Infrared and Raman Spectra of some Phosphorus Sulphides

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The solid-state i.r. and Raman spectra of the four crystalline phosphorus sulphides, P_4S_3, P_4S_5, P_4S_7, and P_4S_{10} are reported. The Raman spectra of the melts formed by all four compounds, and the vapours formed from P_4S_3, P_4S_7, and P_4S_{10} are also recorded. Only P_4S_3 retains the same structure in all three phases. P_4S_5 disproportionates in the melt to P_4S_3 and P_4S_7 and further species which were not identified. Both P_4S_7 and P_4S_{10} lose terminal sulphur in the gase phase. The Raman spectrum of sulphur obscures the Raman spectra of remaining phosphorus sulphur species. The melt spectra of both these compounds are identical with the solid state spectra, although the dark colour of the melts suggests that some terminal sulphur is already dissociating. The spectra of P_4S_3 and P_4S_{10} are assigned in terms of the solid state symmetry.

ALTHOUGH many compounds of phosphorus and sulphur have been reported, only four discrete crystalline compounds have been established, *viz*, P_4S_3, P_4S_5, P_4S_7, and P_4S_{10}. The structures in the solid state have been determined by *X*-ray diffraction [1-7] and are given in the Figure. Since all the structures are based on a tetrahedron of phosphorus atoms, P_4 is shown for comparison. Electron diffraction studies on P_4S_3 are not inconsistent with the same structure in the gas phase [8,9] while ^{31}P

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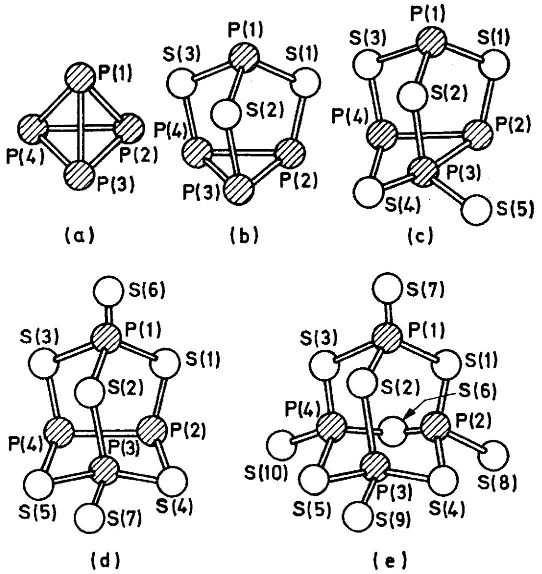

The structures of the phosphorus sulphides
(a) P_4, (b) P_4S_3, (c) P_4S_5, (d) P_4S_7, (e) P_4S_{10}

n.m.r. studies on P_4S_3 and P_4S_{10} in carbon disulphide solution [10] are consistent with the same structures in solution. However, vibrational spectroscopy is the only technique for structure investigation which is readily applicable to solids, solutions, liquids, and gases. Since vibrational studies in the literature are far from complete,[11-14] we have studied, and now report, the Raman spectra of the solid, liquid, and gaseous phosphorus sulphides and the i.r. spectra of the solids.

EXPERIMENTAL

Commercial samples of P_4S_7 and crystalline P_4S_{10} were sublimed *in vacuo* prior to use. A commercial sample of P_4S_3 was recrystallised from carbon disulphide. P_4S_5 was synthesised from P_4S_3 and sulphur in carbon disulphide solution, with a trace of iodine as catalyst, and was recrystallised prior to use.

I.r. spectra were recorded using Beckman IR-11 and Perkin-Elmer 225 spectrometers.

Raman spectra of solids were recorded on a Cary 81 spectrometer fitted with a spectra physics 125 He/Ne laser operated at 632·8 nm. Raman spectra of melts and gases were obtained using a Spex 1401 double monochromator coupled with a Spectra Physics 165 or 140 Ar^+ laser operated at 574·5 nm, a Spectra Physics 125 He/Ne laser operated at 632·8 nm, or a CRL 52 mixed-gas laser operated at 647·1 nm.

