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# NEW VISIBLE BAND SYSTEMS OF THE PO MOLECULE

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Plate VIII

**ABSTRACT.** Two new band systems attributed to the PO molecule, have been observed in the visible region in a high frequency discharge, when moist red phosphorous is excited under low pressure conditions. Of the four new groups of bands observed, two are assigned to one system designated as $D$—$B$ while the other two groups are assigned to another system designated as $D'$—$B$. The common lower state $B$ is identified as the upper state of $B$—$X$ ultraviolet system of PO. The $D$ level is identified as the upper state of the $D$—$X$ system of PO having a doublet separation of 27 K. The structure of the two systems seem to indicate $^2\Delta_a - ^2\Pi_b$ and $^2\Delta_a - ^2\Pi_b$ transitions for the systems $D'$—$B$ and $D$-$B$ systems respectively, the upper states being different. The $D'$ level has a doublet separation of 97 K.

The electronic states of PO and related molecules are discussed in terms of electron configurations.

## INTRODUCTION

The band spectrum of the PO molecule long since has been known to give rise to two characteristic band systems one near $\lambda 2600$ Å and the other near $\lambda 3300$ Å. Of these two systems the former which is analogous to the well known 'γ' system of NO has been investigated in detail by Ghosh and Ball (1931) and Sen Gupta (1935). It is well known from this year's work that this system is due to an electronic transition $^2\Sigma \longrightarrow ^2\Pi$ with a $^2\Pi$ ground state having a doublet separation of 223.8 cm$^{-1}$. The band system near $\lambda 3300$Å was investigated by many workers (Curry, Herzberg and Herzberg 1933), Ramanatham, Rao and Ramasastry (1946) and more recently by K Dressler (1955).) The recent work of this latter author (Dressler) has shown that these bands occurring in the region $\lambda 3190$Å $-\lambda 3560$Å belong to a single system having for its lower state the $^2\Pi$ ground state, identified as the ground state of PO and for its upper state a Hund's case (b) state. In addition to the above two systems Dressler reported three new systems of doublet bands occurring in the regions $\lambda 1975$Å$-\lambda 2140$Å, $\lambda 2050$Å$-\lambda 2170$Å, and $\lambda 1825$Å$-\lambda 1930$Å in a Geissler discharge tube used as a light source. The vibrational analysis of these band systems indicate that the lower state is common and identified as the $^2\Pi$ ground state of PO, the upper states corresponding to different excited electronic states of the PO molecule. The various excited electronic levels

identified from the analysis of the above mentioned systems were designated by Dressler as $B$, $A$, $C$, $D$, $E$ written in the order of increasing energy. Of these '$D$' level is known to be a doublet state having a separation of about 30 cm$^{-1}$, while the $B$ and $E$ levels are known to belong to Hund's case (b). The $\wedge$ value of these two states and the nature of the '$C$' level are however not yet known.

Besides the discrete band systems reported for PO, a number of diffuse and unresolved bands have been observed by Karl Rumpf in the visible region extending from $\lambda6500 - \lambda4750$. These bands were observed in the flame of burning phosphorous in the presence of $CO_2$ and photographed under low dispersion of about 80Å per mm. at $\lambda5000$ Å. A tentative analysis of these bands on the basis of two systems given by the above author is, however, not convincing.

As compared to NO, our knowledge of the nature of the excited electronic levels of PO is less complete, the authors considered it worthwhile to reinvestigate the emission spectrum of the PO molecule. The present paper describes the new results obtained in this reinvestigation.

## EXPERIMENTAL

*Method of excitation ·*

The two band systems $A-X$, $B-X$ were reported by early workers as occurring in a carbon arc source fed with $P_2O_5$. The $B-X$ system was observed by Dressler as occurring in a Geissler discharge tube in which a free flow of oxygen is maintained over heated phosphorous. The remaining systems were also reported as occurring in the same source. The diffuse bands occurring in the region $\lambda6500$ Å $- \lambda4750$ Å were reported by Karl Rumpf in the flame of burning phosphorous in the presence of $CO_2$.

