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Raman Intensities and the Force Field of Phosphorus Pentafluoride[1]

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Raman intensities have been measured for the totally symmetric modes of PF_5 and used to calculate P–F bond polarizability derivatives. The latter are highly sensitive to the degree of interaction of axial and equatorial P–F stretching. Consequently they can be used to constrain the general valence force field. Together with Levin's[8] previous analysis of Coriolis constants and vibrational amplitudes, the intensity data allow estimates of the P–F stretching force constants. The primary constants are $f_{eq} = 5.17$ and $f_{ax} = 4.59$, and the interaction constants are $f_{eqeq} = 0.98$, $f_{axax} = 0.50$, and $f_{axeq} = 0.37$, all in mdyn/Å.

Few molecules have been studied more thoroughly than phosphorus pentafluoride which occupies a central position for testing theories of "non-octet" bonding and of intramolecular dynamics.[2-4] Although the vibrational spectrum has been well characterized,[5-7] and the molecule has been subjected to several approximate normal coordinate analyses,[7-14] there remains an important indeterminacy in the force field which has prevented reliable evaluation of the P-F stretching force constants. Because there are two kinds of P-F bonds, equatorial and axial, in the trigonal-bipyramidal molecule, there are two symmetric stretching vibrations. Each has an associated symmetry force constant, but in addition the two vibrations are connected by an interaction force constant. Only by arbitrarily fixing the interaction constant (often at zero) can the two stretching force constants be calculated from the observed frequencies.

Independent data are needed to determine the interaction force constant. Levin[8] tried to use for this purpose vibrational amplitudes determined by electron diffraction[15] but found that the calculated values are insensitive to the choice of force constant. Woodward long ago pointed out that Raman intensities can provide additional data to restrict force fields,[16] but intensity measurements have rarely been applied for this purpose. In the case of PF_5 Selig, *et al.*,[9] have noted that the very low polarized Raman intensity of the lower energy symmetric stretching mode (generally assigned to axial P-F stretching) is consistent with the high degree of mixing suggested by their orbital valency force-field calculation. Here we show that the observed Raman intensities can be used to determine the degree of mixing with the aid of bond polarizability theory. With this new information the principal stretching force constants of PF_5 can be evaluated.

Experimental Section

The laser Raman spectrometer and its intensity calibration have been described elsewhere.[17] The 5308-Å line of an Ar-Kr mixed gas laser was used for excitation. Phosphorus pentafluoride (Matheson Gas Co.) and methane, which served as an internal standard, were metered into a dry 5-cm cylindrical spectrophotometer cell equipped with a vacuum stopcock. The laser beam was passed through the flat windows and multipassed with a spherical mirror, and the scattered light was collected through the cylinder wall. Intensities were corrected for instrument response and converted to normal mode polarizability derivatives, $\bar{\alpha}'_Q$, in the usual fashion,[17] using the known absolute value of $\bar{\alpha}'_Q$ for the ν_1 mode of methane.[18]

Results and Discussion

Relative intensities, R, depolarization ratios, ρ_1, and normal mode polarizability derivatives $\bar{\alpha}'_Q \equiv \partial\bar{\alpha}/\partial Q$ are given in Table I for the two $A_1{}'$ vibrations of PF_5. These values are estimated to be accurate to within ±10%.

Bond polarizability derivatives, $\bar{\alpha}'_{u_j} \equiv \partial\bar{\alpha}/\partial_{u_j}$, where u_j is a bond of the jth set, can be calculated *via* the transformation

$$\bar{\alpha}'_{Q_p} = \sum_j \sqrt{N_j} l_{jp} \alpha'_{u_j} \qquad (1)$$

where N_j is the number of internal coordinates in the symmetry coordinate S_j, and l_{jp} is the eigenvector element connecting S_j with the normal coordinate Q_p. There are two equations (1), for the two A_1 modes, and two unknowns, $\bar{\alpha}'_{ax}$ and $\bar{\alpha}'_{eq}$, the bond polarizability derivatives for axial and equatorial P-F bonds, respectively. Since the Raman intensity is proportional to the square of the normal mode polarizability derivative, there is a sign ambiguity in the measured $\bar{\alpha}'_Q$ values. The magnitude of $\bar{\alpha}'_{Q_2}$ is so small, however, that the choice of sign is of no significant consequence to the magnitudes of the bond polarizability derivatives. In the ensuing analysis positive values are assumed for both $\bar{\alpha}'_{Q_1}$ and $\bar{\alpha}'_{Q_2}$.