For gas-phase experiments, samples were sublimed *in vacuo* into silica ampoules and sealed off *in vacuo*

For liquid-state experiments, samples were melted under a stream of nitrogen, dried by passage through a molecular sieve, then filtered directly into cells suitable for Raman studies and sealed off.

RESULTS AND DISCUSSION

The observed spectra of the four compounds are given in Tables 1—4. P_4S_3 is the only compound for which the spectra are the same in all three phases, almost certainly due to the absence of terminal sulphur atoms in this compound. The four compounds are discussed separately.

TABLE 1

I.r. and Raman spectra of P_4S_3*

Symmetry species	I.r.		Raman				Assignment
	Nujol mull	KBr disc	gas (550 °C)	melt (250 °C)	CS_2 solution	solid	
e				142vw dp		145vw	ν_{10}
a_1		184s		187vw p?		187w	ν_4
e	222s	218s	221w dp	218w dp	223w dp	220 227 } m	ν_9
e	285m	286m	292m dp	287m dp	291m dp	288m	ν_8
e	341w	339w	347m dp	339m dp	343m dp	343 347 } s	ν_7
		390vw				373vw	Impurity
a_1	423s	414s	420w p	420w p	423w p	422m	ν_3
a_1	440vs	438vs	446vs p	440vs p	444vs p	443vs	ν_2
a_1 (+*e*?)	484m	488m	480w p?	483w p?	490w p?	489m	$\nu_1 + \nu_6$
						599vw	446 + 142
						626vw	446 + 187
						690vw	347 + 347
						766w	420 + 347
						819w	480 + 327
						946vw	480 + 480
Laser line for Raman (nm)			514·5	Various	632·8	Various	

* (For all Tables) all wavenumbers in cm^{-1}. w, weak; m, medium; s, strong; v, very; p, polarised; dp, depolarised; ?, uncertain, sh, shoulder.

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Tetraphosphorus Trisulphide.—The observed spectra are given in Table 1 together with the proposed assignment. The Raman spectra of all three phases, and of solutions, are very similar, and all except one of the observed bands has a counterpart in the i.r. region.

The structure, as determined by *X*-ray diffraction for P_4S_3 [1-3] has C_{3v} symmetry. The 15 normal modes transform as 4 a_1 modes, 1 a_2 mode, and 5 e modes. The a_2 mode is inactive in both the i.r. and Raman. The a_1 and e modes are both Raman and i.r. active, and the a_1 modes are polarised in the Raman.

In the gas-phase, melt, and solution Raman spectra, the two bands at 446 and 420 cm^{-1} are clearly polarised, while 3 bands, at 347, 292, and 221 cm^{-1} are clearly depolarised in all 3 spectra. From the melt spectrum, the weak band at 142 cm^{-1} appears to be depolarised, while the weak band at 187 cm^{-1} appears to be polarised. One a_1 and one e band still remain to be located, and only one further band is observed—which is clearly a fundamental—at 480 cm^{-1}. The state of polarisation of this band is very difficult to determine in all the relevant spectra, but in general it appears slightly polarised, suggesting that it is the remaining a_1 band. The last e band is not located. The bands at 373 cm^{-1} in the solid-state Raman spectrum and 390 cm^{-1} in the solid-state i.r. spectrum are of variable intensity and are probably due to an impurity. There are 3 P–P bonds and 6 P–S bonds which would be expected to give 3 a_1 and 3 e bands between 300 and 500 cm^{-1} so the appearance of 3 a_1 and one e bands in this region is extremely unlikely. The remaining, unlocated e band almost certainly lies in this region. It is possibly coincident with the a_1 band at 480 cm^{-1}, thus explaining why the state of polarisation of this band is so difficult to determine. In a cage molecule such as this, the redundancies in the angle co-ordinates are complicated, so that a normal co-ordinate analysis in terms of internal co-ordinates is difficult. There are 12 angles in the molecule which transform as 3 a_1, 1 a_2, and 4 e modes. In the angle bending region below 300 cm^{-1} 1 a_1 and 3 e modes are located. The a_2 mode is inactive. For the 21 internal co-ordinates given there are 6 redundancies, 2 a_1 and 2 e.