In our present experiments the spectrum was excited in a high frequency discharge from a high power (100 watt) oscillator. Red phosphorous in the wet condition was taken in an ordinary H.F. discharge tube and the tube was evacuated by a Cenco high vacuum pump through a series of absorption towers. No external heating of the substance was found necessary as the R. F. heating of the electrodes was sufficient to maintain a free flow of $P_2$ vapour due possibly to the dissociation of $P_4$ into $P_2$ molecules.

## DESCRIPTION OF THE BANDS AND THEIR ORIGIN

During the first five minutes after the oscillator was switched on, an intense line spectrum was observed in the whole visible region. After this interval of time the line spectrum disappeared and a characteristic pale yellow discharge was observed and the spectrum photographed under these conditions. The photographs of the spectra in the visible region taken on the Fuess instrument (dispersion about 35 Å/mm at $\lambda5600$.) and three prism glass Littrow instrument

PLATE VIII
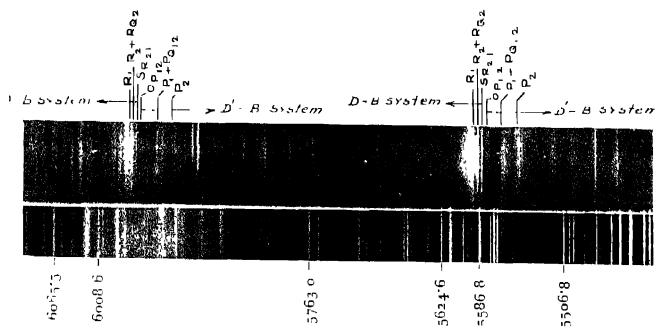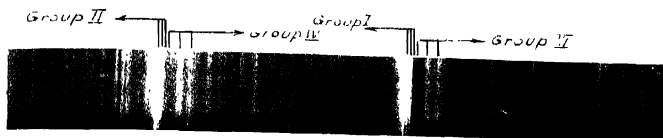


Spectra of the two new systems of PO molecules

(dispersion about 24Å/mm. at $\lambda 5600$ Å) are reproduced in Plates VIII(a) and (b) respectively. In the ultraviolet region the extensive $P_2$ band system and the well known '$\gamma$' system of PO are observed and the spectrum was photographed under the same conditions on a Hilger medium quartz instrument.

Plates VIII(a) and 1(b) are seen to consist of characteristic groups of bands extending from $\lambda 5400$ to $\lambda 6000$. A close examination of Plate VIII(a) reveals a characteristic group of three red degraded bands designated as group I at wavelengths $\lambda 5584.3$, $\lambda 5588.2$ and $\lambda 5592.2$. Strikingly similar in appearance to this group of bands, there is another characteristic group of three red degraded bands designated as group (II) at wavelengths $\lambda 5962.3$ Å, $\lambda 5966.7$ Å and $\lambda 5973.1$ Å. On the short wavelength side of group I bands another group of three violet degraded bands designated as group (III) occurs at wavelengths $\lambda 5549.5$Å, $\lambda 5564.3$ Å and $\lambda 5580.0$ Å. A similar group of violet degraded bands designated as group (IV) is also observed on the short wavelength side of group (II). The spectrum as reproduced in plate 1(b) reveals also a partial resolution of the rotational structure of the groups (I) and (III) bands.

In attempts to identify the emitter of the groups of bands reproduced in plates 1(a) and 1(b) a comparison is made with the spectra of the commonly occurring impurities like CO, $CO^+$, $C_2$, $N_2$, $N_2^+$, CN etc., in the visible region. The measurements of the wavelengths of the band heads of these groups of bands do not agree with any of those given in the list of table of persistent band heads due to impurities as given by Pearse and Gaydon's book "On the identification of molecular spectra". Thus there remain the three following possibilities for the emitter of the bands namely $P_2$, PO and PH. The last two possibilities PO and PH have to be considered in view of the fact that these new bands are observed when phosphorous is excited in the presence of water vapour. A detailed vibrational analysis as described in the following pages has definitely established that the emitter of the bands is PO.

