

## Successive approximation to determine rotational temperature

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**Abstract.** A method using successive approximation is developed for determining the rotational temperatures, when the rotational lines are overlapped. The method is applied to CH ( $B^2 \Sigma^- - X^2 \Pi$ ) band as a test.

**Keywords.** Line intensity; Maxwell-Boltzmann distribution; successive approximation; rotational temperature; rotational lines.

### 1. Introduction

A standard method to determine rotational temperatures from the spectrum of a diatomic molecule is to plot the logarithm of the intensity ( $I$ ) of rotational lines against  $E_J$ , the energy values of the upper state (line intensity graph method) and if the graph is a straight line, the slope yields rotational temperature (Herzberg 1950).

Sometimes the method leads to a nonstraight line graph indicating the possibility of the existence of a non-Maxwellian distribution (Kini and Savadatti 1977; Brennen and Currington 1967; Suzuki and Kuchitsu 1977; Mohlmann *et al* 1976; Oldenberg 1934; Edels 1950; Gorbal and Savadatti 1980; Math 1980) and hence is useful in understanding the mechanisms operating under the prevailing experimental conditions. However, in many experiments involving weak sources it is not feasible to use high resolution to separate all the lines and still have adequate intensity to employ the method in a straightforward way. Quite often one has to deal with experimental situations where a number of lines are overlapped. In such cases the measurements do not normally lead to reliable determination of rotational temperatures. In order to overcome this difficulty a method using successive approximation is developed. This method along with its application to the determination of rotational temperature of CH( $B^2 \Sigma^- - X^2 \Pi$ ) band is described in the following sections.

### 2. Successive approximation theory

The intensity of a rotational line is represented by (Herzberg 1950)

$$I_{K'K''} = C(\nu) \nu^4 S_{K'K''} N_0 \exp(-E_{K'}/kT), \quad (1)$$

or 
$$\log_{10} I_{K'K''}/S_{K'K''} \nu^4 = \text{const} - 0.6247 \times E_{K'}/T, \quad (2)$$

where  $C(\nu)$  is the instrument constant,  $\nu$  is the frequency of the transition,  $S_{K'K''}$  is the line strength,  $N_0$  is the population in  $K' = 0$ ,  $E_{K'}$  is the rotational energy of level  $K'$ ,  $k$  is the Boltzmann constant,  $T$  is the rotational temperature and 0.6247 is the numerical value of  $(hc/k) \log_{10} e$ .

If two lines ( $p$  and  $q$ ) overlap and appear as an unresolved or a poorly-resolved line, then the resultant intensity  $I_{p+q}$  can be represented as follows:

$$\begin{aligned} I_{p+q} &= I_p + I_q \\ &= C S^p \nu_p^4 \exp(-E_{K'}^p/kT) + C S^q \nu_q^4 \exp(-E_{K'}^q/kT), \end{aligned} \quad (3)$$

$C = c(\nu) N_0$ ,  $S^p$  and  $S^q$  are intensity factors for  $p$  and  $q$  lines. Since  $\nu_p = \nu_q (= \nu)$ , expression (3) can be rewritten as

$$I_{p+q} = C \nu^4 \exp(-E_{K'}^q/kT) \{S^q + S^p \exp(E_{K'}^q - E_{K'}^p)/kT\} \quad (4)$$

