Pseudorotation Pathway and Quadratic Force Field for PF$_5$, by *Ab Initio* Calculations

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Extensive *ab initio* calculations have yielded a detailed mechanism for Berry pseudorotation in PF$_5$, for which a barrier of 16 ± 2 kJ mol^{-1} is obtained, and a complete quadratic force field which gives an excellent account of observed vibrational frequencies.

As the prototype five-co-ordinate species, phosphorus pentafluoride occupies a position of pivotal importance in the understanding of fluxional molecules and their dynamics. The Berry pseudorotation (or inversion) process,[1] which rapidly interconverts axial and equatorial fluorine atoms in the trigonal bipyramid, has never been directly observed, and the energy barrier to pseudorotation is not known experimentally with any precision. In this communication, an extensive series of *ab initio* molecular orbital calculations are reported, which have established the mechanism by which pseudorotation occurs. The complete quadratic force field of PF$_5$, which previously was unknown, has also been calculated, since it cannot be established from the experimental data available.[2,3]

The program Gaussian 80[4] was used, with a basis of better than double-zeta quality (11s7p1d/6s4p1d on P, 9s5p/4s3p on F). Geometries were optimized and forces obtained by gradient techniques. Calculated parameters for the equilibrium D_{3h} geometry are indistinguishable from experimental values:[5] P–F$_{ax}$ 157.5 pm (expt. r_g 157.7 $\pm$ 0.5 pm[5]), P–F$_{eq}$ 153.7 pm (r_g 153.4 $\pm$ 0.5 pm[5]).

During pseudorotation, two F–P–F angles increase from 90° to 120°, while two others decrease from 120° to 90°, as shown in Figure 1. The minimum energy pathway for

inversion was determined by fixing the angle F^1–P–F^4 at seven equally spaced values between 90 and 120°, then optimizing the four remaining geometrical parameters under the constraint of C_{2v} symmetry. Results are presented in Table 1 and Figure 1. Changes in bond lengths and angles are coupled, so as to minimize repulsive interactions between F atoms. The closest F· · ·F separation is found to be only 4.3 pm less than the equilibrium F$_{ax}$· · ·F$_{eq}$ distance. Also included in Table 1 are the optimized parameters for the C_{4v} square pyramidal structure. Its geometry and relative energy interpolate smoothly into the C_{2v} pathway, thereby establishing that the pseudorotation transition state has C_{4v} symmetry. This has hitherto always been assumed, rather than demonstrated; it is not necessary.

An energy barrier to pseudorotation of 20.1 kJ mol^{-1} is obtained at the SCF level. Correlation energies were estimated by second-order Møller–Plesset perturbation theory at the SCF D_{3h} and C_{4v} geometries, lowering the barrier to 17.1 kJ mol^{-1}. Similar small reductions in barrier height have been found in correlated studies of PH$_5$[6] and SiH$_5^-$.[7] An earlier SCF calculation on PF$_5$,[8] using a smaller basis than here, produced a barrier of 20.2 kJ mol^{-1}; assuming the geometries of ref. 8, addition of polarization functions to the fluorine
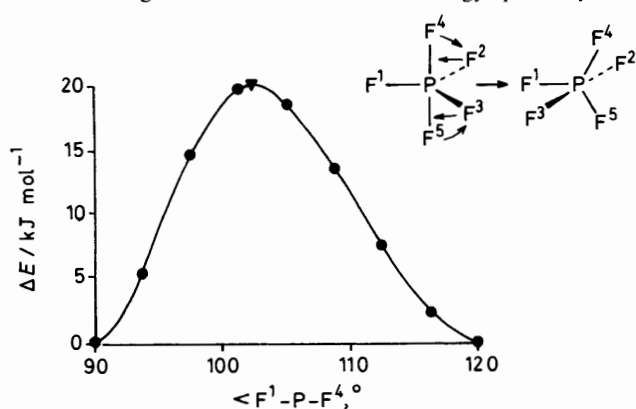

Figure 1. Minimum energy pathway for pseudorotation in PF$_5$; ●: points of C_{2v} symmetry, apart from initial and final D_{3h} geometries; ▲: optimised C_{4v} geometry, shown to be the transition state.

