

Supporting Information:

Equilibrium Structures of the Phosphorus Trihalides PF_3 and PCl_3 , and the Phosphoranes PH_3F_2 , PF_5 , PCl_3F_2 , and PCl_5

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Table S1. Computed Vibrational Contributions ΔX_{vib} ($X = A, B, C$; MHz) to the Ground-State Rotational Constants X_0 , Rotational g Tensors (Dimensionless), and Electronic Contributions ΔX_{el} (MHz) to X_0 of Selected Molecules^{a,b}

Molecule	ΔA_{vib}	ΔB_{vib}	ΔC_{vib}	g_{bb}	g_{cc}	ΔB_{el}	ΔC_{el}
PH ₂	-481.18	-440.16	-2468.5				
PD ₂	-191.37	-154.86	-909.01				
PF ₂	+68.07	-46.11	-39.78				
P ³⁵ Cl ₃	-6.937	-6.937	-5.700	-0.02639	-0.01883	-0.0377	-0.0151
P ³⁷ Cl ₃	-6.500	-6.500	-5.292	-0.02507	-0.01781	-0.0340	-0.0135
P ³⁵ Cl ₂ ³⁷ Cl	-6.941	-6.640	-5.559	-0.02552 ^c	-0.01849	-0.0353 ^c	-0.0146
PF ₅	-15.99	-12.96	-12.96	-0.03524	-0.03314 ^d	-0.0604	-0.0682 ^d
P ³⁵ Cl ₃ F ₂	-5.219	-5.219	-3.897	-0.02477	-0.01235	-0.0222	-0.0081
P ³⁷ Cl ₃ F ₂	-4.917	-4.917	-3.625	-0.02384	-0.01168	-0.0206	-0.0072
P ³⁵ Cl ₅	-4.020	-3.318	-3.318	-0.02583	-0.01513 ^d	-0.0135	-0.0098 ^d
P ³⁷ Cl ₅	-3.737	-3.085	-3.085	-0.02443	-0.01431 ^d	-0.0121	-0.0088 ^d

^aThe terminology is chosen such that X_0 is decomposed as follows: $X_0 = X_e + \Delta X_{\text{vib}} + \Delta X_{\text{el}}$, with X_e denoting the equilibrium rotational constant. ΔX_{vib} and ΔX_{el} are defined as in ref 74 of the main paper.

^bThe ΔX_{vib} values were computed at the level of UHF-CCSD(T)/AVQZ for PH₂, PD₂, and PF₂, CCSD(T)/AVQZ for PCl₃, CCSD(T)/VQZ for PF₅ and PCl₃F₂, and CCSD(T)/VTZ for PCl₅ at the associated optimized equilibrium geometries (see Tables 3-5 of the main paper; the UHF-CCSD(T)/AVQZ geometries of PH₂ and PF₂ are as follows: $r_e(\text{PH}) = 141.90$ pm, $\theta_e(\text{HPH}) = 91.884^\circ$; $r_e(\text{PF}) = 158.24$ pm, $\theta_e(\text{FPF}) = 98.243^\circ$). The g factors as well as ΔX_{el} were always calculated at the CCSD(T)/AWCVTZ level at the corresponding best estimated equilibrium geometries (see Tables 3-5 of the main paper). Due to program limitations, the g factors could not be calculated for the open-shell species (PH₂, PD₂, PF₂).

^cIn addition, $g_{\text{aa}} = -0.02637$ and $\Delta A_{\text{el}} = -0.0377$ MHz, respectively.

^dThe entry refers to g_{aa} and ΔA_{el} , respectively, due to the fact that PF₅, P³⁵Cl₅, and P³⁷Cl₅ are prolate tops.

Table S2. Computed Vibrational Contributions ΔX_{vib} ($X = B, C; 10^{-2} \text{ cm}^{-1}$) to the Ground-State Rotational Constants X_0 , Rotational g Tensors (Dimensionless), and Electronic Contributions ΔX_{el} (10^{-5} cm^{-1}) to X_0 of Selected Symmetric Top Molecules^{a,b,c}

Molecule	ΔB_{vib}	ΔC_{vib}	g_{bb}	g_{cc}	ΔB_{el}	ΔC_{el}
PH ₃	-5.215	-4.259	+0.02246	-0.03409	+5.512	-7.358
PD ₃	-1.931	-1.527	+0.009707	-0.01706	+1.236	-1.842
PF ₃	-0.09313	-0.09126	-0.06673	-0.03897	-0.9509	-0.3413
PH ₃ F ₂	-0.1062	-4.306 ^d	-0.05868	-0.3091 ^d	-0.5119	-48.99 ^d
PD ₃ F ₂	-0.09665	-1.519 ^d	-0.05711	-0.1547 ^d	-0.4849	-12.27 ^d

^aSee footnote *a* of Table S1.

^bThe ΔX_{vib} values were computed at the level of CCSD(T)/AVQZ for PH₃, PD₃, and PF₃, and CCSD(T)/VQZ for PH₃F₂ and PD₃F₂ at the associated optimized equilibrium geometries (see Tables 3-4 of the main paper; the CCSD(T)/AVQZ geometry of PH₃ is as follows: $r_{\text{c}}(\text{PH}) = 141.51 \text{ pm}$, $\theta_{\text{e}}(\text{HPH}) = 93.559^\circ$). The g factors as well as ΔX_{el} were always calculated at the CCSD(T)/AWCVTZ level at the corresponding best estimated equilibrium geometries (see Tables 2-4 of the main paper).

^cFor PH₃, PD₃, PF₃, and PH₃F₂ the respective experimental ground-state rotational constants used to determine a semiexperimental equilibrium structure (see Tables 2-4 and relevant references in the main paper) are given in cm^{-1} . Therefore, we report the ΔX_{vib} and ΔX_{el} values of these species in the same unit (instead of MHz as in Table S1). The computed values for PD₃F₂ serve as predictions.

^dThe entry refers to ΔA_{vib} , g_{aa} , and ΔA_{el} , respectively, due to the fact that PH₃F₂ and PD₃F₂ are prolate tops.