### ANALYSIS OF BANDS

Intensity considerations point to the group of bands designated as group (I) as constituting unambiguously the $\Delta v = 0$ sequence and group (II) as forming the $\Delta v = -1$ sequence. The wavenumber intervals between the first, second and third members of groups I and II are obtained as 1136.0, 1134.8 and 1136.9 respectively. The average $\Delta G_{1/2}''$ difference as shown in Table I is obtained as 1133.9 cm$^{-1}$. This first $\Delta G_{1/2}''$ interval agrees very well with the first $\Delta G_{1/2}''$ interval of the $B$ upper state of the two subsystems $B - {}^2\Pi_{1/2}$ and $B - {}^2\Pi_{3/2}$ as shown in Tables (II and III). This agreement shows conclusively that the lower state of this new system shown in Table (I) is upper state $D$ of the PO molecule. This also confirms the view that the emitter of this new band system is PO. Further this $\Delta G_{v1/2}'$ interval does not agree with the $\Delta G_{v1/2}$ interval of the upper or lower

states of any of the band systems of either $P_2$ or PH molecule, this interval being too big for $P_2$ and too small for PH. As the $\Delta v = -2$ sequence is expected to occur at $\lambda 6400$ Å and is not recorded on our plates. The $x_e \omega_e$ value of 14.1 derived by Dressler for the $B$ state has been adopted by us. The vibrational frequency of the lower state of the new system is thus obtained as 1164 cm$^{-1}$. The bands in groups III and IV which are degraded to shorter wavelengths and are comparatively weaker in intensity, obviously seem to belong to another system. From intensity considerations the groups III and IV are regarded as $\Delta v = 0$ and $\Delta v = -1$ sequences respectively. The vibrational scheme shown in Table (IV) indicates that the first average $\Delta G''_{v,1/2}$ interval is again 1132 cm$^{-1}$. This suggests that the two systems have a common lower state which is to be identified as the $B$ state of PO. The two systems shown in Tables (I and IV) may be designated as $D-B$ and $D'-B$ systems respectively.

### TABLE I

$D-B$ system $^2\Delta_{3/2, 5/2} \to {}^2\Pi_b$

| | $v''$ | 0 | | 1 |
|---|---|---|---|---|
| $S_{R21}$ | | 17903·7 | 1136·0 | 16767·7 |
| $R_2 + RQ_{21}$ | 0 | 17891·5 | 1134·8 | 16756·7 |
| $R_1$ | | 17876·8 | 1136·9 | 16739.9 |

Average value of $\Delta G''_{1/2} = 1135·9$ 

Position of $^2\Delta_{3/2}$ above the ground state $= 48718$

$\omega'' = 1135.9 + 2x_e''\omega_e'$
$\omega'' = 1135·9 + 2 \times 14.1$

Position of $2\Delta_{5/2}$ above the ground state $= 48745$

$\omega'' = 1164$
$\omega' \leqslant 1164$

$^2\Delta_{5/2} - {}^2\Delta_{1/2} = 27 = A$
Coupling constant (approximately).

### TABLE II

$^2\Pi_{\frac{1}{2}} \to {}^2\Pi_b$

| $v''$ $v'$ | 0 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| 0 | 30796·4 | 1217.3  29579.1 | 1204.7  28374.4 | | |
| $\Delta G'_{1/2}$ | | 1131.2 | 1134.0 | — | |
| 1 | | 30710·3 | 1201.9  29508.4 | 1191·1  28317·3 | |
| $\Delta G'_{3/2}$ | | | 1077.0 | 1105.1 | |
| 2 | | | 30585.4 | 1163.0  29422·4 | 1177·1  28245.3 |
| | | | | | 1073·0 |
| 3 | | | | | 29318.9 |

## TABLE III

$${}^{2}\Pi_{3/2} \longrightarrow {}^{2}\Pi_{b}$$

| $v''$    $v'$ | 0 | | 1 | | 2 | | 3 |
|---|---|---|---|---|---|---|---|
| 0 | 30567.6 | 1213.4 | 29354 2 | 1203.5 | 28150.7 | | |
| | | | | | 1131.2 | | |
| 1 | | | | | 29281.9 | 1189 7 | 28092.2 |
| | | | | | | | 1100.0 |
| 2 | | | | | | | 29192.2 |