$$= C \nu^4 X \exp(-E_{K'}^q/kT), \quad (5)$$

$$\text{where } X = S^q + S^p \exp(E_{K'}^q - E_{K'}^p)/kT. \quad (6)$$

The intensities of unoverlapped lines are initially used and an approximate value of rotational temperature ( $T_0$ ) is determined using the line intensity graph method (equation (2)). This value of  $T_0$  as well as the relevant values of  $S^p$ ,  $S^q$  (calculated by the formula of Mulliken 1927) and  $E_{K'}^p$ ,  $E_{K'}^q$  (approximated as  $E_{K'} = B_v K'(K'+1)$  where  $B_v$  is the rotational constant) are substituted in (6) to obtain  $X$  for the observed lines. Using the experimentally measured  $I_{p+q}$  and also the  $I$  values of unoverlapped lines  $\log I/X \nu^4$  is plotted against  $E_{K'}^q$ . These points are fitted to a straight line (equation (5)) and from its slope the rotational temperature  $T_1$  is determined. The value of  $T_1$  is substituted back in (6) and the  $X$  values are redetermined (say  $X_1$ ) which are used in (5) to determine the rotational temperature again. If this temperature is  $T_2$ , then  $T_2$  is used to determine  $X_2$  using (6) from which  $T_3$  is determined by (5). This procedure is continued till the temperature so determined is not different from the preceding one. The resulting temperature is taken as the true temperature. The method can be extended if more than two lines overlap.

### 3. Determination of rotational temperature of CH ( $B^2 \Sigma^- - X^2 \Pi$ ) band

#### 3.1 Experimental

A  $\pi$  type discharge tube with fused tungsten electrodes and the associated vacuum system with provision for metering of gases were fabricated in pyrex glass. CH bands were excited in a condensed discharge through flowing  $C_2H_2$  and  $C_2H_4$ . A 15 kV transformer was used to charge 0.005  $\mu$ F capacitor which discharged *via* a spark gap through the gases in the discharge tube.

The bands were photographed on a Hilger Littrow Quartz Spectrograph using

Ilford R-40 plates and the integrated intensities of the lines were measured using microphotometric technique. A typical microphotometer record of the (0-0) band of CH is shown in figure 1.

### 3.2 Results and determination of rotational temperatures

Figure 1 shows that all the rotational lines are not resolved, and some are overlapped. Therefore, the system has been chosen to apply the procedure as outlined above.

For the (0,0) band the wavelength spread is about 50 Å at 3900 Å; the change in  $\nu^4$  is not appreciable and hence is treated as a constant. Table 1 gives the lines used for intensity measurement along with other molecular parameters. The measured intensities of the seven unoverlapped lines were plotted against  $E_K$ , on a semi-logarithmic plot and  $T_0$  was determined (equation (1)) (see figure 2a). Using  $T_0$  and the calculated  $S^p$  and  $S^q$  values,  $X$  values were determined (equation (6)) which were then used along with measured intensity values for all the lines to determine  $T_1$  (equation (5)) (see figure 2b). Now  $T_1$  was used to redetermine  $X$ , (say  $X_1$ ). This  $X_1$  was used in (5) to determine  $T_2$  which was in turn used to determine  $X_2$ .  $X_2$  in turn yielded  $T_3$  which was identical with  $T_2$  in all cases examined and hence no further approxima-

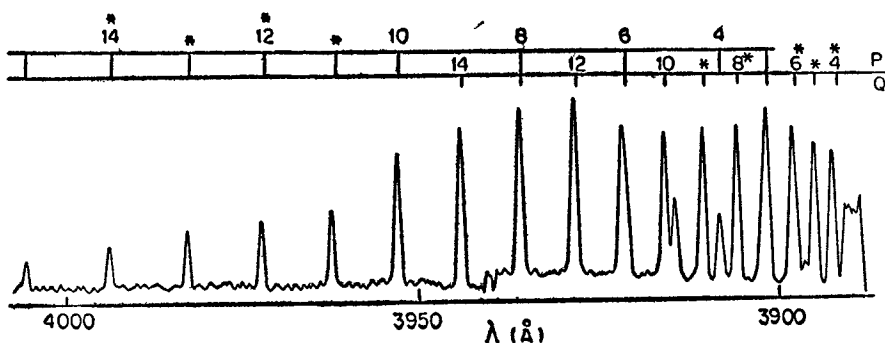


Figure 1. A typical microphotometer record of the 0-0 band of CH ( $B^2 \Sigma^- - X^2 \Pi$ ). \*unoverlapped lines.

