

The Green Flame of Phosphorus Hydride

E. B. Ludlam

Citation: [The Journal of Chemical Physics](#) **3**, 617 (1935); doi: 10.1063/1.1749563

View online: <http://dx.doi.org/10.1063/1.1749563>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/3/10?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Photoelectron spectroscopy of phosphorus hydride anions](#)

J. Chem. Phys. **122**, 194303 (2005); 10.1063/1.1881153

[Reply to “Comment on ‘Ultraviolet light amplification by cool green phosphorus chemiluminescence flame’”](#)

J. Appl. Phys. **53**, 7073 (1982); 10.1063/1.330009

[Ultraviolet light amplification by the cool green phosphorus chemiluminescence flame: PO diatomic and POexcimer electronic excited states](#)

J. Appl. Phys. **53**, 143 (1982); 10.1063/1.331589

[Electron attachment and compound formation in flames. VII. Electron attachment in flames containing phosphorus and potassium](#)

J. Chem. Phys. **69**, 3709 (1978); 10.1063/1.437032

[Source of Green Bands from BoronContaining Flames](#)

J. Chem. Phys. **32**, 1273 (1960); 10.1063/1.1730899



The Green Flame of Phosphorus Hydride

E. B. LUDLAM, *Edinburgh University, Scotland*

(Received July 30, 1935)

The rotational structure of the bands in the green flame of phosphorus indicates that the emitting molecule is PH.

THE green flame associated with the burning of phosphorus has been known for many years. It had been examined by Salet and de Boisbaudran, but more in detail by Geuter¹ in 1907. Geuter also noticed that the same bands were produced in an electric discharge through a tube containing phosphorus if the air (moisture?) had not all been pumped out, the lines disappeared after passing the current for a short time; simultaneously with the green bands the many-lined spectrum of hydrogen appeared, then the Balmer lines and finally the green bands disappeared. He came to the conclusion that the spectrum was a hydride and suggested P_2H_4 . He thought the same spectrum was emitted in the glow of phosphorus, but even with instruments of low dispersion the intensity of the emission from the glow is not sufficient to give a spectrum which can be measured.

Our own interest in the spectrum first arose from a study of the glow of phosphorus and the initiation of the chain reaction between phosphorus vapor and oxygen.² The vapor of white phosphorus consists of P_4 molecules and it had been suggested that the initial stage in the reaction between oxygen and phosphorus was the dissociation of P_4 into $2P_2$.

Recent work on the blue flame of sulphur had shown that the blue color was due to radiation emitted by the excited S_2 molecule, and it was thought possible that the green flame might be due to P_2 molecules; on the contrary, it turns out to be a hydride and most probably PH.

EXPERIMENTAL

After trying a number of different methods of producing the flame, it was found most satisfactory to burn air at a jet in a current of hydrogen which had been passed over white phosphorus. Oxygen was tried instead of air but

was not quite so good. A current of air was regulated by means of a side tube dipping into water and was led upwards into a wide glass tube by a silica tube drawn out into a jet passing through a rubber bung in which it fitted rather loosely, so that it could be pushed easily up and down. Electrolytic hydrogen from a cylinder was passed through two bottles containing sticks of white phosphorus and entered the main tube through a side tube. The top of the main tube was slightly constricted and a short cylinder of mica inserted. The current of hydrogen was started and lighted at the top of the tube, then the air tube was pushed up until the jet was in the constriction, and a gentle stream of air was regulated so that, on pulling the air tube slowly down, the flame remained resting steadily on the jet. Several forms of jet were employed; there was not much to choose between them, but one which gave a fish-tail shape, placed edge-wise to the slit of the spectro-scope was the best.

The spectroscope first used was one made by Bellingham and Stanley. It contained two dense glass prisms and the collimator and camera lenses were of six-foot focus. Its dispersion in the blue-green was about 10A per millimeter. Another instrument of about the same dispersion in the green but better in the yellow was fitted with a first quality Wallace one-meter concave replica grating of 25,000 lines to the inch. Neither of these were first-class instruments but they were the best available. As exposures lasting a whole week were necessary and no regulation of the temperature of the spectroscope was possible, the temperature variation would in itself account for some lack of definition; the gases were, of course, at atmospheric pressure and this also would cause broadening of the lines; the slit width used was a tenth of a millimeter. Attempts to get a brighter flame by raising the temperature of the bottles containing the phosphorus, to increase the amount of

¹ Geuter, *Zeits. f. wiss. Phot.* **5**, 1 (1907).

