

# The gas-phase on-line production of phosphoryl halides, $\text{POX}_3$ and their identification by infrared spectroscopy

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Received 28 October 1997; received in revised form 19 December 1997; accepted 23 December 1997

## Abstract

A new route has been devised, leading to the production of  $\text{POX}_3$  molecules where  $X = \text{F}, \text{Br}$  and  $\text{I}$  by an on-line process using phosphoryl chloride,  $\text{POCl}_3$  as a starting material passed over heated sodium fluoride,  $\text{NaF}$ , potassium bromide,  $\text{KBr}$  and potassium iodide,  $\text{KI}$  at 535, 690 and 480°C, respectively. The products have been characterised by the infrared (IR) spectra of their vapours. The low resolution gas-phase Fourier transform infrared spectra reported for the first time show strong bands centered at 1416.6, 1312.9, 1297.9 and 1285  $\text{cm}^{-1}$ , assigned to  $\nu_1(\text{a}_1)$ , the O=P stretching fundamental of  $\text{POF}_3$ ,  $\text{POCl}_3$ ,  $\text{POBr}_3$  and  $\text{POI}_3$ , respectively. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Gas-phase; Phosphoryl halides; Infrared spectroscopy

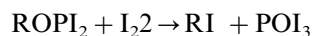
## 1. Introduction

Phosphoryl chloride,  $\text{POCl}_3$  can be made by the oxidation of  $\text{PCl}_3$  with pure oxygen or slightly above room temperature similar to that used on an industrial scale [1]. Phosphoryl bromide,  $\text{POBr}_3$  can be made also by a similar method using  $\text{PBr}_3$  instead of  $\text{PCl}_3$ . Another route for preparing  $\text{POX}_3$  where  $X = \text{Cl}$  and  $\text{Br}$  is as follows:



Phosphoryl fluoride,  $\text{POF}_3$  can be made by the fluorination of  $\text{POCl}_3$  using a metal fluoride (ea.  $\text{M} = \text{Na}, \text{Mg}, \text{Zn}, \text{Pb}, \text{Ag}$ , etc.).  $\text{POI}_3$  was first

made in 1973 by the iodination of  $\text{POCl}_3$  with  $\text{LiI}$ , or by reacting  $\text{ROPI}_2$  with iodine [2]:



Most of the phosphoryl halide compounds are colourless gases or volatile liquids but  $\text{POI}_3$  is dark violet, m.p. 53°C. All of them are monomeric tetrahedral ( $C_{3v}$ ) symmetry point group molecules.  $\text{PO}_2\text{Cl}$  produced by a photochemical reaction between ozone and  $\text{OPCl}$  (obtained from  $\text{POCl}_3$ ) in solid argon has been investigated by IR spectroscopy and ab initio SCF calculations [3]. The same molecule is formed by the high temperature reaction between  $\text{POCl}_3$ ,  $\text{O}_2$  and  $\text{Ag}$ . The paper includes all the frequencies observed for the above molecule. The frequencies were: 1122, 586 and 1429  $\text{cm}^{-1}$ , as-

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signed to  $a_1$  ( $\text{PO}_2$  s-stretch), PCl stretch and  $b_2$  ( $\text{PO}_2$  a-stretch) of  $\text{PO}_2\text{Cl}$ , respectively. Andrews and Withnall reported the formation of  $\text{P}_4\text{O}$ ,  $\text{P}_2\text{O}$ , PO and  $\text{PO}_2$  species and their matrix isolation infrared spectra by the photolysis and discharge reaction of oxygen atoms with  $\text{P}_4$  [4]. Binnewies and Schnöckel mentioned five types of reactions that may lead to OEX or SEX molecules production where, E = P, AS and Sb. One of these reactions is the reduction of phosphoryl halides,  $\text{POX}_3$  with elementary silver at high temperature [5]. Boghosian et. al. recorded the gas phase Raman and UV/Vis spectra of the liquid and solid complexes of  $\text{POCl}_3\text{-FeCl}_3$  molten mixtures under static equilibrium conditions [6]. Moores and Andrews reported some interesting work concerning the oxidation of phosphorus(III) halides by red photolysis of ozone complexes in solid argon [7]. The photolysis of  $\text{PCl}_3/\text{O}_3$  and  $\text{PBr}_3/\text{O}_3$  complexes by red visible radiation in solid argon gives phosphoryl halides. This work has been extended by examining the photolysis of ozone in matrices containing the phosphorus(III) halides  $\text{PF}_3$ ,  $\text{PCl}_3$  and  $\text{PBr}_3$  to generate simple compounds of phosphorus halogen and oxygen and to explore how the products depended on applied wavelength [7].

