

Rotational analysis of the ultraviolet bands of PS

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Abstract. The 2-0, 1-0 and 0-0 bands of the ultraviolet system of PS have been analysed for their rotational structure. It is shown that they involve the transition $C^2\Sigma - X^2\Pi, (a)$. The $C^2\Sigma$ state shows a significant spin doubling.

Keywords. Band system; rotational analysis; spin splitting.

1. Introduction

Two band systems are now known for the PS radical (Dressler and Miescher 1955; Dressler 1955). They lie in the spectral regions 2700-3300Å and 4200-6000Å. Both form doublet systems consisting of red-degraded bands and involve a common lower state assigned as the $X^2\Pi$ state of the molecule in analogy with molecules like NO, PO, NS, etc. In a thorough investigation of these systems using the ^{34}S isotope of sulphur, Narasimham and Balasubramanian (1969) added several new bands to the ultraviolet system and revised the v'' assignments for the visible system earlier proposed by Dressler (1955). Later Narasimham and Balasubramanian (1971) analysed a few of the ultraviolet bands for their rotational structure and concluded that they involved the transition $C^2\Sigma - X^2\Pi, (a)$ deferring publication of the details in order to complete the analysis of more bands. In the present paper we report details of the analysis of the 2-0, 1-0 and part of 0-0 bands of the ultraviolet system.

2. Experimental

The PS spectrum was excited in sealed quartz electrodeless discharge tubes containing traces of elemental phosphorus and sulphur together with the rare gas neon. The tubes were excited by microwaves of 2450 MHz. Details of preparation of the tubes may be found elsewhere (Narasimham and Balasubramanian 1969).

The ultraviolet bands of PS happen to fall in a region where strong bands belonging to the extensive band systems of P_2 and S_2 are known to occur. The present method of excitation always produced the spectra of P_2 and S_2 as well. However by controlling the relative amounts of phosphorus and sulphur and carefully optimising the microwave power employed, it was possible to excite the bands of PS relatively strongly although the bands due to P_2 and S_2 were still present. The bands 2-0, 1-0 and 0-0 being fairly free from overlap and reasonably strong, were chosen for the rotational structure analysis. The bands were photographed on a 3.4 m Ebert

grating spectrograph in the third order at a dispersion of 0.73Å/mm, employing Kodak 103-a-0 emulsion. Exposure times of the order of 1-2 hr were needed. Thorium atomic lines emitted from an electrodeless discharge lamp served as wavelength standards, their wavelengths being taken from the tables of Zalubus (1960). The plates were measured on a Zeiss Abbe comparator. The resolution achieved was such that two lines 0.2 cm^{-1} apart were just resolved.

3. Results and discussion

3.1. Identification of the transition

The ultraviolet bands of PS form a doublet system with a doublet separation of about 321.3 cm^{-1} . Each band consists of two close heads separated by roughly 4 cm^{-1} . As has been stated earlier the lower state of this system is the same as the lower state of the visible system now known to involve the transition $B^2\Pi_r(a) - X^2\Pi_r(a)$ (Jenouvrier and Pascat 1978). Thus the ultraviolet bands represent a transition to a $^2\Pi(a)$ lower state. That this state must be identical with the ground state of PS has already been established by Dressler (1955). In figures 1 a, b and c are shown the rotational structure of the 2-0 and one sub-band of the 1-0 bands. Examination reveals the presence of six branches per sub-band of which two are relatively more intense suggesting that these must be Q branches. The presence of Q branches indicates a transition for which $\Delta\Lambda = \pm 1$. This implies that the upper state C must be either $^2\Sigma$ or $^2\Delta$. The presence of two distinct Q branches rather than one rules out a $^2\Delta$ (case a) state as the initial state. On the other hand, the unmistakable presence of a total of 6 branches in each sub-band shows that we are in fact dealing with a $^2\Sigma - ^2\Pi_r(a)$ or $^2\Delta(b) - ^2\Pi_r(a)$ transition. It was not possible to invoke the criterion of 'first lines' to decide between these alternatives as the structure right up to the head was not clearly resolved. A careful examination of the lines of the strong branches in the sub-band involving the $X^2\Pi_{1/2}$ sub-state, failed to reveal any doubling or even a broadening up to the highest members ($J \sim 50.5$); we were thus forced to conclude that the initial state must be non-degenerate, i.e. $^2\Sigma$. This conclusion is further corroborated by the observation that the N doublet separation in the upper state increases linearly with N which is characteristic of a $^2\Sigma$ state. For a $^2\Delta(b)$ state, on the other hand, the N doublet separation decreases rather rapidly for the first few N values and increases, if at all, only at large N values (Herzberg 1950). The transition therefore is $C^2\Sigma - X^2\Pi_r(a)$.

