibiting sharp rotational lines. The rotational analysis of (1,0) band has 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 molecule has been calculated.

EXPERIMENTAL

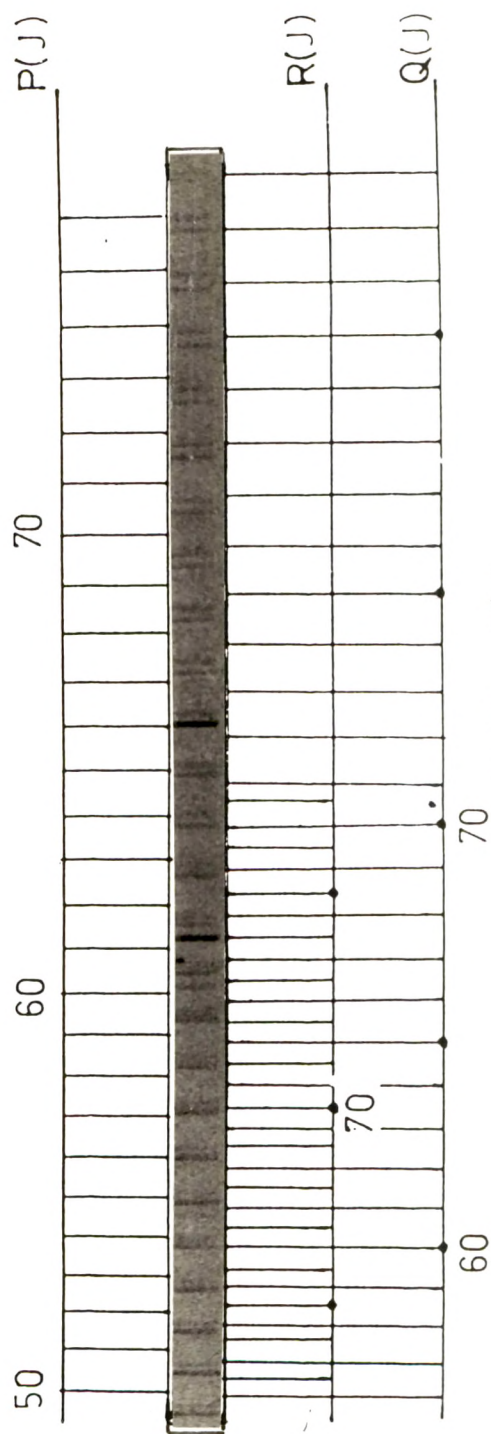
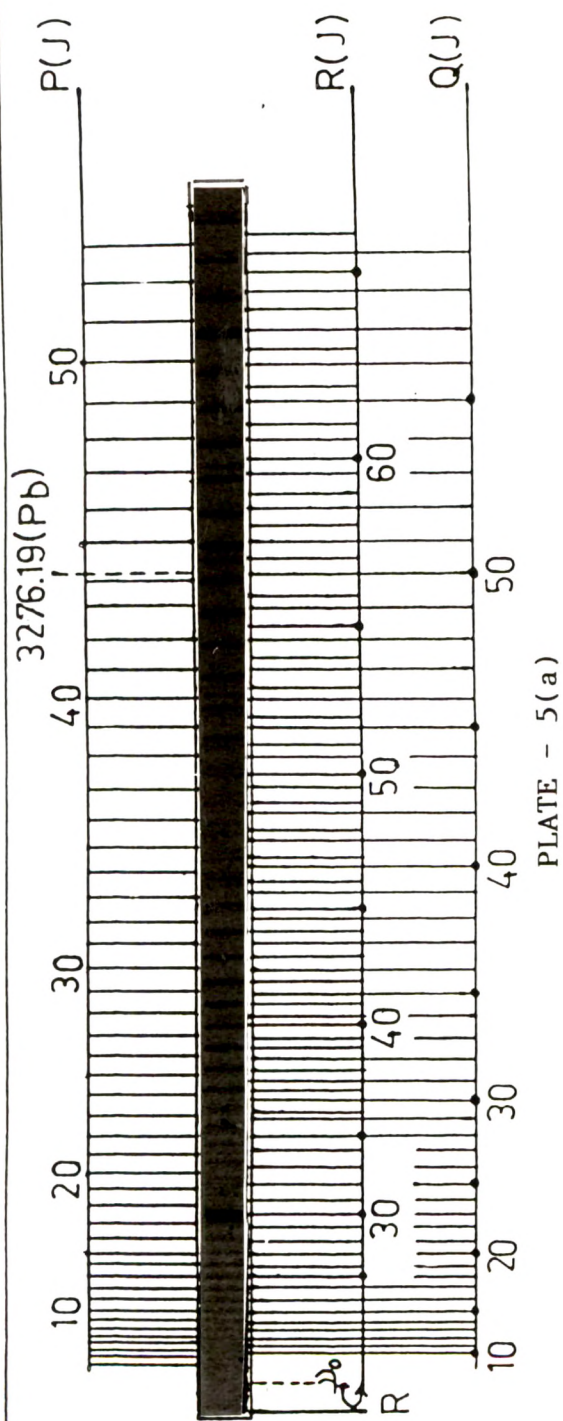
The spectrum of lead monoxide has been excited in RF discharge source. A pure sample of lead oxide (B.D.H.) was taken in a quartz tube 25 cm. in length and 8 mm. in diameter. The characteristic sky blue discharge was established by employing high

frequency oscillator giving an output power of 125 watts at 10-15 MHz. An 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. A strong emission in the blue-green region was seen to develop strong in intensity. The (1,0), (0,1) and (0,2) bands of $D \longrightarrow X$ system at 3264 Å, 3401 Å, 3485 Å respectively were photographed in the 2 meter plane grating spectrograph (Carl-Zeiss) providing a dispersion of 0.7 Å/mm in the seventh order of the plane grating blazed at 10500 Å and 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 of about 10 hours duration 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 measurement is within the limit of $\pm 0.05 \text{ cm}^{-1}$ 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 colour temperature T° Kelvin 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.

ANALYSIS

The (1,0) band of $D \longrightarrow X$ system at 3264 \AA of PbO molecule reproduced in plate 5(a) and 5(b) as seen on negative exhibits a fine rotational structure well resolved upto the origin and comprising of R, Q and P branches of which R and Q are head forming. The branch lines are correctly picked up using the intensity records. The rotational analysis has been performed using the standard method of Herzberg (1950)



ROTATIONAL STRUCTURE OF 3264 Å BAND OF PbO MOLECULE. DISPERSION 0.7088 Å/mm

and by plotting the graphs of ${}_2 F(J) \longrightarrow J$ and

$$\frac{{}_2 F(J)}{(J + \frac{1}{2})} \longrightarrow (J + \frac{1}{2})^2 . \quad \text{The criterion for the}$$

correctness of J numbering suggested by Younger and Winans (1960) 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 square 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 difference of observed and calculated line frequencies ($\text{obs} - \text{cal}$) to a minimum within $\pm 0.1 \text{ cm}^{-1}$.

