Gas-phase Raman Spectroscopy of Phosphorus, Arsenic, and Saturated Sulphur Vapours

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Summary The gas-phase Raman spectra of P_4, As_4, P_2, and As_2 are recorded and compared with literature values for P_2 and As_2 derived from electronic spectroscopy, and for sulphur, the gas-phase Raman spectra of S_8 and S_6 are obtained, together with a polarized band at 237 cm.$^{-1}$ which is probably due to S_7.

RAMAN spectroscopy is an important technique for studying equilibria in the gas-phase. We report the results of a preliminary study of the Raman spectra of phosphorus, arsenic, and sulphur vapours.

Electron diffraction data have shown that arsenic vapour, at approximately 800°, consists mainly of tetrahedral As_4 molecules and a small quantity of As_2 molecules.[1,2] Similarly, phosphorus vapour consists of tetrahedral P_4 molecules, where the tendency to dissociate to P_2 molecules is not so pronounced.[1] At 1700° phosphorus vapour consists of nearly equal quantities of P_4 and P_2 molecules. The Raman spectra of solid, liquid, and gaseous phosphorus have been interpreted in terms of P_4 tetrahedra.[3]

We have now obtained the Raman spectra[‡] of phosphorus and arsenic vapours at temperatures up to 1000°. The results are consistent with the presence of P_4 and As_4 molecular tetrahedra together with small, but detectable, quantities of the diatomic species P_2 and As_2, respectively. The intensity of the Raman-active stretching mode of the diatomic molecule relative to the intensity of the stretching mode of the respective tetra-atomic molecule increases with temperature, in accordance with the tendency of the M_4 species to dissociate to the M_2 species at high temperatures.

For a tetrahedral molecule M_4, in which the metal atoms are equivalent, there are only three fundamentals of species a_1, e, and f_2. All three modes are Raman-active but only the f_2 mode is i.r. active. Two of these modes should occur as depolarised lines (e and f_2) and one as a totally polarised line (a_1) in the Raman spectra of the liquid or gas.

The Raman spectra of gaseous P_4 and As_4 are assigned as in Table 1 where the assignments in the case of P_4 follow those previously suggested.[3] Figures 1 and 2 show the gas-phase Raman spectra of phosphorus and arsenic vapours at 500° and 900°, respectively. It is interesting to apply the central force field approximation to P_4 and As_4, in which cross terms are assumed to be zero. The values of the metal–metal stretching force constants obtained by this approximation are $k_{PP} = 1{\cdot}67$ md./Å and $k_{AsAs} = 1{\cdot}27$ md./Å. One also predicts in this approximation that the ratio $\nu_1 : \nu_2 : \nu_3$ is $2 : \sqrt{2} : 1$. In practice we observe the ratios $1{\cdot}66 : 1{\cdot}28 : 1{\cdot}0$ for P_4 and $1{\cdot}70 : 1{\cdot}25 : 1{\cdot}0$ for As_4.

TABLE 1

The Raman spectra of gaseous phosphorus (P_4/P_2) *and arsenic* (As_4/As_2)

Phosphorus (500°)			Arsenic (900°)		
~807vvw	$\nu_2+\nu_3$	P_4			
775vvw[a,b]		P_2			
720vw (p)	$2\nu_3$	P_4			
			421vw (p)[a]		As_2
			400vvwsh (p)	$2\nu_3$	As_4
600s (p)	ν_1	P_4	340s (p)	ν_1	As_4
450m	ν_2	P_4	250m	ν_2	As_4
360wsh[c]	ν_3	P_4	200wsh[c]	ν_3	As_4
240vvw	$\nu_1 - \nu_3$	P_4	~40vvw	$\nu_2 - \nu_3$	As_4

[a] These bands became more intense with increasing temperature. [b] Observed only at higher temperatures (~1000°) and low pressures. [c] Position of central branch quoted.

Although the results on P_2 and As_2 obtained in this study may appear to be novel, it must be remembered that the

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[‡] The gas-phase Raman spectra of phosphorus, arsenic, and sulphur were recorded on a Spex Raman spectrometer using an argon ion laser (4880Å and 5145Å) with approximately 700mw power in each line. The gaseous samples were contained in silica-glass cells. The Raman spectrum of molten sulphur was recorded at 120° on a Cary 81 Raman spectrometer using a He/Ne laser (6328Å) of about 50mw power. The designs of the gas and melt cells and their respective furnaces were similar to those previously described (refs. 15, 16).

vibrational and rotational constants of many diatomic molecules have been known for many years from detailed analysis of their electronic spectra. Thus for P_2 and As_2, Herzberg recorded values of 775 and 427 cm.$^{-1}$, respectively[4] which may be compared with our gas-phase Raman results of 775 and 421 cm.$^{-1}$.

