Variable-temperature Raman Spectra of Phosphorus(v) Chloride and Bromide deposited at 15 K

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Summary Variable-temperature (15 K—ambient) Raman spectra of solid PCl_5 and PBr_5 deposited at 15 K from the vapour phase are interpreted in terms of ionic and covalent species.

PHOSPHORUS PENTACHLORIDE exists in a variety of forms: (i) in the solid state as ionic species[1] (*e.g.*, phase II, the normal room-temperature modification, PCl_4^+ PCl_6^- and phase III, the so-called metastable form,[2] $2PCl_4^+PCl_6^-Cl^-$), (ii) in the gas phase as a trigonal-bipyramidal (t.b.p.) species[3,4] and (iii) in solution as either the t.b.p. form or an ionic species depending on the nature of the solvent.[5] The low-temperature infra-red spectrum of PCl_5 condensed from the vapour phase on to a cooled plate at 90 K is consistent with the t.b.p. species; on warming, this irreversibly isomeries to the phase II modification, PCl_4^+ PCl_6^-.[6] The Raman spectrum[7] of a similar low-temperature sample is also consistent with the t.b.p. form.

Phosphorus pentabromide is very different, existing as $PBr_4^+Br^-$ in the solid state,[8,9] but fully dissociated into PBr_3 and Br_2 in a wide variety of solvents.[10] No structural data have been reported on the nature of the vapour-phase species above solid PBr_5, but vapour-pressure measurements[11,12] suggest complete dissociation into PBr_3 and Br_2, at least above 305 K.

In this Communication we present the Raman spectrum of the sublimation products of PBr_5 and contrast this with the very different results obtained for PCl_5.

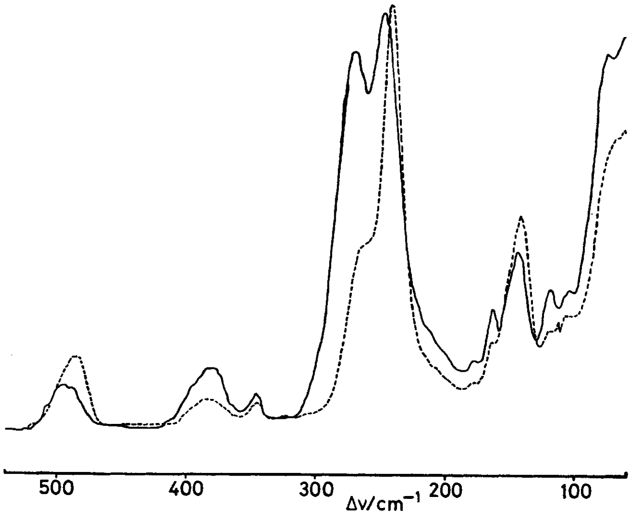
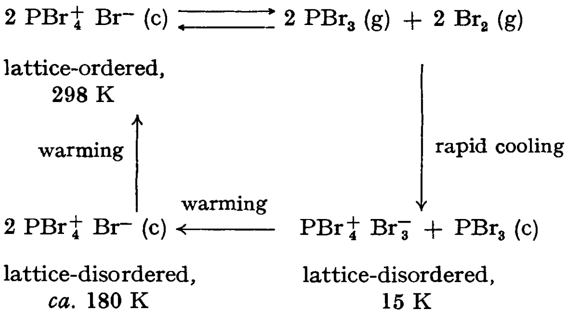


FIGURE 1. Raman spectra of PBr_5 deposited at 15 K (———) and warmed to 125 K (-----).

The Raman spectrum of a sample of PBr_5, sublimed from *ca.* 273 K on to a liquid helium-cooled (Air Products Displex system) copper plate at *ca.* 15 K is shown in Figure 1; wavenumbers are listed in the Table. This spectrum is not interpretable as resulting either from an intact t.b.p. PBr_5 molecule (analogous to the PCl_5 system) or from the simple dissociation products PBr_3 and Br_2. The presence of PBr_3 is confirmed by the positions and intensities of the bands at 119, 163, and 381 cm^{-1}, compared with those from an authentic sample deposited and maintained under the same conditions. However, the characteristic Br–Br stretching mode at 297 cm^{-1} associated with solid-phase elemental Br_2 is *not* observed. The strong band at 269 cm^{-1} is reasonably attributed to a polybromide species such as Br_3^-.[13] Other bands in the spectrum are clearly associated with the PBr_4^+ ion,[14] and we propose the formulation $PBr_4^+Br_3^-$ for this species (see Table for assignments). Comparison of the rather broad bands in this spectrum with those of an authentic sample of $PBr_4^+Br_3^-$[13,15] suggests that the low temperature, vapour-condensed sample consists of randomly orientated crystallites, consistent with the very rapid condensation from the gas phase. On slow warming from 15 K the bands attributed to Br_3^- (269 cm^{-1}) and PBr_3 (119, 163, and 381 cm^{-1}) gradually reduce in intensity (Figure 1) until only the bands due to PBr_4^+ remain. The disappearance of these bands is complete at *ca.* 180 K and presumably results from the solid-phase reaction of PBr_3 and Br_3^-, since vaporisation loss of bromine from the tribromide ion, or of PBr_3 from the solid is unlikely at these low temperatures. At *ca.* 230 K the remaining bands have sharpened to give the characteristic spectrum of polycrystalline PBr_4^+ Br^-, presumably owing to an ordering of the crystal lattice with increasing temperature (Scheme 1 and Figure 2). Preliminary attempts to isolate the vapour-phase products in a matrix of solid argon resulted only in the spectrum of the dissociation products PBr_3 and Br_2 being observed. Hence this work provides no evidence for the existence of the t.b.p. form of PBr_5, consistent with earlier measurements.[10–12]

TABLE. Raman wavenumbers/cm^{-1} of phosphorus pentabromide deposited at 15 K and warmed to 200 K and 230 K.