Table 1. *Ab initio* minimum energy pathway for PF$_5$ pseudorotation.[a]

∠F^1–P–F^4	∠F^1–P–F^2	r(P–F^1)	r(P–F^2)	r(P–F^4)	ΔE[b]
90.0	120.0	153.74	153.74	157.50	0.0
93.75	115.93	152.65	154.36	157.45	5.19
97.5	110.02	152.11	155.28	157.18	14.68
101.25	103.86	152.08	156.05	156.48	19.83
102.33[c]	102.33	152.14	156.25	156.25	20.08
105.0	99.18	152.30	156.63	155.72	18.74
108.75	95.82	152.62	157.03	155.05	13.75
112.5	93.21	152.98	157.30	154.46	7.47
116.25	91.45	153.39	157.43	154.02	2.20
120.0	90.0	153.74	157.50	153.74	0.0

[a] Bond lengths in pm, converged to 0.03 pm, angles in degrees, converged to 0.03°. [b] Energy above the D_{3h} equilibrium geometry, in kJ mol^{-1}. [c] Optimized under C_{4v} symmetry.

Table 2. *Ab initio* quadratic force field, with calculated and observed vibrational wavenumbers, for PF_5.[a]

				$v_{calc.}$/cm⁻¹	$v_{obs.}$[b]/cm⁻¹
A_1'	6.462[c]			812	816
	1.250	5.703[c]		653	648
A_2''	5.176[c]			943	947
	1.399	2.643		603	575
E'	6.278[c]			1023	1024
	1.169	2.434		554	533
	−0.083	−0.604	0.458	171	174
E''	2.185			533	520

[a] Symmetry co-ordinates are those of ref. 14, but with S_6 and S_7 interchanged. S_1, S_2, S_3, and S_5 are stretching co-ordinates, with S_1 and S_5 involving the equatorial bonds. S_4 and S_8 are symmetric and antisymmetric out-of-plane motions of the equatorial fluorines. S_6 and S_7 are axial and equatorial bending motions. Units are aJ Å⁻ᵐ rad ⁻ⁿ, for m stretching and n bending co-ordinates. [b] From ref. 15. [c] Value reported here has been scaled by 0.85.

basis reduces the barrier to 18.9 kJ mol⁻¹.[9] By combining the effects of electron correlation and basis enlargement, a final barrier of 16 ± 2 kJ mol⁻¹ is obtained, where the uncertainty allows for residual limitations in the calculations. Earlier experimental values are 16.4,[10] 12.7 ± 0.9,[11] and 14.3 kJ mol⁻¹.[12]

Quadratic force constants calculated for PF_5 are presented in Table 2. The diagonal stretching force constants F_{11}, F_{22}, F_{33}, and F_{55} have been scaled, since parameters of this type are systematically overestimated at the Hartree–Fock level. To establish the most appropriate scale factor, stretching force constants were also calculated, using exactly analogous procedures, for the two molecules most closely related to PF_5 whose force fields are known experimentally. Factors of 0.88 and 0.82 were obtained for PF_3 and SF_6, and the average of these, 0.85, was adopted for PF_5. No scaling has been applied to the bending force constants or to any of the off-diagonal elements. Calculated harmonic vibrational frequencies are compared in Table 2 with experimental results. The agreement is most satisfactory, with no gross discrepancies and an average deviation of only 1.5%.

A pleasing correlation is found between valence force constants (N m⁻¹) and bond lengths (pm) in PF_5 and PF_3: $P–F_{eq}$, 634 and 153.4; P–F in PF_3, 550 and 157.0; $P–F_{ax}$, 544 and 157.7. There is much greater resistance to axial than equatorial bending in PF_5, shown by F_{66} being substantially larger than F_{77}. In the initial stages of pseudorotation, the 90° angle F^1–P–F^4 therefore opens up more slowly than the 120°

angle F^1–P–F^2 closes, as shown in Table 1. Coupling of these two angular changes is governed by the strikingly large off-diagonal element F_{67}. Since this is negative, an in-phase combination of axial and equatorial bending, the pseudorotation co-ordinate, requires less energy than either separately. Behaviour of this type is expected if non-bonded repulsions are important in PF_5, and is also predicted by the VSEPR approach.[13] The particularly small discrepancy between calculated and observed frequencies for v_7, which can be regarded as the first phase of pseudorotation, suggests that the mechanism reported here for pseudorotation is essentially accurate.

Vibrational amplitudes calculated for PF_5 from the theoretical force field match the experimental values[5] to within the latter's uncertainties, but agreement between calculated and observed[3] Coriolis coupling constants is no better than moderate. Efforts to use all the experimental data to improve the *ab initio* force field have, so far, failed to give satisfactory results. In addition to potential problems caused by hot bands, Fermi and/or second-order Coriolis resonances may perturb the vibrational band contours from which the experimental coupling constants were derived, as there are several near-degeneracies involving the E' vibrational levels.

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