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Millimeter-Wave Spectra, *ab Initio* Calculations, and Structures of Fluorophosphane and Chlorophosphane

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The structures of fluorophosphane, PH_2F, and chlorophosphane, PH_2Cl, have been calculated *ab initio* at the SCF, MP2, CCSD, and CCSD(T) levels using a quadruple ζ polarized basis set. Equilibrium and ground state rotational constants as well as centrifugal distortion constants have been predicted for several isotopomers of PH_2F and PH_2Cl. Theoretical CCSD(T) geometries were also determined for the series of PH_nX_{3-n} (X = F, Cl; $n = 0-3$) molecules using a triple ζ polarized basis set. The millimeter-wave spectra of the short-lived molecules PH_2F, PH_2Cl, and their perdeuterated species were measured in the frequency range 100−470 GHz. For PH_2F and PH_2Cl, accurate ground state parameters have been obtained by a combined fit of the millimeter-wave data and the infrared ground state combination differences. The r_o, r_z, and r_e structures of PH_2F and PH_2Cl, as well as PH_3, PCl_3, and PHF_2 have been determined. The experimental results are found in excellent agreement with their *ab initio* predictions.

I. Introduction

Unlike the isovalent silyl halides SiH_3X (X = F, Cl, Br, I), the monohalogenophosphanes, PH_2X, have remained almost unknown until recently, mainly because they are short-lived species which cannot be isolated. PH_2F was first identified among the products of the reaction of PH_3 with F_2 in an Ar matrix at 16 K[1] by comparing its experimental and *ab initio* infrared spectra[2] and by observing the isotopic H/D shifts obtained upon replacing PH_3 by PD_3. Quite recently the harmonic and anharmonic force fields of the PH_2X molecules have been calculated at the *ab initio* self-consistent field level, permitting accurate prediction of many rovibrational constants.[3]

The spectra simulated with the *ab initio* data enabled the identification of PH_2F and PH_2Cl by low- and high-resolution Fourier transform infrared spectroscopy.[3,4] At room temperature and a pressure < 2 mbar the half-lifes of PH_2F and PH_2Cl were found to be ca. 10 and 1 min, respectively. Most fundamental bands were observed and in the high-resolution infrared spectra, the rotational J- and K-structure of bands, typical of asymmetric rotors near the prolate symmetric top limit (PH_2F, $\kappa = -0.9971$; PH_2Cl, $\kappa = -0.9998$) were resolved. The ground state rotational and centrifugal distortion constants were determined from ground state combination differences (GSCD). However, it was not possible to obtain all of the constants with good accuracy, in particular, the quartic centrifugal distortion constants of $PH_2{}^{37}Cl$ could not be determined. Furthermore, the available experimental data were not sufficient for determining an accurate structure.

As the PH_2X molecules are made up from only four atoms, such a structure determination should not be too difficult. Moreover it should be interesting to compare with the structures of PH_3,[5] PF_3,[6] and PHF_2 [7] and of the analogous nitrogen derivatives which are already known. These are the reasons why we undertook the study of the pure rotational spectra of PH_2F, PH_2Cl, and their perdeuterated species PD_2F and PD_2Cl. In order to make comparisons of the experimental rotational constants and structures with corresponding theoretical predictions, we have performed new state-of-the-art *ab initio* calculations on PH_2F and PH_2Cl.

II. *Ab Initio* Calculations

II.a. Computational Details. The quantum chemical calculations were carried out at the Hartree−Fock self-consistent field (SCF) level of theory[8] and at the correlated levels of second-order Møller−Plesset perturbation theory (MP2),[9] coupled-cluster theory with single and double excitations (CCSD),[10,11] and CCSD augmented by a perturbational estimate of the effects

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of connected triple excitations (CCSD(T)).[12] The correlation consistent polarized basis sets (cc-pVnZ) of Dunning et al.[13,14] were employed: the valence triple ζ basis (cc-pVTZ) denotes a [5s4p2d1f/4s3p2d1f/3s2p1d] contraction of a (15s9p2d1f/10s5p2d1f/5s2p1d) primitive set for P,Cl/F/H, whereas the quadruple ζ basis (cc-pVQZ) corresponds to a [6s5p3d2f1g/5s4p3d2f1g/4s3p2d1f] contraction of a (16s11p3d2f1g/12s6p3d2f1g/6s3p2d1f) primitive set. A convergence study on PH_3 made use of the quintuple ζ basis (cc-pV5Z)[15,16] but without h functions at P and g functions at H, i.e., a [7s6p4d3f2g/5s4p3d2f] contraction of a (20s12p4d3f2g/8s4p3d2f) primitive set for P/H. Only the spherical harmonic components of d, f, and g functions were included. Unless noted otherwise, the core molecular orbitals (F, 1s; P,Cl, 1s, 2s, 2p) were constrained to be doubly occupied in the MP2, CCSD, and CCSD(T) calculations (frozen core approximation).

The molecular geometries were optimized within the constraint of C_{3v} (PH_3, PF_3, PCl_3) and C_s (PH_2F, PHF_2, PH_2Cl, $PHCl_2$) point group symmetry, respectively, using numerical gradients (stepsizes 0.01 Bohr for bond distances and 1° for the angles) as implemented in the MOLPRO94 program system.[17] The largest internal gradient components at the stationary points were always less than 10^{-4} au.