The plots of ${}_2 F(J) \longrightarrow J$ and

$$\frac{{}_2 F(J)}{(J + \frac{1}{2})} \longrightarrow (J + \frac{1}{2})^2 \quad \text{are given in}$$

fig. 16 and 17.

The J numbering, vacuum wave numbers of R, Q and P lines and combination differences are given in Table 13 . The rotational constants obtained from the present analysis of (1,0) band are collected in Table 14 . The electronic transition giving rise to the emission of $D \longrightarrow X$ system is considered to be $1 \longrightarrow o^+$ both the levels belonging to Hund's Case (c) rightly ascribed by Ram et al. However, well resolved and extremely sharp lines do not show perturbation of any rotational levels as observed in case of (0,2) and (0,1) band structure. 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 $^{208}\text{Pb}^{16}\text{O}$.

PART II

ESTIMATION OF ROTATIONAL TEMPERATURE OF PbO MOLECULE

The variation of the intensity of the lines in a rotation vibration bands as a function of J is given essentially by the thermal distribution of the rotational levels. i.e. the intensity is given by the expression

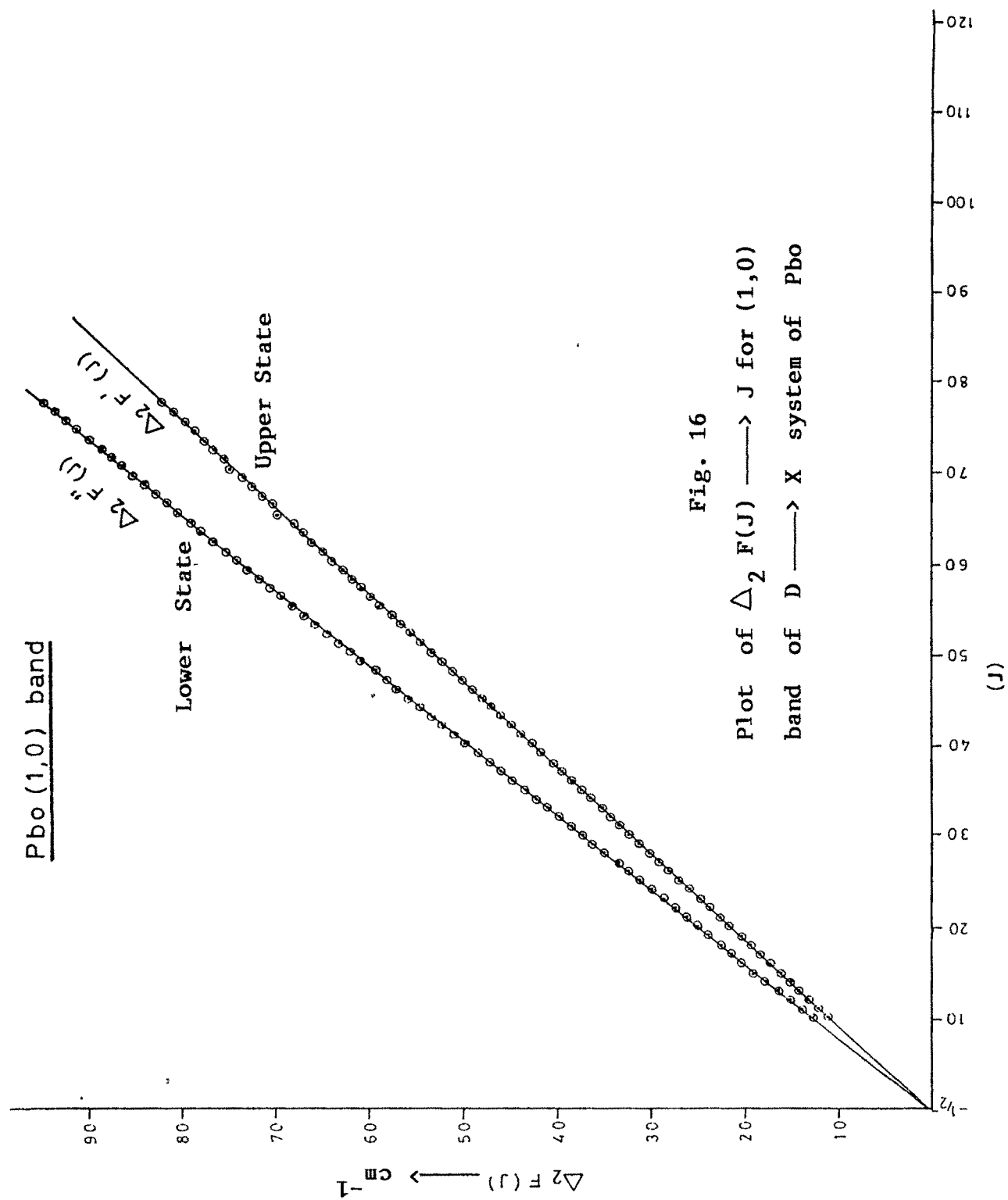
TABLE - 13

J ASSIGNMENTS, VACUUM WAVENUMBERS AND COMBINATION
DIFFERENCES OF D \longrightarrow X SYSTEM OF $^{208}\text{Pb}^{16}\text{O}$

J	Q (J) cm^{-1}	P(J) cm^{-1}	R (J) cm^{-1}	$\Delta_2\text{F}'(\text{J})$ cm^{-1}	$\Delta_2\text{F}''(\text{J})$ cm^{-1}
1	2	3	4	5	6
4		30620.19			
5		30619.24			
6		30618.20			
7		30617.08			
8		30615.88			
9		30614.59			
10	30618.51	30613.22	30624.34	11.12	12.89
11	30617.58	30611.76	30623.94	12.18	14.12
12	30616.57	30610.22	30623.46	13.24	15.35
13	30615.48	30608.59	20622.89	14.30	16.58
14	30614.29	30606.88	30622.24	15.36	17.80
15	30613.03	30605.09	30621.50	16.41	19.03
16	30611.68	30603.21	30620.68	17.47	20.26
17	30610.24	30601.24	30619.77	18.53	21.48
18	30608.73	30599.20	30618.78	19.58	22.70
19	30607.12	30597.07	30617.71	20.64	23.93
20	30605.44	30594.85	30616.55	21.70	25.16
21	30603.66	30692.55	30615.30	22.75	26.39
22	30601.80	30590.16	30613.98	23.82	27.61
23	30599.86	30587.69	30612.56	24.87	28.84
24	30597.84	30585.14	30611.06	25.92	31.15
25	30595.16	30581.41	30608.40	26.99	32.44
26	30593.12	30578.62	30606.83	28.21	32.50
27	30590.87	30575.90	30605.16	29.26	33.80

