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The supplementary material collects the scaled theoretical quadratic force fields in symmetry coordinates for the fluoroarsines AsH_nF_{3-n} (n=0-3), the most stable tbp-isomers of the fluoroarsoranes AsH_nF_{5-n} (n=0-5), and the analogous phosphorus compounds (see Tables S1-S5). The symmetry coordinates have been defined in Tables I and II of ref. 1 for the arsines and phosphines, and in Tables I - III of ref. 2 for the arsoranes and phosphoranes. The corresponding scale factors are shown in Tables S6 and S7 for the arsenic and phosphorus compounds, respectively. The rms deviations between the scaled theoretical and observed frequencies of PH_3, PHF_2, and PF_3 are of the same magnitude as those for AsH_3 and AsF_3 (see Tables S6-S7).

The standard set of transferable scale factors for the phosphines and phosphoranes is comprised of the optimized scale factors for PH_3 (c_r, c_α), PHF_2 (c_γ), and PF_3 (c_R, c_β). In the case of the arsenic compounds, four of the standard scale factors were obtained analogously from AsH_3 (c_r, c_α) and AsF_3 (c_R, c_β) while the fifth one was approximated as $c_\gamma = (c_\alpha + c_\beta)/2$ since $AsHF_2$ is still unknown experimentally. This approximation holds quite well for the phosphorus case where the mean value of c_α and c_β (0.8314) is close to the optimized value of c_γ (0.8195, see Table S7). It is expected to be even more appropriate for the arsenic compounds where c_α and c_β differ much less than in the phosphorus case (see Tables S6-S7).

Finally we note that the present scaled theoretical force fields for the fluorophosphines and fluorophosphoranes obtained from valence-electron calculations with effective core potentials are generally very similar to corresponding all-electron results at the 6-31G** level (see refs. 1-2). In the vast majority of cases the deviations between individual force constants are smaller than 0.05 mdyn/Å so that the rms deviations between two such sets of force constants belonging to the same molecule lie between 0.005 and 0.045 mdyn/Å.

TABLE S1. Scaled Theoretical Force Fields for AsH_3, PH_3, AsF_3 and PF_3 (mdyn/Å) [a]

	AsH_3	PH_3	AsF_3	PF_3
F_{11}	2.633	3.124	5.068	5.937
F_{12}	0.128	0.146	0.124	0.387
F_{22}	0.594	0.615	1.430	2.019
F_{33}	2.641	3.103	4.322	4.935
F_{34}	-0.040	-0.045	-0.076	-0.236
F_{44}	0.644	0.679	0.896	1.225

[a] Angle-bending coordinates have been multiplied by a unit bond length of 1 Å .

TABLE S2. Scaled Theoretical Force Fields for AsH_2F, PH_2F, $AsHF_2$ and PHF_2 (mdyn/Å) [a]

	AsH_2F	PH_2F	$AsHF_2$	PHF_2 [b]
F_{11}	4.124	4.746	2.541	2.889
F_{12}	0.238	0.344	-0.045	-0.002
F_{13}	0.110	0.137	0.126	0.154
F_{14}	-0.003	-0.015	0.022	0.031
F_{22}	0.876	1.028	1.032	1.251
F_{23}	0.007	0.039	0.190	0.263
F_{24}	0.083	0.105	0.171	0.239
F_{33}	2.585	3.073	4.565	5.219
F_{34}	0.087	0.102	0.062	0.214
F_{44}	0.671	0.712	0.967	1.291
F_{55}	0.775	0.898	0.760	0.884
F_{56}	0.054	0.036	-0.173	-0.271
F_{66}	2.595	3.052	4.148	4.687

[a] Angle-bending coordinates have been multiplied by a unit bond length of 1 Å .

[b] Analogously to PH_3 and PF_3 the theoretical force field of PHF_2 has been scaled by scale factors especially optimized for this molecule (see Table S6).

TABLE S3. Scaled Theoretical Force Fields for MH_5, MH_3F_2 and MF_5 (M = P, As) (mdyn/Å) [a]

	AsH_5	PH_5	AsH_3F_2	PH_3F_2	AsF_5	PF_5
F_{11}	2.444	2.880	3.046	3.519	5.670	6.294
F_{12}	0.349	0.376	0.234	0.283	0.664	1.085
F_{22}	1.863	2.095	3.799	4.145	5.180	5.513
F_{33}	1.711	1.959	3.477	3.938	5.017	5.494
F_{34}	0.240	0.259	0.583	0.789	0.774	1.299
F_{44}	0.694	0.739	0.743	0.894	1.567	2.322
F_{55}	2.528	2.944	3.072	3.509	5.557	6.142
F_{56}	0.076	0.071	-0.027	-0.022	-0.048	-0.106
F_{57}	0.246	0.250	0.070	0.110	0.626	1.008
F_{66}	0.159	0.154	0.280	0.297	0.337	0.461
F_{67}	-0.138	-0.146	-0.196	-0.257	-0.374	-0.517
F_{77}	0.978	1.117	1.054	1.378	1.445	2.221
F_{88}	0.626	0.681	0.634	0.787	1.239	1.927

[a] Angle-bending coordinates have been multiplied by a unit bond length of 1 Å.

