Indian Journal of Pure & Applied Physics
Vol. 30, September 1992, pp. 463-464

Near IR electronic spectrum of NiCl

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Received 11 March 1992, accepted 5 June 1992

Electronic transition $I^2\Delta_{5/2}\rightarrow X_1^2\Delta_{5/2}$ of nickel chloride molecule has been identified for the first time from the rotational analysis of 8395 Å band, which was excited in high frequency discharge source and recorded at an inverse dispersion of 1.41 Å/mm in a Carl-Zeiss PGS-2. Observation of rotational isotopic shifts supports the analysis Rotational constants of the upper and lower states are evaluated.

The diatomic nickel chloride molecule is known to exhibit its electronic spectrum in emission and thermal emission in the visible and near IR regions. The visible spectrum has been well studied by several workers while the work reported on the near IR spectrum is not complete and satisfactory. Survey of the work done on the spectrum of NiCl has been nicely described by Darji and Sureshkumar[1]. Recently they[2,3] have reported rotational analysis of 4598 Å band of $G_2^2\Delta_{5/2}\rightarrow X_2^2\Delta_{3/2}$ system and 4284 Å band of $I_2^2\Pi_{3/2}\rightarrow X_1^2\Delta_{5/2}$ system establishing that the ground state of NiCl is $^2\Delta$ state belonging to Hund's Case (a) with multiplet separation of 484 cm^{-1}. The near IR spectrum in the region 6350-8750 Å has not been satisfactorily studied and our knowledge regarding the low-lying electronic states is rather meagre. Poor intensity, high complexity due to large multiplicity of the energy states and limited number of V' and V'' progressions make the study of the spectrum particularly in near IR region more difficult. In continuation of our study, we report here the rotational analysis of 8395 Å band of NiCl for the first time.

The near IR spectrum of NiCl was excited in RF discharge and recorded in a Carl-Zeiss plane grating spectrograph by the experimental arrangements described earlier by Darji and Sureshkumar[4]. The 8395 Å band of $I\rightarrow X_1$ system is found to be so weak in intensity that a very long exposure of about 30 hrs was just enough to photograph it using a slit as wide as 80 μ and high speed Kodak IR Films 4143 and 2481 and aerographic Film 2424. The spectrum of (0,0) band of $I\rightarrow X_1$ system at 8395 Å exhibits the presence of two main branches, clearly identified as R and P, of which R is the head forming one. The rotational lines are quite broadened and badly overlap with each other due to large slit width. Thus the band shows poorly resolved rotational structure. The branch lines are picked up using the intensity trace of the band obtained from microdensitometer. The measurements of rotational lines are made on Abbe comparator using internal standards and the error of measurement is within the limit of ± 0.05 cm^{-1}.

As the structure clearly reveals the presence of two main branches, the electronic transition should be of the type for which $\Delta\Lambda=0$. The lower state of this system is reported to be $^2\Delta_{5/2}$ by Rao *et al.*[4]. The ground state of NiCl molecule is established to be $X_1{}^2\Delta_{5/2}$ by Darji and Sureshkumar[5] from the rotational analyses of $L_1^2\pi_{3/2}\rightarrow X_1{}^2\Delta_{5/2}$ system of NiCl. Thus it is quite reasonable to consider that the lower state of $I\rightarrow X_1$ system is $X_1{}^2\Delta_{5/2}$. Further, no other band of this system is found to possess well resolved and overlapping-free rotational structure. Therefore, the authors are constrained to report the analysis of a single band by using the combination differences of the $X_1{}^2\Delta_{5/2}$ state reported earlier by them. Thus rotational analysis of the 8395 Å has been carried out by following the standard methods[5]. The combination differences for the upper state are formed from the line wave numbers and J numbering is assigned to rotational lines. The

