

# INTENSITIES IN THE BANDS OF THE VIOLET CYANOGEN SYSTEM.

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## *Introduction.*

THE application of Maxwell-Boltzmann distribution to vibrational levels in a band system has yielded very interesting results in many cases. The Franck-Condon theory of maximum transitions examined in relation to different functions expressing the nuclear potential energy of a diatomic molecule in a given electronic state gives different results which require to be verified by experiment. For this reason the subject of vibrational intensities in band spectra has assumed a great importance.

The violet bands of cyanogen form a system which is associated with violet glow when a carbon arc is struck in air. Other methods of exciting these bands are (a) active nitrogen, (b) electric furnace and (c) cyanogen gas burning in flame. The method of carbon arc in air has been chosen here on account of the easy occurrence of the bands and its nearer approach to conditions of thermal equilibrium.

In a paper by Ornstein and Brinkman,<sup>1</sup> one of the aspects, namely, of temperature by intensity measurements in this system, has been studied by the authors. In order to tackle the problem in all aspects and in view of the recent systematic work on gross intensities in some band systems, a thorough investigation of these bands was undertaken and the results are presented in this paper.

For the purposes of this paper, only the peak intensities near the heads of unresolved bands will be taken. Sufficient justification for taking the unresolved bands has been provided by Johnson and Tawde<sup>2</sup> and by Johnson and Dunston<sup>3</sup> in recent papers. This is further supported by the work of Ornstein and Brinkman<sup>1</sup> who have proved by measurements that peak intensities near the heads are in the ratio of the sum of intensities of all the lines into which the band is resolved.

## *Experimental.*

The technique of intensity measurements is the same as that indicated in previous papers<sup>2,3,4</sup> in which further references relevant to the subject

can be found. The carbon arc was run at 3 amps. on 100 volts, the arc length being on an average 8 mm. The band system was photographed on Hilger E<sub>1</sub> spectrograph having quartz system, along with the intensity marks taken with a step-slit having 8 elements. For this, a standard lamp of known energy distribution was used. The calibration of the lamp was done on Hilger quartz double monochromator of the Government Chemical Laboratory, London. The plates used were the Ilford Rapid Process Panchromatic and sufficient number of photographs were taken so as to enable a set of bands to come with measurable density. All observations were taken from microphotometer records. The measured intensities were duly corrected for energy distribution ( $E\lambda: \lambda$  curve) of the lamp and the varying sensitivity of the photographic plate in different regions of the spectrum.

*Results.*

(1) *Intensities.*

The results of intensity measurements are entered in the following  $v'-v''$  (Table I) with 0—0 band as 100. The 0—0 band being very strong in

TABLE I  
*Intensities and  $I/\nu^4$  Values.*

$v' \backslash v''$	0	1	2	3	4	5	6	7	$\Sigma I/\nu^4$
0	100 22.57	11.27 3.54	1.26 .74						26.85
1	10.26 1.68	50.23 11.19	12.08 3.72	2.09 0.91					17.50
2		12.45 2.04	28.64 6.32	10.75 3.26	1.37 0.58				12.20
3			5.22 0.85	16.44 3.60	10.15 3.04	1.04 0.43			7.92
4					10.82 2.35	8.15 2.42	1.01 0.41		5.18
5							7.26 2.13	0.87 0.35	2.48

comparison to 0, 1 or 0, 2, a number of intermediate exposures had to be made to express it on the relative scale.

The intensity of a band connected with a given pair of vibrational levels  $v'-v''$  is proportional to  $\nu^4$ , to the number of molecules in the initial level and to the probability of the transition from the initial to the final level. If the distribution in the initial level corresponds to thermal equilibrium

at an absolute temperature T, the number of molecules with the vibrational energy  $E_{v'}$  is proportional to the Boltzmann factor  $e^{-\frac{E_{v'}}{kT}}$  and the intensity of a band can be written down as  $I = C \cdot \nu^4 \cdot p_{v'v''} \cdot e^{-\frac{E_{v'}}{kT}}$  where  $p$  = transition probability,  $C$ =constant, the other symbols having their usual significance. Consequently  $I/\nu^4$  values are calculated separately for each band and these are put below the intensity values in the above table. The sum  $\Sigma I/\nu^4$  for each initial level is put in the last column of the table and these numbers represent values proportional to the statistical weight of the level.