The eigenvectors are obtained by solving the vibrational secular equation. Only the A_1 block is needed, involving 2×2 G and F matrices.[19] The diagonal symmetry force constants F_{11} and F_{22} correspond to equatorial and axial P-F stretching, respectively. The off-diagonal term is F_{12} =

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Table I

Mode	Frequency, cm^{-1}	R^a	$\rho_1{}^b$	$\bar{\alpha}'_Q$
ν_1	818	0.426	0.037	0.59
ν_2	652	0.043	0.63	0.066

[a] R = molar intensity, relative to the ν_1 band of CH_4. [b] ρ_1 = depolarization ratio for linearly polarized light.

$\sqrt{6}f_{\mathrm{axeq}}$, where f_{axeq} is the axial-equatorial interaction force constant. There is, of course, no way to calculate these three force constants uniquely from the two observed frequencies. Rather, the secular equation provides a family of solutions[20] which can be represented by the circle shown in Figure 1. If we consider eigenvectors arising from the whole family of solutions, they provide a corresponding family of bond polarizability derivatives, *via* eq 1, which are plotted in Figure 2. The curve shows that $\bar{\alpha}'_{\mathrm{P-F_{eq}}} = 1.32$ at $F_{12} = 0$, and decreases, slowly at first and then more rapidly, as F_{12} increases in either a positive or negative direction. On the other hand, $\bar{\alpha}'_{\mathrm{P-F_{ax}}}$ is very close to zero at $F_{12} = 0$ but increases rapidly with increasing F_{12} and in the same direction.

Since $\bar{\alpha}'_{\mathrm{P-F_{ax}}}$ is highly sensitive to the assumed value of F_{12}, the Raman intensities cannot be used to evaluate the axial P-F bond order in PF_5. Rather, the intensities can be used to constrain the value of F_{12} and provide the extra information needed to determine the force field, as discussed in the introduction.

A connection between bond polarizability derivatives and bond orders is given by the δ function potential equation of Long and Plane [21]

$$\bar{\alpha}'_u = \frac{2}{3}\frac{g\sigma}{za_0}\left(\frac{n}{2}\right)r^3 \qquad (2)$$

where r is the bond distance, n is the number of electrons in the bond, σ is the Pauling covalent character, z is the effective nuclear charge (taken as the atomic number minus the number of inner shell electrons), and g is the δ function strength (taken as the square root of the Pauling electronegativity). For heteronuclear bonds the geometric mean of g/z is taken. While based on a highly simplified model of the chemical bond, this equation gives good results for a number of molecules.[21] For others the calculated values of $\bar{\alpha}'_u$ are substantially in error, but consistent results are obtained for related kinds of bonds.[17] The equation is particularly appropriate for evaluating the ratio of $\bar{\alpha}'_u$'s for different bonds connecting the same elements in a single molecule, as in PF_5. In this ratio all the parameters cancel except the bond order and the bond distance, *viz.*

$$\bar{\alpha}'_{\mathrm{P-F_{ax}}}/\bar{\alpha}'_{\mathrm{P-F_{eq}}} = (n_{\mathrm{ax}}/n_{\mathrm{eq}})(r_{\mathrm{eq}}/r_{\mathrm{ax}})^3 \qquad (3)$$

From electron diffraction data, $r_{\mathrm{eq}} = 1.534$ Å and $r_{\mathrm{ax}} = 1.577$ Å.

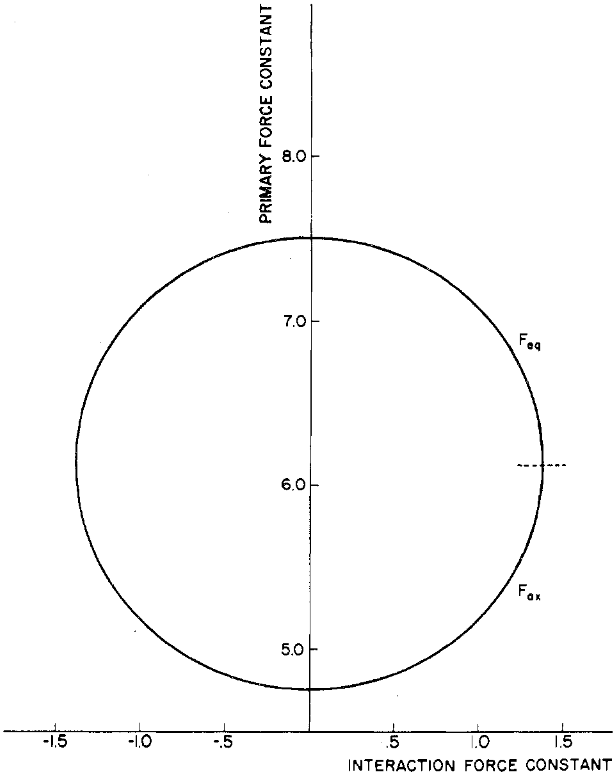

Figure 1. Family of solutions to the A_1 block of the secular equation for PF_5

$$\begin{vmatrix} G_{11}F_{11} + G_{12}F_{21} - \lambda & G_{11}F_{12} + G_{12}F_{22} \\ G_{22}F_{21} + G_{21}F_{11} & G_{21}F_{12} + G_{22}F_{22} - \lambda \end{vmatrix} = 0$$