Table 1 – Rotational constants of 8395 Å band of NiCl

State	Constant	Value	Value reported by Darji and Sureshkumar[2]
$I^2\Delta_{5/2}$	B_0'	0.15967($\pm$67)cm^{-1}	
	D_0'	1.28×10^{-7}cm^{-1}	
	I_0'	175.25($\pm$74)$\times$ 10^{-40} g cm^2	
	r_0'	2.2018($\pm$46) Å	
$X_1{}^2\Delta_{5/2}$	B_0''	0.16708($\pm$33)cm^{-1}	0.16715 cm^{-1}
	D_0''	1.07×10^{-7}cm^{-1}	0.75×10^{-7}cm^{-1}
	I_0''	167.47($\pm$33)$\times$ 10^{-40} g cm^{-2}	167 40($\pm$10)$\times$ 10^{-40} g.cm^2
	r_0''	2.1524($\pm$21) Å	2 1519 ($\pm$6) Å
	ν_0	11905.34 cm^{-1}	

correctness of *J* numbering is verified by applying the criterion of Youngner and Winans[6]. From the graphical plots rotational constant B_0', B_0'', D_0' and D_0'' have been evaluated. B_0' and B_0'' have also been computed from the combination differences. Then the least square fit has been employed to calculate the standard deviations with a confidence level of 95%. The line frequencies are calculated using the rotational constants, which gives the differences ν_{obs}-ν_{cal} within the limits of experimental observations. The rotational constants obtained from the present analysis are listed in Table 1, together with the ground state constants recently reported by Darji and Sureshkumar[4]. From the analysis it is proposed that the electronic transition in all probability should be $I^2\Delta_{5/2} \rightarrow X_1{}^2\Delta_{5/2}$, lower level belonging to Hund's case (a). Absence of an intense *Q* branch confirms this proposition. The rotational isotopic shift due to Cl^{37} has been observed for *P* branch lines, which supports the analysis.

The authors are thankful to Prof S K Shah for providing excellent facilities.

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PRAMANA
— journal of
physics

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Vol 42, No 1,
January 1994
pp 33–40

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

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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 $20\,\mu$ 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 $\pm 0{\cdot}05\,\mathrm{cm}^{-1}$ 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 $X \rightarrow Y$ potentiometeric 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 $10^{-4}\,\mathrm{cm}^2$. 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 $(\nu_{\mathrm{obs}} - \nu_{\mathrm{cal}})$ to a minimum of within $\pm 0{\cdot}1\,\mathrm{cm}^{-1}$. The J numbering, vacuum wave-numbers of R, Q and P lines and combination differences are given in table 1. The rotational constants

