

*Original Investigations***Equilibrium Structure and Harmonic Force Field of the Known PH_3 and the Unknown PH_5 ***

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The equilibrium geometries and harmonic force fields of PH_3 and PH_5 are calculated in an *ab initio* way including electron correlation. The results for PH_3 are in very good agreement with experimental values, whereas those for PH_5 have to be regarded as predictions. We find for PH_5 in its equilibrium D_{3h} structure $r_{\text{ax}} = 1.47 \text{ \AA}$, $r_{\text{eq}} = 1.42 \text{ \AA}$ and the harmonic vibration frequencies in Table 7 given under the heading "CEPA". The barrier for Berry inversion is 2 kcal/mol. The *ab initio* calculation of phosphoranes such as PH_5 not only requires the inclusion of polarization functions (*d* on P and *p* on H) but is also very sensitive to the choice of these polarization functions. This problem is taken care of by a detailed comparison of various basis sets. It is confirmed that a (10/6) basis for P in "double zeta contraction" is better balanced than a (12/9) basis in "double zeta contraction" and that the total energy is not a good criterion for the quality of a basis.

Key words: PH_3 , equilibrium structure of $\sim -\text{PH}_5$, equilibrium structure of $\sim -\text{PH}_3$, force field of $\sim -\text{PH}_5$, force field of $\sim -\text{PH}_3$, inversion barrier of \sim

1. Introduction

PH_5 is the prototype of the phosphoranes. However, it has, in contrast to many substituted compounds such as PF_5 , PH_2F_3 , $\text{P}(\text{C}_6\text{H}_5)_5$ or $\text{P}(\text{CH}_3)_4\text{OCH}_3$, so far not been observed experimentally. Several theoretical investigations of PH_5 have been published [1–5], but this molecule served mainly as a model compound for the known substituted species and the prediction of the properties of PH_5 have only played a minor role.

* Dedicated to Professor Hermann Hartmann on the occasion of his 65th birthday.

Previous studies of PH_5 have indicated [1–4] that the energy of the most stable structure of PH_5 lies 40–50 kcal/mole above the sum of the energies of $\text{PH}_3 + \text{H}_2$. Since the decomposition of PH_5 to $\text{PH}_3 + \text{H}_2$ is Woodward–Hoffmann allowed [2] (i.e. there is at least one symmetry allowed path for this decomposition) one might guess that the reaction $\text{PH}_5 \rightarrow \text{PH}_3 + \text{H}_2$ requires only a very small barrier, if at all (see however Refs. [5] and [6]), and that the failure to produce PH_5 experimentally might be due to the fact that it is not a stable molecule. The calculations on PH_5 published so far have led to the prediction of an equilibrium structure with D_{3h} symmetry [1–5]. However, this does not prove that this structure represents a local minimum of the potential hypersurface, since the energy has been minimized with certain symmetry restrictions. A definite statement about whether or not a molecular structure represents a local minimum of the potential hypersurface can only be made on the basis of the knowledge of the whole harmonic force field.

We have calculated this force field with a twofold aim, namely to prove that PH_5 exists and to give a guide to experimentalists to identify PH_5 via its vibrational spectrum. In order to give sufficiently reliable values for the harmonic force constants and vibration frequencies a good basis set including polarization functions had to be used and correlation effects had to be taken into account. We automatically got a refined geometry, since in previous studies (except Ref. [3]) not all geometrical parameters were optimized [1, 4] or the basis sets were too poor [5].

