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Supplementary material to: On the effect of neglecting anharmonic motion in charge density studies

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1. Supplementary material

The following Table gives the details of the density- and thermal motion parameters of the P atom after multipole refinement. The same data was used for the graphical representations in the main paper. Estimated standard uncertainties (s.u.) are also given.

Table 1
Selected geometry-, density-, and thermal motion parameters of the P atom in **1** in the noise-free, ideal reference model (= true parameters) (**a**), after refinement excluding noise and anharmonic motion in the refinement (**b**), after introduction of noise including full anharmonic motion (**c**), after refinement neglecting anharmonic motion at the Al atom (**d**), after refinement excluding anharmonic motion of 4th order at the P atom (**d**) and finally excluding anharmonic motion at all (**f**) but including experimental noise. Distances are given in Å, Uij in Å^2, Cijk in Å^3, Dijkl in Å^4, monopoles in e, *R* in %.

	(**a**)	(**b**)	s.u.	(**c**)	s.u.	(**d**)	s.u.	(**e**)	s.u.	(**f**)	s.u.
noise*	off	off		on		on		on		on	
3rd order GC	P/Al	off		P/Al		P		P		off	
4th order GC	P	off		P		P		off		off	
d(P−C1)	1.791	1.791		1.791		1.791		1.791		1.791	
d(P−C6)	1.786	1.786		1.786		1.786		1.786		1.786	
x	0.270116	0.270027	0.000001	0.270100	0.000015	0.270101	0.000015	0.270102	0.000015	0.270023	0.000007
y	0.704204	0.704138	0.000001	0.704204	0.000016	0.704206	0.000016	0.704208	0.000016	0.704132	0.000007
z	0.401967	0.401986	0.000001	0.401974	0.000010	0.401974	0.000010	0.401975	0.000010	0.401987	0.000004
U11	0.022306	0.022018	0.000006	0.022202	0.000077	0.022201	0.000077	0.022039	0.000029	0.022035	0.000029
U22	0.017633	0.017668	0.000005	0.017465	0.000063	0.017467	0.000063	0.017660	0.000023	0.017655	0.000023
U33	0.016227	0.015992	0.000004	0.016080	0.000061	0.016080	0.000061	0.015964	0.000022	0.015960	0.000022
U12	0.002181	0.002081	0.000003	0.002197	0.000045	0.002197	0.000045	0.002090	0.000017	0.002089	0.000017
U13	0.000556	0.000599	0.000003	0.000528	0.000047	0.000528	0.000047	0.000610	0.000017	0.000612	0.000017
U23	0.002778	0.002660	0.000003	0.002803	0.000042	0.002803	0.000042	0.002649	0.000016	0.002649	0.000016
U_{eq}	0.019525	0.019342		0.019385		0.019385		0.019335		0.019330	
C111	0.000029	—	—	0.000031	0.000016	0.000033	0.000016	0.000033	0.000016	—	—
C222	-0.000003	—	—	0.000011	0.000020	0.000012	0.000020	0.000015	0.000021	—	—
C333	0.000012	—	—	0.000013	0.000005	0.000013	0.000005	0.000013	0.000005	—	—
C112	0.000043	—	—	0.000045	0.000009	0.000045	0.000009	0.000045	0.000009	—	—
C122	0.000004	—	—	-0.000008	0.000010	-0.000008	0.000010	-0.000008	0.000010	—	—
C113	-0.000033	—	—	-0.000024	0.000006	-0.000024	0.000006	-0.000023	0.000006	—	—
C133	0.000039	—	—	0.000035	0.000004	0.000036	0.000004	0.000036	0.000004	—	—
C223	0.000000	—	—	-0.000004	0.000007	-0.000004	0.000007	-0.000004	0.000007	—	—
C233	0.000022	—	—	0.000018	0.000004	0.000018	0.000004	0.000019	0.000004	—	—
C123	-0.000020	—	—	-0.000024	0.000004	-0.000024	0.000004	-0.000024	0.000004	—	—
D1111	0.000039	—	—	0.000033	0.000010	0.000033	0.000010	—	—	—	—
D2222	-0.000005	—	—	-0.000034	0.000014	-0.000034	0.000014	—	—	—	—
D3333	0.000007	—	—	0.000004	0.000002	0.000004	0.000002	—	—	—	—
D1112	0.000008	—	—	0.000008	0.000005	0.000008	0.000005	—	—	—	—
D1222	0.000006	—	—	0.000005	0.000006	0.000005	0.000006	—	—	—	—
D1113	-0.000003	—	—	0.000000	0.000003	0.000000	0.000003	—	—	—	—
D1333	0.000001	—	—	-0.000002	0.000001	-0.000002	0.000001	—	—	—	—
D2223	0.000009	—	—	0.000014	0.000004	0.000014	0.000004	—	—	—	—
D2333	0.000005	—	—	0.000005	0.000002	0.000005	0.000002	—	—	—	—
D1122	-0.000005	—	—	-0.000013	0.000004	-0.000013	0.000004	—	—	—	—
D1133	0.000006	—	—	0.000003	0.000002	0.000003	0.000002	—	—	—	—
D2233	0.000002	—	—	0.000000	0.000002	0.000000	0.000002	—	—	—	—
D1123	0.000001	—	—	0.000001	0.000002	0.000001	0.000002	—	—	—	—
D1223	-0.000001	—	—	-0.000005	0.000002	-0.000005	0.000002	—	—	—	—
D1233	0.000003	—	—	0.000004	0.000001	0.000004	0.000001	—	—	—	—