A factor group analysis of P_4S_3 space group *Pnmb* (D_{2h}^{16}) and site symmetry C_s, with four molecules per unit cell, shows that each gas phase a_1 band should give rise to two Raman-active and two i.r.-active bands in the solid-state spectrum. Each gas-phase e band should give rise to three i.r.-active and four Raman-active bands and one inactive band, and in addition there should be two extra Raman- and i.r.-active bands arising from the inactive a_2 mode.

The bands at 343 and 220 cm^{-1} are clearly split into two bands in the solid-state Raman spectrum and in addition have shoulders indicating a third band. This provides additional evidence that they correspond to e vibrational modes. The band at 288 cm^{-1} also has slight shoulders on both sides, suggesting that this is also an e mode.

The spectra show similarities to those previously recorded [11,12] but the assignment is different. The band at 290 cm^{-1} previously classed as an a_1 mode is depolarised in all three relevant spectra, and is therefore reassigned as an e mode. No trace was found of the band at 87 cm^{-1}, previously classed as an a_1 mode, or the band at 154 cm^{-1}, previously classed as an e mode, in the Raman spectrum, but new bands at 187 and 142 cm^{-1}, were observed in the Raman spectra of the solid and the liquid.

TABLE 2

I.r. and Raman spectra of P_4S_5*

	Solid-state i.r.		Solid-state Raman laser line 632·8 nm	Liquid-state Raman 647·1 nm (300 °C)
Assignment	This work (Nujol mull)	Ref. 12 (AgBr disc)		
P_4S_6?				110ms
ν_{21}			114m	
ν_{20}	125vw		122m	
P_4S_6?				130m
ν_{19}	134w		135m	
ν_{18} + P_4S_6?			180ms	180vs
ν_{17}	188m		187s	
P_4S_6?				197m
ν_{16} + P_4S_7	212m		211m	210m
ν_{15} + P_4S_7 + P_4S_3	226m		227m	226s
ν_{14}	244vw		239m 244m	
P_4S_6?				259vw
P_4S_6?				265vw
P_4S_3				286m
P_4S_7				298m
ν_{13}	302w		302ms	
ν_{12} + P_4S_7	336vw		332m	336ms
P_4S_3				347s
P_4S_6?				370s
ν_{11}	378m	377s	379sh	
ν_{10}	388s	387vw	386vs	
ν_9	401w		400ms	
ν_8	412sh		410s	
ν_7 + P_4S_3	418s	420sh	420sh	417ms
ν_6	434s	435s	430m	
P_4S_3				439vs
ν_5	452s	455m	452w	
P_4S_3				485w
ν_4	490m	493?vw	490sh	
ν_3	498sh	498?vw	498m	498w
P_4S_7				515vw
ν_2	525s	529m	524w	
ν_1	670vs 676sh	667sh 677vs	666w	

It seems clear that the 'bird-cage' structure of solid P_4S_3 is retained in the liquid and gaseous states.

Tetraphosphorus Pentasulphide.—P_4S_5 exists only in the solid state. The Raman and i.r. spectra of the solid are given in Table 2 together with a previous i.r. study.[12] The Raman spectrum of molten P_4S_5 is also given from which it is clear that the compound disproportionates in the melt to P_4S_3, P_4S_7, and further species which were not identified. This could be the non-stoicheiometric phase prepared by Rodley and Wilkins [15] from melts in the composition range P_4S_5 to $P_4S_{6\cdot9}$. The phase has been shown by *X*-ray diffraction to have the same

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[15] G. A. Rodley and C. J. Wilkins, *J. Inorg. Nuclear Chem.*, 1960, **13**, 231.

structure as P_4S_7 with some terminal sulphur atoms missing.[16] The approximate composition is $P_4S_{6\cdot5}$.