Complementary to the qualitative question whether or not PH_5 represents a local minimum of the potential hypersurface is that concerning the depth of this minimum, or equivalently the lowest barrier for the disintegration of the molecule. We have studied this problem in detail and found that it is a very delicate one. The results will be published separately [6]. We found that the lowest barrier for the decomposition of PH_5 into $\text{PH}_3 + \text{H}_2$ is roughly 40 kcal/mol, i.e. that PH_5 has a rather comfortable valley and should hence be a good metastable molecule. Other disintegration processes like $\text{PH}_5 \rightarrow \text{PH}_4 + \text{H}$ (possibly followed by $\text{PH}_4 + \text{H} \rightarrow \text{PH}_3 + \text{H}_2$) are hardly competitive, since PH_4 is, if at all, only slightly bound with respect to $\text{PH}_3 + \text{H}$ [7]. One can guess that the binding energy of PH_4 with respect to $\text{PH}_3 + \text{H}$ is at most 10 kcal/mol if it is not even unbound. Howell and Olsen [7] found from 4-31G SCF calculations that PH_4 is 13 kcal/mol higher in energy than $\text{PH}_3 + \text{H}$ and they claim that this result is not significantly changed by inclusion of d -functions. We have in fact performed an SCF calculation of PH_4 with polarization functions at Howell's geometry and found its energy 11 kcal/mole above the sum of the energies of PH_3 and H. We did not attempt a geometry optimization. Electron correlation may stabilize PH_4 somewhat with respect to $\text{PH}_3 + \text{H}$ since it stabilizes PH_5 with respect to $\text{PH}_3 + \text{H}_2$ by some 10 kcal/mol. From these data and those for PH_3 and PH_5 we conclude that $\text{PH}_4 + \text{H}$ lies at least 50–60 kcal/mol above PH_5 .

A two-step disintegration of PH_5 in which first an H^- is abstracted, that removes an H^+ before it leaves the field of PH_4^\ddagger seems, however, competitive [5] with the concerted H_2 abstraction [6].

The calculation of the force field of PH_3 on the same level of approximation as that

of PH_5 served mainly as a check of the accuracy of our approach, but it turned out that our calculations allow discrimination between two sets of harmonized vibration frequencies proposed in the literature.

The harmonic force field of PH_3 has been studied extensively. Based on the experimental vibrational spectrum of McConaghie and Nielsen [8] (see also Ref. [9]) several authors have attempted to extract the harmonic force field [10–15], which is a less trivial task than is usually believed. We shall comment on this in Sect. 4.

We are finally interested in the force field of PH_5 because it gives some additional insight into the chemical bond of this molecule and of phosphoranes in general, especially if one compares the force constants (and bond lengths) not only with those of PH_3 in its equilibrium configuration but also with planar PH_3 and with PH_4^+ , where different hybrids of P are supposed to participate in bonding.

2. Methods of Calculation and Basis Sets Used

The calculations reported are either of SCF type or with inclusion of the valence shell electron correlation in the IEPA-PNO, PNO-CI and CEPA-PNO schemes in a localized representation. These methods have been described elsewhere in detail [16–20]. All those PNO configurations were included that contributed more than 10^{-7} a.u. to the energy.

Several basis sets of different quality have been used. They are all constructed from Gaussian lobes as indicated in Ref. [21].

Basis *A* can be regarded as the standard basis of the present work. It consists of a (10*s*/6*p*) Huzinaga basis [22] for P in the double zeta quality contraction ($4,6 \times 1/3,3 \times 1$) augmented by a *d*-set with $\eta = 0.57$ and a 4*s* basis in the contraction (3,1) plus a *p*-set with $\eta = 0.65$ for H. This basis was essentially taken over from Ref. [4], except that in Ref. [4] the *d*-exponents for equatorial and axial *d*-AO's in PH_5 had been optimized independently which led to different values ($\eta = 0.925$ for equatorial, $\eta = 0.5$ for axial bonds). The η_d value 0.57 of basis *A* is optimum for PH_3 .

Basis *B* is the same as basis *A*, but with $\eta_d = 0.925$, i.e. the larger of the two values optimized previously for PH_5 [4].

Basis *C* is basis *A* plus an extra flat *s*-AO on H with $\eta = 0.03$.

Basis *D* is like basis *A*, but with two *d*-sets on P ($\eta = 0.30$ and $\eta = 0.85$) and no *p*-set on H.

