Supporting information for:

Ab initio computation for solid-state ^{31}P NMR of inorganic phosphates: Revisiting X-ray structures†

E-mail:

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Gamma centered k-point grids were created using automated k-mesh generation, built into the VASP code. The density of k-points was determined by the formula:

$$N_x = max(1, l \times |\vec{b_x}| + 0.5) \tag{1}$$

where N_x is the number of k-points along the reciprocal lattice vector, $\vec{b_x}$, corresponding to lattice vector $\vec{x}$. l is the input length parameter which dictates k-spacing, which was found to converge at 15. Larger values for l correspond to greater k-point densities.

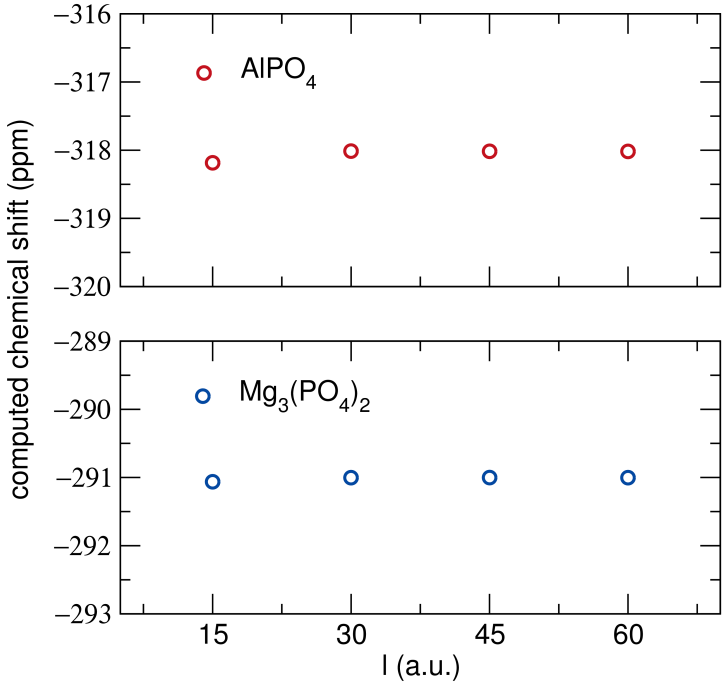

Figure S1: k-spacing was tested for convergence with $AlPO_4$ and $Mg_3(PO_4)_2$.

Table S1: Unit cell parameters for 22 inorganic phosphate compounds studied in this work as reported in ICSD and fully relaxed structures below in italics