For comparison with the present experimental data, the quadratic and cubic force fields of PH_2F and PH_2Cl are required to provide theoretical values for the centrifugal distortion constants and for the differences between the equilibrium and ground state rotational constants. These force fields have been computed previously[3] but have now been recalculated with a larger basis set using the same computational procedure as before.[3,18] This TZ2Pf basis (see, e.g., ref 19) is of valence triple-ζ quality with double polarization plus f functions: P and Cl are described by a (12s9p)/[6s5p] basis[20] with two sets of d and one set of f polarization functions;[14] F is represented by a (10s6p)/[5s3p] basis[21] with two sets of d and one set of f polarization functions;[13] and H is described by a (5s)/[3s] basis (scale factor 1.2)[21] with two sets of p and one set of d polarization functions.[13]

The MP2/TZ2Pf harmonic force fields of PH_2F and PH_2Cl were evaluated analytically in Cartesian coordinates using the GAUSSIAN92 program.[22] The required SCF/TZ2Pf anharmonic force fields of PH_2F and PH_2Cl which are not reported explicitly were determined by a finite difference procedure[3,18] using the GRADSCF program[23] and Cartesian basis functions. The cubic normal coordinate force constants of the less abundant isotopomers (PD_2F, $PD_2{}^{35}Cl$, $PH_2{}^{37}Cl$, $PD_2{}^{37}Cl$) were obtained from those for PH_2F and $PH_2{}^{35}Cl$ by appropriate nonlinear transformations[24,25] via intermediate internal coordinate representations of the cubic force fields.

Table 1. Theoretical Equilibrium Structures of PH_2F and PH_2Cl[a]

	PH_2F				PH_2Cl			
method[b]	PH	PF	HPH	HPF	PH	PCl	HPH	HPCl
SCF	1.4075	1.5783	93.87	98.37	1.4030	2.0685	94.47	97.46
MP2	1.4130	1.6090	92.16	98.02	1.4101	2.0620	92.66	96.89
CCSD	1.4172	1.6020	92.33	97.91	1.4133	2.0693	92.88	96.83
CCSD(T)	1.4198	1.6081	92.08	97.88	1.4161	2.0735	92.59	96.73

[a] Bond lengths in angstroms; bond angles in degrees. [b] cc-pVQZ basis.

Table 2. Theoretical Equilibrium Structures of PH_3[a]

	cc-pVTZ		cc-pVQZ		cc-pV5Z[b]	
method	PH	HPH	PH	HPH	PH	HPH
SCF	1.4081	95.47	1.4055	95.58	1.4043	95.59
MP2	1.4117	93.64	1.4093	93.69	1.4078	93.71
CCSD	1.4165	93.78	1.4138	93.85	1.4124	93.86
CCSD(T)	1.4185	93.51	1.4160	93.55	1.4145	93.56
CCSD(T)[c]	1.4143	93.31	1.4108	93.48	1.4088	93.46

[a] Bond lengths in angstroms; bond angles in degrees. [b] Without h functions at P and g functions at H. [c] Including all molecular orbitals in the correlation procedure.

II.b. Results. Table 1 reports the optimized molecular geometries of PH_2F and PH_2Cl at the SCF, MP2, CCSD, and CCSD(T) levels using the cc-pVQZ basis. The CCSD(T)/cc-pVQZ results are our most reliable predictions. The basis set convergence can be judged from Table 2, which contains the theoretical geometries of PH_3 for the cc-pVTZ, cc-pVQZ, and cc-pV5Z basis sets. Table 3 compares the optimized structures of the halogenophosphanes PH_nX_{3-n} ($n = 0-3$; X = F, Cl) at the CCSD(T)/cc-pVTZ level with experimental data.

Inspection of Tables 1−3 indicates that the theoretical bond angles are not very sensitive to the choice of the correlation treatment (MP2, CCSD, CCSD(T)) or to basis set refinement (cc-pVTZ, cc-pVQZ, cc-pV5Z) since the calculated angles lie in a narrow range (e.g., within 0.3° for PH_2F and PH_2Cl). Hence, we expect an accuracy of 0.2° for our best predictions from CCSD(T)/cc-pVQZ, in agreement with the documented average errors from this approach.[26]

The theoretical bond lengths show a slight systematic decrease when going from the cc-pVTZ to the cc-pVQZ basis, e.g., at the CCSD(T) level by about 0.003 Å for P−H, 0.006 Å for P−F, and 0.012 Å for P−Cl (see Tables 1−3). Further basis set saturation has less effect in the case of PH_3 (see cc-pV5Z in Table 2). The CCSD(T)/cc-pVQZ approach is known to overestimate equilibrium bond lengths typically by a few thousandths of an angstrom,[26] mostly because of the neglect of core−valence correlation.[26] Abandoning the frozen core approximation and including the core orbitals in the correlation treatment indeed shortens the PH bond length in PH_3 by about 0.005 Å (see Table 2), even though it should be noted that the cc-pVnZ basis sets do not provide an optimum description of core−valence correlation. We conclude that the best theoretical bond lengths for PH_2F and PH_2Cl (CCSD(T)/cc-pVQZ, Table 1) are probably too large due to the neglect of core−valence correlation, with errors of about 0.005 Å.

