INTENSITY MEASUREMENTS IN MOLECULAR BANDS

N. R. TAWDE, B. G. JYOTI and M. I. SAVADATTI

DEPARTMENT OF PHYSICS, KARNATAK UNIVERSITY, DHARWAR

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ABSTRACT. Peak and integrated intensities of N_2 II positive bands have been measured. The peak values have been corrected according to the procedure of Floyd and King. The data have been obtained with a view to assess the reliability of peak intensity measurements and also the correction due to Floyd and King.

Intensity of a band to be accurate has to be obtained by summing over the intensities of the rotational lines that form the band. Phillips (1957) tried to use this principle for the C_2 (Swan) system excited in a furnace of known temperature. Since the lines were badly blended he calculated band profiles by combining the profiles of individual rotational lines. He concludes that the results so obtained may be quite uncertain for weak bands. However, a rigorous application of the method is too laborious and many times it is not practicable or even possible. So simpler, but reliable, methods of estimating intensity are to be thought of. The method—known as integrated intensity method—of measuring intensities with a low dispersion spectrograph by integrating over the entire intensity contour of the bands is the one which gives intensity values nearest to the true intensity of a band. The requirements for the results to be reliable are (i) the band structure should not be resolved and (ii) there should be no overlapping from the neighbouring bands. The first requirement can be easily met by a proper choice of the spectrograph, but the second requirement is too rarely satisfied, because in almost all actual band systems there is an overlapping from neighbouring bands. When the overlapping is present, the band profiles are judiciously extrapolated and the effect of overlapping separated. But such a procedure is purely subjective and the results might be in great error for weaker bands overlapped by strong bands.

In case of overlapping, the intensity at the head of the band may be taken to represent band intensity (peak intensity method) or a known fraction of band intensity near head may be used to derive band intensity (fractional band intensity method, Robinson and Nicholls, 1958).

Ornstein and Brinkman (1931) were the earliest to use the peak intensity of CN bands to represent band intensity and concluded that the rotational energy distribution varies from band to band and hence the method is not valid. Tawde and Patankar (1943) have shown for N_2 second positive system that the ratio of

the band head intensity to integrated intensity is not a constant, while Young (1954) has shown experimentally for the same system that the mean deviation for this ratio is only 6.2%.

Floyd and King (1955) have developed a method of obtaining total band intensity from the band head intensity, by assigning a representative rotational quantum number for the band head (J_h) and also taking into account the number of lines forming the head (ΔJ). This method finds immediate application to singlet systems or for those systems which can be approximated to singlet systems. A difficulty in applying the method is that the temperature of the source (emitting the band system) which enters into the equation is, in general, not precisely known. For many sources true temperatures are not easily available or estimable. So the method might not find rigorous application to all the band systems. However, a fairly satisfactory intensity value may be obtained, if we can assume some reasonable temperature or approximate the term containing temperature to a constant. This can be done provided the rotational quantum number at the band head has a small range of variation in the bands considered.

Robinson and Nicholls (1958) have developed a fractional band intensity method which correlates the sum of intensities of a few rotational lines at and near the head with the band intensity. This method also suffers from lack of knowledge of temperature which has therefore to be assumed.

A possible error in peak intensity and fractional band intensity measurements is the effect of self-absorption on the intensity at the peak. This effect becomes appreciable when the intensity of the blended rotational lines reaches a significant fraction of the intensity of a black body at the same temperature and wavelength. In that case one will have to consider the manner of blending of rotational lines at the band head.

Robinson and Nicholls (1958) have developed a rotational line intensity method, where the intensities of rotational lines are plotted against the energy of upper levels of transition. The intercept on this graph can be used to obtain band intensity. The method is satisfactory provided rotational thermodynamic equilibrium exists in the source.

Intensities of $NO(\beta)$ and O_2 (II negative) systems were measured by these methods by the above authors and the results were found to compare satisfactorily with the integrated intensity values. But it may be noted here that the integrated intensity values are subject to the error due to overlapping by the neighbouring bands.