Basis *E* was constructed according to the prescription of Shih *et al.* [23]. It is a (12/9) Veillard basis [24] for P in the contraction (6,2,1,1,1,1/4,2,1,2) plus two *d*-sets with $\eta = 0.85$ and $\eta = 0.30$ and a 5*s* Huzinaga basis in the contraction (4,1) scaled with $\eta^2 = 2$. Basis *E* has hence the same polarization functions as basis *D*. For the *s* and *p* part it is of double-zeta type contraction as e.g. basis *D* but constructed from a larger primitive basis. (In Ref. [23] a 5*s* basis of H different from that of Huzinaga was used.)

Basis *F* is based on the Huzinaga (12/9) set for P, but in a triple-zeta quality contraction ($5,7 \times 1/4,5 \times 1$), with a *d*-set ($\eta = 0.57$) and a 4*s*-basis for H in the

contraction (2,1,1) with a p -set ($\eta = 0.65$). The polarization functions are hence as in basis A .

Basis G is like basis F but with two d -sets on P ($\eta = 0.3$ and 1.0) instead of one and with an additional s -AO ($\eta = 0.03$) on H, and of course a p set on H ($\eta = 0.65$).

Geometry optimization and determination of force constants were based on multi-dimensional fits to a sufficient number of points, e.g. 15 points for the A_1 vibrations of PH_3 . Fits with different numbers of points and different degrees of the polynomial were compared in order to assess the convergence of the results. A full documentation is available on request.

3. Total Energies for Different Basis Sets and Their Analysis

When we realized that basis sets A and B (that differ only in the exponent of the d -AO on P) lead to significantly different equilibrium geometries for PH_5 and that in a recent paper of Shih *et al.* [23] (in the title of which the term “large AO basis” is explicitly used) again different geometries are reported, we decided to study this unexpected basis set dependence of the equilibrium geometry in more detail. To judge the quality of the geometry predictions one needs a criterion to judge basis sets.

The quality of a basis is usually discussed in terms of total energies. Looking at the SCF energies of PH_5 (Table 1) the “quality” of the basis increases in the order D, A, B, C, E, F, G . However, although B is better than A on the SCF-level, their order is inverted if one considers the CI energies. One might think that one should use two rather than one d -AO on P. However, comparison of basis sets A and B with D reveals that one d -set on P and one p -set on H leads to a much lower energy than two d -sets on P. Comparison of bases F and G also confirms that the second d -set has less influence on the energy than one might have suspected.

In order to compare basis sets with different s - p parts the total energy is no appropriate criterion since the larger s - p parts (12/9 *vs.* 10/6) mainly serve to approximate the intra-atomic cusps and have little effect on molecular properties. A better criterion of the quality is the “Hartree–Fock-binding energy”, i.e. the difference of the Hartree–Fock energy of the molecule and the sum of the corresponding energies of the constituent atoms.

One sees from Table 1 that in this sense the “small” basis sets A, B, C are of comparable quality as the “large” basis sets F and G , that D is somewhat poorer and E much poorer (it has a defect of ~ 0.03 a.u. ≈ 20 kcal/mol in the binding energy). The reason for this pooriness is twofold. On the one hand two d -sets on P are poorer than one P on d and one p on H. On the other hand the Veillard “contraction 8” [24] for P is rather unfortunate (it is in disagreement with Dunning’s rules [25]).

A complementary criterion of the quality is the correlation energy (either on CI or CEPA level). Here we see that the basis sets A, C and F are quite comparable, that B is slightly poorer and that D and E are much poorer. With basis D or E one misses more than 0.04 a.u. ≈ 25 kcal/mol of the correlation energy as compared to the other sets.