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Table 3. Theoretical and Experimental Structures of PH_nX_{3-n} (X = F, Cl; $n = 0-3$)[a]

molecule	method[b]	r(PH)	r(PX)	∠(YPY)[c]	∠(HPX)	ref
PH_3	r_z(E)	1.42774(9)		93.3(1)		5
	r_e(E)	1.4114(10)		93.45(9)		
	r_e(T)	1.4185		93.5		
PF_3	r_z(E)		1.565(1)	97.6(2)		54
	r_e(E)		1.5610(1)	97.57(4)		6
	r_e(T)[d]		1.576	97.5		
PCl_3	r_z(E)		2.043(2)	100.28[e]		
	r_e(E)		2.039(3)	100.28[e]		
	r_e(T)		2.065	100.28		
	r_e(C)		2.043	100.28		
PHF_2	r_z(E)	1.432(1)	1.584(1)	98.9(1)	95.7(1)	
	r_e(E)	1.421(2)	1.579(2)	98.9(2)	95.7(2)	
	r_e(T)	1.427	1.593	99.0	95.7	
	r_e(C)	1.420	1.578	99.0	95.7	
$PHCl_2$	r_e(T)	1.418	2.072	102.4	94.9	
PH_2F	r_z(E)	1.429(1)	1.607(1)	92.0(1)	97.8(1)	
	r_e(E)	1.415(2)	1.602(2)	92.0(2)	97.8(2)	
	r_e(T)	1.423	1.614	92.0	97.9	
	r_e(C)	1.415	1.599	92.0	97.9	
PH_2Cl	r_z(E)	1.423(1)	2.068(1)	92.8(1)	96.4(1)	
	r_e(E)	1.411(2)	2.063(2)	92.8(2)	96.4(2)	
	r_e(T)	1.419	2.085	92.6	96.7	
	r_e(C)	1.412		92.6	96.7	

[a] Bond lengths in angstroms; bond angles in degrees. This work, unless otherwise stated. [b] r_z(E) and r_e(E) denote experimental structures (see text for the determination of r_e(E). r_e(T) corresponds to the theoretical CCSD(T)/cc-pVTZ equilibrium structure. The bond lengths in r_e(T) may be corrected to r_e(C) by using constant bond-specific offsets taken from PH_3 for P−H, from PF_3 for P−F, and from PH_2Cl for P−Cl. [c] Y = H, F, Cl. [d] Including all molecular orbitals in the correlation procedure results in r(PF) = 1.574 Å, ∠(FPF) = 97.5°. [e] Fixed at the *ab initio* value.

Table 4 lists the predicted equilibrium and ground-state rotational constants for several isotopomers of PH_2F and PH_2Cl. From the discussion of the CCSD(T)/cc-pVQZ bond lengths, the corresponding rotational constants should be slightly too small. Table 5 collects the MP2/TZ2Pf predictions of the equilibrium centrifugal distortion constants, again for several isotopomers. The theoretical values are expected to be internally consistent and slightly smaller than the observed ground state constants. Tables 4 and 5 also contain the measured ground state constants and the percentage deviations between the theoretical and experimental values.

III. Experimental Details

The millimeter-wave spectra were measured with a computer-controlled source-modulated spectrometer using phase-stabilized sub-millimeter-wave backward-wave oscillators (Thomson-CSF) as sources and a He-cooled InSb bolometer as detector (QMC).

As PH_2F and PH_2Cl are short-lived species, they must be generated in the gaseous phase. This was done in the present study by mixing H_3PF_2 and BCl_3 in the absorption cell.[27,28] In the case of PH_2F, BCl_3 acts as a dehydrofluorination reagent. The cell is first filled with an excess of BCl_3 (5 mbar) so that the walls of the cell are conditioned with BCl_3. The cell is then evacuated, and H_3PF_2 is admitted into the cell at a pressure of 0.1 mbar. Measurements are immediately started after the admission of H_3PF_2. Because of the decomposition of PH_2F, the cell must be refilled every 10 min. When no lines of PH_2F are seen just after the admission of H_3PF_2, it generally means that the cell had not been well-pretreated with BCl_3.

For the generation of PH_2Cl, H_3PF_2 and BCl_3 are successively introduced into the cell (about 1 mbar of each precursor), and the measurements are immediately started after the admission of the last precursor and after having reduced the total pressure to about 0.1 mbar. PH_2Cl is much less stable than PH_2F, and the cell must be refilled every 2 or 3 min.

To generate the deuterated species PD_2F and PD_2Cl, D_3PF_2 was used instead of H_3PF_2.[27,28]

All measurements were made at room temperature, and the accuracy of the frequency measurements is generally better than 50 kHz.

IV. Analysis of the Spectra

The assignment of the spectra was not easy because the phosphanes are highly unstable species and the spectra are crowded by strong lines due to precursors and decomposition products. In fact, when a line quickly disappeared, this was a good indication that it is due to a PH_2X species.

For PH_2F, the a-type transitions were first predicted from the constants resulting from the infrared spectra[3] and were found close to their calculated values. With the improved constants, it was possible to predict c-type transitions with an uncertainty of only a few tens of a megahertz. They could be easily found because they are rather strong. Finally a combined fit of the GSCD obtained from the infrared spectra and the rotational data enabled us to determine all of the rotational and quartic centrifugal distortion constants with good precision. The measured rotational lines are deposited as Supporting Information (Tables A1−A6) and the derived constants are listed in Table 6. They are given for the A-reduction in the I^r representation. In the least-squares fit, the GSCD had a unit weight, whereas the rotational transitions had weights as set out in the frequency tables, typically 250−1000. As these molecules are near-symmetric tops, the S-reduction might be more appropriate. In fact, for the PH_2X species, both reductions give a fit of the same quality (same standard deviation of fit, same number of fitted parameters, and comparable standard deviations for comparable constants). For consistency with previous work we have chosen the A-reduction. We also tried to determine the sextic constants. Only Φ_{JK} could be determined, but as its inclusion did not significantly improve the fit, we did not retain it in the final fit.

