

## FLUORESCENCE EXCITATION SPECTROSCOPY OF PHOTOFRAGMENTS OF PH<sub>3</sub>

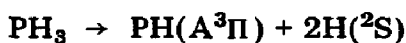
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### Summary

Phosphine (PH<sub>3</sub>) has been photodissociated in the vacuum ultraviolet and the electronically excited primary products PH<sub>2</sub>( $\tilde{A}^2A_1$ ) and PH(A<sup>3</sup>Π) have been detected by emission. The results have been explained in terms of the following processes:



Fluorescence excitation curves for both products are given and from the energy thresholds the following thermochemical values were calculated:  $D(\text{PH}_2 - \text{H}) = 3.69 \pm 0.05$  eV ( $85.1 \pm 1$  kcal mol<sup>-1</sup>),  $D(\text{PH} - \text{H}) = 2.93 \pm 0.15$  eV ( $67.6 \pm 3$  kcal mol<sup>-1</sup>),  $\Delta H_f(\text{PH}_2) = 1.76 \pm 0.05$  eV ( $40.5 \pm 1$  kcal mol<sup>-1</sup>),  $\Delta H_f(\text{PH}) = 2.45 \pm 0.2$  eV ( $56.4 \pm 4$  kcal mol<sup>-1</sup>). The first process seems to correlate mostly with states  $\tilde{A}$ ,  $\tilde{B}$  and  $\tilde{C}$  of PH<sub>3</sub>. The third process is more likely to be associated with an absorption continuum in the more energetic part of the absorption spectrum, while the role of the second process remains uncertain.

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### Introduction

The photolysis of phosphine has been the subject of many previous studies. Melville [1] performed both Hg sensitized and direct photolysis with final product analysis. Ramsay [2] identified PH<sub>2</sub>( $\tilde{X}^2B_1$ ) as a product by absorption spectroscopy, and Norrish and Oldershaw [3] found PH and P<sub>2</sub>

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as secondary products of flash photolysis, the primary product being  $\text{PH}_2$ . A photoionization potential was reported by Price and Passmore [4]. Welge and coworkers detected  $\text{PH}(\text{X}^3\Sigma^-)$ ,  $\text{PH}_2(\tilde{\text{X}}^2\text{B}_1)$  in quartz ultraviolet flash photolysis [5] and  $\text{PH}(\text{A}^3\Pi_1)$  in vacuum ultraviolet photolysis [6]. The photodissociation of  $\text{PH}_3$  was also employed to study the rotational features of the first electronic transition of  $\text{PH}_2$  [7 - 9]. Most of the spectroscopic information on the higher electronic states of  $\text{PH}_3$  is due to Walsh and coworkers [10, 11]. Rather scanty data are available [12] on the heat of formation of  $\text{PH}$  and  $\text{PH}_2$ , apart from the value of McAllister and Lossing [13], and on the P-H bond strengths in  $\text{PH}_3$  and  $\text{PH}_2$  [14].

This paper describes the study of the production of  $\text{PH}(\text{A}^3\Pi_1)$  and  $\text{PH}_2(\tilde{\text{A}}^2\text{A}_1)$  in the photolysis of  $\text{PH}_3$  in terms of fluorescence excitation curves. The latter species has been observed for the first time as a primary product in the photolysis of phosphine. Some thermochemical values have been derived. Preliminary results on this subject have appeared elsewhere [15].

## Experimental

The experimental arrangement for measurements of absorption, emission and fluorescence excitation spectra was the same as described previously [16, 17]. The photolysis source for both types of experiment was a hydrogen discharge lamp (Hanovia type 906 A 0320) operated on an a.c. power supply at 3500 V and 1.5 Torr  $\text{H}_2$  pressure. This lamp emits a many-line (85 - 165 nm) and a continuum spectrum (165 - 300 nm) and was provided with either a LiF or a Suprasil window.

The small fluorescence signals (highest intensity about 100 count  $\text{s}^{-1}$ ) were detected by an EMI 6256 SA photomultiplier having 13 stages and an  $S(Q)$  spectral response ranging from about 170 to 600 nm. Signals were processed by counting techniques and the output of a ratemeter was recorded. The time constants of the detection branch were 5 s for the fluorescence analysis and the  $\text{PH}_2(\tilde{\text{A}}^2\text{A}_1)$  excitation fluorescence spectra and 10 s for the  $\text{PH}(\text{A}^3\Pi)$  excitation spectrum.