1	2	3	4	5	6
28	30588.57	30573.03	30603.48	30.45	35.03
29	30586.28	30570.13	30601.75	31.62	36.24
30	30584.09	30567.22	30599.76	32.54	37.49
31	30584.41	30564.26	30597.80	33.54	38.72
32	30578.87	30561.04	30695.42	34.38	39.96
33	30575.80	30557.84	30593.12	35.28	41.28
34	30572.93	30554.14	30590.87	36.73	42.49
35	30570.13	30550.63	30588.28	37.65	43.65
36	30566.92	30547.22	30585.59	38.37	44.91
37	30563.66	30543.37	30582.68	39.31	46.14
38	30560.19	30539.45	30579.95	40.50	47.35
39	30556.84	30535.33	30577.12	41.79	48.58
40	30553.39	30531.37	30574.25	42.88	49.82
41	30549.87	30527.30	30571.29	43.99	51.05
42	30546.32	30523.20	30568.24	45.04	52.29
43	30542.73	30519.00	30565.08	46.08	53.52
44	30539.00	30514.22	30561.83	47.11	54.75
45	30535.00	30510.33	30558.45	48.12	55.97
46	30531.11	30505.86	30555.08	49.22	57.21
47	30527.10	30501.24	30551.58	50.34	58.44
48	30523.00	30496.64	30547.93	51.29	59.67
49	30518.80	30491.91	30544.35	52.44	60.90
50	30514.47	30487.03	30540.55	53.52	62.12
51	30510.33	30482.23	30536.88	54.65	63.29
52	30505.86	30477.26	30532.99	55.73	64.57
53	30501.54	30472.31	30529.13	56.82	65.78
54	30496.99	30467.21	30525.15	57.94	67.04
55	30492.33	30462.09	30521.12	59.03	69.27
56	30487.53	30456.88	30516.85	59.97	69.52
57	30482.98	30451.60	30512.54	60.94	70.77
58	30478.04	30446.13	30503.24	62.11	71.90

1	2	3	4	5	6
59	30473.20	30440.64	30503.78	63.14	72.99
60	30468.06	30435.25	30499.18	63.93	74.14
61	30463.22	30429.64	30494.75	65.11	75.41
62	30457.95	30423.77	30490.12	66.35	76.72
63	30452.61	30418.03	30485.15	67.12	77.89
64	30447.28	30412.23	30480.52	68.29	79.04
65	30441.78	30406.11	30475.55	69.44	80.30
66	30436.40	30400.22	30470.56	70.34	81.56
67	30430.77	30393.99	30465.58	71.59	82.78
68	30425.26	30387.78	30460.35	72.57	84.00
69	30419.45	30381.58	30455.25	73.67	85.17
70	30313.58	30375.18	30450.02	74.84	86.32
71	30407.68	30368.93	30444.48	75.55	87.70
72	30401.56	30362.32	30438.90	76.58	88.73
73	30395.46	30355.75	30433.22	77.47	90.01
74	30389.32	30348.89	30427.35	78.46	91.26
75	30382.98	30341.96	30421.56	79.60	92.36
76	30376.45	30334.99	30415.89	80.90	93.56
77	30370.20	30328.00	30410.12	82.12	94.74
78	30363.70	30321.15	-	-	-
79	30357.08	30314.13	-	-	-
80	30350.32	-	-	-	-
81	30343.53	-	-	-	-
82	30336.66	-	-	-	-
83	30329.57	-	-	-	-