² Ludlam, *Nature* **128**, 271 (1931).

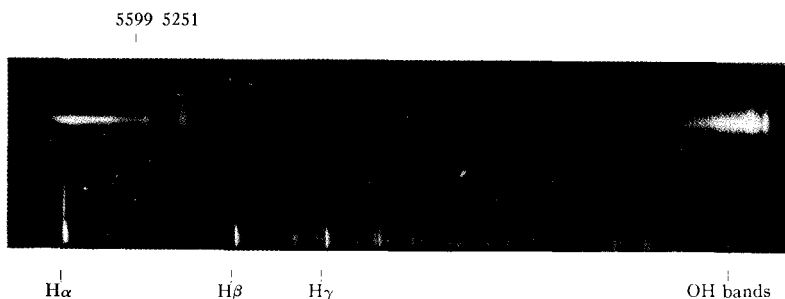


FIG. 1B. Low dispersion.

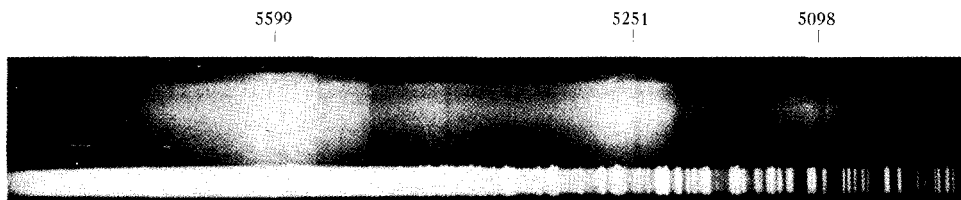


FIG. 1A. Photograph of system of bands from green to yellow. Ilford 'Chromatic' plate, 100-hour exposure, prism spectrograph, bromide enlargement.

phosphorus vapor in the flame, only led to the necessity for more frequent stoppage of the exposure to clean off the red phosphorus which deposits on the tube and cuts off the light from the slit. After trying a number of different brands of plate the fastest for the green region was found to be Ilford 'Chromatic.' These are plates of medium speed emulsion (HD 120) and fine grain, specially sensitized for the green. Later, in order to get the bands in the yellow, Ilford hypersensitive plates were used satisfactorily.

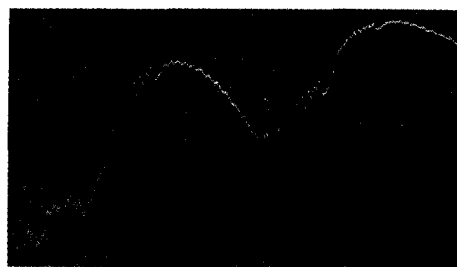
From the point of view of a thoroughgoing analysis of the spectrum the results are poor; the lines are very hazy and this is made much worse by overlapping of bands. They are, however, the best so far obtainable and settle the question quite definitely that the emitter is not P, but a hydride, probably PH.

Numerous attempts were made to photograph this spectrum excited by other methods. In the electric discharge using a tube containing P vapor over which hydrogen was passed (as in Pearse's work on PH in the ultraviolet³) the spectrum was easily *visible*; so, also, in a discharge through streaming PH₃; also when active hydrogen from

a Wood's tube met vapor of phosphorus in a side tube; but in none of these cases was photography with a spectrograph possible. Any exposure that could have shown the least trace of the green bands in the electric discharge would have given many other lines of hydrogen and phosphorus heavily overexposed. It is one great advantage of the flame burning in excess of hydrogen that no lines due to any other spectrum appear on the plate.

The general appearance of the band system is shown in the plate (Fig. 1A). This is from a bromide enlargement of a photograph obtained with one hundred hours exposure, using the glass spectrograph. The band at 5098 is obtained conveniently free from overlapping, and the photo-micrograph (Fig. 2) brings out the intensity relations much more clearly than the enlargement. Another photograph (Fig. 1B) given eighty hours exposure in the first order of the meter grating, gave a negative which could be used for measuring the bands at 5251 and 5599 and although it was underexposed for the 5098 band, several of the faint and hazy lines were just measurable and they are included in the table for direct comparison with the others taken on the same plate (Tables I and II).

³ Pearse, Proc. Roy. Soc. A129, 328 (1930).