The P_4S_5 molecule has no symmetry at all, so all the 21 vibrational modes will be both Raman- and i.r.-active. There are 19 bands which appear in both the solid-state Raman and i.r. spectra. P_4S_5, space group $P2_1$, contains 2 molecules per unit-cell of site-symmetry C_1, so that each band in the solid-state spectrum should be a doublet. There is only one P–S terminal bond so that only one band would be predicted in the P–S terminal stretching region above 650 cm^{-1}. The extra shoulder in the i.r. spectrum is almost certainly due to correlation splitting. There are 10 P–S and P–P bonds which would give 10 bands in the stretching region. There are 10 bands in the region 350 to 550 cm^{-1} which can be identified as the P–P and P–S stretching region. Once again the structure is a cage molecule, giving complex redundancies in the angle-bending co-ordinates. Below 350 cm^{-1} there are 12 bands in the solid-state Raman spectrum, of which one is assigned as due to correlation splitting.

Tetraphosphorus Heptasulphide.—The Raman spectra of solid, liquid, and gaseous P_4S_7 and the i.r. spectrum of the solid are given in Table 3. The spectrum of the melt was of very poor quality, due to the intense brown colour so that no polarisation measurements were possible. It is likely that the brown colour is due to dissociation of terminal sulphur atoms. Molten sulphur shows a gradual colour change from yellow at the melting point of 113 °C through reddish brown to almost black at the boiling point of 444 °C; similar difficulties have been experienced in obtaining the Raman spectrum of liquid sulphur above 250 °C.[17] The colour change for liquid sulphur has been ascribed to at least two different causes in a recent paper on the subject.[18] The absorption edge shows a monotonous shift towards the red of 23·6 cm^{-1}/°C between 114 and 700 °C—the boiling point of liquid sulphur at 10 atm—at an optical density of 0·6. Between 114 and 250 °C this appears to be primarily due to absorption by thermally populated excited vibrational levels of the S_8 ring and also to absorption by polymers. Above this temperature, the colour change is mainly caused by new absorption peaks assigned to S_3 and S_4 species.

TABLE 3

I.r. and Raman spectrum of P_4S_7*

I.r. solid (Nujol mull)	Raman (laser line 647·1 nm)		
	solid	melt (310 °C)	gas (600 °C)
	125sh		
	128sh		
	137s	136vs	
	153w		148vvs dp
	189s		182w dp
	217s	210m	
	232s	226vs	226w dp
	238m		
	248m		
	303s	298m	305s dp
	320w		
	346vs	336vs	366m p
403m	400s	396m	395m p
	426w		
435m	437m	439m	445s p
	444s		
	453sh		
475s		470vw	
	484m		495w p
521s	525vw	515vw	
540s	546vw		555m dp
			621s p
665vs		666w	
675sh	675m		
683sh	685m	686m	696s dp

The similar effects observed in molten P_4S_7 and also in molten P_4S_{10} are probably due to the formation of sulphur by dissociation of terminal atoms. Support for this theory comes from the existence of such sulphur-deficient species as P_4S_6 [15] and P_4S_9.[19] Alternatively the effect could be due to fragmentation of the phosphorus sulphide cages to give smaller, highly absorbing species, as occurs with S_8. Before the spectra are totally extinguished (*ca.* 320 °C) no new Raman bands are evident, indicating that the species causing total absorption are only present in low concentration.