The rotational spectrum of the $v_4 = 1$ excited state ($\nu_4 = 807\ cm^{-1}$) of PH_2F studied previously in the infrared[3] was measured and analyzed in the same way. The derived constants are given in Table 6.

To calculate a structure for PH_2F, it is quite useful to first determine the rotational constants of PD_2F. At the outset of this investigation, no experimental data were available for PD_2F, but the *ab initio* rotational constants were already known.[29] To predict the spectrum, these constants were corrected by the relative offset observed for PH_2F, and the first assigned a-type lines were measured about 250 MHz away from their predicted value. The derived parameters are given in Table 6.

The ground states of $PH_2{}^{35}Cl$ and $PH_2{}^{37}Cl$ were analyzed in the same way as for PH_2F. Because only high-J lines were measured, only the c-type lines were found split by the nuclear quadrupole interaction. However, the few measured splittings did not allow us to determine nuclear quadrupole coupling constants. For the centrifugal distortion analysis, we used the hypothetical unsplit frequencies obtained by intensity weighted averaging of the hyperfine components. The spectrum of $PD_2{}^{35}Cl$ was predicted and analyzed as the PD_2F one. No c-type line could be assigned with certainty. The rotational parameters are collected in Table 6. For PD_2Cl, the A-reduction seems to be definitely better than the S-reduction.

Tables 4 and 5 compare the experimental ground state constants with the results of the *ab initio* calculations. The differences are about 1% for the rotational constants and less

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Table 4. Theoretical Equilibrium (A_e, B_e, C_e)[a] and Theoretical and Experimental Ground State (A_0, B_0, C_0)[b] Rotational Constants (MHz) for PH_2F and PH_2Cl

	PH_2F	PD_2F	$PH_2{}^{35}Cl$	$PD_2{}^{35}Cl$	$PH_2{}^{37}Cl$	$PD_2{}^{37}Cl$
A_e	131 684.9	68 268.2	131 203.1	67 752.0	131 201.5	67 750.1
B_e	15 076.8	13 901.6	6 687.7	6 299.3	6 516.4	6 136.1
C_e	14 911.1	13 525.3	6 654.8	6 223.0	6 485.2	6 063.7
A_0						
calcd	130 378.9	67 803.7	130 065.6	67 342.6	130 063.0	67 340.0
expt	130 843.8	68 109.0	130 494.8	67 630.1	130 323.0	
expt − calcd (%)	0.36	0.45	0.33	0.43	0.20	
B_0						
calcd	14 997.9	13 832.4	6 656.5	6 272.7	6 486.3	6 110.3
expt	15 126.7	13 949.2	6 735.2	6 345.8	6 563.0	
expt − calcd (%)	0.85	0.84	1.17	1.15	1.17	
C_0						
calcd	14 825.7	13 448.8	6 622.2	6 194.6	6 453.7	6 036.2
expt	14 958.5	13 569.9	6 701.4	6 268.3	6 530.8	
expt − calcd (%)	0.89	0.89	1.18	1.17	1.18	

[a] CCSD(T)/cc-pVQZ. [b] Theoretical corrections $A_e - A_0$, $B_e - B_0$, $C_e - C_0$ from SCF/TZ2Pf.

Table 5. Theoretical[a] and Experimental[b] Quartic Centrifugal Distortion Constants (kHz) for PH_2F and PH_2Cl

							deviation	
	PH_2F	PD_2F	$PH_2{}^{35}Cl$	$PD_2{}^{35}Cl$	$PH_2{}^{37}Cl$	$PD_2{}^{37}Cl$	max	median
Δ_J								
expt	21.64	17.00	4.94	4.10	4.69			
calcd[c]	20.15	15.83	4.63	3.84	4.40	3.65		
expt − calcd (%)	6.87	6.86	6.23	6.24	6.16		6.87	6.24
calcd[d]	21.27	16.74	4.94	4.10	4.69			
expt − calcd (%)	1.57	1.76	0.00	0.00	0.00		1.76	0.00
Δ_{JK}								
expt	250.62	180.84	70.41	54.80	66.98			
calcd[c]	235.82	169.15	68.61	52.37	65.41	49.86		
expt − calcd (%)	5.91	6.47	2.55	4.44	2.34		6.47	4.44
calcd[d]	250.10	179.97	73.22	55.98	69.75			
expt − calcd (%)	0.25	0.47	−3.99	−2.15	−4.14		4.14	2.15
Δ_K								
expt	1897.21		1989.38					
calcd[c]	1719.63	371.97	1815.92	463.47	1819.03	465.96		
expt − calcd (%)	9.36		8.72				9.36	9.04
calcd[d]	1980.45	435.50	2077.24	531.22	2080.59			
expt − calcd (%)	−4.42		−4.42				4.42	4.42
δ_J								
expt	0.253	0.441	0.031	0.055				
calcd[c]	0.233	0.402	0.028	0.051	0.026	0.047		
expt − calcd (%)	7.91	8.84	10.54	7.27			10.54	8.37
calcd[d]	0.245	0.425	0.030	0.054	0.028			
expt − calcd (%)	3.16	2.49	3.23	1.82			3.23	2.83
δ_K								
expt	391.2	223.6	125.50	59.83				
calcd[c]	340.4	193.1	79.37	52.03	75.48	49.53		
expt − calcd (%)	12.99	13.60	36.76	13.27			36.76	13.43
calcd[d]	370.4	208.7	86.46	56.40	82.17			
expt − calcd (%)	5.42	6.49	31.11	5.98			31.11	6.24