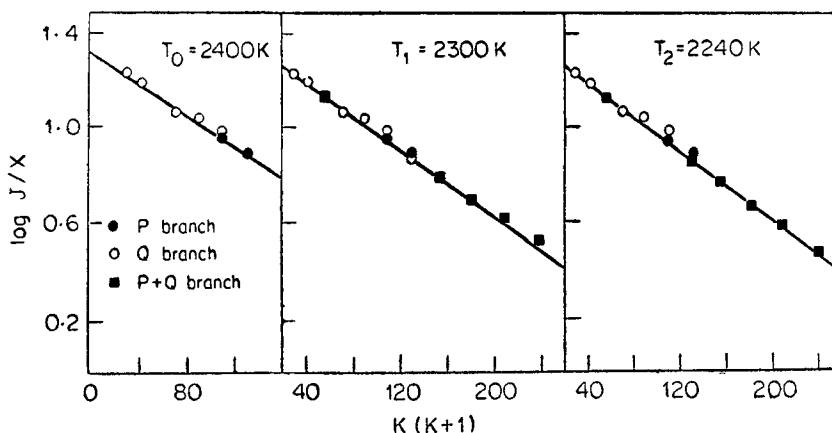


Figure 2. Rotational temperature determination of the 0-0 band of CH ( $B^2 \Sigma^- - X^2 \Pi$ ) obtained from discharge through  $C_2H_2$  (5.0 torr).

tions were necessary. A similar procedure was used for the CH rotational lines excited under different experimental conditions. In each of these cases there was no need to determine beyond  $T_3$ . The different rotational temperature under different experimental conditions reflect the changed experimental conditions and will be analysed in another paper. All these results are collected in table 2.

In order to check the reliability of the method the intensities of these lines are calculated using the determined rotational temperature and the intensity values are reproduced within experimental errors. A typical result of the calculation is given in

**Table 1.** Rotational lines used for measurements and their energy and line strength values.

Rotational lines	$E_{K'}$	Line strengths	
		$P$	$Q$
$Q(5)$	30	—	10·8091
$Q(6)$	42	—	12·8431
$Q(7) + P(3)$	56	7·9590	14·8633
$Q(8)$	72	—	16·8812
$Q(9)$	90	—	18·8944
$Q(10)$	110	—	20·9044
$Q(11) + P(6)$	132	6·9510	22·9130
$Q(12) + P(7)$	156	7·9590	24·9200
$Q(13) + P(8)$	182	8·9647	26·9260
$Q(14) + P(9)$	210	9·9690	28·9310
$Q(15) + P(10)$	240	10·9724	30·9355
$P(11)$	110	11·9752	—
$P(12)$	132	12·9774	—

**Table 2.** Measured rotational temperatures of CH ( $B^2 \Sigma^- - X^2 \Pi$ ) 0-0 band.

Pressure (torr)	Temperature ( $^{\circ}$ K)			
	$T_0$	$T_1$	$T_2$	$T_3$
Source: Discharge through $C_2H_4$				
0·4	1800	1750	1700	1700
1·6	1900	1850	1750	1750
5·0	2200	2100	1950	1950
Source: Discharge through $C_2H_2$				
0·38	2200	2000	1900	1900
1·50	2300	2100	2000	2000
2·30	2300	2150	2100	2100
5·00	2400	2300	2240	2240

**Table 3.** Comparison of the measured intensities with calculated ones for the 0-0 band of the  $B^2 \Sigma^- - X^2 \Pi$  system of CH.

Rotational lines	Intensities	
	measured	calculated (at $T = 2240^\circ\text{K}$ )
$Q(5)$	16.98	17.77
$Q(6)$	19.25	18.93
$Q(7) + P(3)$	26.30	27.74
$Q(8)$	19.50	20.00
$Q(9)$	20.89	19.40
$Q(10)$	19.25	18.18
$Q(11) + P(6)$	25.12	28.05
$Q(12) + P(7)$	26.30	26.75
$Q(13) + P(8)$	23.44	24.37
$Q(14) + P(9)$	22.90	21.85
$Q(15) + P(10)$	20.40	20.40
$P(11)$	10.00	9.49
$P(12)$	9.12	8.70

Condition:  $\text{C}_2\text{H}_2$  discharge at 5 torr

table 3. Successive approximation method has also been applied to this data using least squares technique, in place of the graphical methods, and this leads to same final temperatures. Hence the method can be used with confidence wherever lines overlap.

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