3.2. Identification of the branches and rotational assignments

The twelve branches that arise for a $^2\Sigma - ^2\Pi_r(a)$ transition are illustrated in figure 2. They fall into two groups of six branches each separated by the spin-splitting in the $^2\Pi$ state. The rotational line strengths of the lines of the various branches were first calculated from the expressions of Earls (1935) using a preliminary $Y(=A/B)$ value of 1100. These calculations showed that the branches Q_{11} , Q_{21} and Q_{12} , Q_{22} were the most intense while the branches R_{11} , P_{11} , R_{21} , P_{21} and P_{22} , R_{22} , P_{12} , R_{12} were weaker by a factor of roughly 2.5. The Q branches and the branches

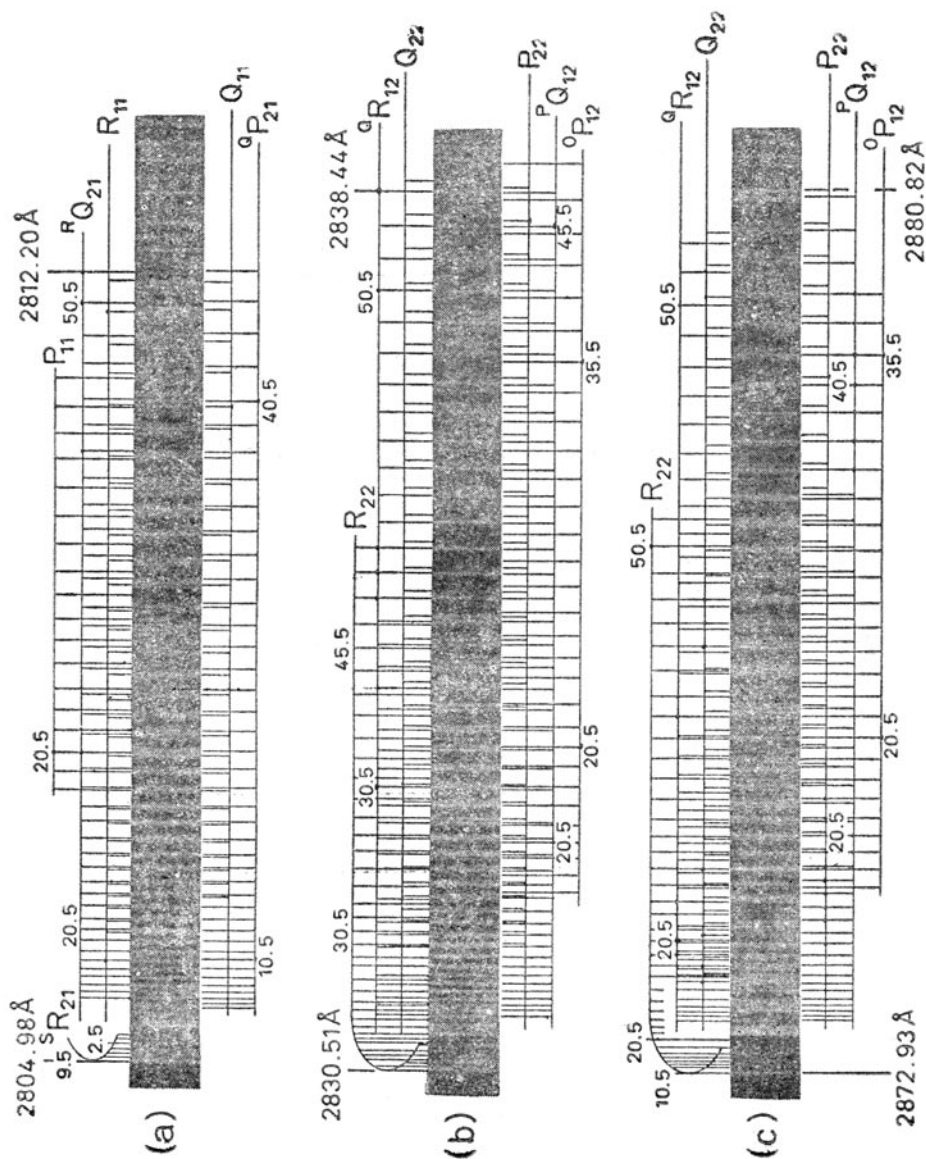


Figure 1. Rotational structure of the PS ultraviolet system. a. 2.0 band of $C^2\Sigma^- - X^2\Pi_{1/2}$. b. 2.0 band of $C^2\Sigma^- - X^2\Pi_{3/2}$. c. 1.0 band of $C^2\Sigma^- - X^2\Pi_{1/2}$.

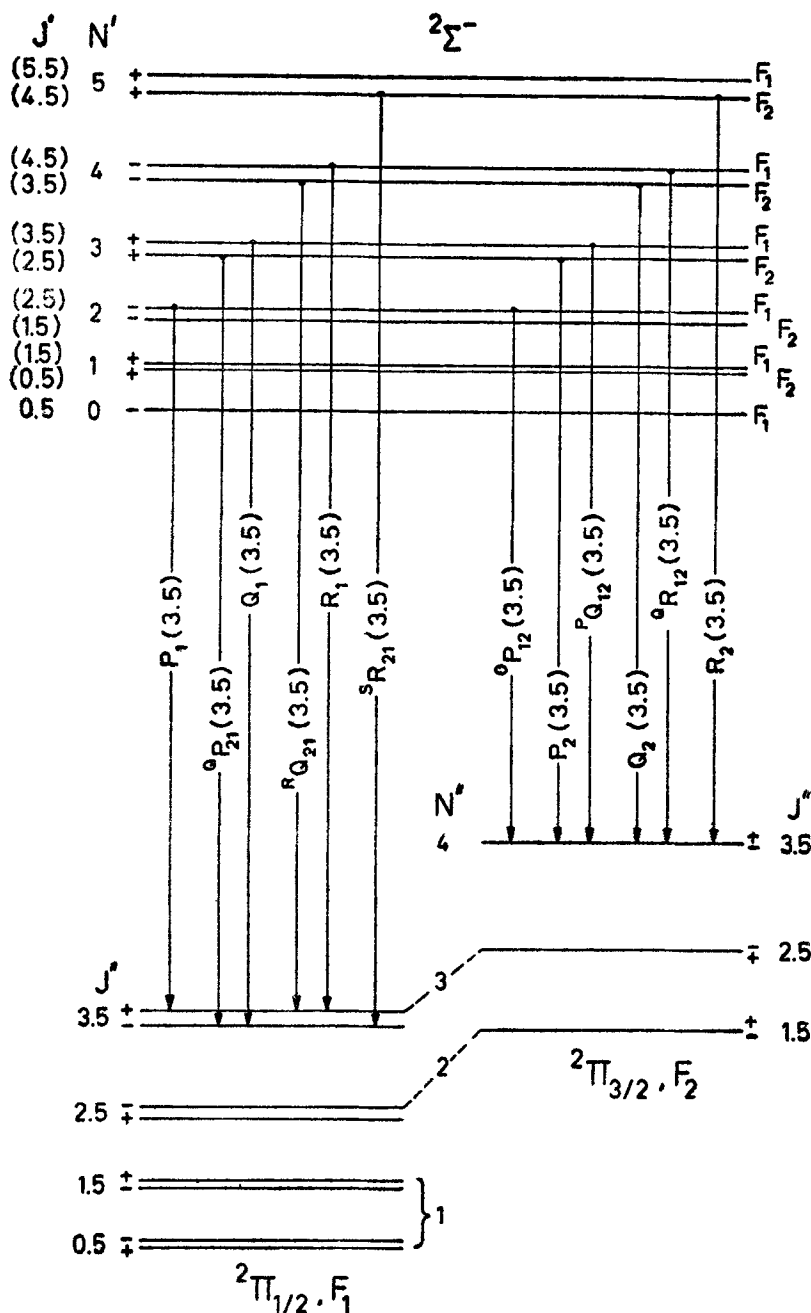


Figure 2. Rotational transitions in ${}^2\Sigma^- - {}^2\Pi(a)$ electronic transition.

R_{21} , R_{22} forming heads quite away from the origins were readily picked out. Thereafter the other branches could be readily identified from their expected intensities.