[a] MP2/TZ2Pf, equilibrium values. [b] Ground state values. [c] Unscaled force field. [d] Scaled force field.

than 10% for the quartic centrifugal distortion constants, except for δ_K where a larger deviation is observed: it is only 13% for PH_2F and PD_2Cl but as large as 37% for PH_2Cl. It may be noted that, for the molecules studied so far, the agreement is quite generally worse for the δ_K constant. But, the theoretical δ_K values are known to be very sensitive to the choice of the structure (either equilibrium or ground state).[30] Indeed, if we compare the *T*-constants instead of the Δ-constants, the maximum deviation is only 8%. The experimental *T*-constants are systematically greater than the theoretical ones by about 6.7%.

V. Harmonic Force Field

The determination of the structure from experimental data (next section) requires the knowledge of harmonic corrections to the rotational constants and the mean square amplitudes of vibration. Both quantities may be derived from the harmonic force field. Since the PH_2X molecules have C_s symmetry, their normal coordinates transform as $4A' + 2A''$. There are thus 13 force constants to be determined. We did not have enough data for a complete experimental determination of the force field. On the other hand, the MP2/TZ2Pf force field is rather accurate (and less expensive in computer time and memory than the CCSD(T)/cc-pVTZ calculation), although it still shows some small systematic deviations (see preceding sections). Hence, it was scaled according to the scheme

$$F_{ii}^{scaled} = C_i F_{ii}^{theor} \tag{1a}$$

$$F_{ij}^{scaled} = [C_i C_j]^{1/2} F_{ij}^{theor} \tag{1b}$$

where C_i and C_j are the scale factors. Four different scale factors

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Table 6. Experimental Ground State Parameters of PH_2F, PD_2F, $PH_2{}^{35}Cl$, $PH_2{}^{37}Cl$ and $PD_2{}^{35}Cl$ and $v_4 = 1$ Parameters of PH_2F, *A*-reduction, I^r-representation

	PH_2F $v = 0$	PH_2F $v_4 = 1$	PD_2F $v = 0$	$PH_2{}^{35}Cl$ $v = 0$	$PH_2{}^{37}Cl$ $v = 0$	$PD_2{}^{35}Cl$ $v = 0$
A, MHz	130 843.812 (37)	130 792.997 (32)	68 109.0 (11)	130 494.771 (26)	130 323.03 (10)	67 630.1 (57)
B, MHz	15 126.684 (10)	14 991.542 (72)	13 949.1765 (50)	6 735.192 (8)	6 563.008 (12)	6 345.8438 (72)
C, MHz	14 958.495 (12)	14 882.821 (75)	13 569.8920 (49)	6 701.362 (9)	6 530.840 (12)	6 268.2477 (70)
Δ_J, kHz	21.636 5 (62)	21.056 (15)	16.9952 (39)	4.937 6 (11)	4.688 9 (56)	4.0954 (10)
Δ_{JK}, kHz	250.622 (81)	296.95 (15)	180.841 (27)	70.408 (32)	66.98 (22)	54.801 (35)
Δ_K, kHz	1 897.21 (36)	1 873.99 (26)	371.97[a]	1 989.38 (24)	1 989.38[d]	463.47[a]
δ_J, kHz	0.253 0 (22)	0.122 (13)	0.4410 (57)	0.031 30 (51)	0.031 30[d]	0.0550 (19)
δ_K, kHz	891.2 (55)	164 (36)	223.6 (14)	125.5 (42)	125.5[d]	59.83 (52)
Φ_{JK}, Hz			1.849 (76)			0.168 (19)
Φ_{KJ}, Hz			1.069 (94)			0.896 (39)
ν_4^0, cm^{-1}		807.358 97 (3)[e]				
no. of lines[f]	35	27	40	27	24	34
σ(fit), kHz	703	653	14	425	408	14
no. of IR data	6129[b]	949[c]	0	9410[b]	663[b]	0
J_{max}/K_{max}	42/13	42/13		55/13	45/6	
σ(fit), MHz	15.14	11.72		17.99	21.59	

[a] Fixed at the *ab initio* value. [b] GSCD's, dimensionless. [c] IR transitions, dimensionless. [d] Constrained to $PH_2{}^{35}Cl$ value. [e] Reference 3. [f] Rotational transitions.

Table 7. Geometry, Symmetry Coordinates, Scale Factors Used in the Harmonic Force Field Refinement, and Scaled *ab Initio* MP2/TZ2Pf Force Constants of PH_2X (X = F, Cl)

Symmetry Coordinates

A′ block	$S_1 = {}^1/_{\sqrt{2}}[r(PH) + r(PH')]$	A″ block	$S_5 = {}^1/_{\sqrt{2}}[r(PH) - r(PH')]$
	$S_2 = \angle(HPH')$		$S_6 = {}^1/_{\sqrt{2}}[\angle(HPX) - \angle(H'PX)]$
	$S_3 = {}^1/_{\sqrt{2}}[\angle(HPX) + \angle(H'PX)]$		
	$S_4 = r(PX)$		

Internal Coordinates and Geometry (Distances, Å; Angles, deg)

	PH_2F (X = F)	PH_2Cl (X = Cl)		PH_2F (X = F)	PH_2Cl (X = Cl)
$r(PH)$	1.4152	1.4121	$\angle(HPH)$	92.25	92.70
$r(PX)$	1.6158	2.0703	$\angle(HPX)$	97.89	96.90