In contrast, the gas-phase Raman spectrum of P_4S_7 bears no resemblance to the solid-state spectrum. The strongest band in the spectrum at 148 cm^{-1} corresponds to the strongest band in the gas-phase spectrum of P_4S_{10}. However, P_4S_{10} does not go into the gas phase as discrete P_4S_{10} molecules (see below). Another strong band at 445 cm^{-1} corresponds to the strongest band in the gas-phase spectrum of P_4S_3 (Table 1). Many of the other bands can be correlated with the spectrum of sulphur at this temperature.[20] It seems reasonable to suggest that in the gas phase, P_4S_7 disproportionates to give P_4S_3 and P_4S_{10}, which itself dissociates giving sulphur.

In the absence of polarisation data, no assignment of the solid-state spectrum was attempted.

Tetraphosphorus Decasulphide.—The Raman spectra of solid, liquid, and gaseous P_4S_{10} and the i.r. spectrum of the solid are given in Table 4. The liquid- and gas-phase spectra were difficult to record because of the intense brown colour which developed in the melt and persisted into the gas phase. The Raman spectrum of the liquid was eventually recorded using a horizontal cell at right angles to both incident and scattered light, a 90° collection system (Spex Instruments Ltd.) and a laser line at 647·1 nm from a CRL 52 mixed-gas laser. The quality of the spectrum was not very good because of the high percentage of the laser light which was absorbed by the sample. The melt spectrum showed many similarities with the solid-state spectrum, but the gas-phase spectrum was completely different. The Raman spectrum of the condensed gas was identical with

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[17] A. T. Ward, *J. Phys. Chem.*, 1968, **72**, 4133.

[18] B. Meyer, T. V. Ommen, and D. Jensen, *J. Phys. Chem.*, 1971, **75**, 912.

[19] M. Meisel and H. Grunze, *Z. anorg. Chem.*, 1969, **366**, 152.

[20] K. K. Yee, R. F. Barrow, and A. Rogstad, *J.C.S. Faraday II*, 1972, **68**, 1808.

the original solid-state spectrum. Vapour-density measurements[21] have previously suggested that the compound decomposes in the gas phase, and our results confirm this. The decomposition is reversible. Apart from a very strong band at 148 cm^{-1} the Raman spectrum of P_4S_{10} in the gas phase corresponds precisely to the Raman spectrum of sulphur vapour at the same temperature.[20]

TABLE 4

I.r and Raman spectra of P_4S_{10}

		Raman (laser line 647·1 nm)		
T_d Species	I.r. solid	solid	melt 310 °C	gas 550 °C
e		112sh		
		117		
		123s		
t_2	132sh	128sh	126vs dp	
	138m	135sh		
				148s dp
a_1	162vw	162m	162m p	
	189w	191sh		
t_2	192sh	195vvs	198s dp	198m p
	205sh	204sh		
	260sh			
t_2	264m			
	267sh	272s	266s dp	
t_2? or		305 variable	304s dp	
impurity				310s dp
sulphur				367m p
2 × 162		325vw		
sulphur	377m	378 variable	381s p	
a_1	398w	395m	406s p	398m p
		408w		
162 + 266	426vvw	427vvw		
		437vvw		
		459vvw		452w p
198 + 266	467vvw			
		527w		
t_2	533vs	533sh		
		540w		
e?	564w	567vvw		561m dp
	588vvw	581vvw		
sulphur				612w p
	644w	641w		
		665vvw		670m p?
t_2	690vs	688sh		
		695m	707w dp	692m p?
a_1	718vw	718ms	716w p	
	758vw	753w		
567 + 198		771vvw		
533 + 266		789vvw		
2 × 406		814vw		
718 + 162		871vw		
688 + 126		907vvw		
567 + 406		969vvw		
		1053		
2 × 533		1065vvw		

The free molecule symmetry of P_4S_{10} is T_d. There are 36 vibrational modes which transform as 3 a_1 modes, 3 e modes, 3 t_1 modes, and 6 t_2 modes. The t_2 modes are both i.r.- and Raman-active while the a_1 and e modes are only Raman-active. The t_1 modes are inactive in both the i.r. and Raman. The 3 a_1 modes should be completely polarised in the Raman.