The pairs of branches (R_{11} , Q_{21}) and (Q_{11} , P_{21}) in the ${}^2\Sigma^- - {}^2\Pi_{1/2}$ subband and (R_{12} , Q_{22}) and (Q_{12} , P_{22}) in the ${}^2\Sigma^- - {}^2\Pi_{3/2}$ sub-band are split only by the spin-splitting in the ${}^2\Sigma$ state. This splitting in the present case was considerable ($\gamma \sim 0.015 \text{ cm}^{-1}$)

and led to a certain complication in the structure of the 2-0 band (see figure 1a, b). The J assignments were carried out using the combination relation

$$\begin{aligned} R_{22}(J) - Q_{22}(J+1) &= Q_{22}(J) - P_{22}(J+1) \\ &= R_{12}(J) - Q_{12}(J+1) = Q_{12}(J) - P_{12}(J+1) = 2B'_{v \text{ eff}}(2)(J+1). \end{aligned}$$

These relations utilise branches from the longer wavelength sub-band and are readily established from a look at figure 2. Terms due to D and other terms due to Λ -doubling in ${}^2\Pi_{3/2}$, expected to be small from theory, have been neglected in the above relation. To effect the J assignments for the lines in the ${}^2\Sigma - {}^2\Pi_{1/2}$ sub-band we utilise a somewhat different relation (since in this case the Λ -doubling in ${}^2\Pi_{1/2}$ cannot be ignored at least in principle). The relations employed were

$$R_{21}(J) - Q_{11}(J) = Q_{21}(J+1) - P_{11}(J+1) = (4B'_{v \text{ eff}} - \gamma)(J+1)$$

(neglecting D terms). Since the P_{21} branch closely follows its parent main branch Q_{11} , its assignment is straightforward and likewise the main R_{11} accompanying its satellite Q_{21} could be readily assigned. These assignments could be checked employing the relation

$$\begin{aligned} R_{21}(J) - Q_{11}(J) &= Q_{21}(J+1) - P_{11}(J+1) = R_{22}(J) - Q_{12}(J) \\ &= Q_{22}(J+1) - P_{12}(J+1) \text{ etc.} \end{aligned}$$

Of course, several other relations are possible but we chose to use only those relations that employ branches that are strong or are free from overlap. As a final check on these assignments the various branch lines were calculated using the rotational constants derived and these were then compared with the observed spectrum. Most of the lines of the ${}^2\Sigma - {}^2\Pi_{1/2}$ sub-bands could be reproduced to within 0.08 cm^{-1} while for the ${}^2\Sigma - {}^2\Pi_{3/2}$ sub-bands the deviations seldom exceeded 0.04 cm^{-1} . The larger error in the former case was due to the fact that the corresponding sub-bands of 2-0 and 1-0 were badly overlapped while the 0-0 band was relatively weak.

The frequencies of the rotational lines of the various branches along with their assignments may be obtained on request from the authors.

3.3. Determination of the rotational constants

3.3a. *The $X^2\Pi$ state:* The lower $X^2\Pi$ state with a large spin-splitting parameter $A \sim 322 \text{ cm}^{-1}$ conforms to Hund's case (a) scheme of coupling. Because of this, the rotational terms of ${}^2\Pi_{1/2}$ (F_1) and ${}^2\Pi_{3/2}$ (F_2) may be described separately using 'effective' rotational constants. For the ${}^2\Pi_{1/2}$ terms we have

$$F_1(J) = B'_{v \text{ eff}}(1) J(J+1) - D'_{v \text{ eff}}(1) J^2(J+1)^2 \pm (p/2)(J+1/2).$$

The constant p takes account of the Λ -doubling in the ${}^2\Pi_{1/2}$ substate. For the ${}^2\Pi_{3/2}$ terms, likewise, we have

$$F_2(J) = (A-2B) + B_{v \text{ eff}}^{(2)} J(J+1) - D_{v \text{ eff}}^{(2)} J^2(J+1)^2$$

The term describing Λ -doubling, expected to be small for ${}^2\Pi_{3/2}$, has been ignored.