where $G_{11} = G_{22} = 1/m_{\mathrm{F}} = 0.05263$; $G_{12} = G_{21} = 0$; $\lambda = 0.58851 \cdot (\nu/1000)^2$; $\nu_1 = 818\ \mathrm{cm}^{-1}$; $\nu_2 = 652\ \mathrm{cm}^{-1}$.

The bonding in PF_5 is the subject of enduring controversy.[2] The three equatorial bonds can be accommodated by conventional sp^2 hybrid orbitals on phosphorus, giving unit bond order. The phosphorus $3p_x$ orbital is then available for bonding to the axial fluorine atoms. Since there are two axial P-F bonds, one has a choice between three-center bonding, with a bond order of 0.5, or hybridization with the $3d_{z^2}$ orbital. Full hybridization would allow a bond order of 1.0 while partial utilization of the $3d_{z^2}$ orbital would result in a bond order between 0.5 and 1.0. In the free phosphorus atoms, the 3d orbitals lie at much higher energy than the 3p orbitals, but the gap is expected to diminish appreciably through polarization by the strongly electronegative fluorine atoms. Molecular orbital calculations[22,23] suggest, however, that the involvement of d orbitals is unimportant in any of the filled molecular orbitals of PF_5.

On the basis of these arguments $n_{\mathrm{ax}}/n_{\mathrm{eq}}$ can range from 1.0 to 0.5 whence (eq 3) $\bar{\alpha}'_{\mathrm{P-F_{ax}}}/\bar{\alpha}'_{\mathrm{P-F_{eq}}}$ should lie between 0.92 and 0.46, with the lower end of the range more probable. This interval is marked by dashed lines in Figure 2. The values of $\bar{\alpha}'_{\mathrm{P-F_{eq}}}$ and $\bar{\alpha}'_{\mathrm{P-F_{ax}}}$ at the extremes of this range are, respectively, 1.08 and 1.00 ($n_{\mathrm{ax}}/n_{\mathrm{eq}} = 1.0$) and 1.24 and 0.57 Å^2 ($n_{\mathrm{ax}}/n_{\mathrm{eq}} = 0.5$). The corresponding range for F_{12} is 1.08-0.86 mdyn/Å, a variation of only 20%. A further 10% reduction in F_{12} from 0.86 mdyn/Å would require that $\bar{\alpha}'_{\mathrm{P-F_{ax}}}/\bar{\alpha}'_{\mathrm{P-F_{eq}}} = 0.24$, 50% lower than the value corresponding to a bond order ratio of 0.5. This seems a generous allowance for the uncertainty associated with the use of the δ function equation.

This equation requires that bond polarizability derivatives be positive. Because of the sign ambiguity inherent in the determination of $\bar{\alpha}'_Q$, there is in general no way to test this point experimentally. Consideration of atomic and molecular polarizabilities has led to the conclusion that, at least for C-C and C-H bonds, $\bar{\alpha}'_Q$ should indeed be positive.[24]

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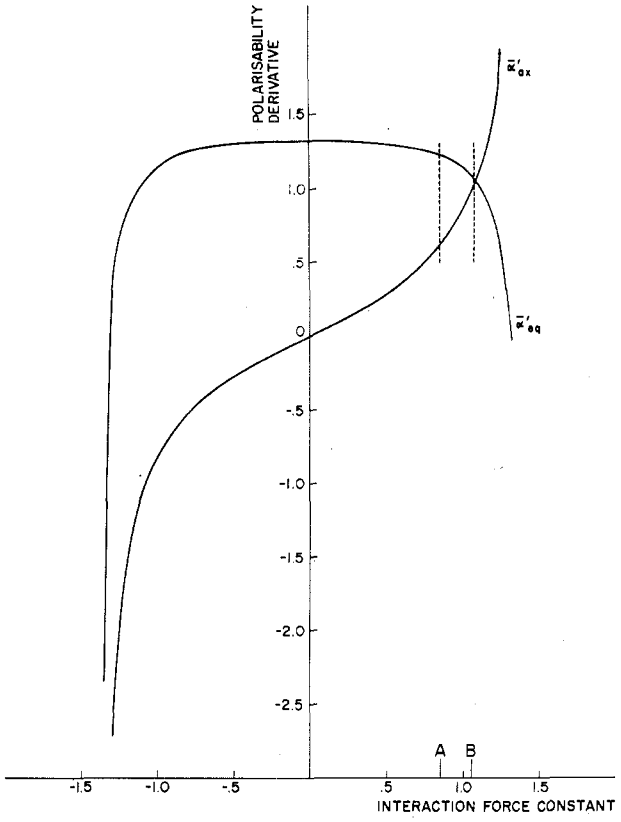