15 K (disordered PBr_4^+ Br_3^- and PBr_3)	200 K (disordered PBr_4^+ Br^-)	230 K (lattice-ordered PBr_4^+ Br^-)	Assignment
494 (w,br.)	477 (m,br.)	482 475 (w) 470	$\nu_3(t_2)$ PBr_4^+
381 (w,br.)			$\nu_1(a_1)$- and $\nu_3(e)$-PBr_3
346 (vw)			?
269 (vs)			$\nu_1(\Sigma_g^+)$ Br_3^-
247 (vs)	233 (s,br.)	229(vs)	$\nu_1(a_1)$ PBr_4^+
177 (vw)			?
163 (m-w)			$\nu_2(a_1)$ PBr_3
144 (m)	144 (s)	141 147 (m) 157	$\nu_4(t_2)$ PBr_4^+
119 (w)			$\nu_4(e)$ PBr_3
103 (vw)			?
74 (w)	73 (m)	73 (m)	$\nu_2(e)$ PBr_4^+



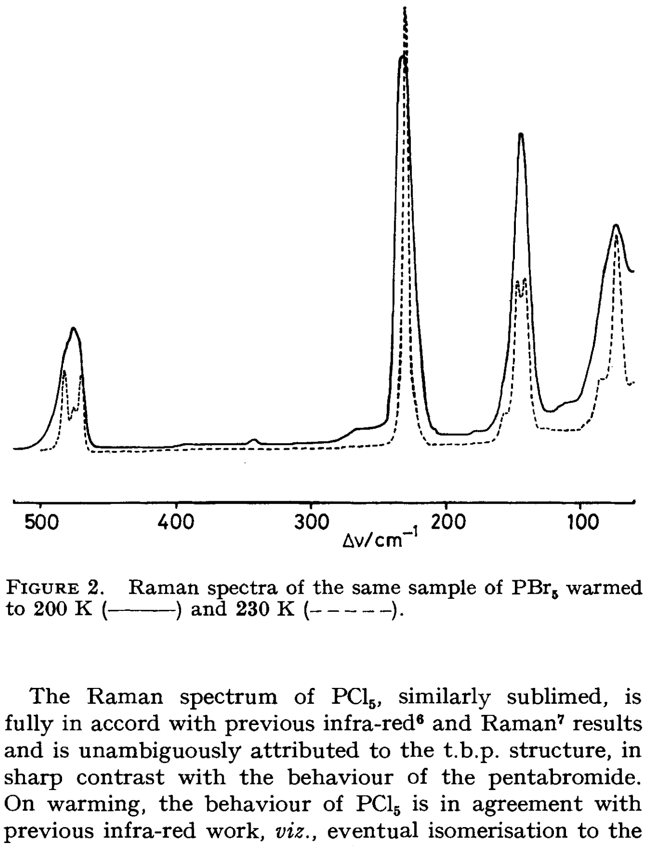
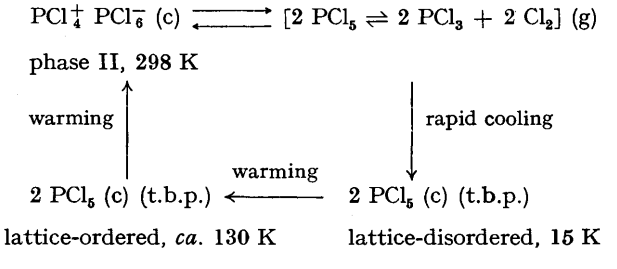


FIGURE 2. Raman spectra of the same sample of PBr_5 warmed to 200 K (———) and 230 K (– – – – –).

The Raman spectrum of PCl_5, similarly sublimed, is fully in accord with previous infra-red[6] and Raman[7] results and is unambiguously attributed to the t.b.p. structure, in sharp contrast with the behaviour of the pentabromide. On warming, the behaviour of PCl_5 is in agreement with previous infra-red work, *viz.*, eventual isomerisation to the ionic phase-II modification, PCl_4^+ PCl_6^-. However, as with the PBr_5 system, a distinct sharpening of the bands occurs at about 130 K, indicative of an ordering of the lattice from the disordered state resulting from the initial vapour deposition (Scheme 2). Interestingly, there is no evidence



for the phase-III modification which might have been expected to form under these conditions.[16] Apparently the production of this phase from vapour deposition procedures is critically dependent on, *inter alia*, apparatus geometry.

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