In both 2-0 and 1-0 bands the longer wavelength component (${}^2\Sigma - {}^2\Pi_{3/2}$) were 'clean' and a high accuracy was realised in their measurements. We therefore thought it best to determine the rotational constants from these bands and to determine the other constants relative to these. The relation

$$\begin{aligned} \Delta_1 F''_2(J) &= R_{22}(J) - Q_{22}(J+1) = Q_{12}(J) - P_{12}(J+1) \\ &= 2B_{v \text{ eff}}^{(2)} (J+1) - 4D_{v \text{ eff}}^{(2)} (J+1)^2, \end{aligned}$$

was used to determine the effective B and D constants by the usual graphical procedure as described by Herzberg (1950).

The difference $B_{v \text{ eff}}^{(2)} - B_{v \text{ eff}}^{(1)}$ was evaluated from the relation

$$\begin{aligned} Q_{11}(J) - Q_{12}(J) + Q_{21}(J) - Q_{22}(J) \\ = 2(A-2B) + 2 \left(B_{v \text{ eff}}^{(2)} - B_{v \text{ eff}}^{(1)} \right) J(J+1), \end{aligned}$$

which utilises the strong Q branches.

To determine the Λ -doubling constant p , it is essential to observe the so-called combination defect characteristic of any ${}^2\Sigma - {}^2\Pi$ transition. In the present case since the weaker P_{11} , R_{11} , and R_{21} lines were severely overlapped it was desirable to use a relation involving the Q branches. We tried the relation

$$| \{ Q_{21}(J) - Q_{11}(J) \} - \{ Q_{22}(J) - Q_{12}(J) \} | = | p | (J+1/2).$$

However, a combination defect could not be established in any of the bands analysed in the present case pointing to the fact that the constant p is quite small for the $v=0$ level of $X^2\Pi$.

The coupling constant A of the $X^2\Pi$ state was evaluated from the relations

$$\begin{aligned} F_2(J) - F_1(J) &= (1/2) [\{ Q_{11}(J) - Q_{12}(J) \} + \{ Q_{21}(J) - Q_{22}(J) \}] \text{ and} \\ \{ F_2(J) - F_1(J) \}^2 + 16B_v D_v (J+1/2)^4 &= A(A-4B_v) + 4\tilde{B}_v^2 (J+1/2)^2. \end{aligned}$$

A plot of the left hand side quantity against $(J+1/2)^2$ yielded a straight line with slope $= 4\tilde{B}_v^2$ and intercept equal to $A(A-4B_v)$. From this A was solved and the positive root for A was chosen. The parameter B_v appearing in the above relation, in general, differs from the 'true' or inertial B_v , the difference stemming from the

effect of centrifugal distortion on A as has been discussed in detail by James (1964). In the present case, for the $v=0$ level, B was found to be 0.2965 cm^{-1} while \tilde{B} was 0.258 cm^{-1} .

3.3b. *The $C^2\Sigma$ state:* The rotational terms of a $^2\Sigma$ state are given by

$$F_1(N) = T_v + B_v N(N+1) - D_v N^2(N+1)^2 + N\gamma/2,$$

$$F_2(N) = T_v + B_v N(N+1) - D_v N^2(N+1)^2 - (N+1)\gamma/2,$$

where γ represents the spin-rotation interaction parameter. We used the following relations for the determination of B_v and D_v .

$$\Delta_1 F_1'(N=J-1/2) = Q_{12}(J+1) - P_{12}(J+1)$$

$$= \gamma/2 + 2B_v(J+1/2) - 4D_v(J+1/2)^3,$$

$$\Delta_1 F_2'(N=J-1/2) = R_{22}(J-1) - Q_{22}(J-1)$$

$$= -\gamma/2 + 2B_v(J+1/2) - 4D_v(J+1/2)^3.$$

A graph of

$$\frac{\Delta_1 F_1'(N) + \Delta_1 F_2'(N)}{2(J+1/2)}$$

against $(J+1/2)^2$ readily yielded the values for B_v and D_v .

The differences

$$R_{11}(J-1) - Q_{21}(J-1), Q_{11}(J) - P_{21}(J), R_{12}(J-1) - Q_{22}(J-1)$$

and $Q_{12}(J) - P_{22}(J)$,

directly give the separation between the N doublets viz. $\Delta v_{12}(N)$ of the upper state. To obtain the splitting parameter γ use was made of the relation

$$\Delta v_{12}(N) = \gamma(N+1/2),$$

for the $v=1$ level. For the $v=2$ level, an indirect procedure had to be resorted to as in the 2-0 band the relevant branches suffered from blending. The relation

$$\Delta_1 F'_{21}(N=J-1/2) = Q_{22}(J) - Q_{12}(J) = (2B_v - \gamma)(J+1/2) - 4D_v(J+1/2)^3,$$

is readily established from which the quantity $(2B_v - \gamma)$ was evaluated. This was combined with the value of B_v obtained earlier to yield a fairly accurate value of γ . The value of γ ranged between 0.013 to 0.015 cm^{-1} .