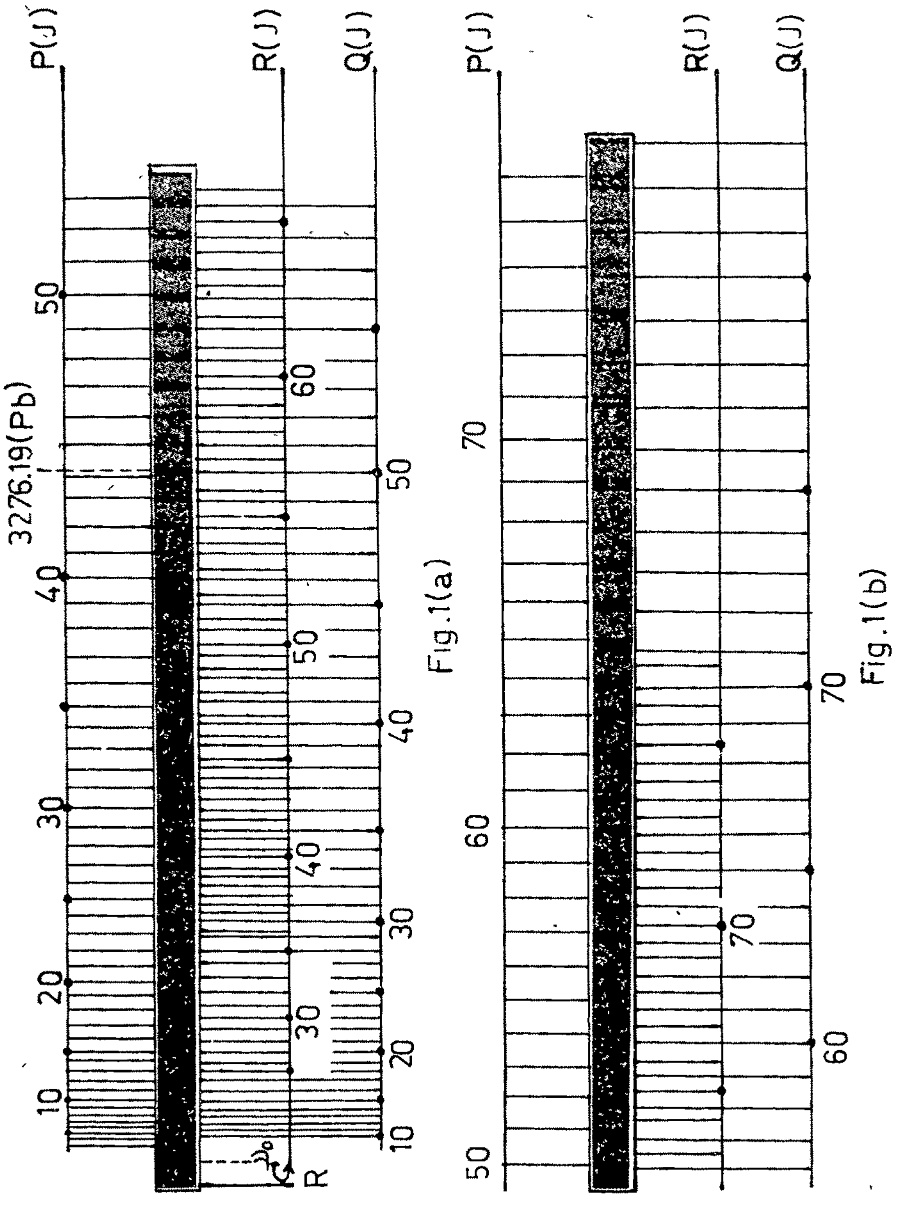

Figure 1. Rotational structure of (1, 0) band of $D \rightarrow X$ system of ^{208}Pb ^{16}O molecule at 0 7088 Å/mm

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

J	$Q(J)$ cm^{-1}	$P(J)$ cm^{-1}	$R(J)$ cm^{-1}	$\Delta_2F'(J)$ cm^{-1}	$\Delta_2F''(J)$ 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*)

Table 1. (*Continued*)

J	$Q(J)$ cm^{-1}	$P(J)$ cm^{-1}	$R(J)$ cm^{-1}	$\Delta_2F'(J)$ cm^{-1}	$\Delta_2F''(J)$ 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}Pb ^{16}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}Pb ^{16}O molecule

State	Constant	Values	Values reported by Ram *et al* [14]
$D1$	B'_1	$= 0{\cdot}26487\,\mathrm{cm}^{-1}$	—
	D'_1	$= 2{\cdot}81 \times 10^{-7}\,\mathrm{cm}^{-1}$	—
	r'_1	$= 2{\cdot}069\,\text{Å}$	
	I'_1	$= 105{\cdot}64 \times 10^{-40}\,\mathrm{g\,cm}^2$	
$X0^+$	B''_0	$= 0{\cdot}30703\,\mathrm{cm}^{-1}$	$0{\cdot}3063\,\mathrm{cm}^{-1}$
	D''_0	$= 2{\cdot}34 \times 10^{-7}\,\mathrm{cm}^{-1}$	$2{\cdot}27 \times 10^{-7}\,\mathrm{cm}^{-1}$
	r''_0	$= 1{\cdot}922\,\text{Å}$	—
	I''_0	$= 91{\cdot}13 \times 10^{-40}\,\mathrm{g\,cm}^2$	—
Band Origin	ν_0	$= 30623{\cdot}15\,\mathrm{cm}^{-1}$	—

(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 $T = 4738{\cdot}5(\pm 126{\cdot}3)\,\mathrm{K}$

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

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

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

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

where

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

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

Estimation of rotational temperature

By ploting $\log (I_{em}/(J' + J'' + 1)$ 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 (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

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