Table 1. Comparison of the calculations with different basis sets^a

Basis	$r_{ax}(r)^b$	$r_{eq}(\alpha)^b$	$-E_{SCF}$	$-E_{CI}$	$-E_{CEPA}$	$-\Delta E_{SCF}^c$	$-E_{CI}^{d,e}$	$-E_{CEPA}^{d,e}$	$t_{SCF}^{e,h}$	$t_{CI}^{e,i}$
PH ₅										
A	2.77	2.665	343.45794	343.64192	343.65667	0.33397	0.18398	0.19873	33	135
B	2.749	2.653	343.45820	343.63451	343.64778	0.33423	0.17631	0.18958		
C	2.77	2.665	343.45820	343.64262	343.65751	0.33423	0.18442	0.19931	47	210
D	2.78	2.68	343.43892	343.58197	343.59219	0.31495	0.14306	0.15328	14	25
E	2.80	2.70	343.51006	343.65677	343.66752	0.29888	0.14671	0.15746	26	20
E ^d	2.80	2.70	343.50301	343.65311	343.66428 ^a	0.29183	0.15010	0.16127	(5.7) ^j	(3.3) ^j
F	2.77	2.665	343.53341	343.72223	343.73775	0.32223	0.18883	0.20434	64	300
G ^o	2.77	2.665	343.54331	—	—	0.33313	—	—	120	—
PH ₃										
A	2.677	92.51°	342.39706	342.54489	342.55507	0.27164	0.14783	0.15801	27	68
F	2.677	92.51°	342.47596	342.62834	342.63926	0.26439	0.15238	0.16331	45	143
G ^o	2.677	92.51°	342.47962	342.64076	342.65360	0.26805	0.16144	0.17398	88	260
t	2.66	95.78°	342.46304	—	—	0.25147	—	—	—	—

^a All energies in a.u., all bond lengths in a_0 , computer times in minutes.

^b The geometries are close to the minimum structures (D_{3h} -symmetry) for the respective basis sets, either computed or guessed (for exact geometries see Table 2).

^c Is $E_{SCF}(PH_3) - E_{SCF}(P) - nE(H)$.

^d Only SCF calculations were performed with this basis.

^e Values from Ref. [26], with a (12/9) basis of P in the contraction (6, 2, 1, 1, 1/3, 3, 1, 1, 1) and $\eta(d_p) = 0.6$; $\eta(p_B) = 0.67$.

^f Total time on the INTERDATA8/32 minicomputer.

^g CI and CEPA calculation.

^h CPU times on an IBM 370-168 reported in Ref. [23].

ⁱ Values from Ref. [23], E_{CEPA} is rather "CI full estimate".

^j Integral evaluation plus SCF calculation.

We conclude that basis *A* is a good basis, but that basis *E* is, in spite of the lower total energy, only of medium quality. Our criteria of the quality of a basis set are in a way a quantification of the property to be well-balanced.

The computer time necessary for calculations with the different basis sets are also given in Table 1.

The energy of PH_5 lies above that of $\text{PH}_3 + \text{H}_2$. The following values were obtained for this energy's difference (in kcal/mol)

	SCF	CEPA
basis <i>A</i> :	43	39
basis <i>F</i> :	46	43
basis <i>G</i> :	42	

The CEPA value with basis *G* was not computed but it can be estimated to be ≈ 38 kcal/mol. This should be close to the exact value.

4. Equilibrium Geometries and Inversion Barrier

The geometrical parameters for the equilibrium structures of PH_3 and PH_5 are collected in Table 2.

For PH_3 we note good agreement between the present SCF results and those of a previous SCF study [26] with a comparable basis, while $r(\text{PH})$ from a CEPA calculation is much closer to the experimental $r(\text{PH})$. However, the experimental $r(\text{PH})$ is not known as accurately as one might think. Bartell and Hirst [27] in an

Table 2. Equilibrium geometry of PH_3 and PH_5^a

		Basis	SCF	CI	CEPA	exptl.	other theoretical			
PH_3	r	<i>A</i>	1.409	1.413	1.417	1.424 ^b	1.419 ^{c,o}	1.42 ^d	1.408	
	α	<i>A</i>	94.6	92.9	92.5	93.8			95.8 ^f	
PH_5 (D_{3h})	r_{ax}	<i>A</i>	1.471	1.468	1.471			1.485 ^e	1.48 ^b	1.55 ^l
		<i>B</i>	1.457	1.450	1.452			1.47 ^j	1.48 ^k	1.49 ^l
		<i>G</i>	1.473							
	r_{eq}	<i>A</i>	1.410	1.416	1.419			1.365 ^e	1.41 ^b	1.43 ^l
		<i>B</i>	1.401	1.405	1.409			1.41 ^j	1.43 ^k	1.44 ^l
		<i>G</i>	1.409							
PH_5 (C_{4v})	r_{ap}	<i>A</i>	1.392	1.398	1.395			1.39 ^j	1.41 ^k	1.41 ^l
	r_{bas}	<i>A</i>	1.445	1.451	1.447			1.44 ^j	1.46 ^k	1.47 ^l

^a Distances in Å, angles in degrees.