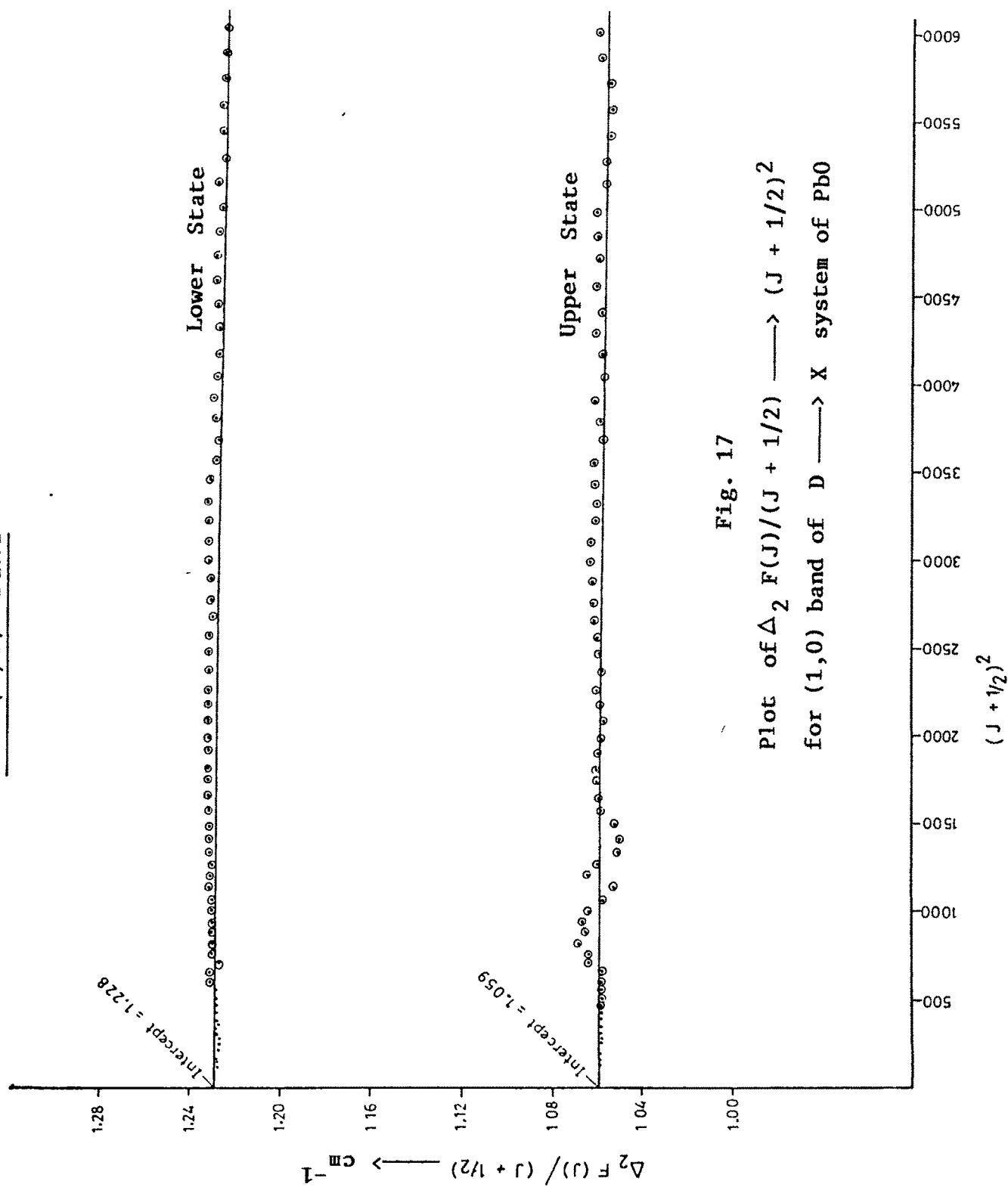


TABLE - 14

(i) ROTATIONAL CONSTANTS OF D — X SYSTEM OF $^{208}\text{Pb}^{16}\text{O}$ MOLECULE

State	Constant	Values	Values reported by Ram et al
D ₁	B'_1	$= 0.26487 \text{ cm}^{-1}$	-
	D'_1	$= 2.81 \times 10^{-7} \text{ cm}^{-1}$	-
	r'_1	$= 2.069 \text{ \AA}$	-
	I'_1	$= 105.64 \times 10^{-40} \text{ g cm}^2$	-
XO ⁺	B''_0	$= 0.30703 \text{ cm}^{-1}$	0.3063 cm^{-1}
	D''_0	$= 2.34 \times 10^{-7} \text{ cm}^{-1}$	$2.27 \times 10^{-7} \text{ cm}^{-1}$
	r''_0	$= 1.922 \text{ \AA}$	-
	I''_0	$= 91.13 \times 10^{-40} \text{ g cm}^2$	-
Band Origin	ω_0	$= 30623.15 \text{ cm}^{-1}$	

$$N_J = \frac{N}{Q_r} (2J + 1) e^{-BJ(J + 1)hc/kT}.$$

The intensity distribution resembles closely to the distribution of the rotational levels. The total intensity of the band remains constant as long as the temperature is not so high that the number of molecules in the lower vibrational level ($v = 0$) is appreciably reduced.

The intensity distribution in a band can be used for determining the temperature of the source of emission or absorption.

The maximum of the intensity in a branch shifts towards higher J values with rotational increasing temperature, according to

$$J_{\max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} = 0.5896 \sqrt{\frac{T}{B}} - \frac{1}{2}$$

Thus from the position of the maximum, the temperature of the source can be determined. More accurate and reliable values are obtained when the whole intensity distribution is measured.

In the case of $\Sigma - \Sigma$ bands, the observed

values of $\log I / (K' + K'' + 1)$ are plotted against $K (K + 1)$ and a straight line is obtained whose slope gives an accurate value of the temperature. Even if the fine structure of the bands is not resolved the shape of the band profiles varies as a function of temperature and may be used for determination of the temperature. It must be emphasized that the temperatures thus obtained are effective (Rotational or Vibrational) temperatures. They represent true temperature only if either the excitation is strictly thermal or is of such a type that it does not affect the thermal distribution.

Intensity distribution in the rotational structure of (1,0), (0,1) and (0,2) bands together with constants and J numbering has been employed to calculate the rotational temperature of the molecule. The area under the intensity profile of a rotational line is measured by taking the base line corresponding the background intensity of the emulsion. A standard source of continuous emission spectrum is used for a calibration of colour temperature T° Kelvin 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 lines of rotation or rotation-vibration bands in emission is given by

$$I_{em} = \frac{C_{em} \nu^4}{Q_r} (J' + J'' + 1) \exp \left[-B_{v'} J'(J'+1) \frac{hc}{kT} \right] \quad \dots(98)$$

where C_{em} is a constant depending upon the change of dipole moment and the total number of molecules in the initial vibrational level and Q_r is the rotational state sum. From expression (98), one obtains immediately

$$\log \frac{I_{em}}{J' + J'' + 1} = A - \frac{B_{v'} J'(J' + 1)hc}{kT} \quad \dots(99)$$

where

$$A = \log \frac{C_{em}}{Q_r}$$

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

By plotting $\log \left\{ \left(\frac{I_{em}}{J' + J'' + 1} \right) \right\}$ against $J'(J' + 1)$ a straight line is obtained whose slope

is $(B'v hc/kT)$. Thus by measuring line intensities and using rotational constants and J numbering, the temperature of the source can be determined. Strictly speaking, expression (98) 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 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 {(Fig. 18 (a), (b) and (c) }. Area under the peak of each rotational line is measured with the help of planimeter. The averages of area under the peak are 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. Intensity measurements of rotational lines of P and Q branches of (1,0), (0,1) and (0,2) bands are given in Tables 15(a) and (b), 16(a) and (b) and 17(a) and (b) respectively. Thus $\log I/(2J + 1)$ is plotted against $J(J + 1)$ for P and Q branch lines of (1,0) band. The plots for (1,0), (0,1) and (0,2) are given in figs. 19(a) and (b), 20(a) and (b) and 21(a) and (b). Using the J numbering and rotational constant B' 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 (1973). The constants obtained from the present study are given Table 18. The rotational temperature so obtained is the effective rotational temperature. 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

TABLE - 15 (a)

INTENSITY MEASUREMENT OF ROTATIONAL LINES OF
(1,0) BAND AT 3264 Å

P branch

J = K	K(K - 1)	Area under peak = $I_{em} \text{ cm}^2$	$\ln \frac{I_{em}}{2J}$
57	3192	1.15	-4.5964
58	3306	1.80	-4.1658
59	3402	2.25	-3.9598
60	3540	2.40	-3.9120
62	3782	1.05	-4.7715
64	4032	2.10	-4.1101
68	4556	1.95	-4.2448
69	4692	2.5	-4.0109
70	4830	2.9	-3.8769
71	4970	2.65	-3.9813
72	5112	2.70	-3.9766

73	5256	2.20	-4.1951
74	5402	1.65	-4.4964
75	5550	2.05	-4.2928
76	5700	2.35	-4.1695
77	5852	2.30	-4.2040
78	6006	2.70	-4.0566
79	6162	2.65	-4.0693
80	6320	2.10	-4.3332

TABLE - 15.(b)

Q branch
 RELATIVE INTENSITY MEASUREMENT OF ROTATIONAL LINES OF
 (1,0) BAND AT 3264 Å

J = K	K (K + 1)	Area under peak = $I_{em} \text{ cm}^2$	$\ln \frac{I_{em}}{(2K+1)}$
57	3306	3.05	-3.62979
58	3422	2.45	-3.86609
59	3540	3.05	-3.66398
60	3660	2.30	-3.96288
61	3782	3.00	-3.71357
62	3906	2.70	-3.83506
63	4032	2.85	-3.79686
64	4160	3.05	-3.74467
65	4290	2.40	-3.99973
66	4422	3.15	-3.74295
67	4556	3.05	-3.79013
68	4692	3.40	-3.69620
69	4830	2.45	-4.03838
70	4970	3.20	-3.78560
71	5112	3.00	-3.86423
72	5256	2.80	-3.94711
73	5402	2.40	-4.114964
74	5700	1.80	-4.42949

TABLE - 16 (a)

INTENSITY MEASUREMENT OF ROTATIONAL LINES OF
(0,1) BAND AT 3402 Å .

