

894. *The Raman Spectrum and Vibrational Assignments of the Phosphorus Pentachloride Molecule.*

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The complete Raman spectra of the phosphorus pentachloride molecule in benzene and carbon tetrachloride solutions have been observed. The results, together with recent infrared absorption data, are used as the basis for a new assignment of fundamental frequencies.

INFRARED and Raman spectra of phosphorus pentachloride solutions were reported by Wilmshurst and Bernstein in 1957.¹ Taking earlier work into account, they suggested a vibrational assignment, but this seems doubtful in view of subsequent results.

The phosphorus pentachloride molecule is trigonal bipyramidal with the two axial bonds slightly longer than the three equatorial bonds.² The point group is D_{3h} and thus the number of fundamental frequencies is eight; six are Raman-active ($2a_1' + 3e' + e''$) and five are infrared-active ($2a_2'' + 3e'$). Wilmshurst and Bernstein, working with solutions which admittedly contained impurities, observed more frequencies, some of which they assigned to fundamentals of phosphorus pentachloride and others to overtones or combinations. Very recently Beattie and Webster³ reported infrared spectra of phosphorus pentachloride solutions, making due allowance for small amounts of phosphorus oxychloride present. Their measurements with benzene and carbon disulphide as solvents extended to 250 cm.^{-1} (*i.e.*, lower than in previous work) and showed only four bands due to phosphorus pentachloride: 274m, 301m, 441vs, and 578vs cm.^{-1} . All four are likely to be fundamentals of the phosphorus pentachloride molecule. The fifth infrared-active fundamental doubtless lies below the experimental range.

It was suggested that the conclusions of Wilmshurst and Bernstein¹ might have been impaired by bands due to impurities, and our observations on the Raman spectra of phosphorus pentachloride in solutions support this. We find that solutions which have been in contact with moisture can show, in addition, the complete Raman spectrum of phosphorus oxychloride.⁴ However, solutions carefully prepared under anhydrous conditions in a vacuum system show no trace of the phosphorus oxychloride spectrum and give the following six frequencies: 100m (depolarised), 261w (depol.), 281m (depol.), 370vw (?), 395vs (highly pol.), 581w (depol.) cm.^{-1} . These probably constitute the complete Raman spectrum of the phosphorus pentachloride molecule.

Taken together with recent infrared findings of Beattie and Webster,³ our results appear to decide all eight of the fundamental frequencies of phosphorus pentachloride and to make possible a straightforward assignment on the basis of the D_{3h} selection rules. Two of the frequencies (441 and 301 cm.^{-1}) are found only in infrared absorption and so must be assigned to the a_2'' class (ν_3 and ν_4). Three (395, 370, and 261 cm.^{-1}) are observed only in the Raman spectrum; the first of these is polarised and so must be assigned to $\nu_1(a_1')$ and the last is depolarised and so must be $\nu_8(e'')$. It follows that 370 cm.^{-1} must be $\nu_2(a_1')$ (see below). Of the remaining three fundamentals found in the Raman spectrum (which must belong to class e'), 581 and 281 cm.^{-1} both have counterparts in the infrared (at 578 and 274 cm.^{-1} , respectively), as is required by the selection rules. (The observed infrared value of 274 cm.^{-1} may be somewhat low owing to the presence of a little phosphorus oxychloride, which has a band at 267 cm.^{-1} .) The infrared counterpart of the last Raman frequency (100 cm.^{-1}) lies well below the experimental range. For four fundamentals (ν_2 , ν_4 , ν_6 , and ν_8) the new assignment here presented (see Table) differs from that of Wilmshurst and Bernstein.¹

¹ Wilmshurst and Bernstein, *J. Chem. Phys.*, 1957, **27**, 661.

² L. E. Sutton *et al.*, "Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.* No. 11, 1958.

³ Beattie and Webster, *J.*, 1963, **38**.

⁴ Ziomek and Piotrowski, *J. Chem. Phys.*, 1961, **34**, 1087.

Assignments of fundamental frequencies of phosphorus pentachloride.

Class	Activity	Vibrations and approx. descriptions of modes †	Frequencies (cm. ⁻¹)	
			Present assignment	Previous assignment ¹
<i>a</i> ₁ '	Raman, pol.	ν_1 PCl ₂ Cl ₃ sym. stretch. (in phase)	395	394
		ν_2 PCl ₂ Cl ₃ sym. stretch. (out of phase)	370	394
<i>a</i> ₂ ''	Infrared	ν_3 PCl ₂ antisym. stretch.	441	440
		ν_4 PCl ₃ out-of-plane bending	301	(176) *
<i>e</i> '	Raman, depol., i.r.	ν_5 PCl ₃ stretching	581	585
		ν_6 PCl ₂ bending	281	338
<i>e</i> ''	Raman, depol.	ν_7 PCl ₃ in-plane bending	100	100
		ν_8 Cl'PCl bending	261	280

* Calc., not observed. † Cl and Cl' refer to equatorial and axial chlorine atoms, respectively.