This paper investigates the gas phase IR spectra and the on-line productions of phosphoryl halides,  $\text{POX}_3$  where X = F, Br and I which have

not been reported previously, using  $\text{POCl}_3$  as a precursor passed over heated NaF, KBr and KI for  $\text{POF}_3$ ,  $\text{POBr}_3$  and  $\text{POI}_3$  productions, respectively.

## 2. Experimental

The first step was to optimize the production conditions of phosphoryl chloride,  $\text{POCl}_3$ , before attempting to observe  $\text{POF}_3$ ,  $\text{POBr}_3$  and  $\text{POI}_3$ .  $\text{POCl}_3$  (Merck, 99.9%) was degassed in the vacuum system before use with liquid nitrogen. The on-line process involved warming the  $\text{POCl}_3$  with heating tape to  $55^\circ\text{C}$  to obtain enough vapor pressure and then pass through an empty tube kept at  $475^\circ\text{C}$ . The remaining conditions were the fast flow reaction under 0.3 Torr pressure.

Fig. 1 shows the experimental set up for the synthesis and spectrometric observation of phosphoryl halide,  $\text{POX}_3$  where X = F, Br and I. The synthesis routes for  $\text{POF}_3$ ,  $\text{POBr}_3$  and  $\text{POI}_3$  can be written as follows:

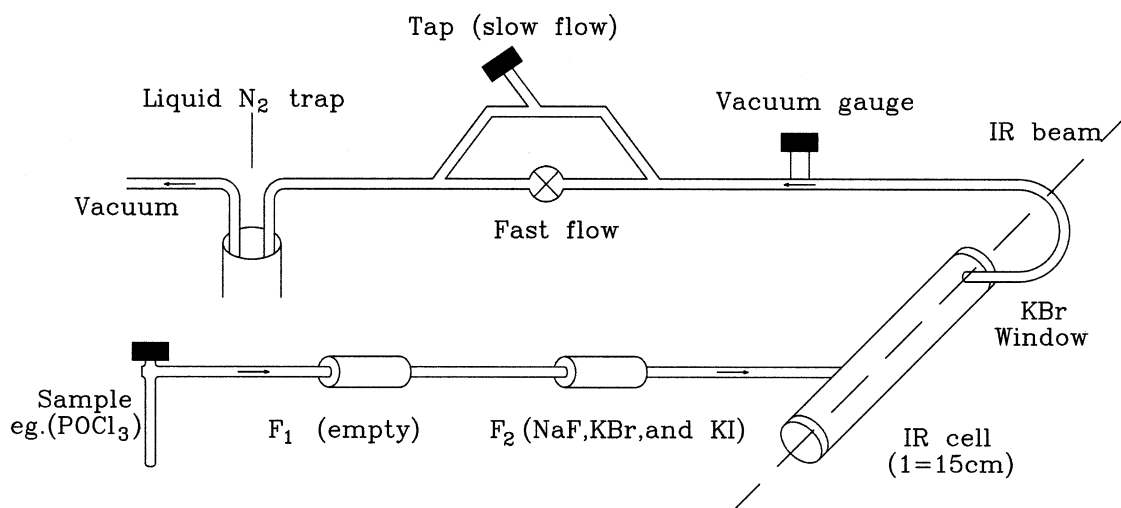
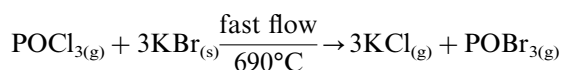
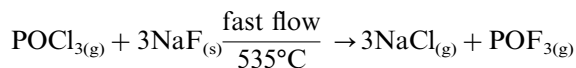


Fig. 1. The experimental set-up for the synthesis and spectrometric observation of phosphoryl halide,  $\text{POX}_3$ .