The analysis of the emission bands was carried out with the photolysis cell assembled at the entrance slit of a 0.3 m Czerny-Turner monochromator (McPherson Model 218) with the discharge lamp at right angles. The grating was blazed at 500 nm with 1200 line  $\text{mm}^{-1}$  and the slits were 0.5 mm wide corresponding to a half-height bandwidth of 1.5 nm.

The fluorescence excitation spectra of the detected photofragments were obtained by irradiating a photolysis cell with the hydrogen discharge lamp assembled at the entrance slit of a normal incidence vacuum ultraviolet monochromator (McPherson model 225). A 600 line  $\text{mm}^{-1}$  concave grating, coated with  $\text{MgF}_2$  and blazed at 200 nm in the first order, was used. When working at wavelengths longer than 200 nm a fused quartz window was interposed to avoid irradiation by the second order vacuum ultraviolet. Slits were 0.4 mm wide corresponding to a 0.7 nm half-height bandwidth. The photo-

lysis cell was T-shaped to allow measurement of emission and absorption and was placed at the exit slit of the monochromator. The fluorescence excitation spectra were detected after passing through the appropriate filters as shown in Fig. 1. Absorption was d.c. detected with an in-line photomultiplier and a picoammeter.

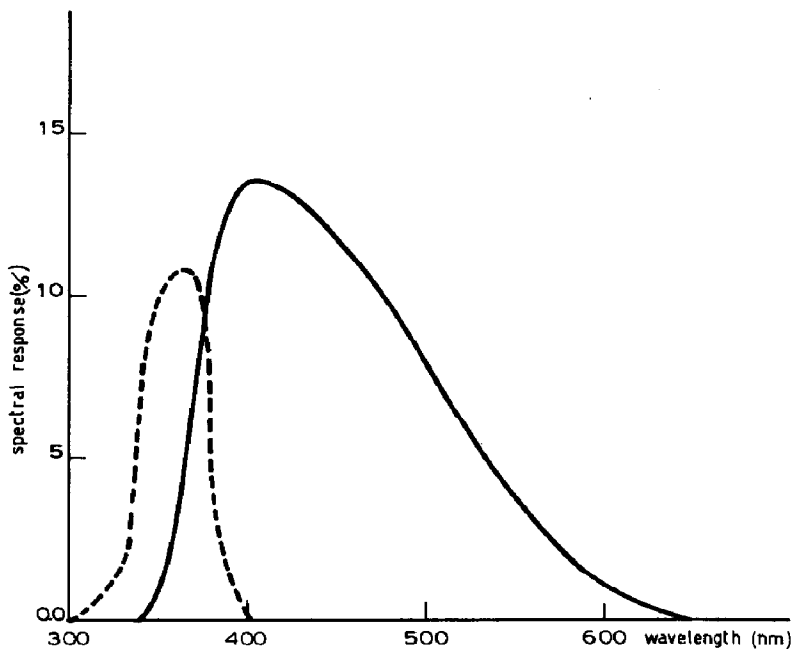


Fig. 1. Spectral response of the photomultiplier plus colour filter assembly used for the detection of the transitions: (a)  $\text{PH}(\text{A}^3\Pi_1 \rightarrow \text{X}^3\Sigma^-)$ , broken curve; (b)  $\text{PH}_2(\tilde{\text{A}}^2\text{A}_1 \rightarrow \text{X}^2\text{B}_1)$ , solid curve.

Commercially available (Matheson)  $\text{PH}_3$  was used without further purification. The assessed purity was 99.5%, and the experiments were carried out with the gas flowing through the photolysis cell. An approximate residence time of 0.1 s was obtained using a 2 in oil diffusion pump.

## Results

The emission of photofragments of  $\text{PH}_3$  was analysed by scanning the spectral region between 300.0 and 650.0 nm. Two main features were apparent in the pressure range from  $5 \times 10^{-2}$  to 0.5 Torr. The emission spectrum shown in Fig. 2 has a 1.5 nm resolution and 25 count  $\text{s}^{-1}$  maximum intensity over the scattered light, the signal-to-noise ratio being about 5. The bands can be attributed to the transition  $\text{PH}(\text{A}^3\Pi \rightarrow \text{X}^3\Sigma^-)$  previously seen in the photolysis of  $\text{PH}_3$  with rare gas resonance lamps [6]. The assignments given in Fig. 2 are from ref. 18. The emission in the region 410 - 630 nm is shown in Fig. 3; the long wavelength limit is due to the sensitivity of the photo-