In order to judge the merits and demerits of any method for intensity measurements, it is necessary to possess integrated intensity values on bands which have no appreciable overlapping. So it was decided to measure the intensities of bands N_2 (II positive) system with a view to ascertain the reliability of peak intensities and peak intensities corrected according to the method of Floyd

and King (1955). The reason for selecting only these two is that such values are easily available and an evaluation of their reliability is naturally much useful. The bands (1–6), (2—7), (3—8), (1—5), (2—6) and (3-7) have almost negligible overlapping from neighbouring bands and hence they have been particularly chosen for this study. The intensities have been measured photographically using an a.c. discharge through air as a source of N_2 (II positive) bands. The measurements have been repeated with two spectrographs to ascertain the effect of varying dispersion on the intensity measurements and also as a general check on the measurements.

TABLE I

Intensity measurements · N_2 II P. (small quartz spectrograph)

Transition	$*I_p$	$*I_{pc}$	$*I$	$\dfrac{I_p}{I}$	Devn. from mean	$\dfrac{I_{pc}}{I}$	Devn. from mean
1–6	25.36	26.92	30.61	0.83	0.09	0.88	0.07
2–7	32.64	34.93	38.13	0.86	0.06	0.92	0.03
3–8	28.69	31.19	32.89	0.87	0.05	0.95	0.00
1–5	93.94	92.11	95.34	0.99	0.07	0.97	0.02
2–6	100.00	100.00	100.00	1.00	0.08	1.00	0.05
3–7	65.01	65.72	66.24	0.98	0.06	0.99	0.04

Mean 0.92 Mean 0.95
Mean % devn.: 7.5 Mean % devn.: 4.2

TABLE II

Intensity measurements—N_2 II P. (medium quartz spectrograph)

Transition	$*I_p$	$*I_{pc}$	$*I$	$\dfrac{I_p}{I}$	Devn. from mean	$\dfrac{I_{pc}}{I}$	Devn. from mean
1–6	20.43	21.39	19.09	1.07	0.07	1.12	0.09
2–7	23.27	24.65	22.53	1.03	0.03	1.09	0.05
3–8	21.16	22.78	21.89	0.97	0.03	1.04	0.00
1–5	99.98	98.14	98.16	1.02	0.02	1.00	0.04
2–6	100.00	100.00	100.00	1.00	0.00	1.00	0.04
3–7	70.20	71.58	74 83	0.94	0.06	0.96	0.08

Mean 1 Mean 1.04
Mean % devn.: 5 Mean % devn.: 5

* I_p Peak intensity,
I, Integrated intensity, and
I_{pc}, Peak intensity corrected according to Floyd and King (see Appendix).

The results are collected in Tables I and II. It is observed that the percentage mean deviation is not more than 7% in the case of uncorrected peaks and not more than 5% in the case of corrected peaks. Considering the fact that photographic photometry has errors of these magnitude, we feel that the peak values compare fairly well with integrated values; and corrected peak values, in general, give a better comparison with integrated values. In connection with corrected values, it may be noted that the exponential term containing the rotational temperature has been approximated to a constant. However, if a temperature, say $300^\circ C$, is assumed for the discharge, the change in value of intensities is $\backsim 2\%$ and hence the approximation of the term might be justified.

<center>APPENDIX</center>

$$I_{pc} - I_p \left[J_h \Delta J \right]^{-1} \exp \left[\frac{B_{v'} J_h (J_h - 1)}{kT} \right]$$

where J_h the rotational quantum number at band head, is expressed as

$$J_h = \frac{B_{v'} + B_{v''}}{2(B_{v'} - B_{v''})}$$

and ΔJ the number of lines forming band head is given by

$$= \frac{Const}{\lambda_h} \left[\frac{d\lambda}{ds} \middle/ (B_{v'} - B_{v''}) \right]^{\frac{1}{2}}$$

where λ_h — wavelength at band head.

The symbols in the above have their usual meaning (Herzberg, 1950).

<center>ACKNOWLEDGMENT</center>

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