^b Ref. [33].

^c Ref. [32].

^d Ref. [8].

^e Ref. [27], estimated r_0 , all other experimental values are rather averaged over the zero point vibration.

^f Ref. [26], SCF.

^g Ref. [4], CEPA, not fully optimized.

^h Ref. [3], SCF.

ⁱ Ref. [7], SCF without polarization functions.

^j Ref. [23], SCF.

^k Ref. [23] "MRD-CI".

^l Ref. [23], "CI full estimate".

electron diffraction study report a r_0 of $1.437 \pm 0.004 \text{ \AA}$ and a root-mean square amplitude of the PH stretching vibration of $\pm 0.085 \text{ \AA}$. This r_0 involves an averaging over the zero point vibration and the authors extrapolate an equilibrium distance $r_e \approx 1.419 \text{ \AA}$ [27]. Microwave and IR results for $r(\text{PH})$ that represent rather r_z (in the Kuchitsu notation [28]) between 1.412 and 1.424 are quoted in Ref. [27], but the assumptions on which the extraction of r_z from the moments of inertia is based, are criticized and according to Ref. [27] the true r_z should rather be $\sim 1.43 \text{ \AA}$, i.e. $\approx 0.01 \text{ \AA}$ larger than r_e . If we accept the r_e of Ref. [27] as the experimental value the agreement with the CEPA value is excellent and confirms our observation [29, 30] that r_e from CEPA with double-zeta-plus-polarization type basis sets are accurate to within 0.003 \AA (see also Ref. [31]).

An experimental geometry of PH_5 is not known. In order to give a reliable prediction, rather severe intrinsic criteria have to be applied, especially since there is (unlike for PH_3) no good agreement between different theoretical results. The bond lengths reported by Howell [7] are much off all other values (r_{ax} is too large by 0.08 \AA) and this is obviously due to the absence of polarization functions in Howell's calculations. The too small r_{eq} of Ref. [4] is due to the fact that it was assumed to be equal to the bond length in planar PH_3 . This assumption, based on the idea that in both cases sp^2 hybridization is realized, turned out to be invalid. The too large r_{ax} of Ref. [4] is probably a consequence of the unrealistic r_{eq} .

It is somewhat intriguing that bases A and B , which differ only in $\eta(d_p)$, lead to rather different geometries. Although the considerations of Sect. 2 give more weight to basis A , we decided to do an additional geometry optimization with the very large basis G . The SCF geometry of basis A is confirmed, we are hence confident that the CEPA geometry of basis A is also reliable and the parameters for the equilibrium structure of PH_5 are:

$$r_{\text{ax}} = 1.47 \text{ \AA}, \quad r_{\text{eq}} = 1.42 \text{ \AA}.$$

The effect of electron correlation on the bond lengths is as expected for the "ordinary" bonds such as $r(\text{PH})$ in PH_3 and r_{eq} in PH_5 , namely to lengthen the bond by $\sim 0.01 \text{ \AA}$. The bond lengthening by correlation is related to the incorrect dissociation behaviour of covalent bonds in the SCF approximation. The axial bonds are to a large extent ionic and hence suffer less from defects of the SCF approach, and are consequently less affected by correlation.

(The very large correlation effect on the bond lengths in Ref. [23] is not confirmed by us.)

We have also optimized the geometry of PH_4^+ and found the following equilibrium distance: $r_e = 1.39 \text{ \AA}$.

For the geometry optimization of the C_{4v} structure of PH_5 , only basis A was used. The angle α was kept fixed at 100° , since pilot calculations and results from the literature confirm that the energy is very insensitive to small variations of α near 100° .