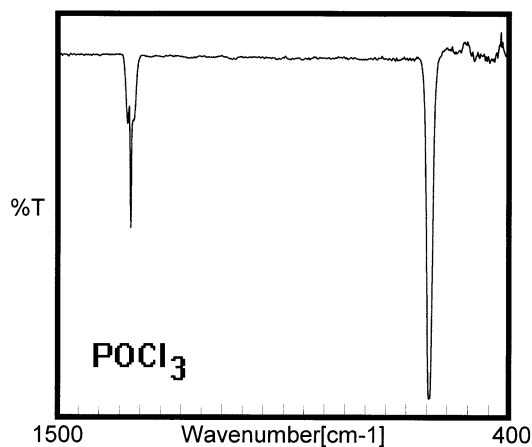
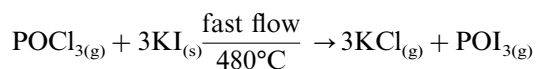


Fig. 2. The gas phase IR spectrum of POCl<sub>3</sub>.



Note that, the first empty furnace ( $F_1$ ) is kept at 475°C in all the above reactions. The salts containing halogens used in these experiments, placed in the second furnace ( $F_2$ ), were obtained from Aldrich with a purity (99.9%).

The products from these reactions were passed directly into an IR cell (Fig. 1) fitted with two KBr windows. The distance between the second furnace ( $F_2$ ) and the IR cell is 3 cm. The cell was pumped out via a liquid nitrogen trap with a rotary pump (E2M8, Edwards) displacing 9.5 m<sup>3</sup> h<sup>-1</sup>. The IR-spectra were obtained on a JASCO 300E FTIR spectrometer at a resolution of 2 cm<sup>-1</sup>.

### 3. Results and discussion

Fig. 2 shows the result of passing POCl<sub>3</sub> gas over an empty tube heated at 475°C. Two strong bands were observed within the spectrometer range at 1312.9 and 590 cm<sup>-1</sup>. The first band centered at 1312.9 cm<sup>-1</sup> is assigned to  $\nu_1(a_1)$ , the O=P stretching mode of POCl<sub>3</sub> and shows typical PQR-type structure and with a strong Q-head. The second band at 590 cm<sup>-1</sup> is assigned to  $\nu_4(e)$ , mode of POCl<sub>3</sub>. It is known empirically that there could be a shift in the band position between the matrix isolation method and the gas-phase technique of

about +1%. Comparison between the 1312.7 cm<sup>-1</sup>,  $\nu_1(a_1)$  stretching mode in POCl<sub>3</sub> observed by the matrix isolation technique after photolysis of PCl<sub>3</sub>/O<sub>3</sub> using 520 nm filter [7,8], with that observed by