TABLE S4. Scaled Theoretical Force Fields for AsH_4F and PH_4F (mdyn/Å) [a]

	AsH_4F	PH_4F
F_{11}	2.842	3.296
F_{12}	0.124	0.152
F_{13}	0.258	0.279
F_{14}	-0.021	-0.045
F_{22}	2.226	2.453
F_{23}	0.102	0.052
F_{24}	0.171	0.195
F_{33}	3.017	3.475
F_{34}	-0.406	-0.521
F_{44}	0.674	0.759
F_{55}	2.889	3.312
F_{56}	0.006	0.008
F_{57}	0.129	0.134
F_{58}	0.094	0.128
F_{66}	0.240	0.245
F_{67}	-0.076	-0.086
F_{68}	-0.150	-0.185
F_{77}	0.757	0.860
F_{78}	0.192	0.243
F_{88}	0.802	1.002

[a] Angle-bending coordinates have been multiplied by a unit bond length of 1 Å .

TABLE S5. Scaled Theoretical Force Fields for MH_2F_3 and MHF_4 (M = P, As) (mdyn/Å) [a]

	AsH_2F_3	PH_2F_3	$AsHF_4$	PHF_4
F_{11}	3.109	3.592	5.491	6.094
F_{12}	0.028	0.024	0.023	0.101
F_{13}	0.026	0.021	0.004	-0.003
F_{14}	0.185	0.233	0.539	0.826
F_{15}	-0.044	-0.068	-0.452	-0.677
F_{22}	0.401	0.448	0.568	0.779
F_{23}	-0.102	-0.127	0.017	0.013
F_{24}	-0.034	0.003	0.023	-0.007
F_{25}	-0.345	-0.487	-0.562	-0.693
F_{33}	5.189	5.768	3.173	3.656
F_{34}	0.360	0.519	0.117	0.159
F_{35}	0.509	0.788	0.099	0.144
F_{44}	4.254	4.613	4.707	5.058
F_{45}	-0.100	-0.056	0.098	0.061
F_{55}	1.794	2.549	1.939	2.713
F_{66}	0.660	0.844	1.214	1.796
F_{77}	3.151	3.604	5.375	5.948
F_{78}	0.007	0.001	-0.090	-0.104
F_{79}	0.088	0.132	0.554	0.885
F_{88}	0.350	0.437	0.280	0.332
F_{89}	-0.294	-0.370	-0.288	-0.395
F_{99}	1.105	1.496	1.363	2.024
$F_{10,10}$	0.742	0.925	1.420	2.043
$F_{10,11}$	0.500	0.683	0.575	0.940
$F_{10,12}$	0.078	0.083	0.080	0.082
$F_{11,11}$	3.953	4.434	4.454	4.935
$F_{11,12}$	0.364	0.579	0.368	0.509
$F_{12,12}$	1.262	1.769	0.708	0.924

[a] Angle-bending coordinates have been multiplied by a unit bond length of 1 Å .

TABLE S6. Scale Factors c_i and rms Deviations σ (cm^{-1}) for the Arsenic Compounds

molecule	c_r	c_R	c_α	c_β	c_γ	σ
AsH_3	0.8147		0.7819			1.8
AsF_3		0.8418		0.8084		2.8
std [a]	0.8147	0.8418	0.7819	0.8084	0.7952 [b]	

[a] Used for AsH_2F, $AsHF_2$, and AsH_nF_{5-n} (n=0-5).

[b] Mean value of c_α and c_β; see text.

TABLE S7. Scale Factors c_i and rms Deviations σ (cm^{-1}) for the Phosphorus Compounds

molecule	c_r	c_R	c_α	c_β	c_γ	σ
PH_3	0.8172		0.7788			3.1
PHF_2	0.7860	0.8076		0.8760	0.8195	3.2
PF_3		0.8207		0.8839		1.4
std [a]	0.8172	0.8207	0.7788	0.8839	0.8195	

[a] Used for PH_2F and PH_nF_{5-n} (n=0-5).