The vibrational quanta $\Delta G_{(3/2)}$ and $\Delta G_{(1/2)}$ and the parameter α_e were evaluated

by suitably combining the Q lines of 2-0, 1-0 and 1-0, 0-0 bands in turn as described by Herzberg (1950). From the two vibrational quanta the value of ω_e and $\omega_e x_e$ for the $C^2\Sigma$ state was obtained. Finally the band origins of the individual subbands were obtained graphically from the relations

$$\begin{aligned}
 Q_{11}(J) + Q_{21}(J) &= \left(2\nu_0^{(1)} + \frac{1}{2} B_{v \text{ eff}}''^{(1)} - \gamma \right) \\
 &+ 2 \left(B_v' - B_{v \text{ eff}}''^{(1)} \right) (J+1/2)^2 \\
 &- 2 \left(D_v' - D_{v \text{ eff}}''^{(1)} \right) (J+1/2)^4. \\
 Q_{12}(J) + Q_{22}(J) &= \left(2\nu_0^{(2)} + \frac{1}{2} B_{v \text{ eff}}''^{(2)} - \gamma \right) \\
 &+ 2 \left(B_v' - B_{v \text{ eff}}''^{(2)} \right) (J+1/2)^2 \\
 &- 2 \left(D_v' - D_{v \text{ eff}}''^{(2)} \right) (J+1/2)^4.
 \end{aligned}$$

The determination of $\nu_0^{(1)}$ and $\nu_0^{(2)}$ in this fashion incidentally yielded accurate values for the differences

$$\left(B_v' - B_{v \text{ eff}}''^{(1)} \right), \left(B_v' - B_{v \text{ eff}}''^{(2)} \right) \text{ and } \left(D_v' - D_{v \text{ eff}}''^{(1)} \right), \left(D_v' - D_{v \text{ eff}}''^{(2)} \right).$$

All the constants thus determined appear in table 1.

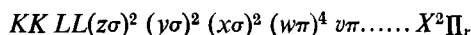
Table 1. Molecular constants (in cm^{-1}) of the $C^2\Sigma$ and $X^2\Pi$ states of P^{32}S

$X^2\Pi$		$C^2\Sigma$
$B_0^{(1)}$ eff	$= 0.2963_2$ $(0.29649)^*$	$T_e = 34688.7$
$B_0^{(2)}$ eff	$= 0.2967_4$ $(0.29695)^*$	$B_0 = 0.2634_6$
$D_0^{(1)}$ eff	$= D_0^{(2)}$ eff $= 2.0 \times 10^{-7}$ $(1.9 \times 10^{-7})^*$	$B_1 = 0.2614_8$
B_0 (true)	$= 0.2965_3$	$B_2 = 0.2595_2$
r_0	$= 1.900_7 \text{ \AA}$	$D_0 = D_1 = D_2 = 2.5 \times 10^{-7}$
\bar{B}_0	$= 0.258$	$\gamma_0 = 0.012_6$
A_0	$= 321.93$	$\gamma_1 = 0.015_8$
		$\gamma_2 = 0.015_1$
		$B_e = 0.2644_2$
		$\alpha_e = 0.00195$
		$D_e = 2.5 \times 10^{-7}$
		$r_e = 2.013 \text{ \AA}$
		$\omega_e = 534.1$
		$\omega_e x_e = 3.07$
	Band origins	
Band	$C^2\Sigma - X^2\Pi_{1/2}$	$C^2\Sigma - X^2\Pi_{3/2}$
0-0	34586.04	—
1-0	35113.97	34792.66
2-0	35635.76	35314.45

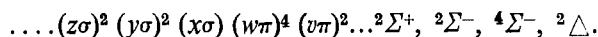
*Values reported by Jenouvrier and Pascat (1978)