P branch

J = K	K(K - 1)	Area under peak = I_{em} cm^2	$\ln \frac{I_{em}}{2J}$
53	2756	3.75	-3.34302
54	2862	5.65	-2.95056
55	2970	5.65	-2.96889
57	3192	3.55	-3.46926
60	3540	4.90	-3.19833
61	3660	6.30	-2.96347
62	3782	6.35	-2.97182
63	3906	5.55	-3.12265
64	4032	6.10	-3.04387
66	4290	9.70	-2.61074

TABLE - 16 (b)
 RELATIVE INTENSITY MEASUREMENT OF ROTATIONAL LINES OF
 ((0,1) BAND AT 3402 Å.
Q branch

J = K	K(K + 1)	Area under peak = I_{em} cm^2	$\ln \frac{I_{em}}{(2K + 1)}$
32	1056	7.35	-2.179687
33	1122	6.30	-2.364143
34	1190	8.85	-2.053689
35	1260	7.40	-2.261199
36	1332	9.75	-2.01319
37	1406	8.30	-2.201232
38	1482	8.60	-2.19204
39	1560	9.35	-2.13407
45	2070	10.15	-2.19339
46	2162	11.15	-2.12116
50	2550	8.20	-2.51099
51	2652	10.80	-2.25518
52	2756	9.15	-2.44021
57	3306	6.80	-2.82801
58	3422	8.05	-2.67650
60	3660	8.50	-2.65572
65	4290	8.45	-2.74103
66	4422	9.50	-2.63906

TABLE - 17 (a)

INTENSITY MEASUREMENT OF ROTATIONAL LINES OF
(0,2) BAND AT 3486 Å

P branch

J = K	K(K - 1)	Area under peak = $I_{em} C_m^2$	$\ln \frac{I_{em}}{2J}$
24	552	1.10	-3.77589
26	650	1.15	-3.81148
27	702	1.0	-3.98898
30	870	1.35	-3.79424
31	930	0.80	-4.35027
32	992	0.65	-4.58966
33	1056	0.75	-4.47733
34	1122	0.65	-4.65029
35	1190	0.50	-4.94164
36	1260	1.15	-4.12690
37	1332	1.05	-4.25527
38	1406	0.65	-4.76151
39	1482	0.55	-4.95454
40	1560	0.85	-4.54454
41	1640	0.75	-4.69440
42	1722	1.30	-4.16845

TABLE - 17 (b)

Q branch

RELATIVE INTENSITY MEASUREMENT OF ROTATIONAL LINES OF
(0,2) BAND AT 3486 Å.

K = J	K (K + 1)	Area under	$\ln \frac{I_{em}}{(2K+1)}$
		peak = $I_{em} \text{ cm}^2$	
30	930	1.75	-3.55127
31	992	1.65	-3.64237
32	1056	1.70	-3.64379
33	1122	2.70	-3.21145
34	1190	1.50	-3.82864
35	1260	2.10	-3.52075
36	1332	0.75	-4.57823
37	1406	1.65	-3.81671
38	1482	0.50	-5.03695
39	1560	0.75	-4.65712
40	1640	0.80	-4.61759
41	1722	0.95	-4.47020
42	1806	0.55	-5.04050
43	1892	0.50	-5.15907
44	1980	0.50	-5.18179
45	2070	0.50	-5.20400
46	2162	0.40	-5.44890
47	2256	0.65	-4.98466
48	2352	0.105	-6.82657
49	2450	0.105	-6.84892

Pbo (1,0) band, P branch

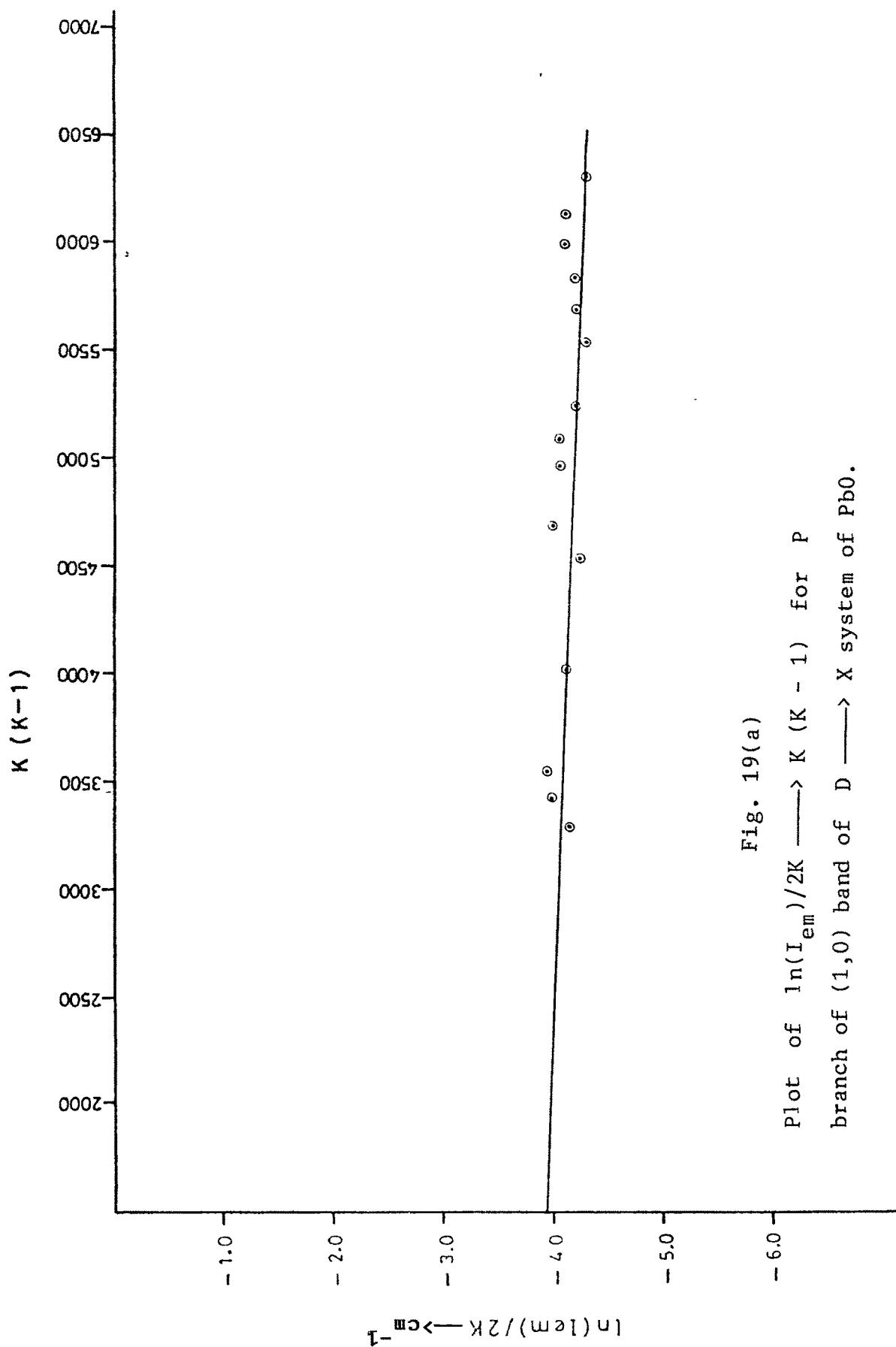


Fig. 19(a)

Plot of $\ln(I_{em})/2K \rightarrow K (K - 1)$ for P
branch of (1,0) band of D \rightarrow X system of PbO.