(2) *Effective Temperature of the Arc.*

The data  $\Sigma I/\nu^4$  from Table I have been utilized to calculate 'effective' temperature of the source. In the case of CN  ${}^2\Sigma \rightarrow {}^2\Sigma$  system, the following equation holds for the vibrational energy in the upper state:

$$2164 \cdot 15 (v' + \frac{1}{2}) - 20 \cdot 25 (v' + \frac{1}{2})^2 = 1 \cdot 6083 T \log_{10} \frac{N_0}{N_{v'+\frac{1}{2}}}$$

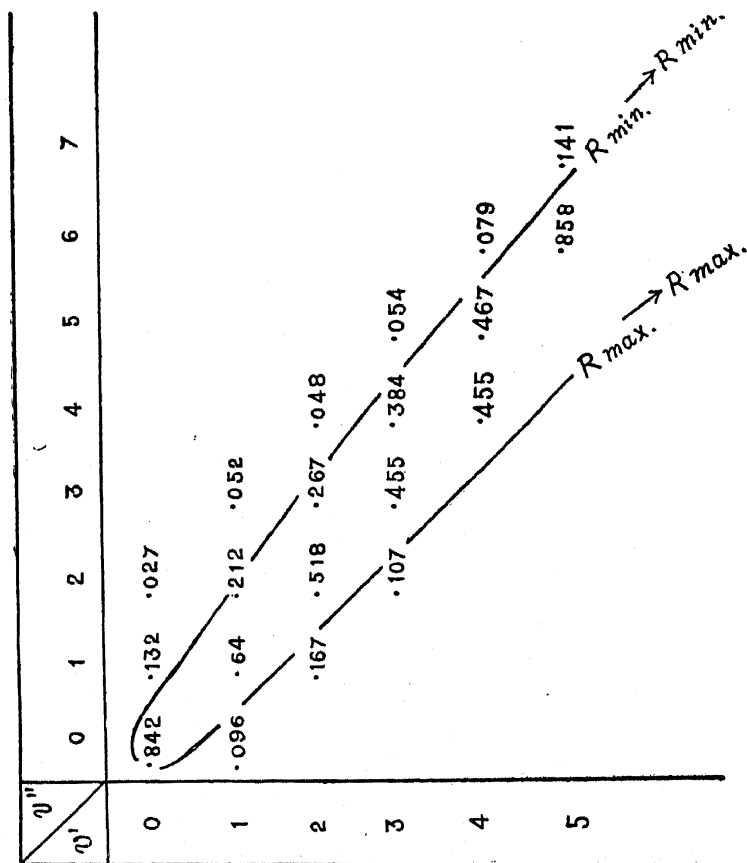


FIG. 1. Transition Probabilities.

The values of N, the number of molecules are taken proportional to  $\Sigma I/\nu^4$  in each initial level. By plotting  $\log_{10} \frac{N_0}{N_{v'+\frac{1}{2}}}$  against the vibrational energy it is possible to get the value of T the absolute temperature from the slope of the linear relation and this has been found in our case to be  $7210 \pm 500K$ .

(3) *Transition Probabilities.*

Fig. 1 above has been constructed giving numbers proportional to vibrational transition probabilities. They have been calculated according to procedure adopted in a previous paper from  $I/\nu^4$  values of Table I. They represent only relative values. The Condon parabola of maximum transitions has been shown as a curve passing through preferred vibrational levels. Its agreement with theory can be judged from the following Table II which gives comparative values.

TABLE II.  
*Transition Probabilities.*  
*Comparative Values.*

Experimental	Morse	Rydberg
$r_{\max} \rightarrow r_{\max}$		
4,4	4, 3 and 4, 4	4, 4
3, 2 and 3, 3	3, 2	3, 2 and 3, 3
2, 2 and 2, 1	2, 1	2, 2 and 2, 1
1, 1	1, 0 and 1, 1	1, 0 and 1, 1
0, 0	—	0, 0
$r_{\min} \rightarrow r_{\min}$		
5, 6 and 5, 7	5, 7	5, 7
4, 5	4, 6	4, 6
3, 4	3, 5	3, 5
2, 3	2, 4	2, 4
1, 2	1, 2	1, 2
0, 1	0, 1	0, 1 and 0, 0

Column 1 of the Table gives experimental transitions, while columns 2 and 3 give the transitions as derived theoretically by graphical method from Morse and Rydberg functions. The potential energy curves drawn to scale according to these are shown in Figs. 2 and 3.