Compound	a/Å	b/Å	c/Å	α/°	β/°	γ/°
Li_3PO_4	4.924	6.115	10.473	90	90	90
	4.974	*6.141*	*10.538*	*90*	*90*	*90*
$Cd_2P_2O_7$	6.623	6.672	6.858	64.62	84.20	82.38
	6.659	*6.619*	*6.807*	*64.950*	*84.087*	*82.011*
$Ca(H_2PO_4)_2$	5.550	7.558	8.223	68.154	70.522	86.320
	5.488	*8.037*	*8.410*	*70.882*	*66.212*	*78.39*
α–$Zn_3(PO_4)_2$	8.14	5.63	15.04	90	105.13	90
	8.215	*5.618*	*15.120*	*90*	*105.046*	*90*
$Na_4P_2O_7$	9.367	5.390	13.480	90	90	90
	9.324	*5.393*	*13.499*	*90*	*90*	*90*
α–$CaZn_2(PO_4)_2$	4.96	8.42	8.94	113.75	102.45	94.20
	4.967	*8.412*	*8.937*	*113.688*	*102.340*	*94.254*
$KZn_4(PO_4)_3$	8.166	9.675	13.810	90	90	90
	8.168	*9.627*	*13.854*	*90*	*90*	*90*
β–$Zn_3(PO_4)_2$	8.270	8.686	9.170	90	90	12.771
	8.270	*8.716*	*9.152*	*90*	*90*	*113.132*
$Ca(H_2PO_4)_2 \bullet (H_2O)$	5.626	6.256	11.889	92.928	96.656	114.229
	5.585	*6.208*	*11.785*	*92.942*	*95.760*	*114.357*
$CaHPO_4 \bullet 2(H_2O)$	5.812	15.180	6.239	90	116.430	90
	5.796	*14.861*	*6.084*	*90*	*115.780*	*90*
$MgZn_2(PO_4)_2$	7.569	8.355	5.059	90	94.95	90
	7.585	*8.314*	*5.061*	*90*	*95.142*	*90*
β–$Ca_2P_2O_7$	6.686	6.686	24.147	90	90	90
	6.664	*6.664*	*24.104*	*90*	*90*	*90*
α–$Ca_2P_2O_7$	5.315	8.542	12.660	90	90.3	90
	5.323	*8.483*	*12.641*	*90*	*89.845*	*90*
$Mg_3(PO_4)_2$	8.512	8.982	9.320	116.34	91.50	114.49
	8.504	*8.982*	*9.325*	*115.944*	*91.356*	*114.378*
α–$Zn_2P_2O_7$	8.259	9.099	10.618	99.350	112.888	90
	8.272	*9.129*	*10.663*	*99.027*	*112.822*	*112.822*
α–$Mg_2P_2O_7$	6.981	8.295	9.072	90	113.999	90
	6.954	*8.300*	*9.067*	*90*	*113.856*	*90*
$NaAlP_2O_7$	7.203	7.710	9.326	90	111.743	90
	7.227	*7.694*	*9.335*	*90*	*111.761*	*90*
$KAlP_2O_7$	7.308	8.025	9.662	90	90	106.69
	7.339	*8.081*	*9.684*	*90*	*90*	*107.096*
α–$Sr_2P_2O_7$	5.404	8.910	13.105	90	90	90
	5.372	*8.899*	*13.151*	*90*	*90*	*90*
$NaZr_2(PO_4)_2$	8.804	8.804	9.132	61.179	61.179	60
	8.855	*8.855*	*9.132*	*60.997*	*60.998*	*60.000*
$Mg_2P_4O_{12}$	7.191	7.191	9.675	98.959	109.792	109.652
	7.195	*7.195*	*9.722*	*99.062*	*109.355*	*109.843*
$AlPO_4$	4.946	4.946	10.953	90	90	120
	4.974	*4.974*	*11.016*	*90*	*90*	*120*

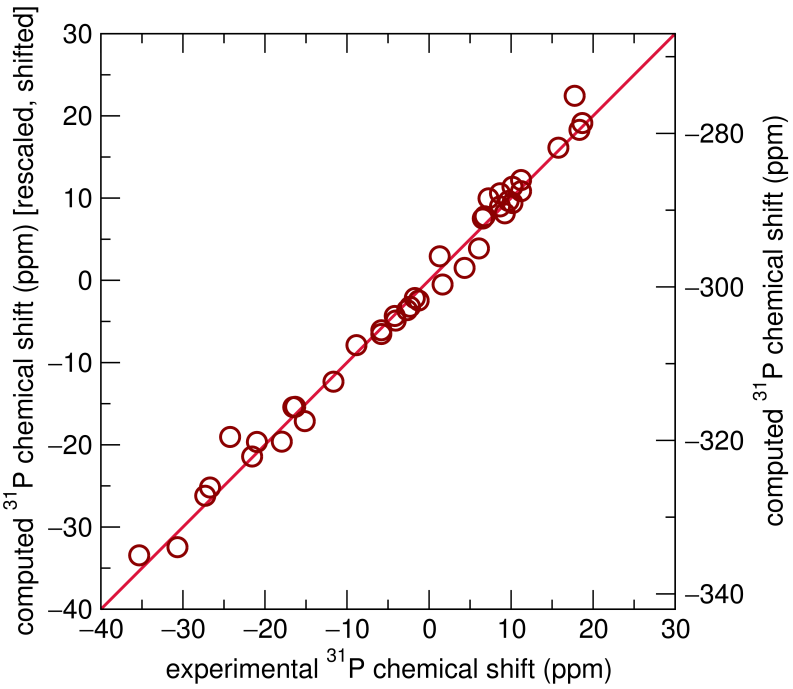

Figure S2: GIPAW calculated isotropic chemical shifts using fully relaxed structures and the PBEsol functional compared to experimentally reported values. $R^2 = 0.987$. Here, the left vertical axis is scaled by a factor of 0.933 and shifted by 299.15 ppm from the VASP calculated shifts.