PbO (1,0) band, Q branch

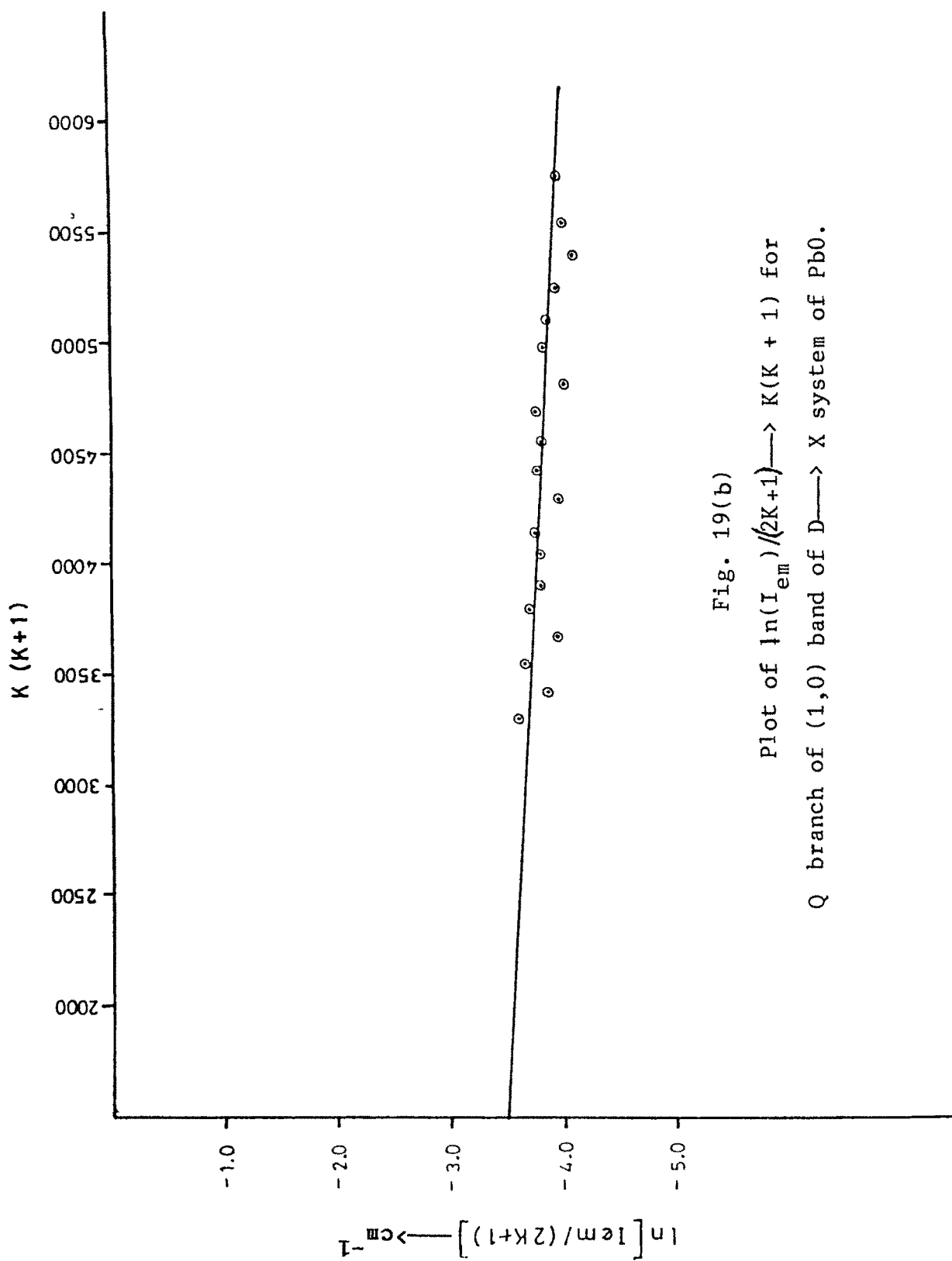


Fig. 19(b)

Plot of $\ln(I_{em})/(2K+1) \rightarrow K(K+1)$ for
Q branch of (1,0) band of D \rightarrow X system of PbO.