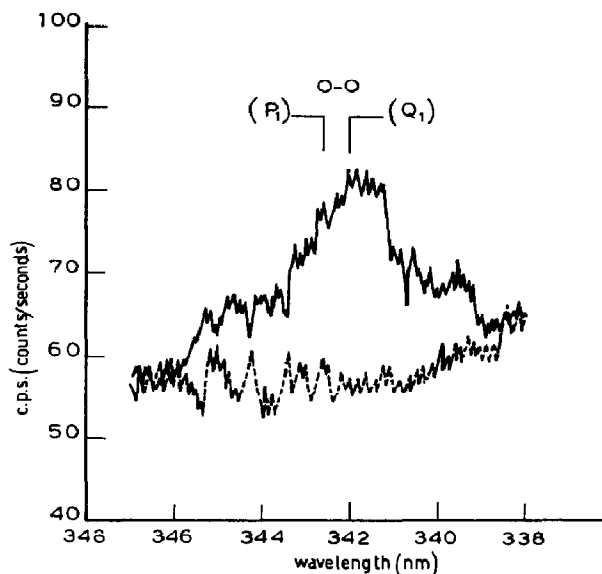


Fig. 2.  $\text{PH}(A^3\Pi_i \rightarrow X^3\Sigma^-)$  emission bands produced by the photodissociation of 0.1 Torr  $\text{PH}_3$ . The resolution is 1.5 nm. The lower curve is the scattered light background.

multiplier. The resolution is the same as for the previous transition. The bands can be attributed to the process  $\text{PH}_2(\tilde{A}^2A_1 \rightarrow \tilde{X}^2B_1)$  first seen in absorption by Ramsay [2], in emission by Guenebaut and Pascat [19, 20] and analysed by Ramsay and coworkers [7 - 9]. The assignments of Fig. 3 are taken from the band heads [19, 20] and  $T_0$  values [9] for the single vibrational levels of the  $v' = n \leftrightarrow v'' = 0$  progression of the  $\nu_2$  bending mode. It may be noted that both  $\text{PH}_2$  states involved in the  $\text{PH}_2(\tilde{A}^2A_1 \rightarrow \tilde{X}^2B_1)$  transition are bent so that the 000 - 000 band should have a more favourable Franck-Condon factor than the corresponding linear-bent transition in  $\text{NH}_2$ . Accordingly, maximum intensity in absorption occurs in the 040  $\leftarrow$  000 band compared with the 090  $\leftarrow$  000 band in  $\text{NH}_2$  [8]. The  $\Delta v = 0$  sequence has band heads in the 546.7 - 556.0 nm region which is fairly well covered by our detection system.

The absorption spectrum of  $\text{PH}_3$  shown in Fig. 4(a) has been obtained at the same pressure as the fluorescence excitation spectra of Fig. 4(b). The upper states of the transitions involved are indicated. According to Walsh *et al.* [10, 11] the first continuum corresponds to a transition to the  $\tilde{A}$  state, and starts with a very low absorption somewhere near 230.0 nm. A second bound state is reached in the region 159.2 - 149.0 nm. The resolution was not sufficient to resolve the vibrational structure of this and of the following transition to the  $\tilde{C}$  state. A  $\tilde{D}$  state is reported in the region 126.0 - 133.0 nm for  $\text{PD}_3$ , and an underlying continuum below about 150 nm. This type of absorption spectrum bears some resemblance to that of ammonia, and the above states could correspond to the  $\tilde{A}^1A_2$ ,  $\tilde{B}^1E''$ ,  $\tilde{D}^1A_2''$  and possibly the  $\tilde{G}$  states of  $\text{NH}_3$ . The symmetry properties of electronically excited  $\text{PH}_3$  are not