## TABLE IV

D' B system    $^{2}\Delta_{3/2,\,5/2} \longrightarrow {}^{2}\Pi$

| $v''$    $v'$ | 0 | | 1 | | 2 |
|---|---|---|---|---|---|
| $^{O}P_{1\,2}$ | 17916 2 | 1136 7 | 16779 5 | | |
| $P_{1} + {}^{P}Q_{1\,2}$  0 | 17965.8 | 1130 3 | 16835.5 | | |
| $P_{2}$ | 18013 4 | 1128 7 | 16884 7 | | |
| $P_{1} + {}^{P}Q_{1\,2}$  1 | | | | | 16976 1 |
| $P_{2}$ | | | | | 17027.6 |

Average value of $\Delta G''_{1/2}$   = 1131.9      Position of $^{2}\Delta_{1/2}$ above the ground state   }   = 48757 5

$\omega''$  = 1131 9 | 2 $\omega_{e}'$       Position of $2\Delta_{5/2}$ above the ground state.  } = 48854.7
$\omega''$  = $-$ 1131.9 $+2 \times 14$  1   $\because$ 
$\omega''$ = 1160       $^{2}\Delta_{5\,2} - {}^{2}\Delta_{1/2}$    $-$ 97 2 cm$^{-1} -A$
$\omega''$ $\simeq$ 1301       $-$ coupling constant (approximately).

From his analysis of the $B$--$^{2}\Pi$ system of PO Dressler concluded that the $B$ state belongs to Hund's case (b). However he did not definitely suggest the $\Lambda$ value of this state. It may be either $a^{2}\Sigma$ or $a^{2}\Pi_{b}$ or $^{2}\Delta_{b}$ state. Of these three alternatives $^{2}\Pi_{b}$ term is considered more likely for the $B$ state, as this would account for the observed double headed nature of the $B$--$X^{2}\Pi$ system and also the coarse vibrational structure of the two new systems reported here.

The vibrational structure of the $D$--$B$ system shown in Table (I) can be interpreted on the basis of $a^{2}\Delta_{a} \rightarrow {}^{2}\Pi_{b}$ transition. Such a transition is expected to give rise to four head forming branches. $^{S}R_{2\,1}$, $R_{2} + {}^{R}Q_{2\,1}$, $R_{1}$ and $Q_{1} + {}^{O}R_{1\,2}$ and the last $Q_{1} + {}^{O}R_{1\,2}$ is generally obscured in the shading of the $R_{1}$ head. Thus both the (0, 0) and (0, 1) bands appear to be triple headed as observed. The appearance of this system is strikingly similar to the well known red CN system arising from a

transition between two doublet states. Since $^SR_2{}_1$ and $R_1$ heads occupy similar positions in the two subsystems of $a^2\Delta_a - {}^2\Pi_b$ transition, they will be separated by a wave number interval which is approximately of the order of the coupling constant $A$ for the upper $^2\Delta$ state. This interval is obtained as 27 cm$^{-1}$ approximately and represents the interval between $^2\Delta_{5/2}$ and $^2\Delta_{3/2}$ components of the $^2\Delta_a$ state. Adopting the $\nu_{H(0\cdot 0)}$ values ($^SR_2{}_1$ and $R_1$ heads) the heights of the $^2\Delta_{3/2}$ and $^2\Delta_{5/2}$ above the ground state are obtained as $30841.3 + 17876.8 = 48718.1$ and $30841.3 + 17903.7 = 48745.0$ respectively. These compare favourably with the approximate value 48690 and 48720 given by Dressler for the two components of the $D$ state of PO from his analysis of $D-X$ system. Thus both the doublet intervals and the positions of these levels suggest that the upper state of the above new system is to be identified as the $D$ state. Further, as in the $D-X$ system of PO, predissociation is observed in the $v' = 1$ level of this new system as well.