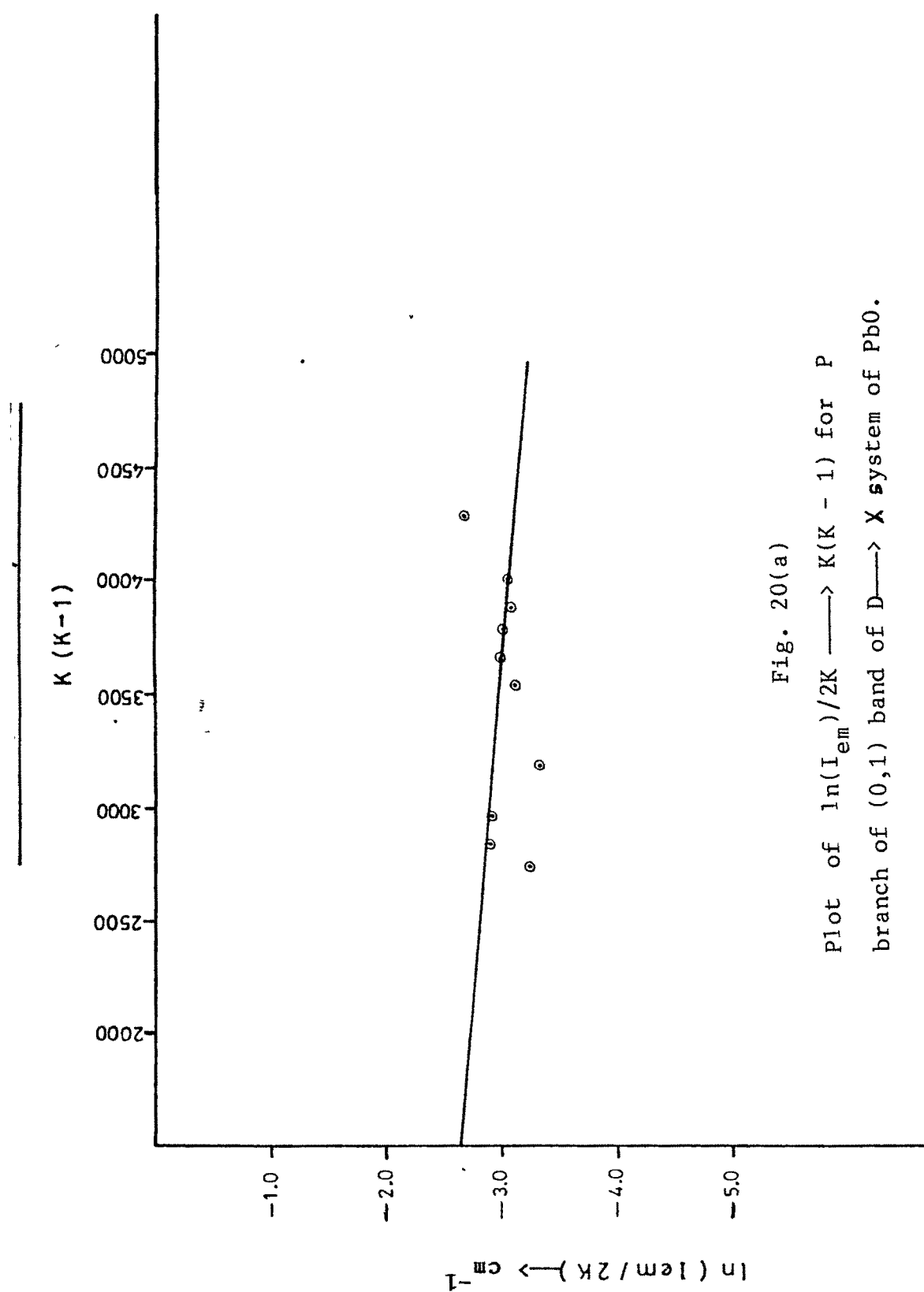


Fig. 20(a)

Plot of $\ln(I_{em})/2K \rightarrow K(K-1)$ for P
branch of (0,1) band of D \rightarrow X system of PbO.

PbO (0,1) band Q branch

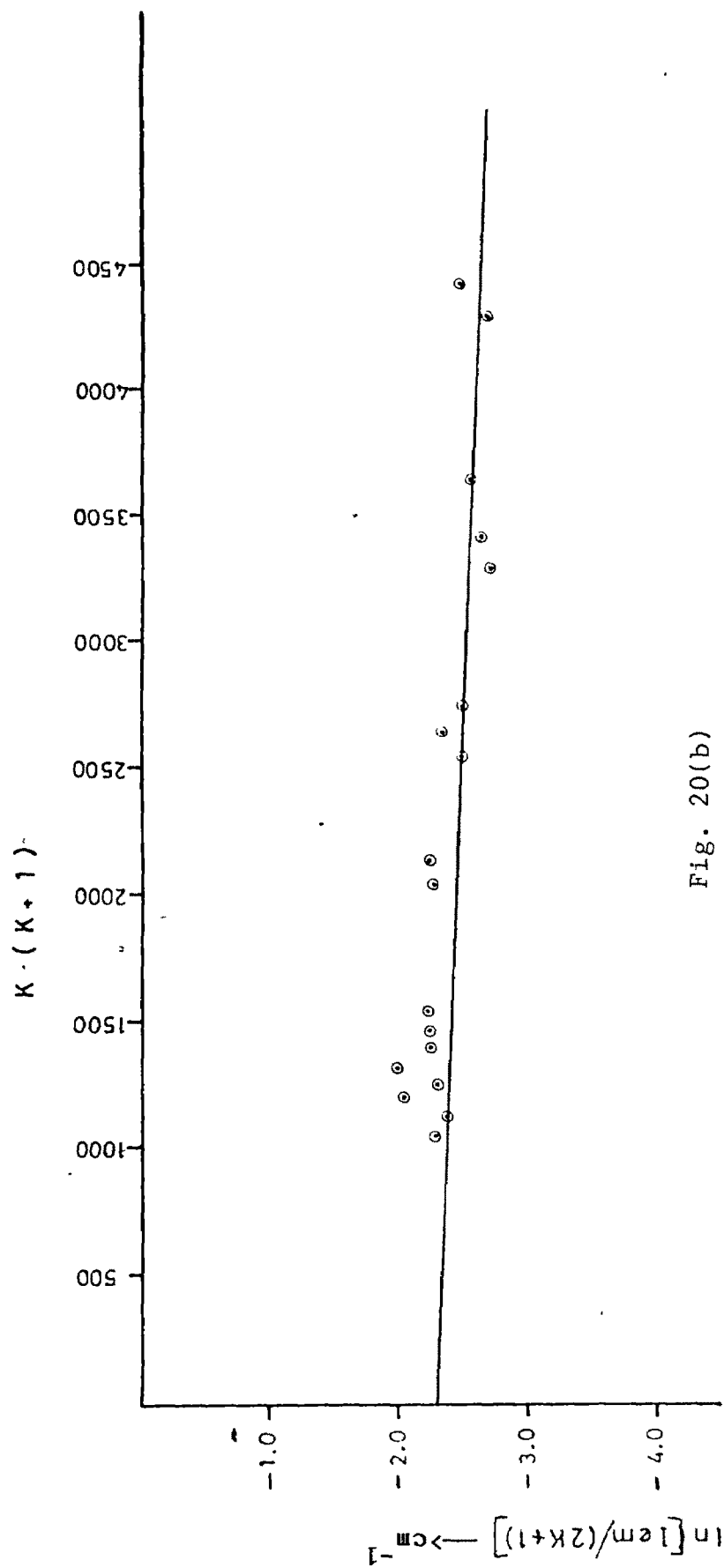


Fig. 20(b)

Plot of $\ln(I_{em})/(2K+1) \rightarrow K(K+1)$ for Q
branch of (0,1) band of D \rightarrow X system of PbO.