Table 3. Berry inversion barrier for PH₅ (in kcal/mol)

Basis	SCF	CI	CEPA
<i>A</i> ^a	2.79	2.13	1.94
<i>B</i> ^b	3.09	2.67	2.50
\bar{E} (Ref. [23])	2.45	1.17	0.87

^a Optimized geometries (see Table 2).

^b Referring to a compromise geometry ($r_{ap} = 1.403$ Å, $r_{bas} = 1.436$ Å), for the C_{4v} structure and a compromise geometry ($r_{eq} = 1.403$ Å, $r_{ax} = 1.455$ Å), for the D_{3h} structure.

The values of the Berry inversion barrier of PH₅ are given in Table 3. The rather large differences between the different approaches reported in Ref. [4] could not be reproduced. They were probably due to incomplete geometry optimizations. Electron correlation does lower the barrier, but we cannot confirm the reduction of the barrier to ≈ 1 kcal/mol found by Shih *et al.* [23].

5. The Force Field of PH₃

In Table 4 the computed force constants of PH₃ (basis *A*) are compared with experiment. We have used the convention that a force constant is equal to 1/2 times the (mixed) second derivative of the energy with respect to inner coordinates, with lengths measured in Å and angles in rad. However, we have tabulated rather the force constants with respect to symmetry coordinates, because those are obtained directly.

It is hard to make a meaningful statement concerning the agreement of theory and experiment since the "experimental" harmonic force constants scatter so much. While the CEPA values are close to their experimental counterparts for F_{11} , F_{22} , F_{33} and F_{44} (and better so than the SCF results), F_{12} and F_{34} seem to be completely arbitrary. In fact they have almost no influence on the frequencies and one can vary them considerably [11] and still reproduce the spectrum. On these grounds the theoretical values should be given more credit.

If one wants to compare theory and experiment one should rather do this on the level of the harmonized vibration frequencies.

This is done in Table 5. The only uncertainty of the experimental values lies in the harmonization procedure. The different sets of harmonized frequencies differ mainly in ν_3 . Our computed values are strongly in favour of the harmonization of Gamo [10], on which also the analysis of Duncan and Mills [13] is based, rather than that of De Alti *et al.* [14].

Table 4. Harmonic force constants of PH₃

	This paper SCF	CEPA	other theoretical ^a	from experiment e	f	g	h	i	j,k
A_1									
$F_{11} = f_r + 2f_{rr}^a$	3.748	3.557	3.49	3.455	3.4774	3.438	3.306	3.402	3.282
$F_{22} = f_a + 2f_{aa}^b$	0.785	0.690	0.74	0.659	0.6942	0.675	0.791	0.685	0.649
$F_{12} = f_{ra} + 2f_{ra}^c$	0.153	0.088	-0.29	-0.078	0.3306	-0.153	0.752	-0.284	-0.298
E									
$F_{3a} = f_r - f_{rr}^a$	3.575	3.553	3.76	3.356	3.2884	3.274	3.270	3.466	3.194
$F_{4a} = f_a - f_{aa}^b$	0.879	0.783	0.80	0.874	0.7668	0.761	0.791	0.757	0.867
$F_{34} = f_{ra} - f_{ra}^c$	-0.048	-0.036	0.12	0.022	0.1590	0.065	-0.014	-0.057	-0.539

^a In mdyn/Å.

^b In mdyn/rad.

^c In mdyn Å rad⁻².

^d Ref. [26].

^e Ref. [10].

^f Ref. [14].

^g Ref. [12].

^h Ref. [34].

ⁱ Ref. [13].

^j Ref. [11].

^k These authors offer 5 sets of force constants with F_{12} varying between 0 and 0.44, and F_{34} varying between 0 and -0.64, with rather small variations of the other constants; the values reproduced here correspond to the "most likely" set.