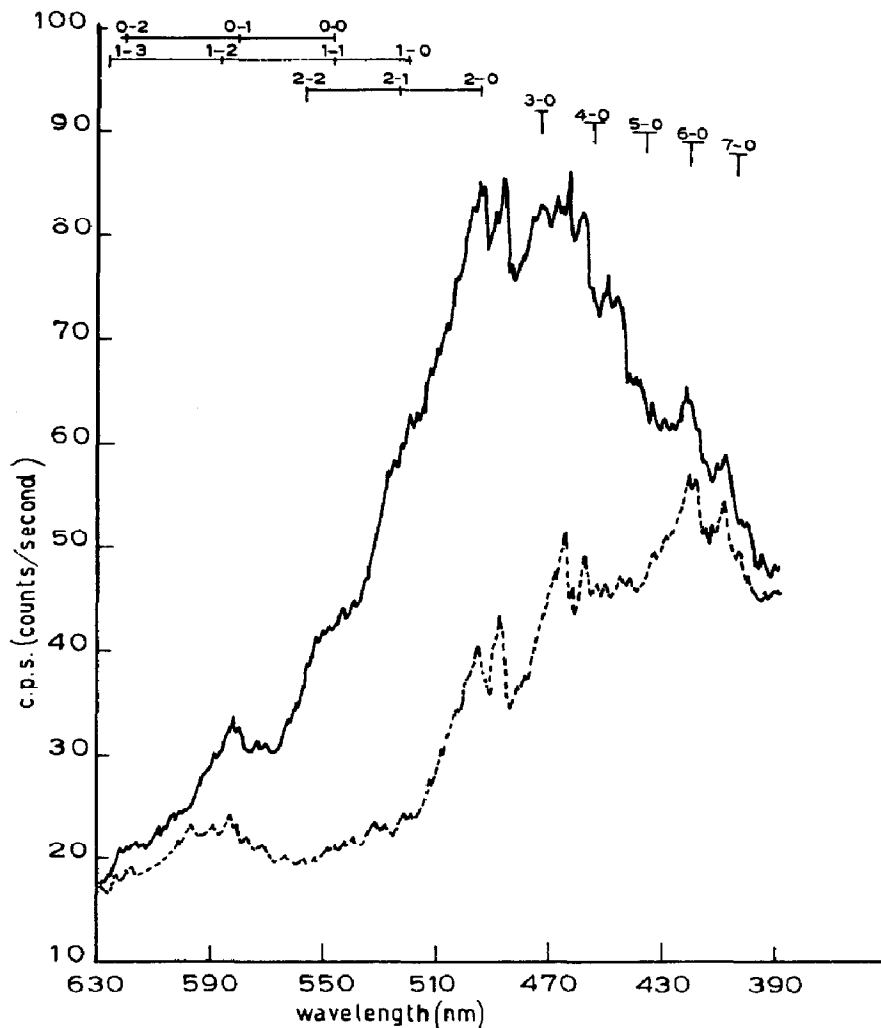


Fig. 3.  $\text{PH}_2(\tilde{\text{A}}^2\text{A}_1 \rightarrow \tilde{\text{X}}^2\text{B}_1)$  emission bands produced by the photodissociation of 0.1 Torr  $\text{PH}_3$ . The resolution is 1.5 nm. The lower curve is the scattered light background.

well known. A pyramidal structure which is virtually planar because of an inversion due to the  $\nu_2$  vibrational mode has been proposed [10, 11].

Fluorescence intensities were measured as a function of incident wavelengths and, after normalization for constant incident light intensity, are given in Fig. 4(b) as fluorescence excitation spectra for both photofragments detected. Arbitrary units are used for the intensity, and they are approximately the same for both transitions shown because a correction was introduced to account for filter transmissions and photomultiplier spectral response. The emission from  $\text{PH}(\text{A}^3\Pi_1)$  begins at  $159 \pm 2$  nm where the signal is very low but a sharp increase appears at about  $121.0 \pm 1$  nm. The emission attributed to  $\text{PH}_2(\tilde{\text{A}}^2\text{A}_1)$  begins at  $208 \pm 1$  nm and extends down to about 120 nm.