Due to the large deviations of lattice parameters during the full relaxation of $Ca(H_2PO_4)_2$, another DFT relaxation was done for this structure including dispersion interactions using the DFT-D2 method.[1] The PBE functional[2] was used as the PBEsol functional is incompatible with the DFT-D2 method within the VASP code. Even with dispersion forces accounted for, lattice cell parameters still largely deviated from the previously reported structure, as shown in Table S2.

Table S2: Unit cell parameters for $Ca(H_2PO_4)_2$ as reported in ICSD and fully relaxed while accounting for dispersion interactions below in italics

Compound	a/Å	b/Å	c/Å	α/°	β/°	γ/°
$Ca(H_2PO_4)_2$	5.550	7.558	8.223	68.154	70.522	86.320
	5.490	*7.918*	*8.312*	*70.613*	*67.926*	*79.041*

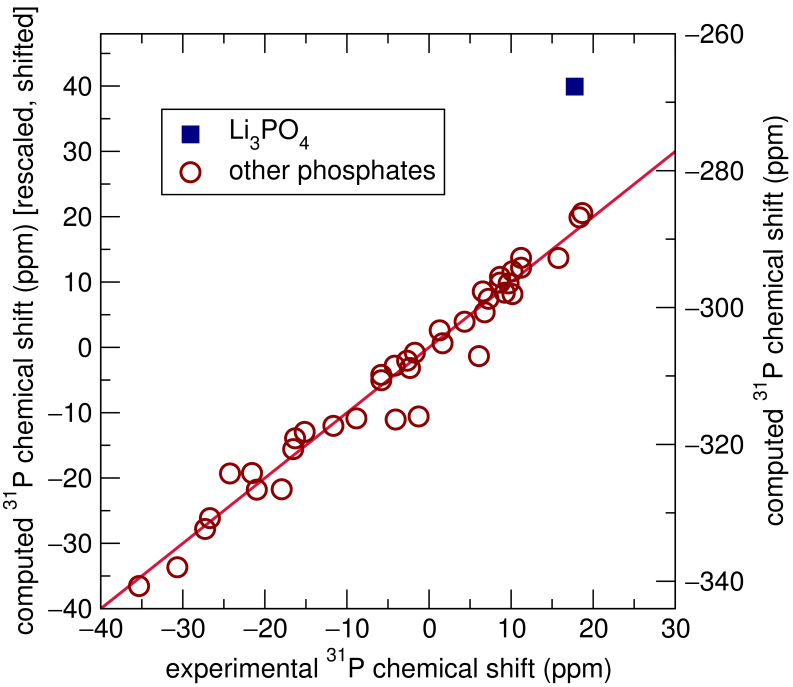

Figure S3: GIPAW calculated isotropic chemical shifts using reported structures from ICSD and the PBE functional compared to experimentally reported values. $R^2 = 0.924$, or $R^2 = 0.963$ if Li_3PO_4 is disregarded. Here, the left vertical axis is scaled by a factor of 1.048 and shifted by 305.80 ppm from the VASP calculated shifts.