(4) *Behaviour in Sequences.*

It has been shown by Ornstein and Brinkman<sup>1</sup> that in the sequences of this system, there is a linear relation between  $\log I/\nu^4$  of a band and the vibrational energy  $E_{v'}$ . This means that the vibrational transition probabilities in each sequence are proportional to  $e^{-\alpha E_{v'}}$  after a certain value of  $v'$ ,  $\alpha$  being a constant. The linearity of this relation in some sequences has been verified by the author in a previous paper.<sup>6</sup> Calculation of the value of  $\alpha$  gives in the case of  $v'-v''=0$  sequence  $\alpha = +1.15 \times 10^{-4}$  and that

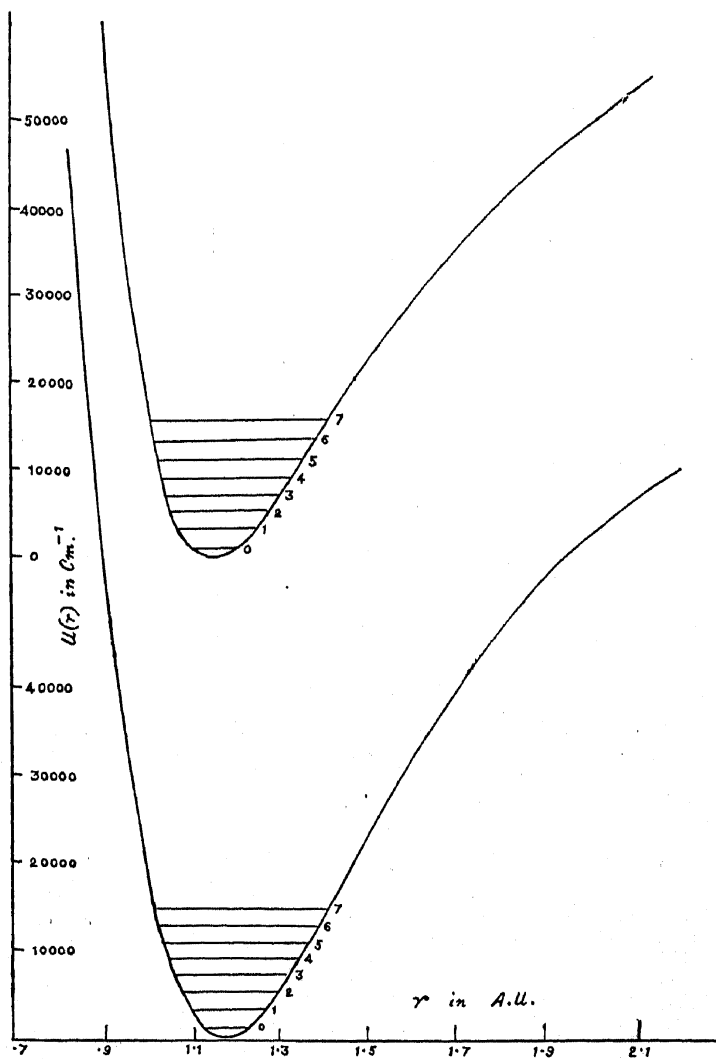


FIG. 2. Morse Potential Energy Curves for Violet CN System.