Worthy of special comment is our assignment of the weak Raman line of uncertain polarisation (370 cm.⁻¹) to ν_2 of class *a*₁'. A similar situation is encountered in the Raman spectrum of antimony pentachloride, our own observations of which confirm earlier findings.⁵ As with phosphorus pentachloride, the spectrum of antimony pentachloride contains only one definitely polarised line (355 vs cm.⁻¹, obviously assignable to ν_1). Again, as with phosphorus pentachloride, there is another line of lower frequency (305 cm.⁻¹) and considerably lower intensity, which is not appreciably polarised, but which has, nevertheless, been assigned^{5,6} to ν_2 . This is supported by the fact that there is no corresponding infrared band.^{3,6}

Wilmshurst and Bernstein¹ took the view that ν_1 and ν_2 of phosphorus pentachloride are accidentally equal, and assigned 394 cm.⁻¹ to both of them. They rejected 370 cm.⁻¹ as a possibility for ν_2 , no doubt on account of its low intensity and apparent lack of polarisation. Our suggestion that 370 cm.⁻¹ be assigned to ν_2 , despite these characteristics, receives support from simple considerations based on the Wolkenstein bond-polarisability theory. The force constant of an axial bond will differ only slightly from that of an equatorial bond, and the interaction between them will be small. Hence ν_1 and ν_2 would be expected to be rather close together, and both normal modes of vibration will involve stretchings of all five bonds. In one of these modes all the bonds will stretch in phase ("breathing" mode) and this will lead to a large value of the mean-value invariant, *a*', of the derived polarisability tensor of the molecule and a small value of the anisotropy γ' . Consequently the degree of depolarisation, ρ , which is equal to $6(\gamma')^2/[45(a')^2 + 7(\gamma')^2]$, will be much lower than 6/7, *i.e.*, the Raman line will be highly polarised, as is observed for ν_1 . In the other totally symmetric mode (ν_2) the stretching of the equatorial bonds will be out of phase with the stretching of the axial bonds, and this will lead to a relatively small value of *a*' (possibly near zero) and a larger value of γ' . Both of these factors will contribute to making ρ relatively high, *i.e.*, the ν_2 Raman line will be only slightly polarised, which may well be inappreciable by the qualitative experimental method used. Rough calculations show that the intensity, which is proportional to $45(a')^2 + 13(\gamma')^2$, will be much lower for ν_2 than for ν_1 , since for the latter the $45(a')^2$ term will make a dominant contribution; this conclusion also agrees with experimental finding.

EXPERIMENTAL

Preparation of Solutions.—All operations were carried out in a vacuum system with exclusion of moisture. Phosphorus pentachloride was purified and sublimed into a trap, and pure benzene or carbon tetrachloride was distilled on to it. The trap, with attached Raman tube, was then sealed off. After the solid had dissolved, the solution was poured over into the Raman tube without opening the system to the air. The concentration of phosphorus pentachloride in the benzene solution studied was ~M; the substance is less soluble in carbon tetrachloride at room temperature, and so a solution saturated at about 75° was used and kept hot during the Raman exposures.

⁵ Siebert, *Z. anorg. Chem.*, 1951, **265**, 303.⁶ Wilmshurst, *J. Mol. Spectroscopy*, 1960, **5**, 343.

Raman Spectra.—The spectra were excited by the Hg 4358 Å line from a Toronto-type mercury arc. Primary lines of lower wavelength were filtered out by a 16% solution of *m*-dinitrobenzene in benzene. The spectra were photographed with a two-prism Hilger E 612 spectrograph, with Kodak special scientific plates of type Oa, G. The phosphorus pentachloride line of lowest frequency (100 cm.^{-1}) was observed with carbon tetrachloride as solvent; with benzene as solvent it was obscured by the "winging" of the Rayleigh line. Frequencies were measured with an iron arc as standard and are probably correct within $\pm 2 \text{ cm.}^{-1}$. The "present" Raman values in the Table are the means of concordant measurements for benzene and carbon tetrachloride solutions. Qualitative information on the states of polarisation of the Raman lines was obtained by using polarised incident light, with suitably oriented Polaroid cylinders around the sample tube.

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