* $p_1 = 0.333$

Table 1
Cont.

	(**a**)	(**b**)	s.u.	(**c**)	s.u.	(**d**)	s.u.	(**e**)	s.u.	(**f**)	s.u.
noise*	off	off		on		on		on		on	
3rd order GC	P/Al	off		P/Al		P		P		off	
4th order GC	P	off		P		P		off		off	
M1	4.727487	4.676929	0.006796	4.766778	0.035572	4.763719	0.035655	4.765609	0.035331	4.734058	0.035354
D1+	-0.083755	-0.071903	0.002139	-0.085138	0.011760	-0.085132	0.011786	-0.088792	0.011736	-0.072019	0.011081
D1-	-0.081504	-0.085901	0.002178	-0.090616	0.011817	-0.090336	0.011843	-0.090206	0.011819	-0.096089	0.011270
D0	0.001121	-0.025834	0.002116	-0.020546	0.011616	-0.020239	0.011640	-0.020483	0.011636	-0.042872	0.010900
Q0	0.132725	0.151436	0.002374	0.122856	0.013037	0.123176	0.013066	0.139514	0.012190	0.145481	0.012271
Q1+	-0.013929	-0.017503	0.001954	-0.022464	0.010662	-0.021950	0.010687	-0.025255	0.010008	-0.025081	0.010090
Q1-	-0.001107	-0.007310	0.002109	-0.005104	0.011417	-0.005518	0.011442	-0.014648	0.010818	-0.013675	0.010907
Q2+	-0.110834	-0.117114	0.002352	-0.114259	0.012862	-0.114010	0.012890	-0.121069	0.012077	-0.119978	0.012161
Q2-	0.052472	0.040644	0.002006	0.053452	0.010966	0.053727	0.010991	0.034707	0.010284	0.037451	0.010362
O0	0.015320	-0.002187	0.002082	0.017933	0.011339	0.017865	0.011364	0.016603	0.011362	0.003446	0.010779
O1+	-0.031655	-0.004174	0.001948	-0.052669	0.010597	-0.053089	0.010621	-0.052267	0.010613	-0.022465	0.010070
O1-	-0.058460	-0.018273	0.001928	-0.045543	0.010443	-0.045506	0.010465	-0.044595	0.010456	-0.010672	0.009958
O2+	-0.004995	-0.003752	0.001983	-0.007394	0.010723	-0.007718	0.010748	-0.007556	0.010754	-0.002912	0.010269
O2-	0.005727	-0.012539	0.001879	-0.001641	0.010138	-0.001348	0.010161	-0.001940	0.010171	-0.017927	0.009726
O3+	0.163272	0.146733	0.001985	0.173834	0.010848	0.173897	0.010874	0.174648	0.010868	0.160071	0.010264
O3-	-0.059161	-0.051805	0.001939	-0.068841	0.010513	-0.068893	0.010537	-0.070104	0.010544	-0.057580	0.010028
H0	0.051373	0.058592	0.002302	0.056404	0.012818	0.056107	0.012846	0.059068	0.011798	0.055525	0.011903
H1+	-0.014073	-0.027446	0.002007	0.014347	0.011175	0.013370	0.011198	0.000989	0.010291	0.001473	0.010382
H1-	0.008756	0.004319	0.002088	-0.007637	0.011541	-0.007029	0.011565	-0.005786	0.010707	-0.007037	0.010803
H2+	-0.013680	-0.017000	0.002134	-0.032721	0.011775	-0.032660	0.011801	-0.038848	0.010945	-0.037983	0.011037
H2-	0.004100	0.004808	0.001952	-0.002287	0.010782	-0.002568	0.010805	-0.002779	0.010003	-0.001916	0.010092
H3+	-0.015033	-0.011876	0.001933	-0.032426	0.010669	-0.032488	0.010691	-0.024275	0.009909	-0.022989	0.009997
H3-	0.022475	0.017539	0.001999	0.014204	0.011022	0.014560	0.011047	0.007084	0.010250	0.005785	0.010341
H4+	0.070642	0.066727	0.001889	0.083409	0.010453	0.084095	0.010477	0.081817	0.009683	0.079208	0.009763
H4-	0.057957	0.060036	0.001843	0.049479	0.010199	0.049387	0.010223	0.052118	0.009457	0.051089	0.009531
$\kappa(P)$	1.079831	1.087263	0.000473	1.081432	0.002607	1.081448	0.002619	1.081018	0.002372	1.082829	0.002407
$\kappa'(P)$	0.938526	0.938526	—	0.938526	—	0.938526	—	0.938526	—	0.938526	—
R	0.00	0.35		1.54		1.54		1.55		1.56	