← *R* branch λ5098 *P* branch → λ5212 λ5251

FIG. 2. 100-hour exposure, Ilford 'Chromatic' plate, prism spectrograph. Shows complete bands at λ5098 and 5257, and the *R* branch at λ5212, the *P* branch overlapping the tail of the *R* branch from λ5251.

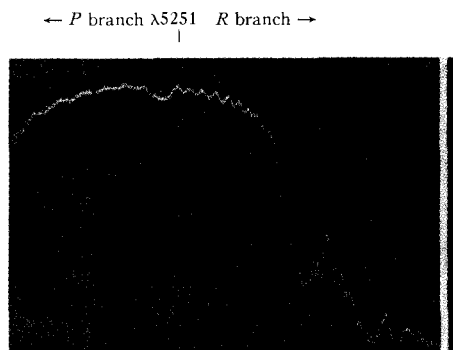


FIG. 3. Grating; 80 hours, hypersensitive panchromatic plate. Enlargement 4.9 times.

TABLE I.

$$R(J) - P(J) = B'(4J+2); \quad R(J-1) - P(J+1) = B''(4J+2)$$

<i>J</i>	λ5098 (PRISM), $\nu = 19,615$				(GRATING)			
	ΔR	ΔP	<i>B'</i>	<i>B''</i>	ΔR	ΔP	<i>B'</i>	<i>B''</i>
1	12.4	33.8(gap)	7.70	8.57	12.5	34.0(gap)	7.75	8.83
2	14.5	17.6	7.83	8.18	14.4	19	7.99	8.45
3	14.5	18.0	7.91	8.16	15.2	19	8.14	8.53
4	13.9	18.0	7.93	8.20	13.7	20.5	8.24	8.52
5	13.5	18.7	7.95	8.22	13.7	19	8.27	8.80
6	12.8	19.4	7.96	8.23	too faint to measure			
7	12.1	19.8	7.97	8.18				
8	11.4	21.6	8.0					
		mean	7.92	8.22		mean	8.08	8.62

TABLE II.

<i>J</i>	λ5251 $\nu = 19,044$ (GRATING)				λ5599 $\nu = 17,860$ (GRATING)			
	ΔR	ΔP	<i>B'</i>	<i>B''</i>	ΔR	ΔP	<i>B'</i>	<i>B''</i>
1	12.6	33.1(gap)	7.61	8.88	11.9	33.6(gap)	7.59	8.80
2	13.7	20.2	7.96	8.75	12.8	19.2	7.75	8.57
3	12.6	21.6	8.13	8.61	13.1	21.0	7.97	8.50
4	11.9	19.5	8.07	8.81	13.1	21.0	8.21	8.64
5	11.2	21.6	8.09	8.90	10.3	23.0	8.23	8.68
		mean	7.97	8.79		mean	7.95	8.64

ROTATIONAL STRUCTURE

As the general appearance of each band is that of a *P* and *R* branch, with one missing line between them, it is concluded that the emission is due to a $^1\Sigma - ^1\Sigma$, or a $^1\Sigma - ^3\Sigma$ transition. One cause of haziness of the lines may be due to the close triplet levels, if the transition is $^1\Sigma - ^3\Sigma$.

Approximate values for *B''* and *B'* are tabulated along with the separations between the lines in each branch. As the 5098 branch shows no sign of doubling back (though some of the other bands in the photograph exhibit an appearance rather as though the *R* branch went to a

head) the moments of inertia in the upper and lower states are not very different. The standard of accuracy does not admit of any calculation of *D*, the term in *B*².

It will be noticed that the first line of the *R* branch is stronger than the second which is weaker also than would be expected from the average of the first and third. This is noticeable in all the bands that are sufficiently free from overlapping to show it.

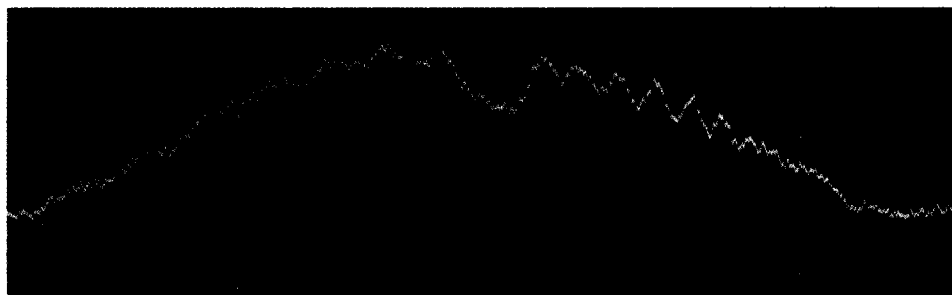
Considering the lack of sharpness in the lines it is obvious from a glance at the tables for the values of *B'* and *B''* for the three bands measured that they are in satisfactory agreement. The band at 5098 in the prism photograph was the clearest and was measured with the greatest care. Taking the value 8.2 as the mean of these values of *B''*, this may be compared with Pearse's value 8.4 for PH in the band at 3400 in the ultraviolet. The less accurate value obtained with the grating was 8.6, the mean of the two giving the value 8.4.