The vibrational scheme shown in Table (1V) relates to the $D'-B$ system of PO. It is seen that the (0, 0) band consists of three sub bands. The vibrational structure of these bands is interpreted on the basis of $^2\Delta_a \to {}^2\Pi_b$ transition, the lower state $^2\Pi_b$ being the common lower state of both the systems. The upper state $^2\Delta$ belongs to a separate higher excited state of the PO molecule. The two doublet components $^2\Delta_{3/2}$ and $^2\Delta_{5/2}$ will give rise to four head forming branches $^OP_1{}_2, P_1 + {}^PQ_1{}_2$ and $P_2, Q_2 + {}^QP_2{}_1$. Of these the $Q_2 + {}^QP_2{}_1$ head is generally being obscured in the shading of the $P_2$ head and the (0, 0) band appears triple headed. The two corresponding heads $^OP_1{}_2$ and $P_2$ which occupy similar positions in the two sub systems are separated by a wave number interval which is approximately equal to coupling constant $A$ of the $^2\Delta$ state. This is obtained approximately as 97 cm$^{-1}$. The heights of the two components above the ground state are derived as $48757.5$ ( $= 30841.3 + 17916.2$) and $48854.7$ ( $= 30841.3 + 18013.4$) for the $^2\Delta_{3/2}$ and $^2\Delta_{5/2}$ respectively.

*Predissociation* :

It is noteworthy that no bands are observed belonging to the $\Delta v = +1$ sequence. This may be due to the occurrence of predissociation at the $v' = 1$ level in the two upper states $D$ and $D'$. This predissociation may then also account for the absence of the (1,0) band in the $D-X$ system analysed by Dressler.

## PREDICTED ELECTRONIC STATES FROM ELECTRONIC CONFIGURATIONS IN PO AND RELATED MOLECULES

The electronic configuration giving rise to a $^2\Pi_r$ state in each of the related molecules NO, NS, PO, PS and SiF is well known to be

$$K.K\ldots\ldots(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)\ldots{}^2\Pi_r \qquad \ldots (1)$$

In this configuration the last $(v\pi)$ electron is an antibonding electron. According to Mulliken the symbols $z, y, x, w, v$ denote the order of decrease in firmness

of binding energy of molecular orbitals of the electrons, from a detailed discussion of the electronic states of NO and $O^+_2$. Assuming that in PO as well the same order of orbitals the first excited electronic configuration of PO may be written as

$$K.K...(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^3(v\pi)^2...{}^2\Pi_i, {}^2\Pi_r, {}^2\Pi, {}^4\Pi_i \text{ states} \qquad ... \quad (2)$$

Of these the $^2\Pi$ term may represent the *B*-state in PO and belongs to Hund's case (b). However the transition of an electron from a $w\pi$ to a $v\pi$ orbital is accompanied by only a slight reduction in frequency from 1232 to 1166 cm$^{-1}$ in contrast to a large diminution in NO. This probably indicates that the $w\pi$ electrons in PO are weakly bonding. The second excited electronic configuration corresponds to the transition of an electron from $x\sigma$ to $v\pi$ orbital giving rise to the states

$$K.K....(z\sigma)^2(y\sigma)^2(x\sigma)(w\pi)^4(v\pi)^2...{}^2\Sigma^+, {}^2\Sigma^-, {}^2\Delta, {}^4\Sigma^- \text{ states} \qquad ... \quad (3)$$

The $^2\Delta$ term belonging to configuration (3) may represent the *D* state of PO. In the $D-B$ transition an $x\sigma$ electron changes into a $w\pi$ electron. This change is accompanied by probably a slight reduction in vibrational frequency as indicated by the evidence of slight degradation of the bands in the $D-B$ system towards the red. This indicates that the $x\sigma$ orbital in PO is slightly more bonding than $w\pi$.

The third excited electronic configuration corresponding to the transition of $y\sigma$ to $v\pi$ as in configuration (4) gives rise

$$K.K...(z\sigma)^2(y\sigma)(x\sigma)^2(w\pi)^4(v\pi)^2...{}^2\Sigma^+, {}^2\Sigma^-, {}^2\Delta, {}^4\Sigma^- \text{ states} \qquad ... \quad (4)$$

to $a^2\Delta$ term in addition to $^2\Sigma^+$, $^2\Sigma^-$ and $^4\Sigma^-$. This $^2\Delta$ term may very well represent the *D′* level in PO. The transition of an antibonding $y\sigma$ electron to a $w\pi$ orbital is expected to be accompanied by an increase in vibrational frequency It is probable that the $x\sigma$ orbital has only slightly greater firmness of binding. In consequence the two $^2\Delta$ states resulting from (3) and (4) lie close to each other. Since the two states satisfy Kronig's selection rules for predissociation the observed predissociation at the $v' = 1$ level can thus be accounted for.

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