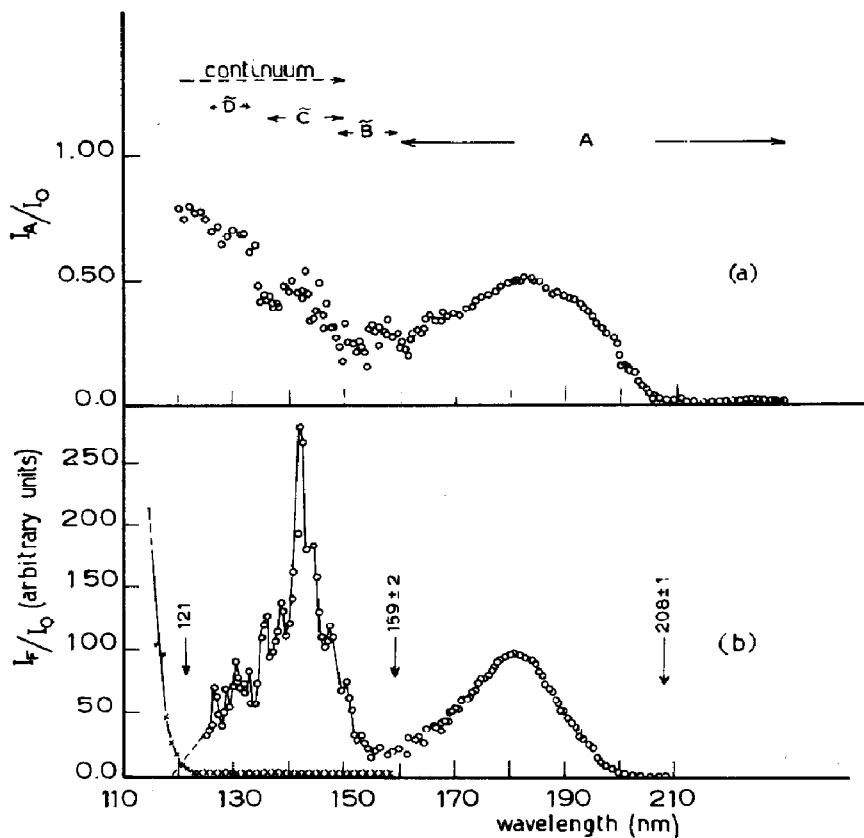


Fig. 4. (a) Absorption of PH<sub>3</sub> normalized to incident light intensity: resolution 0.7 nm, cell length 4 cm. Upper electronic states of PH<sub>3</sub> [10, 11] are indicated. (b) ○ Fluorescence excitation spectrum of PH<sub>2</sub>( $\tilde{A}^2A_1$ ) from PH<sub>3</sub> photolysis: resolution 1 nm. × Fluorescence excitation spectrum of PH( $A^3\Pi_1$ ) from PH<sub>3</sub> photolysis: resolution 1.5 nm. All curves obtained at 0.1 Torr PH<sub>3</sub> pressure.

## Discussion

### *Emission bands in the vacuum ultraviolet photolysis of PH<sub>3</sub>*

The PH( $A^3\Pi$ ) emission has been observed only from the  $v' = 0$  state at 341.9 (Q<sub>1</sub>) and 342.6 (P<sub>1</sub>) nm. The 1–1 and 1–0 band systems at about 346.5 and 322.0 nm were not detected, though the energy of the incident photons was sufficient to produce PH( $A^3\Pi$ ) in the first vibrational state and the Franck–Condon factors of the 1–1 and the 0–1 transitions are comparable. The equilibrium distances of the P–H bond in PH<sub>3</sub>( $\tilde{X}^1A_1$ ) and in PH( $A^3\Pi_1$ ) are reported in Table 1. The PH distance is longer by about 3 pm in PH( $A^3\Pi_1$ ) than in the ground state of the parent molecule. A difference of a few picometres in bond length seems sufficiently significant to account for the vibrational excitation of the departing fragments. This can be deduced from the excitation mechanism proposed by Simons and Tasker [26] which assumes a vertical transition from the ground state of a parent molecule having a

TABLE 1

Thermochemical, spectroscopic and configurational values from the literature used in the Discussion

	$\Delta H_f^0$ (kcal mol <sup>-1</sup> )	$T_0$ (cm <sup>-1</sup> )	$D(\text{PH}_n\text{-H})$ (kcal mol <sup>-1</sup> )	$\theta(\text{H-P-H})$ (°)	$R(\text{P-H})$ (pm)
$\text{PH}_3(\tilde{X}^1A_1)$	7.0 ± 0.4 [12]		83.9 ± 2 [13] 81 ± 4 [25]	93.37 [23]	142.9 [23]
$\text{PH}_3(\tilde{A})$		(43000) [10, 11]		120 [10, 11]	
$\text{PH}_3(\tilde{B})$		62801 [10, 11]		120 [10, 11]	
$\text{PH}_3(\tilde{C})$		66660 [10, 11]		120 [10, 11]	
$\text{PH}_3(\tilde{D})$		(75000) [10, 11]			
$\text{PH}_2(\tilde{X}^2B_1)$	37.3 ± 2 [13]		71.4 [21]	91.7 [9]	141.8 [9]
$\text{PH}_2(\tilde{A}^2A_1)$		18276.6 [9]		123.2 [9]	138.9 [9]
$\text{PH}(\text{X}^3\Sigma^-)$	60.4 ± 8 [12]		81.0 ± 7 [22] 70.4 [21]		142.21 [24]
$\text{PH}(\text{A}^3\Pi_1)$		29318.28 [18]			144.58 [24]
$\text{H}(^2S)$	51.63 [12]				