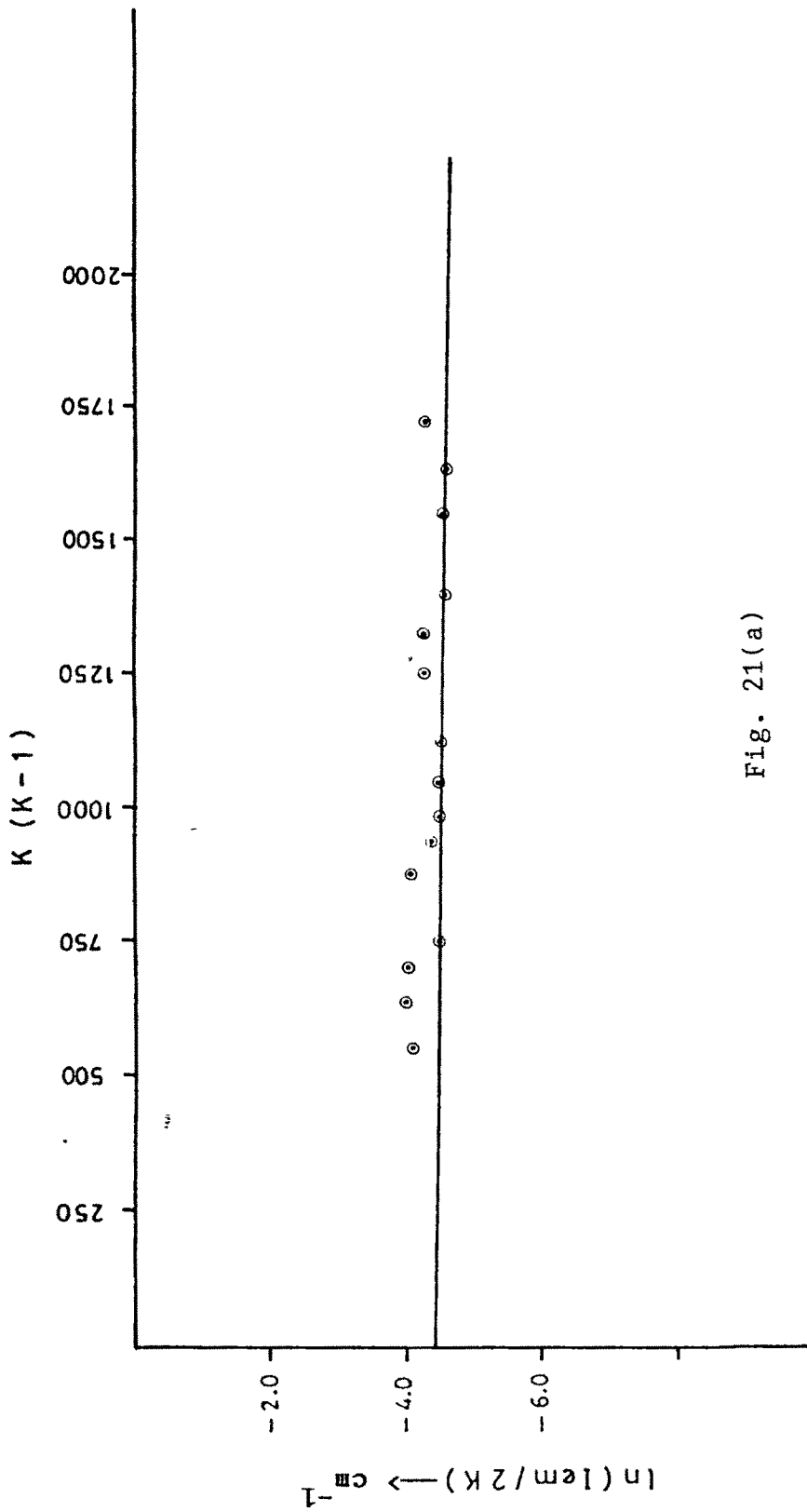


Fig. 21(a)

Plot of $\ln(I_{em})/2K \rightarrow K(K-1)$ for P
branch of (0,2) band of $D \rightarrow X$ system of Pbo.

PbO (0,2) band, Q branch

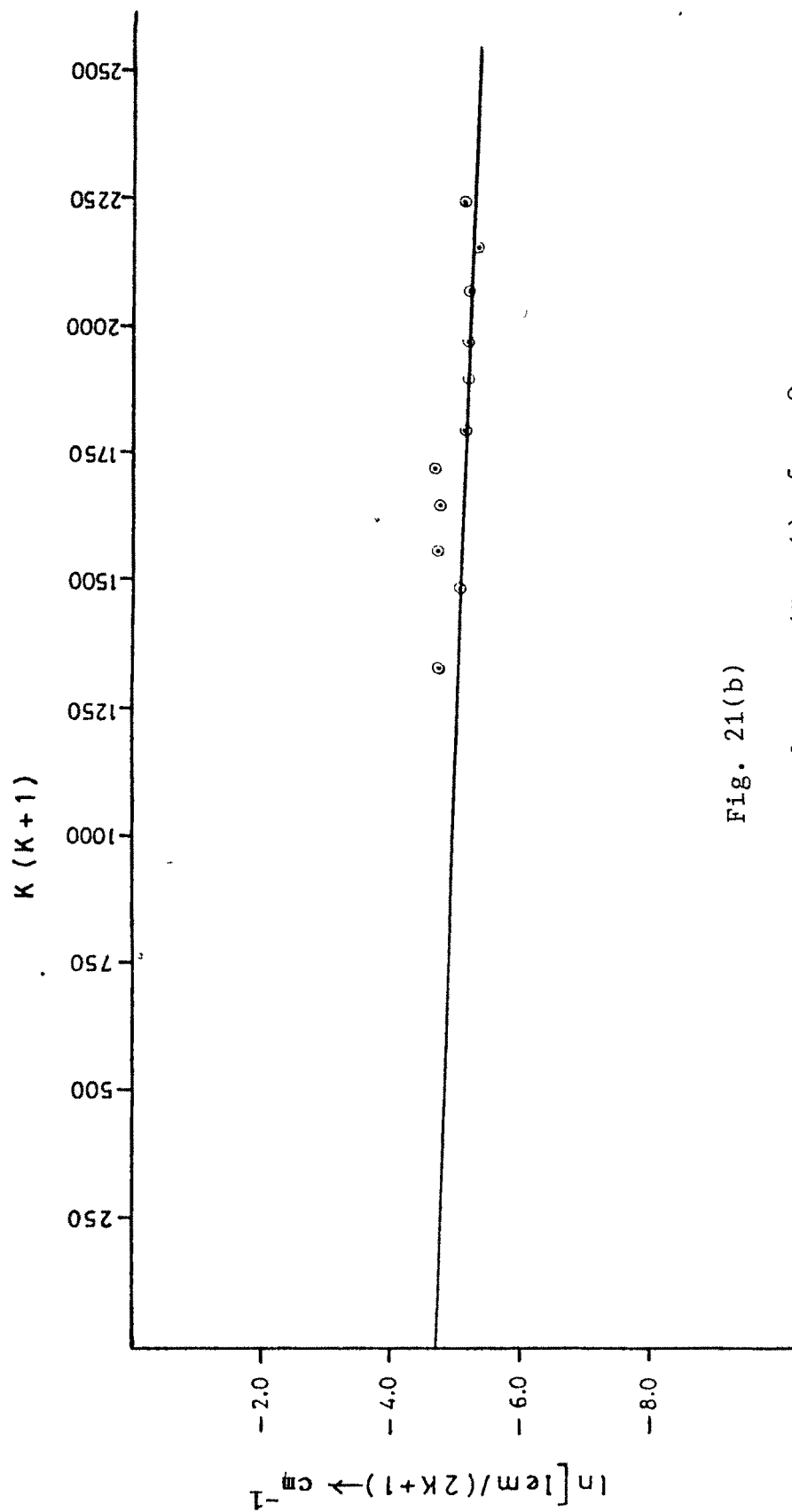


Fig. 21(b)

Plot of $\ln[I_{1m}/(2K+1)] \longrightarrow K(K+1)$ for Q branch of (0,2) band of D \longrightarrow X system of PbO.

TABLE - 18

EFFECTIVE ROTATIONAL TEMPERATURE OF THE SOURCE
 EMITTING THE SPECTRUM OF PbO MOLECULE [D \longrightarrow X
 SYSTEM].

Band	Branch	Rotational Temperature
(1,0)	Q	4897°K
	P	4605°K
(0,1)	Q	5085°K
	P	4591°K
(0,2)	Q	4668°K
	P	4585°K
Effective rotational temperature $T = 4738.5^{\circ} \pm 126.3^{\circ}$ K.		

1