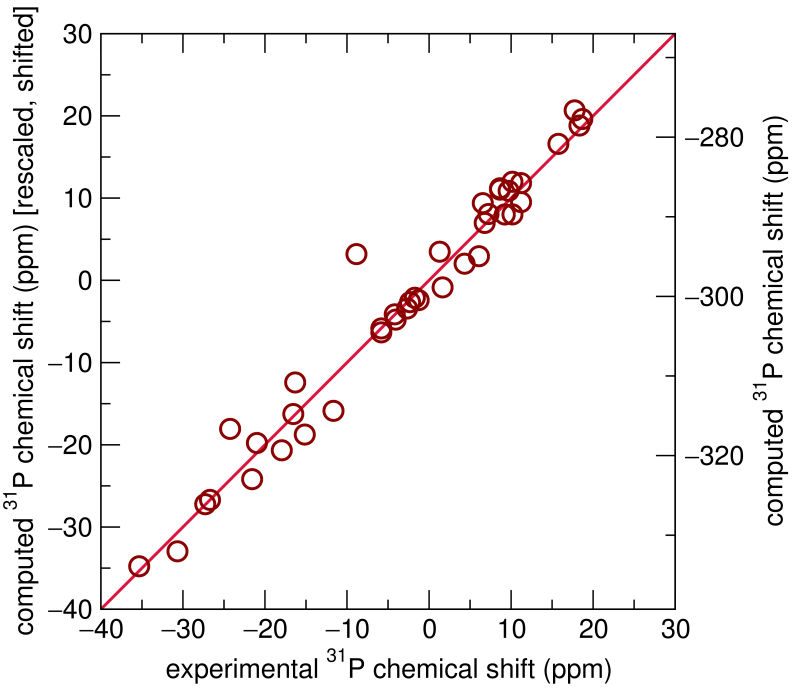

Figure S4: GIPAW calculated isotropic chemical shifts using structures relaxed with rigid cell parameters and the PBE functional compared to experimentally reported values. $R^2 = 0.964$. Here, the left vertical axis is scaled by a factor of 0.968 and shifted by 297.99 ppm from the VASP calculated shifts.

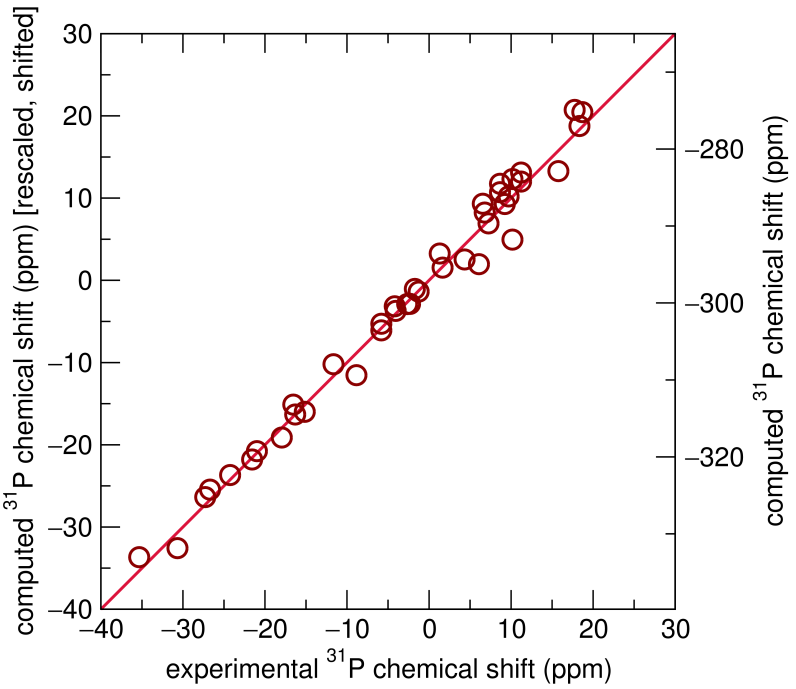

Figure S5: GIPAW calculated isotropic chemical shifts using fully relaxed structures and the PBE functional compared to experimentally reported values. $R^2 = 0.986$. Here, the left vertical axis is scaled by a factor of 0.936 and shifted by 297.05 ppm from the VASP calculated shifts.