Figure 2. Bond polarizability derivatives for axial ($\bar{\alpha}'_{ax}$) and equatorial ($\bar{\alpha}'_{eq}$) P–F bonds, calculated from the Raman intensities, as a function of the interaction force constant F_{12}. The interval (A–B) marked by dotted lines is the range of F_{12} corresponding to the expected $\bar{\alpha}'_{ax}/\bar{\alpha}'_{eq}$ for an axial–equatorial bond order ratio ranging from 0.5 to 1.0 (see text).

Instances have been reported, however, where, for a given molecule, bond polarizability derivatives of opposite sign are required if they are to have physically reasonable magnitudes.[25,26] In the present case it seems intuitively reasonable that the two P–F bond polarizability derivatives should have the same sign. Moreover, if they had opposite signs, then the required interaction constant, F_{12}, would be negative (see Figure 2) which would be inconsistent with analogous force constants for related molecules, as discussed below.

From the above considerations, F_{12} can confidently be set within 10% of 0.9 mdyn/Å, corresponding to $f_{axeq} = 0.37 \pm 0.04$ mdyn/Å. This value compares satisfactorily with the cis stretch–stretch interaction constant, 0.35, 0.42, and 0.38 mdyn/Å, respectively, of the second row octahedral hexafluorides[27] SF_6, PF_6^-, and SiF_6^{2-}. In the octahedral molecules the cis-interaction force constant, which involves orthogonally oriented M–F bonds, as does f_{axeq} in PF_5, is uniquely determined by the difference in two fundamental frequencies, ν_1 and ν_2.

We are now in a position to evaluate the valence stretching force constants of PF_5. A value of 0.9 mdyn/Å for F_{12} fixes F_{11} and F_{22} at 7.15 and 5.09 mdyn/Å, respectively. In terms of valence constants we have

$$F_{11} = f_{eq} + 2f_{eqeq} = 7.15$$
$$F_{22} = f_{ax} + f_{axax} = 5.09$$

where f_{eq} and f_{ax} are the principal stretching constants for equatorial and axial bonds, respectively, f_{eqeq} is the interaction constant between equatorial bonds, and f_{axax} is the interaction constant between axial bonds. Levin[8] estimated the two other required symmetry force constants.

$$F_{33} = f_{ax} - f_{axax} = 4.10 \text{ mdyn/Å}$$
$$F_{55} = f_{eq} - f_{eqeq} = 4.19 \text{ mdyn/Å}$$

Combination of these equations gives (mdyn/Å)

$$f_{eq} = 5.17 \qquad f_{eqeq} = 0.98$$
$$f_{ax} = 4.59 \qquad f_{axax} = 0.50$$

The estimated 10% uncertainty for F_{12} introduces a ~0.1 mdyn/Å uncertainty into F_{11} and F_{12}, which in turn contributes an uncertainty of ~0.03 mdyn/Å into f_{eq} and f_{eqeq} and ~0.05 mdyn/Å into f_{ax} and f_{axax}. The value of F_{55} is well determined through the use of Coriolis constants, and Levin gives an error estimate of only 5%. Unfortunately, the reliability of F_{33} is difficult to assess. Vibrational amplitudes were found to be insensitive to the assumed value of the A_2' interaction constant, F_{34}. A minimum value of F_{34}, 0.75 mdyn, was required to obtain real solutions to the A_2' secular equation, and this value was assumed in reporting F_{33}.[8]

From the known bond distances one can use Badger's rule,[28] as modified[29] by Herschbach and Laurie,[30] to predict $f_{eq}/f_{ax} = 1.17$, which is in good accord with the experimental ratio, 1.12. The interaction constants f_{axeq} and f_{axax} have reasonable values, but f_{eqeq} is unexpectedly high. Since this interaction constant is calculated with well-determined symmetry force constants, F_{11} and F_{55}, its value is considered to be reliable.

Registry No. PF_5, 7647-19-0.

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