

Supplementary Information for “Resolving the Trifecta of Discrepancies Regarding the Phosphorus Suboxide P₄O”

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Vibrational Frequencies

Table S1: Computed Vibrational Frequencies (cm⁻¹) and Harmonic Intensities (km mol⁻¹) for C-P₄O.

Sym.	Fund.	Intensity	Isotope Fund.	CCSD(T) Harm.	CCSD(T) Isotope Harm.	B3LYP Harm.	B3LYP δ VPT2
a ₂	201.0	0	201.0	202.4	202.4	207.0	-1.5
b ₁	298.2	3	287.0	300.0	288.8	307.2	-1.8
b ₂	299.0	1	298.8	301.0	300.8	311.1	-2.1
a ₁	431.7	8	422.8	434.5	425.7	430.0	-2.9
a ₁	459.5	9	457.6	463.9	462.0	461.5	-4.4
a ₁	537.4	3	536.9	542.3	541.8	533.0	-4.9
b ₂	561.1	9	561.1	566.8	566.8	559.3	-5.7
a ₁	651.3	34	634.5	652.7	635.8	639.4	-1.3
b ₂	787.1	33	752.5	806.3	770.8	784.1	-19.2

Table S2: Computed Vibrational Frequencies (cm⁻¹) and Harmonic Intensities (km mol⁻¹) for B-P₄O.

Sym.	Fund.	Intensity	Isotope Fund.	CCSD(T) Harm.	CCSD(T) Isotope Harm.	B3LYP Harm.	B3LYP δ VPT2
b ₁	316.1	4	304.3	320.1	308.1	318.6	-4.0
a ₁	327.0	<1	325.1	332.1	330.2	329.6	-5.1
a ₂	332.1	0	332.1	335.1	335.1	329.6	-3.0
b ₁	414.4	3	414.3	418.7	418.7	410.2	-4.3
a ₁	426.1	2	423.0	430.0	426.9	423.7	-3.9
b ₂	443.0	9	442.9	448.6	448.5	439.4	-5.6
a ₁	550.7	5	550.4	556.1	555.8	546.3	-5.4
b ₂	641.8	30	617.3	656.3	631.3	642.4	-14.5
a ₁	739.9	58	712.1	747.0	718.9	739.2	-7.1

Table S3: Computed Vibrational Frequencies (cm⁻¹) and Harmonic Intensities (km mol⁻¹) for T-P₄O.

Sym.	Fund.	Intensity	Isotope Fund.	CCSD(T) Harm.	CCSD(T) Isotope Harm.	B3LYP Harm.	B3LYP δ VPT2
e	246.8	10	239.8	248.6	241.5	246.1	-1.8
e	321.0	1	320.9	325.5	325.4	323.2	-4.5
a ₁	395.5	<1	391.4	400.0	395.9	396.8	-4.5
e	494.4	6	494.1	501.4	501.1	497.4	-6.9
a ₁	555.3	<1	550.4	562.5	557.6	557.7	-7.2
a ₁	1258.5	143	1218.2	1274.1	1233.3	1267.2	-15.6

Table S4: Computed Vibrational Frequencies (cm^{-1}) and Harmonic Intensities (km mol^{-1}) for D_{2d} -symmetry P_4O_2 .

Sym.	Fund.	Intensity	Isotope Fund.	CCSD(T) Harm.	CCSD(T) Isotope Harm.	B3LYP Harm.	B3LYP δVPT2
e	233.27	2	224.13	237.54	228.23	239.31	-4.27
a ₁	348.26	0	344.23	355.88	351.77	352.39	-7.62
b ₁	353.52	0	353.52	358.45	358.45	353.14	-4.93
e	398.55	2	397.93	403.94	403.31	395.95	-5.39
b ₂	422.24	1	419.38	429.55	426.64	424.10	-7.31
a ₁	504.93	0	501.19	507.63	503.87	493.96	-2.71
e	654.01	23	628.68	666.11	640.31	652.06	-12.10
a ₁	724.58	0	696.28	732.28	703.68	726.06	-7.70
b ₂	729.76	91	701.55	739.69	711.09	733.53	-9.93

Geometries (in angstrom)

Cyclic P_4O , CCSD(T)/cc-pV(T+d)Z

P	0.000000	-1.481222	0.812515
P	0.000000	-1.082799	-1.212523
P	0.000000	1.481222	0.812515
P	0.000000	1.082799	-1.212523
O	0.000000	0.000000	1.536835

Bridge-Bonded P_4O , CCSD(T)/cc-pV(T+d)Z

P	0.000000	-1.119500	0.964412
P	1.245722	0.000000	-0.534651
P	-1.245722	0.000000	-0.534651
P	0.000000	1.119500	0.964412
O	0.000000	0.000000	-1.679452

Terminal P_4O , CCSD(T)/cc-pV(T+d)Z

P	0.663894	-1.149898	-0.731375
P	0.000000	0.000000	0.939617
P	0.663894	1.149898	-0.731375
P	-1.327788	0.000000	-0.731375
O	0.000000	0.000000	2.418162

D_{2d}-Symmetry P₄O₂, CCSD(T)/cc-pV(T+d)Z

P	-0.903365	-0.903365	0.723431
P	0.903365	0.903365	0.723431
P	0.903365	-0.903365	-0.723431
P	-0.903365	0.903365	-0.723431
O	0.000000	0.000000	1.838283
O	0.000000	0.000000	-1.838283

Terminal P₄O, CCSD/cc-pV(T+d)Z

P	-0.659058	-1.141522	0.726345
P	0.000000	0.000000	-0.936443
P	-0.659058	1.141522	0.726345
P	1.318116	0.000000	0.726345
O	0.000000	0.000000	-2.406249

Transition State (Terminal→Intermediate), 271*i* cm⁻¹, CCSD/cc-pV(T+d)Z

P	-0.514364	0.764906	1.163420
P	-0.393151	-1.070185	0.000000
P	-0.514364	0.764906	-1.163420
P	1.301587	0.781955	0.000000
O	0.232944	-2.404291	0.000000

Intermediate, CCSD/cc-pV(T+d)Z

P	-0.452712	0.791185	1.153644
P	-0.579246	-1.214443	0.000000
P	-0.452712	0.791185	-1.153644
P	1.313842	0.855194	0.000000
O	0.330804	-2.368542	0.000000

Transition State (Intermediate→Bridge-Bonded), $382i\text{ cm}^{-1}$, CCSD/cc-pV(T+d)Z

P	-0.444072	-0.866406	1.143067
P	-0.700405	1.156561	0.000000
P	1.283227	-0.430824	0.000000
P	-0.444072	-0.866406	-1.143067
O	0.591248	1.950177	0.000000

Bridge-Bonded P₄O, CCSD/cc-pV(T+d)Z

P	0.000000	-1.112973	0.956750
P	1.245352	0.000000	-0.528521
P	-1.245352	0.000000	-0.528521
P	0.000000	1.112973	0.956750
O	0.000000	0.000000	-1.658772