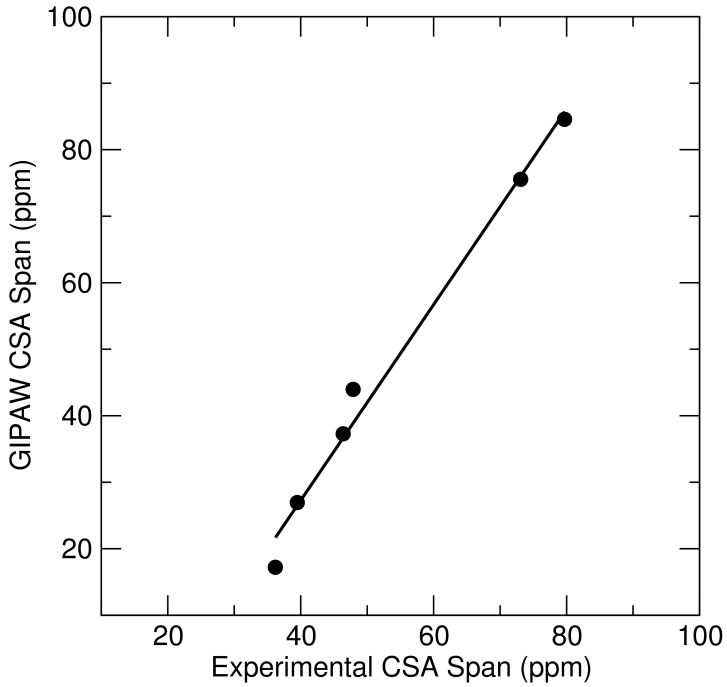

Figure S6: GIPAW calculated CSA span using structures relaxed with rigid lattice parameters and the PBE functional compared to experimentally reported values. $R^2 = 0.987$.

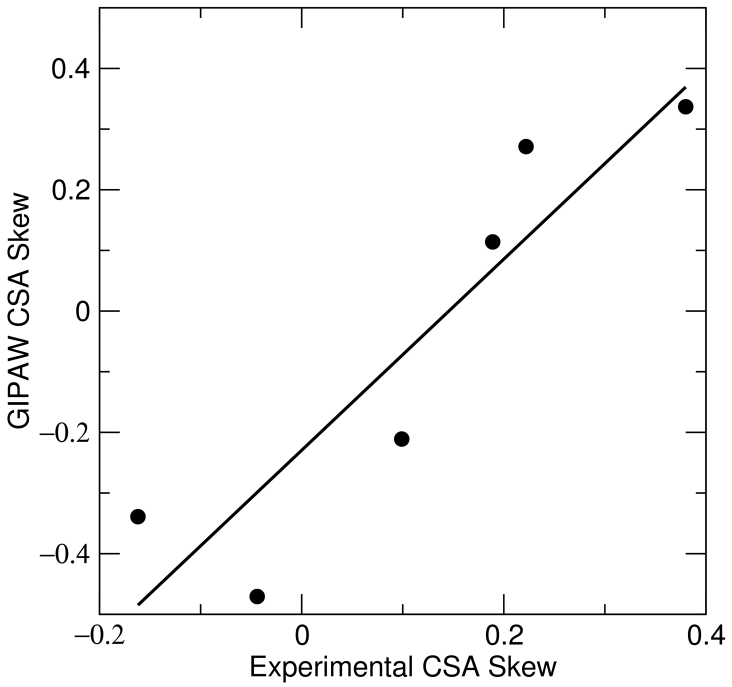

Figure S7: GIPAW calculated CSA skew using structures relaxed with rigid lattice parameters and the PBE functional compared to experimentally reported values. $R^2 = 0.831$.

Table S3: Computed ^{31}P CSA tensor parameters for all 22 compounds computed for structures relaxed with rigid cell parameters using PBEsol and PBE written below in italics.