3.4. Electron configuration dissociation products and the parity of the $C^2\Sigma$ state

The ground electron configuration of PS may be readily written down as



in analogy with similar molecules like NO, PO, NS, etc. The ground state has $\omega_e = 739 \text{ cm}^{-1}$ and $r_e = 1.90 \text{ \AA}$. The excited $C^2\Sigma$ state has $T_e = 34689 \text{ cm}^{-1}$, $\omega_e = 534 \text{ cm}^{-1}$ and $r_e = 2.013 \text{ \AA}$. The decrease in ω_e and the increase in r_e suggest a loosening of the bond which can occur when a bonding electron is promoted to an anti-bonding orbital. Accordingly the possible configuration for $C^2\Sigma$ is



Since ${}^2\Sigma$ states with both parities arise, no conclusion may be drawn regarding the parity of the $C^2\Sigma$ from the above consideration.

To obtain the possible dissociation products of $C^2\Sigma$ we first estimate the dissociation energies of $X^2\Pi$ and $C^2\Sigma$ by Birge-Sponor extrapolation.

$$D_e \sim (0.85) \frac{\omega_e^2}{4\omega_e r_e},$$

the factor 0.85 being included to compensate for the well-known fact that the usual extrapolation overestimates the dissociation energies. In this fashion we obtain

$$D_e(X^2\Pi) \sim 39100 \text{ cm}^{-1},$$

$$D_e(C^2\Sigma) \sim 19600 \text{ cm}^{-1},$$

$$T_e(C^2\Sigma) + D_e(C^2\Sigma) \sim 54300 \text{ cm}^{-1}.$$

The atomic state combination, the molecular states that arise therefrom and the limits of dissociation are summarised below. All the limits are referred to the potential minimum of $X^2\Pi$.

Separated atoms: phosphorus+sulphur	Molecular states	Limits of dissociation (cm^{-1})
${}^4S_u + {}^3P_g$	${}^{2,4,6}\Sigma^+, {}^{2,4,6}\Pi$	39100
${}^4S_u + {}^1D_g$	${}^4\Sigma^-, {}^4\Pi, {}^4\Delta$	48400
${}^2D_u + {}^3P_g$	${}^{2,4}\Sigma^-(1), {}^{2,4}\Sigma^+(2), {}^{2,4}\Pi(2),$ ${}^{2,4}\Delta(1), {}^{2,4}\phi(1)$	50500

We conclude that the $C^2\Sigma$ state should correlate with the atomic combination ${}^2D_u + {}^3P_g$. However, this combination produces ${}^2\Sigma$ states of both parities and the parity of $C^2\Sigma$ state is still left undetermined.

An attempt to understand the origin of the rather large spin-splitting parameter γ of the $C^2\Sigma$ state points to a negative parity for this state. The splitting in $^2\Sigma$ arises largely due to interaction with neighbouring $^2\Pi$ states. The experimental value of γ is $+0.015 \text{ cm}^{-1}$. If it is assumed that the $C^2\Sigma$ and $X^2\Pi$ stand in relation of 'pure precession' to each other, the parameter γ can be estimated from the relation of van Vleck (1929) or of Mulliken and Christy (1931)

$$\gamma, p = \pm \frac{2ABL(L+1)}{T_\pi - T_\Sigma} \quad (\text{with } L = 1 \text{ in the present case}).$$

Here A is the coupling constant (which includes its sign) of the $^2\Pi$ state and B is the mean rotational constant. The positive sign goes with a Σ^+ state and negative sign with a Σ^- state. In the present case $T_\pi - T_\Sigma$ is negative, the $^2\Pi$ state being the ground state. The observed positive γ therefore shows that the $C^2\Sigma$ state is $C^2\Sigma^-$. Inserting the appropriate values for the constants in the above expression a value of $\gamma = 0.01 \text{ cm}^{-1}$ results which is close to the experimental value. One further comment is relevant. If indeed the $X^2\Pi$ state is the source of the spin-splitting in the $C^2\Sigma$ state, the $C^2\Sigma$ state in turn should produce a Λ -doubling in the $X^2\Pi$ state whose magnitude may be estimated from the above expression. The $X^2\Pi_{1/2}$ levels should show a doubling corresponding to a p value of $+0.01 \text{ cm}^{-1}$ —a magnitude large enough to produce a measurable combination defect. In the present case no combination defect could actually be established. Interaction of the $X^2\Pi$ state with other (hitherto unidentified) $^2\Sigma^+$ states might offset the effect due to $C^2\Sigma^+$. No further comments are therefore offered.

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