Scale Factors

	PH_2F (X = F)	PH_2Cl (X = Cl)		PH_2F (X = F)	PH_2Cl (X = Cl)
PH stretch	0.8640	0.8667	HPX bend	0.9513	0.9425
HPH bend	0.9172	0.9180	PX stretch	0.9479	0.9363

Scaled *ab Initio* MP2/TZ2Pf Force Constants F_{ij}[a] of PH_2X

	PH_2F	PH_2Cl		PH_2F	PH_2Cl		PH_2F	PH_2Cl
				A′ Block				
F_{11}	2.999	3.053	F_{22}	0.719	0.691	F_{33}	1.035	0.833
F_{12}	0.111	0.108	F_{23}	0.088	0.035	F_{34}	0.388	0.326
F_{13}	0.025	−0.006	F_{24}	−0.007	0.006	F_{44}	4.672	2.662
F_{14}	0.116	0.029						
				A″ Block				
F_{55}	3.004	3.062	F_{56}	0.052	0.066	F_{66}	0.952	0.807

[a] Units are consistent with aJ for energy, angstroms for distances, and radians for angles.

were used; they were derived by fitting the computed harmonic vibrational wavenumbers of the PH_2X species to the observed ones. In order to obtain a meaningful force field, the calculations were performed on a structure optimized using the same theoretical model (MP2) and basis set (TZ2Pf). The symmetry coordinates, the scale factors, and the scaled force field are given in Table 7. The calculated wavenumbers are compared to the experimental ones in Table 8. The scaled force constants reproduce the experimental data very well, especially when considering that the scaling can account for anharmonicity effects only in an average sense. For the centrifugal distortion constants, the improvement is also very significant (see Table 5), the maximum deviation being now less than 4.4% (instead of 10% with the unscaled force field), except for δ_k, especially for $PH_2{}^{35}Cl$ where the deviation is still 31%. But, it was shown in the preceding section that this large deviation is mainly due to the choice of the structure, not to the quality of the force field.

VI. Determination of the Structures

VI.a. Experimental Structures. The best description of the geometry of a molecule is the equilibrium (r_e) structure. An equilibrium internuclear distance is the distance between two hypothetically motionless nuclei and corresponds to the minimum of the potential energy function. *Ab initio* calculations yield theoretical equilibrium geometries.

As the nuclei undergo vibrational motions about their equilibrium positions, the experimental ground state moments of inertia (I_o) are different from the equilibrium ones (I_e), and the difference depends in a complicated way on the force field (quadratic and cubic). These differences have been calculated

Table 8. Calculated[a] and Observed[b] Vibrational Wavenumbers (cm^{-1}) of PH_2X for Given Mode Description (ν_S, δ, δ_S, ν, ν_{as}, and δ_{as})

		A′ symmetry				A″ symmetry	
		ν_1 $\nu_s(PH_2)$	ν_2 $\delta(HPH)$	ν_3 $\delta_s(HPX)$	ν_4 $\nu(PX)$	ν_5 $\nu_{as}(PH_2)$	ν_6 $\delta_{as}(HPX)$
PH_2F	calcd	2281	1109	977	807	2289	928
	obsd	2283	1109	977	807	2287	
PD_2F	calcd	1636	808	724	798	1646	678
	obsd	1660		701[c]	808	1667	
$PH_2{}^{35}Cl$	calcd	2302	1096	860	511	2311	839
	obsd	2303	1096	861	511	2310	83
$PH_2{}^{37}Cl$	calcd	2302	1096	860	504	2311	839
	obsd	2305	1096	861	505	2310	838
$PD_2{}^{35}Cl$	calcd	1651	787	630	508	1662	603
	obsd	1665		633	510	1670	

[a] Calculated with scaled *ab initio* force constants of Table 7. [b] References 3 and 4. [c] Reference 58.

ab initio in section II, but they are known to be affected by systematic deviations which are difficult to estimate *a priori* and which may be too large to permit an accurate structure determination. However, it is possible to overcome this difficulty by deriving the average structure r_z as described below. The r_z distance is the distance between average nuclear positions in the ground vibrational state at 0 K.[31] Thus, it has a clear physical meaning and permits the comparison of structures of different molecules. Furthermore, the average bond angles are known to be very close to the corresponding equilibrium values, the differences being generally of the same order of magnitude as the experimental accuracy. The average bond length differs from the equilibrium one only because of the anharmonicity of the molecular vibrations. It is also possible to extrapolate the r_z distance to the equilibrium value if we assume that the bond stretching anharmonicity is the dominating term. This assumption was carefully checked in many different molecules and was found to be a reasonable one.[32]

Thus, in order to obtain the zero-point moments of inertia I_z^g ($g = a, b, c$), we corrected the ground state constants for the harmonic contributions to the α's. The harmonic contributions to the rotational constants calculated by the usual expressions[33] are summarized in Table A7 of the Supporting Information. The r_z structure was obtained by doing a least-squares fit of the structural parameters to the I_z^g. It is well-established that the r_z structure may be strongly affected by isotopic effects.[34−36] The isotopic changes in bond lengths were estimated from Kuchitsu's formula:[37,38]

$$r_z = r_e + {}^3/_2 a u^2 - K \tag{2}$$

hence

$$\delta r_z = {}^3/_2 a \delta u^2 - \delta K \tag{3}$$

u^2 is the mean square amplitude for the bond concerned, and K, the mean square perpendicular amplitude correction, both obtained from the harmonic force field, while a is the Morse anharmonicity parameter. This formula (2) is an approximation (diatomic approximation) because it neglects all of the anharmonic constants except the bond stretching anharmonicity. Furthermore the a parameters are often assumed to be equal to those of the corresponding diatomic molecules, for which potential functions have been determined experimentally. Most of them have been tabulated by Kuchitsu and Morino.[39] The parameter a of the P−Cl bond is not listed in ref 39 but may be easily calculated from the known molecular constants of the PCl radical.[40] The result is $a = 1.575$ Å^{-1}. Although it is known that the range of variation of a is small (1.3−2.6 Å^{-1}), it is better, whenever possible, to deduce this effective anharmonic constant a for each molecule, either from isotopic differences in the average structure[41] or from differences in the average structure by vibrational excitation.[42]