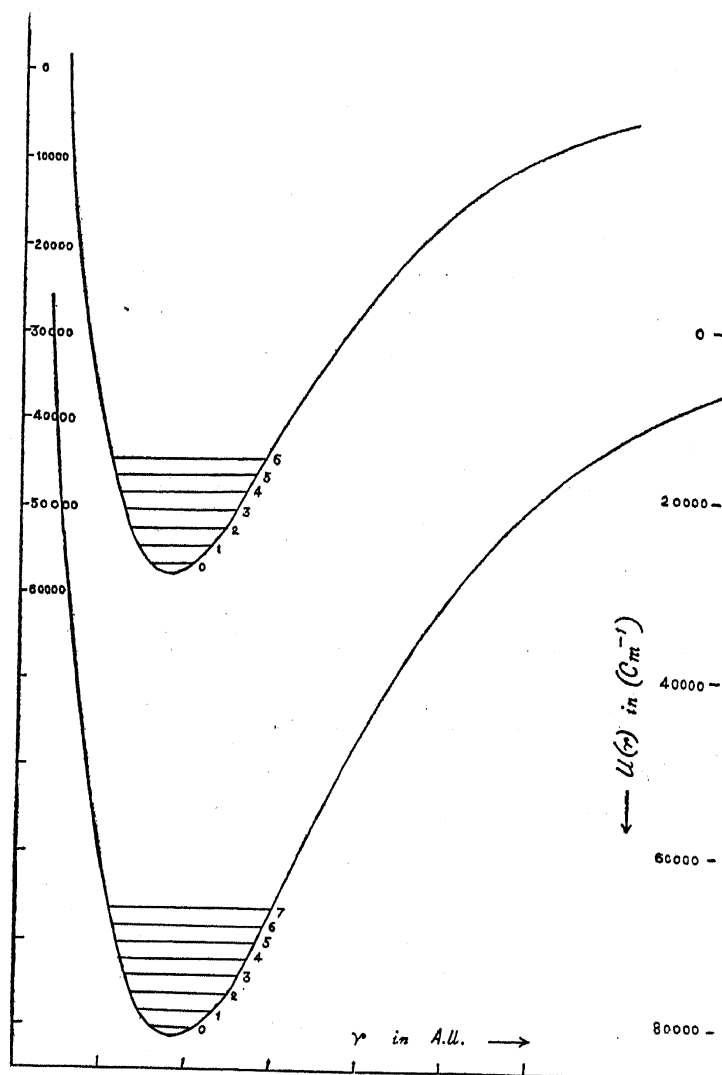


FIG. 3. Rydberg  $U(r)$  Curves for Red CN System.

in the case of  $v'-v'' = -1$  it equals  $-1.38 \times 10^{-4}$  on a relative scale. For  $v'-v'' = +1$  and  $-2$  sequences the value of  $a$  is not very well defined, but it is near about  $-1.317 \times 10^{-4}$  in the case of the latter. In general, it appears that  $a > 0$  in sequences  $v'-v'' = 0$  and  $+1$  and  $a < 0$  in sequences  $v'-v'' = -1$  and  $-2$  as indicated by Ornstein and Brinkman.<sup>1</sup>

#### Conclusions.

In deriving the effective temperature of the radiating source, a linear relation was found between the 'weights' of the various initial levels and the vibrational energy. This shows that there is thermal equilibrium of molecules at the temperature of the source and a vibration temperature does exist in this case, but its value is rather too high for the source used. However, according to Ornstein and Brinkman,<sup>1</sup> temperatures between

5,000°K. and 7,000°K. exist in the carbon arc depending on the current and length of the arc as determined by spectroscopic methods. They have found in the case of CN bands a vibration temperature 5,870° K. for a current of 1.7 amp. in the carbon arc. Considering this, the temperature 7,210°K.  $\pm 500$  in our case (for current strength 3 amps.) is not improbable, especially in view of the probable sources of error due to unknown causes in this type of work. If in different zones of the arc different temperatures exist, it is quite likely that two band systems arising in the same arc source but giving two different effective temperatures for that source, are excited in different zones. This aspect of the problem requires elucidation and work in this direction is in progress.

There is not much to differentiate between the results of maximum transition probabilities as derived from Morse and Rydberg potential energy functions. Both the curves agree well within the observed limits of the vibrational levels of the system. The Condon parabola derived from both is practically the same and there is satisfactory agreement of the experimental curve with this parabola as can be seen from Fig. 1 and Table II. The narrowness of the parabola is to be expected for a molecule of this type where  $r'_e < r''_e$ .

The theoretical aspect of the subject of spectral intensities in band systems has been treated by Hutchisson<sup>5</sup> on the basis of quantum mechanics. Hutchisson considers that his formula for calculating the intensity of vibrational levels is applicable to symmetric molecules only, but Dunham<sup>7</sup> shows that it is of general applicability. Hence in CN which is a non-symmetric molecule, it should be possible by Hutchisson's formula to calculate theoretical intensities and to see their agreement with experiment. It is intended to investigate this in a later paper.

The experimental part in connection with this problem was carried out at the University of London King's College and all the later work was done at the Royal Institute of Science, Bombay. The author is much indebted to Dr. R. C. Johnson for his interest in the work and to Prof. A. Fowler of the Royal College of Science, London, for allowing the use of his microphotometer.

#### *Summary.*

Quantitative estimation of vibrational intensities in  ${}^2\Sigma \rightarrow {}^2\Sigma$  system of CN has been made by the method of heterochromatic spectral photometry.

The results have been utilized to examine some aspects of Condon's theory and effective temperature derived on the assumption of the thermal distribution of molecules in vibrational levels.

Some features of intensities in sequences are discussed.

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