different equilibrium bond distance from that of the dissociation excited state. It is therefore very likely that  $\text{PH}(\text{A}^3\Pi)$  was also produced in vibrational states higher than  $v' = 0$  but was not seen because of a predissociation mechanism, as suggested by Rostas *et al.* [24], which leads to ground state atoms:



The resolution of the  $\text{PH}_2(\tilde{A}^2A_1 \rightarrow \tilde{X}^2B_1)$  emission spectrum is not good enough to allow detailed conclusions to be drawn about the vibrational energy distribution. According to the assignments [9, 19, 20] reported in Fig. 3, upper vibrational levels  $v' = 4 - 5$  of the  $\nu_2$  bending mode seem to be appreciably populated. This can be qualitatively accounted for by the semi-classical mechanism already mentioned [26]. The recoil effect of the departing H atom can be neglected and we may be concerned more with the difference between the bond equilibrium angles of  $\text{PH}_3(\tilde{X}^1A_1)$  and  $\text{PH}_2(\tilde{A}^2A_1)$ , as in Table 1. Ground state phosphine is pyramidal, with point group  $C_{3v}$ , and has a H-P-H equilibrium angle of 93.37° [23]. In the first electronically excited state  $\text{PH}_2$  is a bent molecule having an H-P-H angle of 123.2° [9], close to that of the virtually  $D_{3h}$  excited  $\text{PH}_3$  [10, 11]. The absorption of the photolysing energy by phosphine can be regarded as a vertical transition resulting in excited  $\text{PH}_3$  with an H-P-H angle distorted by about 30° from its equilibrium position. This distortion is also maintained by the departing  $\text{PH}_2(\tilde{A}^2A_1)$  fragment and, using the reported force constant of  $5.45 \times 10^{-12}$  erg rad<sup>-2</sup> [27], would correspond to an energy of 0.46 eV which is about that of the fourth  $\nu_2$  vibrational level.

### The primary processes

In order to determine the primary processes of photolysis of  $\text{PH}_3$  we refer to the thermochemical values available in the literature and listed in Table 1. The  $208.0 \pm 1$  nm energy threshold for the formation of  $\text{PH}_2(\tilde{\text{A}}^2\text{A}_1)$  is attributed to process



This process seems to correspond to the  $\tilde{\text{A}}$  state of  $\text{PH}_3$ . Absorption and fluorescence excitation curves are somewhat different between 208 and 198 nm. In this range the yield of  $\text{PH}_2(\tilde{\text{A}}^2\text{A}_1)$  remains low, possibly because the production of vibrationally cold  $\text{PH}_2(\tilde{\text{A}}^2\text{A}_1)$  is not very likely, as discussed previously. Below 159 nm the resolution of the fluorescence excitation spectrum is not sufficient to assess whether process (1) is associated with the bound states  $\tilde{\text{B}}$  and  $\tilde{\text{C}}$  of  $\text{PH}_3$  or with some underlying continuum. The first case may be preferred because process (1) vanishes below 120 nm where only a continuum is reported.

The energy threshold at  $159 \pm 2$  nm for the formation of  $\text{PH}(\text{A}^3\Pi_1)$  has no obvious thermochemical meaning. Two photolysis mechanisms may be proposed for the production of  $\text{PH}(\text{A}^3\Pi_1)$ :



According to the heats of formation given in Table 1 the experimental energy threshold at 159 nm lies between those of process (2) and process (3). The calculated threshold values are in fact 208.3 and 118.9 nm respectively. The experimental value of the threshold seems to have some spectroscopic meaning as it coincides with the onset of the  $\text{PH}_3(\tilde{\text{B}} \leftarrow \tilde{\text{X}})$  absorption transition. Process (2) is forbidden by spin conservation rules and begins at this point with a very low yield, possibly by predissociation of the  $\text{PH}_3(\tilde{\text{B}})$  state through a non-bonding triplet state. At 121.0 nm there is a very sharp increase in the signal which is probably due to the onset of process (3) which is spin allowed. Further, it may be noticed that in this region the photoionization threshold has been found at 124.2 nm [4], the  $\text{PD}_3(\tilde{\text{D}} \leftarrow \tilde{\text{X}})$  transition ends at 126.0 nm [10, 11] and the formation of  $\text{PH}_2(\tilde{\text{A}}^2\text{A}_1)$  vanishes at 119.0 nm.