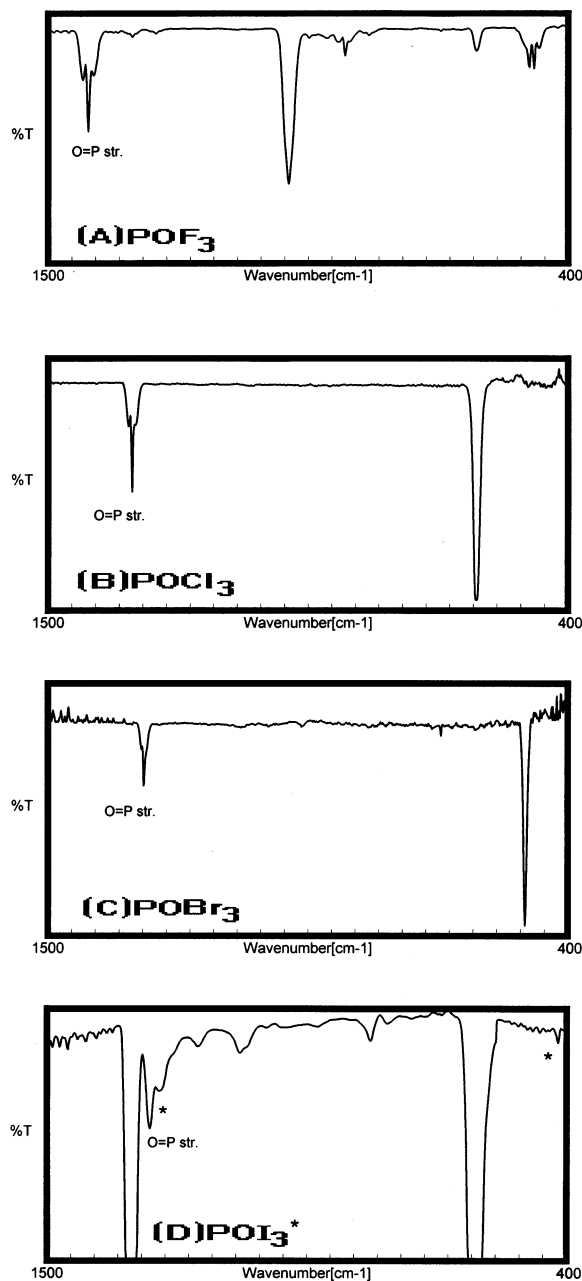


Fig. 3. Full IR spectra of POX<sub>3</sub> where X = F, Cl, Br and I in the range 400–1500 cm<sup>-1</sup>.

Table 1

Observed gas phase IR frequencies of  $\text{POX}_3$  in comparison with matrix isolation and Raman results including the P–R separation ( $\text{cm}^{-1}$ )

Molecule	Mode	Assignment	Observed			P–R separation	
			Matrix [7] isolation	Raman [9] gas-phase	This work (IR) gas-phase	Obs.	Cal.
$\text{POF}_3$	$\nu_1$	$a_1(\text{O}=\text{P str.})$	1410.5	1417	1416.6		
	$\nu_4$	$e(\text{P}-\text{F str.})$	990	991	991.2		
	$\nu_2$	$a_1 \text{ PF}_3 \text{ umbrella}$	875	873	872	43.1	41.6
	$\nu_3$	$a_1 \text{ FPO def.}$	470	472	472.3		
$\text{POCl}_3$	$\nu_1$	$a_1(\text{O}=\text{P str.})$	1312.7	1312.7	1312.9		
	$\nu_4$	$e(\text{P}-\text{Cl str.})$	589	589.5	590	15.4	16.2
$\text{POBr}_3$	$\nu_1$	$a_1(\text{O}=\text{P str.})$	1295.1	—	1297.9		
	$\nu_4$	$e(\text{P}-\text{Br str.})$	488	—	490	8.7	8.8
$\text{POI}_3$	$\nu_1$	$a_1(\text{O}=\text{P str.})$	—	—	1285		
	$\nu_4$	$e(\text{P}-\text{I str.})$	—	—	426	3.9	3.4

gas phase Raman spectroscopy of  $\text{POCl}_3$  at  $1312.7 \text{ cm}^{-1}$  [9] and this gas phase infrared spectroscopy work at  $1312.9 \text{ cm}^{-1}$ , is reasonable and fits very nicely especially with the gas phase Raman results. These gas phase IR results fit also within the expected shift between matrix isolation and gas phase results.