The isotopic shift is particularly large for the substitution H → D. A first set of calculations using the tabulated value a(PH) $= 1.659$ Å^{-1} gave results incompatible with the *ab initio* calculations. A redetermination of a using more recent molecular parameters for the PH radical[43] did not significantly improve the results, the new value, 1.674 Å^{-1}, being in good agreement with the former one. This prompted us to determine a(PH) from the isotopic difference r_z (PH) - r_z (PD) in PH_3, this molecule being much more similar to the molecules under investigation than the radical PH. The r_z and r_e structures of PH_3 have already been determined by different authors.[5,44,45] But, as the structure of PH_3 has been used to "scale" the *ab initio* calculations (see below), it is important to check its accuracy.

We determined the zero-point moments of inertia for PH_3 and PD_3 using the latest ground state rotational constants[5] and the best harmonic force field. They were also corrected for electronic contribution using the g-factors determined by the analysis of the rotational Zeeman effect.[46] The derived r_z structure (Table 3) is in very good agreement with the previous determinations.

There are three ways to estimate the r_e structure of PH_3 from the r_z one:

(1) First is the "diatomic approximation" of Oka and Morino,[47] where r_z is a linear function of $\mu_t^{-1/2}$, μ_i being the reduced mass of the PH or PD group. The resulting equation for the bond length is

$$r_e = \frac{(r_z)_H \mu_H^{1/2} - (r_z)_D \mu_D^{1/2}}{\mu_H^{1/2} - \mu_D^{1/2}} \tag{4}$$

This gives r_e(PH) $= 1.4114$ Å.

(2) Second is the mass-dependence method of Nakata and Kuchitsu.[48] The r_e bond length may be obtained from the

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following equation:

$$r_e = r_z + \left\{\frac{m_D + m_H}{m_D - m_H} + \frac{1}{2}\right\}(r_z(PH) - r_z(PD)) \qquad (5)$$

This gives $r_e(PH) = 1.4113$ Å.

(3) Finally, a may be estimated using eq 3 and δr_z, and then eq 2 is used to calculate the r_e bond length. This gives $r_e(PH) = 1.4116$ Å and $a = 1.993$ Å^{-1}.

The results of the three methods are in excellent agreement, they agree also very well with the r_e structure which was calculated using the α's of PD_3 determined by infrared spectroscopy,[49] $r_e(PH) = 1.4118(5)$ Å. This agreement gives us confidence in the accuracy of the r_e structure of PH_3. Furthermore, the derived anharmonic constant is significantly different from that of the diatomic radical PH. This is one of the main causes limiting the accuracy of eq 2. For the PCl bond, the isotopic change is 2 orders of magnitude smaller, so the accuracy of a(PCl) is much less important.

In the fit, primary as well as secondary isotopic differences in bond lengths were taken into account, while isotopic differences in bond angles were neglected throughout. The estimated differences with respect to the normal species are listed in Table A8 of the Supporting Information and the derived r_z structures in Table 3. The assignment of error limits to the average structural parameters is not straightforward. The final results are affected by systematic errors due to the harmonic corrections of the rotational constants and to the estimates of the isotopic differences. Both contributions depend on the quality of the force field. To calculate the errors, we have assumed that the harmonic correction is known with an accuracy which is at best 1 MHz for the α^b and α^c constants, and worse for the α^a constants (the used accuracies are listed in Table A7 of the Supporting Information). Furthermore, we have assumed that eq 3 gives the isotopic shifts with an accuracy of 30%, which is a rather pessimistic estimate. We also tried a fit neglecting the isotopic shifts. The structural parameters do not vary much, but the standard deviation of the fit is significantly worse.

In order to compare the structures of PH_2F and PH_2Cl with those of structurally similar molecules, we have also determined the r_z structure of PHF_2 and PCl_3. We have used the same procedure as that for PH_2F and PH_2Cl. The ground state rotational constants of PHF_2 and PDF_2 are taken from ref 7, and the harmonic force field, from ref 50. The ground state rotational constants of $P^{35}Cl_3$ and $P^{37}Cl_3$ are taken from ref 51, and the force field from ref 52. In the latter case, it was not possible to accurately determine both the r(P−Cl) distance and the ∠(ClPCl) angle because these two parameters are highly correlated (the rotational constants are too similar). To solve that problem, we have fixed the ∠(ClPCl) angle to its *ab initio* value (Table 3); i.e., we have assumed that the r_z angle and the *ab initio* angle are identical. This assumption seems to be rather reasonable as discussed below.