### Determination of bond dissociation energies and of heats of formation

The bond energies  $D(\text{PH}_2\text{—H})$  and  $D(\text{PH—H})$  are not well known and are not reported by Darwent [14]. From the experimental energy threshold of process (1) at  $208.0 \pm 1$  nm and the  $T_0$  value for  $\text{PH}_2(\tilde{\text{A}}^2\text{A}_1)$  [9],  $D(\text{PH}_2\text{—H})$  is  $3.69 \pm 0.05$  eV ( $85.1 \pm 1$  kcal mol<sup>-1</sup>) in very good agreement with the value obtained by McAllister and Lossing [13] by electron impact methods and that obtained by Smith and Brauman [25] from electron affinity measurements (Table 1).

If it is assumed, as discussed above, that the energy threshold  $h\nu_0$  of process (3) is at  $121.0 \pm 1$  nm corresponding to the sharp increase of the slope of  $\text{PH}(\text{A}^3\Pi_1)$  production, then



$$\begin{aligned}
 D(\text{PH-H}) &= h\nu_0 - D(\text{PH}_2\text{-H}) - T_0(\text{PH } A^3\Pi_1) \\
 &= 2.93 \pm 0.15 \text{ eV } (67.6 \pm 3 \text{ kcal mol}^{-1})
 \end{aligned}$$

Experimental data for comparison are not available. A semi-empirical theoretical value of  $71.44 \text{ kcal mol}^{-1}$  has been calculated by Jordan [21] employing a method requiring, as input data, experimental parameters for  $\text{PH}_3$  such as the heat of formation, bond angles and the electronic excitation energy of the transition  $\text{PH}(A^3\Pi \leftrightarrow X^3\Sigma^-)$ . Cottrell [28] gives an average  $\bar{D}$  value for the P-H bond in  $\text{PH}_3$  of  $77 \pm 2 \text{ kcal mol}^{-1}$ . The average obtained with our results and the two values reported in Table 1 for  $D(\text{P-H})$  in PH is  $\bar{D}(\text{P-H}) = 77.9$  or  $74.4 \text{ kcal mol}^{-1}$ . The latter is probably more reliable because it is based on a fairly recent estimate by Jordan. The difference  $D(\text{PH}_2\text{-H}) - D(\text{PH-H}) = 17.5 \text{ kcal mol}^{-1}$  also compares favourably with the analogous quantity in  $\text{NH}_3$  [14] where  $D(\text{NH}_2\text{-H}) = 103$ ,  $D(\text{NH-H}) = 89$  and  $D(\text{N-H}) = 85 \text{ kcal mol}^{-1}$ . In the molecules  $\text{PH}_n$  ( $1 \leq n \leq 3$ ), as in  $\text{NH}_n$  ( $1 \leq n \leq 3$ ), bond energies appear to vary with  $n$  although bond distances and angles are nearly constant.

Heats of formation of  $\text{PH}_3$ ,  $\text{PH}_2$  and PH reported in the literature are fairly uncertain. The most reliable seems to be  $\Delta H_f^0(\text{PH}_3) = 7 \pm 0.4 \text{ kcal mol}^{-1}$  [12];  $\Delta H_f^0(\text{PH}_2)$  given in ref. 13 is based on this value. The heats of formation of  $\text{PH}_2$  and PH are derived from the bond energies  $D(\text{PH}_2\text{-H})$  and  $D(\text{PH-H})$  and the above  $\Delta H_f^0(\text{PH}_3)$ :  $\Delta H_f^0(\text{PH}_2)$  is  $1.75 \pm 0.05 \text{ eV } (40.5 \pm 1 \text{ kcal mol}^{-1})$ , which is very close to the value of McAllister and Lossing;  $\Delta H_f^0(\text{PH})$  is  $2.45 \pm 0.2 \text{ eV } (56.4 \pm 4 \text{ kcal mol}^{-1})$  and no other experimental data are available for comparison. The value reported in Table 1 is based on a semi-empirical theoretical method [21].

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