Fig. 3 shows three new spectra A, C, and D ( $400\text{--}1500 \text{ cm}^{-1}$ ) where spectrum B is the precursor ( $\text{POCl}_3$ ). Spectrum A is the result of passing  $\text{POCl}_3$  gas over an empty tube kept at  $475^\circ\text{C}$  and also over heated NaF at  $535^\circ\text{C}$ . Four new bands were observed at  $1416.6$ ,  $991.2$ ,  $872$  and  $472.3 \text{ cm}^{-1}$ . The first band at  $1416.6 \text{ cm}^{-1}$  is assigned to  $\nu_1(a_1)$ , the  $\text{O}=\text{P}$  stretching mode of  $\text{POF}_3$  and show a PQR type structure with a very strong Q-head. This result is consistent with expectation and the band is shifted to higher frequency when fluorine replace the chlorine in  $\text{POCl}_3$  to form  $\text{POF}_3$  which is similar to the NSX work [10]. The second band at  $991.2 \text{ cm}^{-1}$  is assigned to  $\nu_4(e)$   $\text{POF}_3$ , the third band at  $872 \text{ cm}^{-1}$  is assigned to  $\nu_2(a_1)\text{POF}_3$ , this band has a PQR type structure and the final band at  $472.3 \text{ cm}^{-1}$  is assigned to  $\nu_3(a_1)\text{POF}_3$  and also has a PQR type structure. The obtained gas phase IR results for  $\text{POF}_3$  are compared with matrix isolation after full arc photolysis of  $\text{PF}_3/\text{O}_3$  [7] and with gas phase Raman results too [9] (see Table 1). Note that, the ob-

served gas phase IR frequencies are identical to those obtained by gas phase Raman technique and lies within an acceptable range with matrix isolation technique.

There is very little trace of  $\text{POCl}_3$  as can be seen in spectrum A and it is estimated that the purity is about 99%. The  $\text{POF}_3$  sample was collected using cold slush bath of acetonitrile mixed with liquid nitrogen at  $-41^\circ\text{C}$  and the IR spectrum was taken for the collected material. The obtained infrared spectrum was exactly identical to that observed by the on-line process.

Spectrum C in Fig. 3 shows the result of passing  $\text{POCl}_3$  gas over heated KBr at  $690^\circ\text{C}$ . Two new bands were observed at  $1297.9$  and  $490 \text{ cm}^{-1}$ . The first band at  $1297.9 \text{ cm}^{-1}$  is assigned to  $\nu_1(a_1)$ , the  $\text{O}=\text{P}$  stretching mode of  $\text{POBr}_3$  and also shows a PQR type structure. The shift to lower frequency again fits with expectation after bromine replaces the chlorine in order to form  $\text{POBr}_3$ . Comparison of the  $1295.1 \text{ cm}^{-1}$  (most intense peak [7]) the  $\nu_1(a_1)$ , the  $\text{O}=\text{P}$  stretching mode of  $\text{POBr}_3$  observed by matrix isolation technique after full arc photolysis of  $\text{PBr}_3$  and ozone [7] and these gas phase IR results at  $1297.9 \text{ cm}^{-1}$ , is justified. The second band at  $490 \text{ cm}^{-1}$  is assigned to  $\nu_4(e)$  of  $\text{POBr}_3$ . To confirm this reaction,  $\text{POBr}_3$  pure sample was obtained from Merck with a purity of 99.9% and replaced in the

gas flow system. The sample has very high vapor pressure so the IR spectrum is recorded without any heating and the result was similar spectrum observed by the new route applied in this work. Therefore,  $\text{POBr}_3$  can be collected by our route below  $55^\circ\text{C}$  which is the melting point of pure  $\text{POBr}_3$ .

