THE BAND SPECTRUM OF PHOSPHORUS—PART II : ALTERNATING INTENSITY AND NUCLEAR SPIN

By K. NARAHARI RAO

(Received for publication, March 5, 1943)

Plate IV

ABSTRACT. Elaborate quantitative measurements have been made of the alternating intensities of the rotational structure lines in the case of the bands (5,21), (5,18), (9,21), and (6,22). The (5,21) band alone gave the anomalous value 3.3 while for the others, the ratio on an average is 3.0. Such a high value (3.4 to 3.5) was obtained for this band also by Jenkins (1935). But the anomaly cannot be ascribed to any effect of perturbations, as the (5,18) band does not show the anomaly and the rotational structure has not revealed any perturbations. The intensity ratio leads to a value of $\frac{1}{2}h/2\pi$ for the nuclear spin of phosphorus as determined by Ashley (1933) and Jenkins (1935).

From a study of the rotational structure of the bands of phosphorus involving the level $v'=5$, the author has considered in a previous paper (Rao, 1943) the possibility of a perturbation of rotational lines associated with the initial vibrational level 5 which has been reported by Herzberg (1932) to show strong perturbations. The present part deals with the determination of the alternating intensities of the lines in the bands (5,21), (5,18), (9,21) and (6, 22) in relation to the nuclear spin of phosphorus. Two of the above bands chosen for study have the initial vibrational level 5. As such, the results of the determination of the alternating intensity ratio of the above bands throw light on the question of perturbation of the level $v'=5$. The method employed for determining the intensities of the lines is a direct one using a standardised quartz lamp and varying slit widths.

EXPERIMENTAL

The experimental arrangement for exciting the bands is the same as that described in the previous paper of the author. The phosphorus bands were photographed with a quartz Littrow spectrograph on Ilford Special Rapid plates. With the usual precautions in adjusting the times of exposure and in developing the plates, the grain effect is found to be negligible.

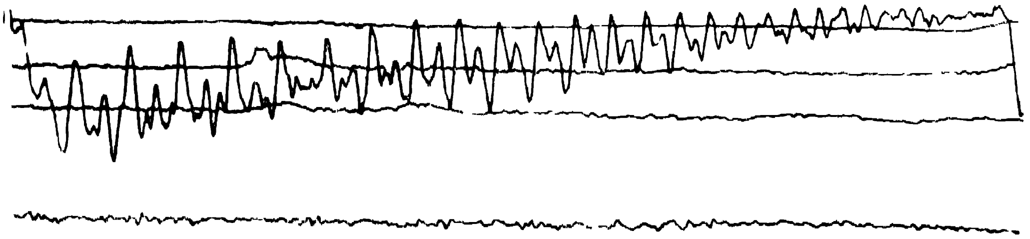
For the purpose of deriving the blackening-intensity curves of the plate at any wavelength, density marks were given with varying slit widths on the same plate as the one utilised for recording the band spectrum of phosphorus. The slit is calibrated by a Hilger photo-measuring micrometer. The slit widths employed were 0.10, 0.25, 0.63 and 1.58 mms. The slit of the spectrograph was directly illuminated from a distance of about half a metre by a quartz standardised lamp, calibrated at Utrecht. The lamp was run on 220 volts D.C.

from high-capacity batteries and a steady current of 16 amperes was sent. The exposures for the density marks were 25 minutes each. (Plate IV.)

The calibration curve of the lamp gave the relation $E_\lambda : \lambda$ in the spectral region investigated and for the current at which the lamp was worked (*i.e.*, for the corresponding temperature of the filament). The value of $E_\lambda : \lambda$ for the regions investigated have been given in the tables supplied by the manufacturer along with the lamp. From these values and the dispersion curve $d\lambda/dm : \lambda$ of the quartz spectrograph (drawn separately) a curve is drawn in two different regions between $E_\lambda/d\lambda/dm$ and λ appropriate to the standard lamp (at the temperature at which it is worked) used in conjunction with the particular spectrograph employed.

The energy falling over a given region of the plate at any wavelength is given by E_λ $(d\lambda/dm)$ W where W is the slit-width.