Compound	δ_{iso}/ppm	Ω/ppm	κ
Li_3PO_4	–276.6878	6.3630	–0.1396
	–276.6414	*6.2621*	*–0.1392*
$Cd_2P_2O_7$	–296.7197	161.3842	–0.5365
	–295.8874	*161.3797*	*–0.5531*
	–299.8709	117.1326	–0.6952
	–298.8751	*116.1794*	*–0.6860*
$Ca(H_2PO_4)_2$	–289.9187	167.5137	0.3432
	–289.6518	*177.1814*	*0.4328*
	–295.8704	140.7196	0.1813
	–294.9645	*143.7031*	*0.1395*
α–$Zn_3(PO_4)_2$	–288.1672	78.4081	0.1582
	–286.7135	*75.5592*	*0.1139*
$Na_4P_2O_7$	–287.7554	143.1338	–0.8727
	–286.5922	*142.5992*	*–0.8725*
	–286.7524	153.2788	–0.8780
	–285.6128	*152.2954*	*–0.8757*
α–$CaZn_2(PO_4)_2$	–290.4665	85.9927	0.2883
	–289.7158	*84.5761*	*0.2712*
	–279.5392	44.6057	–0.4834
	–278.5499	*43.9620*	*–0.4707*
$KZn_4(PO_4)_3$	–288.8791	66.8469	–0.6744
	–286.7518	*64.8321*	*–0.6802*
	–278.4310	73.0178	0.3885
	–277.7230	*74.5302*	*0.3547*
β–$Zn_3(PO_4)_2$	–289.1686	23.4822	–0.0323
	–289.7030	*17.2178*	*–0.2111*
	–281.8146	40.4123	–0.4229
	–280.8441	*37.2953*	*–0.3990*
$Ca(H_2PO_4)_2 \bullet (H_2O)$	–295.1250	124.8185	–0.1526
	–294.3918	*131.1878*	*–0.1121*
	–289.7484	103.1896	0.2026
	–288.2935	*103.1762*	*0.0475*
$CaHPO_4 \bullet 2(H_2O)$	–285.9999	116.8827	0.0249
	–286.4263	*123.1148*	*–0.0670*
$MgZn_2(PO_4)_2$	–285.7051	47.6715	–0.2044
	–285.7744	*47.6568*	*–0.1395*
β–$Ca_2P_2O_7$	–305.8869	174.8703	–0.1685
	–304.5263	*172.4847*	*–0.1742*
	–300.9802	141.3152	–0.5608
	–300.1662	*140.7336*	*–0.5560*
	–302.5808	149.4955	–0.6724
	–301.5242	*148.3881*	*–0.6700*
	–303.2678	145.1390	–0.4339
	–302.2609	*144.7101*	*–0.4379*

Table S4: Computed ^{31}P CSA tensor parameters for all 22 compounds computed for structures relaxed with rigid cell parameters using PBEsol and PBE written below in italics (continuted)

Compound	δ_{iso}/ppm	Ω/ppm	κ
α–$Ca_2P_2O_7$	–301.8591	125.2659	–0.3203
	–300.7201	*123.1066*	*–0.3024*
	–305.1167	123.8306	–0.5170
	–304.0286	*123.9809*	*–0.5428*
$Mg_3(PO_4)_2$	–291.0622	27.4465	0.4335
	–290.7743	*26.9534*	*0.3368*
α–$Zn_2P_2O_7$	–317.9956	135.5742	–0.3852
	–317.3484	*135.0370*	*–0.4140*
	–320.4896	144.9354	–0.3686
	–319.3358	*144.2677*	*–0.3910*
	–313.2307	113.1426	–0.7932
	–314.3873	*115.2942*	*–0.7677*
α–$Mg_2P_2O_7$	–315.3940	146.4777	–0.6315
	–294.6839	*218.8990*	*–0.2985*
	–307.2805	110.9000	–0.9052
	–310.8127	*160.9620*	*–0.2276*
$NaAlP_2O_7$	–315.8403	150.6109	–0.3564
	–314.7761	*149.1990*	*–0.3615*
	–326.3221	130.6143	–0.5731
	–325.5653	*130.1871*	*–0.5751*
$KAlP_2O_7$	–320.1908	112.9544	–0.9751
	–318.4101	*112.4001*	*–0.9479*
	–327.3605	133.2534	–0.2466
	–326.1127	*132.3035*	*–0.2410*
α–$Sr_2P_2O_7$	–304.1691	121.4014	–0.8373
	–302.9232	*119.5529*	*–0.8764*
	–301.9383	109.7637	–0.5855
	–300.4661	*106.8719*	*–0.5980*
$NaZr_2(PO_4)_2$	–322.8137	13.9623	–0.9348
	–322.9771	*16.2592*	*–0.7897*
$Mg_2P_4O_{12}$	–333.8429	230.9511	0.4928
	–332.0204	*230.4921*	*0.4886*
	-335.3001	241.2628	0.5337
	–333.9006	*240.7955*	*0.5354*
$AlPO_4$	–318.0154	8.5019	0.0751
	–316.6491	*9.0072*	*0.0174*

References

(1) S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787.

(2) J. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.