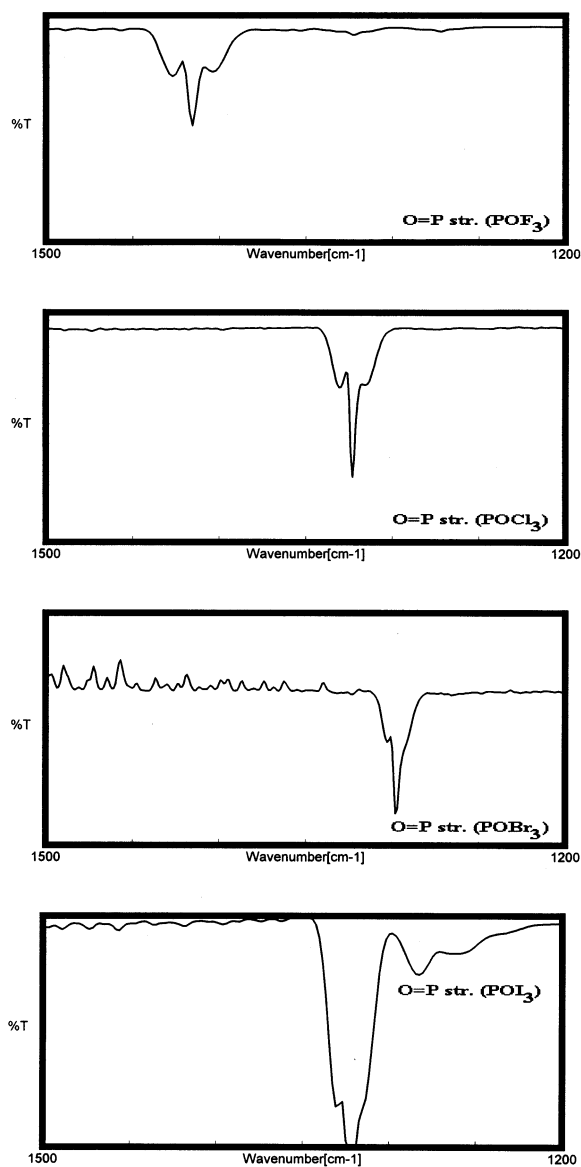


Fig. 4. The  $\nu_1(a_1)$ , O=P stretching band of  $\text{POX}_3$  in the range (1200–1500)  $\text{cm}^{-1}$ .

The final step is shown in Fig. 3 (spectrum D) which is the result of passing  $\text{POCl}_3$  gas over heated KI at  $480^\circ\text{C}$ . The gas phase IR spectrum of  $\text{POI}_3$  is recorded here for the first time and no other spectroscopic data is available. It should be pointed out that the producing of  $\text{POI}_3$  is in general far from being trivial due to easy sublimation of iodine at high temperature of heated KI. Nevertheless, the two characterized bands of  $\text{POI}_3$  are observed. Because, there is no previous experimental spectroscopic data for  $\text{POI}_3$ , the assignment of the obtained spectrum could be analysed considering the previous analogous molecules. The two bands correspond to  $\text{POI}_3$  are centred at 1285 and  $426\text{ cm}^{-1}$ . The first band positioned to the right side  $\text{POCl}_3$  mode centred at  $1285\text{ cm}^{-1}$ , is assigned to  $\nu_1(a_1)$ , the O=P stretching mode of  $\text{POI}_3$ . The observed band has a PR type structure and this experiment has been performed especially under  $1\text{ cm}^{-1}$  resolution in order to resolve this structure. The PR profile can be seen in Fig. 3 (bottom spectrum), the Q-head was not observed but that could be due to decreases in electronegativity from fluorine up to iodine which may be responsible for broader band in  $\text{POI}_3$  than of the other halides in preceding spectra. The second band at  $426\text{ cm}^{-1}$  is very small and tentatively assigned to  $\nu_4(e)$ , of  $\text{POI}_3$ . As can be seen from the bottom spectrum, the concentration of  $\text{POCl}_3$  is too high and it was very difficult to obtain pure  $\text{POI}_3$  from  $\text{POCl}_3$  owing to easy sublimation of iodine at high temperature of heated KI. Therefore, the concentration of iodine in the vacuum system is very low compared with  $\text{POCl}_3$  which could lead to the formation of  $\text{POCl}_2\text{I}$  or  $\text{POClI}_2$  in some stages before forming the interested  $\text{POI}_3$  molecule (Fig. 4).