The melt spectrum shows 4 polarised bands and 5 depolarised bands. The polarised band at 381 cm^{-1} occurs in most of the spectra of the phosphorus sulphides and is probably due to an impurity species not yet identified. The band is of variable intensity. The other 3 polarised bands at 162, 406, and 716 cm^{-1} are assigned as the 3 a_1 modes. Unfortunately, the poor quality of the spectrum prevented a search for weaker depolarised bands

P_4S_{10} crystallises as triclinic crystals, space group $P\bar{1}$ (C_i^1) with two molecules per unit cell. The molecules have site symmetry C_1 and therefore each a_1 mode in the gas phase Raman spectrum should give one Raman- and one i.r.-active band in the solid-state spectra, each e mode should give two Raman- and two i.r.-active bands, and each t_1 or t_2 mode should give three Raman- and three i.r.-active bands. The solid-state spectra show many instances of this splitting, and indeed it is an aid to assignment. The group of five bands between 112 and 135 cm^{-1} in the solid-state Raman spectrum are classed as one e and one t_2 mode. There are two bands in the i.r. spectrum in this region which are considered part of the t_2 mode. In the region of 198 cm^{-1} corresponding to a strong, depolarised band in the melt spectrum, there are three bands in the solid-state Raman spectrum and three in the solid-state i.r. spectrum. This is also classified as a t_2 mode, as is the triplet of bands *ca.* 266 cm^{-1} in the solid-state i.r. spectrum, corresponding to one strong band in the solid-state Raman spectrum, and a strong depolarised band in the melt Raman spectrum.

For the free molecule, only t_2 modes should be i.r. active, so that the strongest bands in the i.r. spectrum are expected to correspond to t_2 vibrations. There are two very strong bands at 533 and 690 cm^{-1}, both of which correspond to three much weaker bands in the solid-state Raman spectrum. The depolarised band at 707 cm^{-1} in the melt Raman spectrum probably also corresponds to the band at 690 cm^{-1} in the solid-state i.r. spectrum. There remains a strong depolarised band in the melt Raman spectrum corresponding to a band of variable intensity in the solid-state Raman spectrum. This might be the remaining t_2 mode but is more probably due to an impurity. Two of the e vibrations are not located on this data. Two of the e vibrations in P_4O_{10} have also not been located,[22] and the indications are that they are very weak for these molecules. An approximate normal co-ordinate calculation using a simple valence force-field indicated that one of the missing e fundamentals should be below 150 cm^{-1}, while the other should be in the region of 530 cm^{-1}. Any weak bands below 150 cm^{-1} would almost certainly be obscured by the strong t_2 band in this region. The weak bands at 567 and 581 cm^{-1} in the solid-state spectra probably correspond to one of the missing e fundamentals.

The data are consistent with essentially the same structure for P_4S_{10} in the solid state and in the melt, although the intense brown colour of the melt indicates some dissociation of terminal sulphur. In the gas

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[21] A. H. Cowley, *J. Chem. Educ.*, 1964, **41**, 530.

[22] A. C. Chapman, *Spectrochim. Acta*, 1968, **24***A*, 1687.

phase, this dissociation becomes so serious that the Raman spectrum of gaseous P_4S_{10} is totally obscured by that of sulphur.

CONCLUSION

P_4S_3 is the only one of the 4 crystalline phosphorus sulphides whose structure remains unchanged into the gas phase. P_4S_7 and P_4S_{10} apparently melt without serious decomposition, although the brown colour suggests some loss of sulphur. Both lose sulphur in the gas phase to such an extent that the Raman spectrum of sulphur is all that can be identified. P_4S_5 decomposes in the melt to P_4S_3, P_4S_7, and at least one further species.

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