* $p_1 = 0.333$

2. Supplementary material to the probability density function of the P atom

The total integrated negative probability is -0.008% and the associated volume 1.36 Å^3 for a 51 × 51 × 51 cube around P with edge lengths 1.6 Å and P in the center.

3. Supplementary material to the section "Quadrupoles, octupoles and hexadecapoles"

Figs. 1 to 3 show the histograms for the higher multipoles. The largest change due to a neglect of anharmonic nuclear motion is for refinement **b** due to a change in the octupoles, which contributes roughly 50 % of the density parameter changes to the total parameter distance from the reference set of parameter values as measured by the parameter R-factor given in Table 3 in the main text. When noise enters the data (**c**), which in reality is always the case, however, the most dominant contribution comes from the hexadecapoles and the error contribution of the octupoles is markedly reduced. A particular strong contribution from $O3+$ is given.

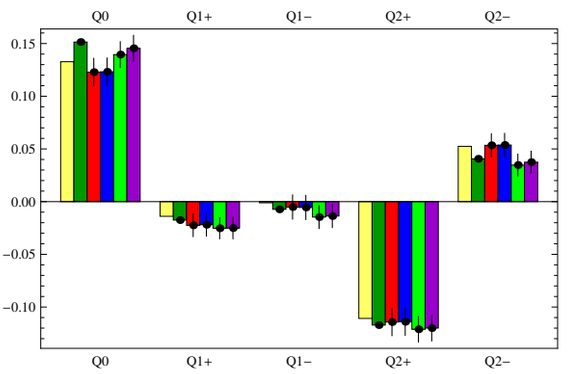

Figure 1
Quadrupole populations for refinements **a**-**f**.

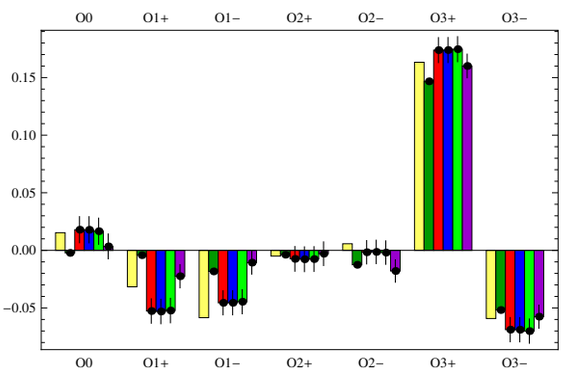

Figure 2
Octupole populations for refinements **a**-**f**.

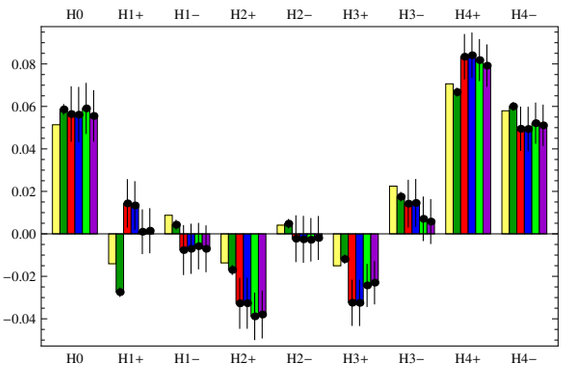

Figure 3
Hexadecapole populations for refinements **a**-**f**.

A pronounced effect on the octupoles can be observed, however, experimental noise induces larger changes in the hexadecapoles.