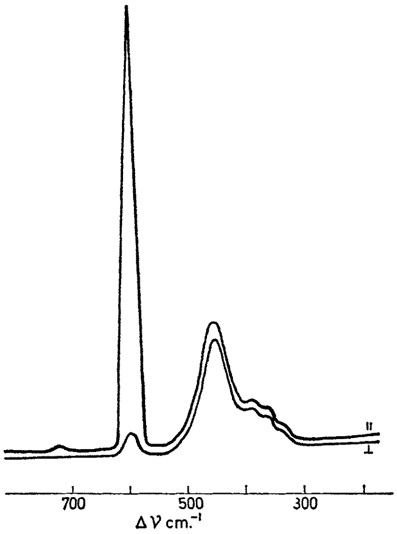

FIGURE 1. *The gas-phase Raman spectrum of phosphorus* (500°)

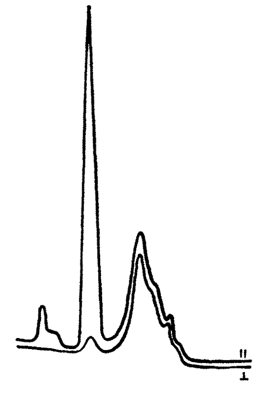

FIGURE 2. *The gas-phase Raman spectrum of arsenic* (900°)

The allotropy of sulphur is well known, as are the physical properties of solid, liquid, and gaseous sulphur.[5] The structure of the gaseous S_8 molecule has been determined by electron diffraction techniques[6] where the puckered, eight-membered ring occurring in crystalline rhombic sulphur[7,8] persists in the vapour. At low temperatures, in the saturated vapour above rhombic sulphur, the predominance of the S_8 species (over less polymeric species) is supported by mass spectroscopy and vapour pressure studies.[9,10] Both techniques can yield values of the relative abundances (at different pressures and temperatures) of the polymeric species S_n where $n > 1$.

Gas-phase Raman spectra may now be recorded as a routine technique, using laser excitation. A gas-phase Raman investigation thus provides a method of monitoring the changes in constitution which occur in sulphur vapour.

At low temperatures (< 200°) the Raman spectrum of saturated sulphur vapour (Table 2 and Figure 3) is almost entirely due to the species S_8. The gas-phase Raman data under these conditions are very similar to those obtained for sulphur as a melt at 120° (recorded in Table 2 for comparison), sulphur in solution in carbon disulphide,[11] and powdered rhombic sulphur[12] and show that the ring-shaped, puckered octagon of D_{4d} symmetry is retained in all phases.

TABLE 2

The Raman spectra of gaseous and molten sulphur

Assignment	Saturated vapour (200°)	Melt (120°)	S_6^{13} (solid or solution)
$S_8 + S_6$	483 (2·2) (p)	474 (5·1) (p)	476s (p)
S_6	451 (0·1)		451w
S_8	445 (0·1)	439 (0·5)	
S_6	269 (0·5) (p)		266m (p)
$S_8 + S_7$	237 (1·2) (p)	239 (0·4)	
S_8	218 (5·5) (p)	219 (8·4)	
S_6	201 (0·3)		204mw
S_8	151 (4·8)	153 (5·3)	
S_8	76 (0·7)	80 (1·0)	

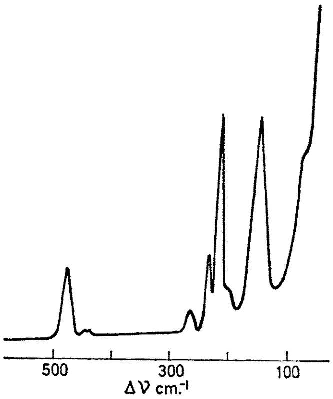

FIGURE 3. *The gas-phase Raman spectrum of saturated sulphur vapour* (ca. 200°)

At slightly higher temperatures (*ca.* 250°) some new bands appear in the Raman spectrum of saturated sulphur vapour, most of which can be satisfactorily assigned to S_6.[13] The strongest remaining, polarised band observed at 237 cm.$^{-1}$ (neglecting the bands assigned to S_8 and S_6) is probably characteristic of S_7 which is expected to have appreciable concentration[9] under the above experimental conditions. As no high-frequency bands were observed, which would be characteristic of terminal S–S stretching modes, the species S_7 may exist in the vapour as a ring, rather than a chain. The three polarised bands at 218, 237, and 269 cm.$^{-1}$ may all be associated with a ring bending or crinkling mode of the species S_8, S_7, and S_6, respectively, in which the rise to higher frequency is in the order expected for decreasing ring size and increasing ring strain.

In a series of higher temperature (250—1000°) and lower pressure experiments, where species less polymeric than S_8, S_7, and S_6 are expected to predominate, the gas-phase spectra were extremely complex and were more characteristic of resonance Raman and resonance fluorescence spectra, rather than Raman spectra. A full account and possible interpretations of these results will be published in detail.[14]

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