The corresponding values for the moment of inertia and radius are:

$$\lambda 3400 \quad B'' = 8.411 \text{ cm}, I = 3.293 \cdot 10^{-40} \text{ g/cm}^2, \\ r'' = 1.43 \cdot 10^{-8} \text{ cm},$$

$$\lambda 5098 \quad B'' = 8.2 \text{ cm}, I = 3.34 \cdot 10^{-40} \text{ g/cm}^2, \\ r'' = 1.41 \cdot 10^{-8} \text{ cm}.$$

These results leave very little doubt that we are here dealing with the molecule PH. No other diatomic or polyatomic compound of phosphorus could have so small a moment of inertia.



← P branch $\lambda 5599$ R branch →

FIG. 4. Exposure 80 hours, grating, hypersensitive panchromatic plate, enlargement 14.8 times.

VIBRATION ANALYSIS

Many attempts have been made to arrive at some plausible analysis of the vibrational structure but nothing satisfactory has been obtained. Even with the longest exposures it was impossible to get measurements in the blue or red although there are faint bands in these regions. If it had not been for the decisive low moment of inertia the system might have been attributed to a polyatomic molecule such as P_2H_4 or P_2H_2 .

The magnitude of the vibration quantum for PH is between 2300 and 2400 cm^{-1} and this is a range of wave-length from $\lambda 5098$ ($19,615\text{ cm}^{-1}$) to, say, $\lambda 5800$. There are faint bands, with apparent overlapping, in this region and even so far as about 6400 , but they are hopeless for measurement. Rough visual measurements are given by the earlier workers, but they are of very little value, except for speculation.

The following points are noteworthy:

(a) The green bands in the flame are not accompanied by any other bands in the ultraviolet (except the OH bands) they are not a continuation of the $\Pi-\Sigma$ bands into the visible region.

(b) The rotational structure shows them to be $\Sigma-\Sigma$ bands.

(c) The moments of inertia in the upper and lower states are only slightly different, the equilibrium diameters are nearly the same, the potential energy curve for the higher state is almost symmetrically above that for the lower state and the Condon parabola will be a very narrow one. The result of this is to exclude transitions between vibration levels which are widely different in quantum number; e.g., $10 \rightarrow 10$ is much more probable than $0 \rightarrow 10$.

(d) The production of the PH and its spectrum in a flame may lead to the electronic excitation of molecules already possessing high energy of vibration, which, together with (c) would lead to a system of bands which would be sequences of high quantum number.

(e) Inter-combinations would have only a low probability and this would account for the difficulty in obtaining sufficient intensity. Consequently, although no exact vibrational analysis can be offered, it seems undesirable to leave the problem there without making a definite suggestion based on these considerations. As a tentative explanation of the spectrum it seems possible that the four brightest bands might be related in some such manner as the following:

	λ	ν	$\nu' - \nu''$
(a)	5098	19615	11-10
(b)	5251	19044	10-10
(c)	5435	18400	11-11
(d)	5599	17860	10-11

A further word of explanation is, perhaps, necessary. (a-c) gives the value of the 11th vibrational quantum in the lower state, 1215 cm^{-1} ; (b-d) gives the 11th quantum in the upper state, 1184 cm^{-1} . There is nothing improbable in the reduction of the quantum from 2300 to 1200 , but whether this would have happened at the tenth, or even the 15th, cannot be decided at present. Possibly work on the ultraviolet bands may lead to some definite decision.

I wish to express my thanks to Dr. R. W. B. Pearce and Dr. G. B. B. M. Sutherland for helpful advice, to the Carnegie Trustees for a Teaching Fellowship, and to Dr. Baker and Professor Sampson of the Royal Observatory for the photometer curves.