VI.b. Comparison with *ab Initio* Results. Generally, the average bond angles are very close to the corresponding equilibrium values. To calculate the r_e bond lengths, eq 2 was used. To estimate the accuracy of the r_e structure, it was assumed that eq 2 allows us to calculate $r_z - r_e$ with an accuracy of 30%. This gives a final accuracy of only 0.004 Å for the PH bond length. But, it is possible to check the results and to improve their accuracy by a joint use of *ab initio* calculations. Comparisons between the experimental and theoretical equilibrium structures may be based on the CCSD(T)/cc-pVTZ predictions which are available for all molecules of the PH_nX_{3-n} series (X = F, Cl; $n = 0-3$), see Table 3. In principle, the CCSD(T)/cc-pVQZ predictions should be more accurate (see Tables 1 and 2), and the deviations from experiment are indeed significantly reduced for the bond lengths when the basis is extended from cc-pVTZ to cc-pVQZ, e.g., by a factor of 2 for P−F in PH_2F and for P−Cl in PH_2Cl. On the other hand, these deviations are quite systematic for both basis sets and may therefore be corrected equally well by empirical offsets.[26] Hence, we use the more economic cc-pVTZ basis to derive such empirical bond length corrections which allow us to cover all PH_nX_{3-n} molecules (see Table 3). No empirical corrections are needed for the bond angles since the CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ values are within 0.1° of each other and also very close to the experimental values. For instance the CCSD(T) bond angles in PH_3 and PF_3 (93.51° and 97.50°, respectively, see Table 3) are in very good agreement with the corresponding experimental values (93.45(9)° and 97.57(4)°, see Table 3). Hence, the *ab initio* angles of PH_2F, PH_2Cl, PCl_3, and PHF_2 are expected to be reliable, too. In fact, the different determinations of the angles are in very good agreement with each other, so the accuracy of the angles is probably better than 0.3°.

Likewise the equilibrium PH bond lengths in PHF_2, PH_2F, and PH_2Cl that have been extrapolated from the r_z value (with eq 2) are in excellent agreement with the CCSD(T)/cc-pVTZ values corrected by a constant offset of 0.0071 Å (from PH_3). Hence, the estimated uncertainty of 0.004 Å for r_e(PH) is probably much too pessimistic, 0.002 Å being probably a more realistic estimate. The two values quoted in Table 3 for the equilibrium PF bond length in PH_2F differ by 0.003 Å, which may be attributed to the inaccuracy of the experimental value, but it would be desirable to check whether the correction $r_e -$ *r(ab initio)* is constant. This requires the experimental determination of the equilibrium PF bond length in several molecules. The experimental PCl bond length in PH_2Cl is more accurate (because it was possible to determine the rotational constants of the two isotopomers with ^{35}Cl and ^{37}Cl). It is much larger than in PCl_3 (2.039−2.043 Å). To correct the *ab initio* value for PH_2Cl, it would be necessary to accurately determine the experimental equilibrium value for the PCl bond length in at least one additional molecule.

VI.c. Comparison with Fluoroamines. With increasing substitution by fluorine the fluorophosphanes PH_nF_{3-n} reveal decreasing PF and increasing PH bond lengths. Although the related fluoroamines NH_nF_{3-n} exhibit analogous H/F substitution effects,[53] their geometrical and spectroscopic properties are different from those of the fluorophosphanes. While the sum of the bond angles at P increases from PH_3 to PF_3, it decreases from NH_3 to NF_3.[53]

Likewise the PF stretching force constants are inversely related to the PF bond lengths. To the contrary the NF stretching force constants decrease from NH_2F to NF_3 with concomitant shortening of the NF bonds.[53] The behavior of the PF bond parameters is in agreement with increasing $P^{\delta+}-$

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Table 9. Comparison of the Valence Force Constants (N/cm) of the Halogenophosphanes PH_nX_{3-n} (X = F, Cl)

	PH_3	PH_2Cl	PH_2F	$PHCl_2$	PHF_2	PF_3
f(PH)	3.17	3.06	3.00	3.02	2.89	
f(PH,PH′)	0.01	−0.005	−0.002			
f(PH,PX)		0.02	0.08	0.01	0.12	
f(PF)			4.67		4.99	5.49
f(PF,PF′)					0.32	0.47
ref	5	*a*	*a*	55	2	56

[a] This work.

$F^{\delta-}$ Coulomb attraction the more F atoms are bonded to phosphorous.

Both the averaged PH stretching frequencies and PH stretching force constants of fluoro- and chlorophosphanes decrease with increasing substitution by halogen, see Table 9. Moreover, the fluorophosphanes PH_2F and PHF_2 have longer PH bonds and smaller PH stretching force constants as well as larger HPX bond angles (X = F, Cl) than the corresponding chlorophosphanes. Analogously the averaged NH stretching frequencies decrease in the order NH_3 (3408 cm^{-1})−NH_2F (3290 cm^{-1})−NHF_2 (3193 cm^{-1}), which is consistent with the observed increase of the NH bond length.[53] This behavior has been attributed to a transition from attractive $H^{\delta+}-N^{\delta-}$ interactions in NH_3 to repulsive forces $H^{\delta+}-N^{\delta+}$ in NHF_2,[53] but the electrostatic model cannot be applied to the corresponding fluorophosphanes. The structures of the latter may be better explained on the basis of stereoelectronic *n*(F)/*σ*(PH) repulsion which should supersede n(F)/*σ**(PH) hyperconjugative effects.[57]

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Supporting Information Available: Tables of rotational frequencies, harmonic contributions to the rotational constants, and isotopic differences r_z(isotopic species) − r_z(parent species) (7 pages). Ordering information is given on any current masthead page.

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