All the observed frequencies ( $\text{cm}^{-1}$ ) of  $\text{POX}_3$  determined by this gas phase IR spectroscopy work in comparison with the data obtained by matrix isolation and gas phase Raman results are listed in Table 1. The Table also includes the observed and calculated values using the method of Paul and Dijkstra [11] for the  $\nu_1(a_1)$   $\text{POX}_3$  where X = F, Cl, Br and I. The overall shift between the matrix isolation and these gas phase IR spectra of  $\nu_1(a_1)$ , the O=P main stretching

mode of  $\text{POF}_3$ ,  $\text{POCl}_3$  and  $\text{POBr}_3$ , is 6.1, 0.2 and  $2.8 \text{ cm}^{-1}$ , respectively. This shift is in agreement with the less 1% shift between matrix isolation and gas phase IR results.

It is concluded that the present work reports for the first time, the on-line production and detection of  $\text{POF}_3$ ,  $\text{POCl}_3$ ,  $\text{POBr}_3$  and  $\text{POI}_3$ , in the gas-phase. These experimental data agree with expectations and are comparable with the data obtained by matrix isolation and gas phase Raman spectroscopy. The frequency shift between matrix isolation and this gas phase IR results is less than 1% and in good agreement with the two techniques. Concerning our gas phase infrared and Raman results, both results are in excellent agreement.  $\text{POF}_3$  can be collected by our route at  $-41^\circ\text{C}$  using cold slush bath of acetonitrile mixed with liquid nitrogen.  $\text{POBr}_3$  can be collected also by the new applied route at around  $55^\circ\text{C}$ .

#### Acknowledgements

I would like to thank Professor Dr I. Othman (DG) and Professor Dr Y. Koudsi (Head of Chemistry Department) for their encouragement as well as Mr N. Odeh and Miss D. Naima for their effort in setting up the experiments and

gratefully acknowledges TWAS for research grant No. 94-025 RG/CHE/AF/AC. I am very grateful to Drs R. Suffolk, D.R.M. Walton, H. Klawi, G. Zazafoon and Z. Ajji for their valuable discussion, as well as Miss Wafa'a Alibrahim and Miss B. Alrez for the help.

#### References

- [1] N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 1st ed., Pergamon Press, Oxford, 1989.
- [2] A.V. Kirsanov, Zh.K. Gorbatenko, N.G. Feshchenko, *Chemistry of phosphorus iodides*, *Pure Appl. Chem.* 44 (1975) 125.
- [3] R. Ahlrichs, C. Ehrhardt, M. Lakenbrink, S. Schunck, H. Schnöckel, *J. Am. Chem. Soc.* 108 (1986) 3596.
- [4] L. Andrews, R. Withnall, *J. Am. Chem. Soc.* 110 (1988) 5605.
- [5] M. Binnewies, H. Schnöckel, *Chem. Rev.* 90 (1990) 321.
- [6] S. Boghosian, G.A. Voyiatzis, G.N. Papatheodoron, *J. Chem. Soc. Dalton Trans* 16 (1996) 3505.
- [7] B.W. Moors, L. Andrews, *J. Phys. Chem.* 93 (1989) 1902.
- [8] A.J. Downs, G.P. Gaskill, S.P. Saville, *Inorg. Chem.* 21 (1982) 3385.
- [9] R.J.H. Clark, D.M. Rippon, *Mol. Phys.* 28 (1974) 305.
- [10] A.W. Allaf, G.Y. Matti, R.J. Suffolk, J.D. Watts, *Electron Spectrosc. Relat. Phenom.* 48 (1989) 411; and *Chem. Phys. Lett.* 155 (1989) 32.
- [11] W.A. Seth Paul, G. Dijkstra, *Spectrochim. Acta Part A* 23A (1967) 2861.