Table 5a. Harmonic vibration frequencies of PH₃

	This paper		Other theoret. ^a	Exptl. harmonized			Observed ^o
	SCF	CEPA		^b	^c	^d	
<i>A</i> ₁ ν_1	2547	2482	2462	2452	2448	2456	2322.9
ν_2	1136	1081	1114	1041	1045	1044	992.0
<i>E</i> ν_3	2501	2487	2560	2457	2390	2402	2327.7
ν_4	1241	1170	1256	1154	1153	1150	1122.4

^a Ref. [26]. ^b Ref. [10]. ^c Ref. [11]. ^d Ref. [14]. ^e Ref. [8].

Table 5b. Harmonic vibration frequencies of PD₃

	This paper		Other theoret.	Exptl. harmonized			Observed ^h
	SCF	CEPA		^b	^f	^g	
<i>A</i> ₁ ν_1	1823	1778	—	1761	1754	1760	1694
ν_2	829	788	—	756	763	759	730
<i>E</i> ν_2	1798	1788	—	1766	1730	(1720)	(1698) ^b
ν_4	885	834	—	822	819	822	806

^b Ref. [10]. ^f Ref. [15]. ^g Ref. [12]. ^h Ref. [9].

We regard the really good agreement between our computed harmonic frequencies both for PH₃ and PD₃ (on CEPA level the largest deviation is 40 cm⁻¹; the SCF values differ by 100 cm⁻¹ and more from experiment) with those extracted from experiment as a positive test of the method and the basis set used and a guarantee that the predictions for PH₅ are rather reliable.

6. The Force Field of PH₅

The force constants of PH₅ are collected in Table 6. Those for the *A*'₁ vibrations were obtained together with the geometry optimization under *D*_{3h} constraint. In order to save computer time the symmetry-lowering deformations on both the SCF and CEPA level were performed starting from an average geometry between the SCF and CEPA equilibrium structure (basis *B*) ($r_{\text{eq}} = 1.404 \text{ \AA}$, $r_{\text{ax}} = 1.455 \text{ \AA}$). The definition convention of the force constants is the same as for PH₃ (see Sect. 5). The angles α (between two equatorial bonds) and β (between an axial and an equatorial bond) are as in Levin's study [35] of the force field of PF₅, where also the symmetry coordinates are given explicitly.

For the potential hypersurface of PH₅, basis *B* was used because it yielded lower SCF energies than basis *A*. When we became aware of the sensitivity of the geometry to variations of the basis, we recalculated the *A*'₁ force constants and vibration

Table 6. Harmonic force constants of PH₅^o

		SCF	CEPA	Other authors ^d
A_1'	$F_{11} = f_a + f_{aa}$ ^a	2.757 (2.441) [2.551]	2.359 (2.477)	
	$F_{22} = f_e + 2f_{ee}$ ^a	3.667 (3.458) [3.514]	3.502 (3.407)	
	$F_{12} = \sqrt{6}f_{ae}$ ^a	0.508 (0.424) [0.499]	0.256 (0.347)	
A_2''	$F_{33} = f_a - f_{aa}$ ^a	2.719	2.678	
	$F_{44} = 2f_\beta + 4f_{\beta\beta}$ ^c	0.961	0.897	
	$F_{34} = 2\sqrt{3}f_{a\beta}$ ^b	-0.303	-0.219	
E'	$F_{55} = f_e - f_{ee}$ ^a	3.667	3.623	3.59
	$F_{66} = \frac{3}{2}f_\alpha$ ^c	0.177	0.185	0.20
	$F_{77} = \frac{3}{2}(f_\beta + f_{\beta\beta})$ ^c	1.470	1.401	1.36
	$F_{56} = \frac{3}{2}f_{\alpha\alpha}$ ^b	0.080	0.088	0.08
	$F_{57} = \frac{3}{2}f_{\epsilon\beta}$ ^b	-0.304	-0.272	0.29
	$F_{67} = \frac{3}{2}f_{\alpha\beta}$ ^c	0.203	0.167	-0.18
E''	$F_{88} = \frac{1}{2}(f_\beta - 3f_{\beta\beta'} - 4f_{\beta\beta''})$ ^c	0.866	0.811	

^a mdyn/Å. ^b mdyn/rad. ^c mdyn Å rad⁻². ^d Ref. [3].