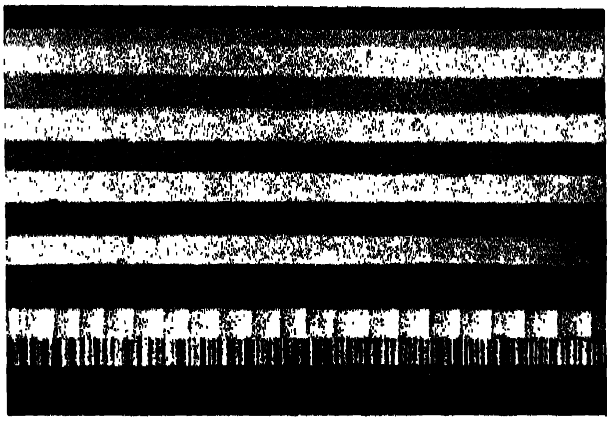
Microphotometer curves were taken for the band system under study and of the different intensity marks successively on a single photographic sheet at a single setting of the microphotometer. Forty-nine times magnified microphotometer records are obtained separately for the individual bands. The curves corresponding to each band in the spectrum are thus superposed on those corresponding to the intensity marks in an exact manner with respect to the wavelength. This special procedure considerably facilitated the evaluation of the densities at the proper wavelengths. The curve of the (5,18) band is given in Fig. 1 as an illustration.



(5,18) band (P_2 molecule)

FIG. 1

The values of the optical density log (u_0/u) ('u_0' being the perpendicular distance of the zero line to the blank plate line and 'u' the distance from the zero line to the point corresponding to which the intensity is required to be evaluated) for the different steps and the line (whose intensity is required) are calculated for a particular wavelength, say λ_1, at which the line under study is situated. The density is plotted against log I (where $I = E_\lambda . d\lambda/dm . W$) From this curve, the intensity corresponding to the density of the line is read off. On account of the variation of sensitivity of the plate, a separate density curve for each wavelength at which a line is situated has to be drawn. As many curves are to be drawn as there are lines whose intensities are to be evaluated. Here each band extends to about 10 Angstrom units at the most.



So in order to minimise the more laborious and tedious calculations one curve is drawn for each band and the intensities of all the lines in the band are read off from that curve.

The intensities thus obtained for all the lines in the band are corrected for the continuous background. The intensity at the depression just preceding the peak corresponding to a particular line is subtracted from the peak intensity to get the actual value of the intensity of the line correcting for the background.

In this manner, the intensities of all the lines (strong and weak) in each band are evaluated. (The influence of frequency in not considered as it does not affect the alternating intensity ratio.) In a particular band the ratio between the sum of all the intensities of the strong lines and that of an equal number of the weak lines lying in between the two gives the mean ratio of the intensity of the strong to the weak lines. This process is utilised for the determination of the mean ratio to minimise errors due to the blends of the P and R branches.

In evaluating the ratio for the various bands those portions of the spectrum only where the structure is well open are chosen. A final value of the ratio of the strong to the weak lines is obtained by finding out the average of the values determined for individual bands.

A large number of plates (more than forty to fifty in all) were taken varying the times of exposures of the standard lamp and the discharge through phosphorus and an equally large number of microphotometer records were also made for the different bands. Only those plates for which the microphotometer record of the lines in the band lies in between the curves for the density marks are utilised for calculating the intensities in the manner indicated above. Great care is taken to see that such developer and hypo solutions are used which are filtered free from dust particles, the developer being of uniform standard in strengths for all the plates. The values obtained for the bands studied are shown in the table given below :

Bands v', v''	Alternating intensity ratio
5,21	3.3
5,18	3.0
6,22	3.1
9,21	2.9
	Average of the last three values is 3.0

The table of alternating intensity ratios given above shows that the intensity ratio is approximately 3.0 for all the bands with the exception of (5,21) which gives a higher ratio. But that this is not due to any effect of strong perturbation (reported by Herzberg as associated with the vibrational level $v'=5$) is obvious as the (5,18) band does not give an anomalous value. The larger value of the (5,21) band must be ascribed to the probable overlapping of a fainter band which has given rise to a difficulty in elucidating the rotational structure.

NUCLEAR SPIN

It is known that the ratio of the intensity of the strong to that of the succeeding weak line in the case of the rotational structure of the bands due to the symmetrical molecules is given by the expression $(I+1)/I$ where I is the spin moment of the nucleus. The experimentally determined ratio 3.0 for the P_2 molecule obtained in the above investigation leads to $I=\frac{1}{2}$, the same as that arrived at by Asley (1933) and Jenkins (1935).

The author is indebted to Dr. K. R. Rao for his advice and guidance in the course of these investigations.

SOLAR PHYSICS LABORATORY,
KODAIKANAL.

REFERENCES

Ashley, 1933, *Phys. Rev.*, **44**, 919.
Jenkins, 1935, *Phys. Rev.*, **47**, 783.
Herzberg, 1932, *Ann. der Phys.*, **15**, 677.
Rao, K. Narahari, 1943, *Ind. J. Phys.*, **17**, 135.