^o Calculations with basis *B*, results with basis *A* are given in parentheses, those with basis *G* in square brackets.

frequencies with both basis *A* and *G*. If we regard the basis *G* results as most reliable, we have to conclude that on the SCF level basis *B* overestimates the diagonal force constants by 4–8%, whereas basis *A* underestimates them by 2–4%. The CEPA force constants obtained with basis *A* and *B* differ much less and for the vibration frequencies the difference is so small that we did not regard it as worthwhile to repeat the calculations for the symmetry species other than A_1' with the somewhat better basis *A* (basis *G* would have been prohibitive anyway). A good cross-check is the rather good agreement of our E' frequencies with those of Ref. [3].

One sees from Table 6 that electron correlation does affect certain force constants. It mainly reduces the diagonal force constants, but the overall effect is not very large. Similar observations have been made for other systems with single bonds. For double and triple bonds correlation effects are very important [29, 30].

In Table 7 the harmonic frequencies of PH₅ and PD₅ are tabulated. We hope that they give some indication where the (anharmonic) frequencies of PH₅ should be observed.

The lowest E' vibration $\nu_7 = 648 \text{ cm}^{-1}$ deserves interest because it initiates the Berry pseudorotation. The zero-point energy of this vibration is $\sim 0.0014 \text{ a.u.} \approx 0.9 \text{ kcal/mol}$ and hence comparable with the barrier height (see Table 2) of 2 kcal/mol. One expects this vibration to be rather anharmonic.

Table 7. Harmonic vibration frequencies of PH₅ and PD₅^b

		PH ₅ SCF	CEPA	^a	PD ₅ SCF	CEPA
<i>A'</i>	ν_1	2561 (2466) [2505]	2337 (2436)	2423	1812 (1744)	1731 (1723)
	ν_2	2064 (1963) [1985]	1970 (1995)	2019	1460 (1388)	1394 (1411)
<i>A''</i>	ν_3	2261	2227		1671	1640
	ν_4	1284	1260		929	914
<i>E'</i>	ν_5	2571	2554	2519	1873	1860
	ν_6	1365	1328	1362	975	951
	ν_7	612	648	651	444	470
<i>E''</i>	ν_8	1585	1534	1333	1121	1085

^a Ref. [3].^b Calculations with basis *B*, results from basis *A* are given in parentheses, from basis *G* in square brackets.

7. Conclusions Concerning the PH-Bonds in PH₅

In a previous paper an analysis of the chemical bond in PH₅ and other phosphoranes was given [4] in terms of energetics, *d*-AO contributions and population analysis. The present results concerning bond lengths and vibration frequencies give additional information.

We see that the length of the equatorial bond in PH₅ (1.42 Å) is close to *r*(PH) in PH₃ (1.42 Å) where a "pure *p*-AO" of P is said to be involved in bonding. PH₄⁺, with supposedly an *sp*³-hybrid on P, has a shorter *r*(PH) of 1.39 Å, and in planar PH₃ with an *sp*² hybrid on P, *r*(PH) is still shorter (1.37 Å). The presence of the axial bonds in PH₅ obviously weakens the equatorial bonds referred to those in planar PH₃. The axial bond itself with *r*(PH) = 1.47 Å is finally the weakest of all PH-bonds.

The force constants (for symmetric stretch) confirm the same trends, PH₃ (planar): 4.61 mdyn/Å [4], PH₄⁺: 4.29, PH₅ (equatorial): 3.40, PH₃ (equilibrium): 3.55, PH₅ (axial): 2.48 mdyn/Å.

It is somewhat unexpected that the equatorial bonds in PH₅ have nearly the same distance and force constant as the PH-bonds in PH₃ (equilibrium) and not as in PH₃ (planar).

There is a rather large coupling between the axial and equatorial bonds as seen from the off-diagonal force constant *F*₁₂ in Table 6 which confirms that either bond would be different without the presence of the other.

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Professor H. Hartmann to whom this work is dedicated was one of the first to use quantum chemical methods for the calculation of normal frequencies of a polyatomic molecule [36] and this without an electronic computer.

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