Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

^{95}Mo Nuclear Magnetic Resonance Parameters of Molybdenum Hexacarbonyl from Density Functional Theory: Appraisal of Computational and Geometrical Parameters

SUPPORTING INFORMATIONS

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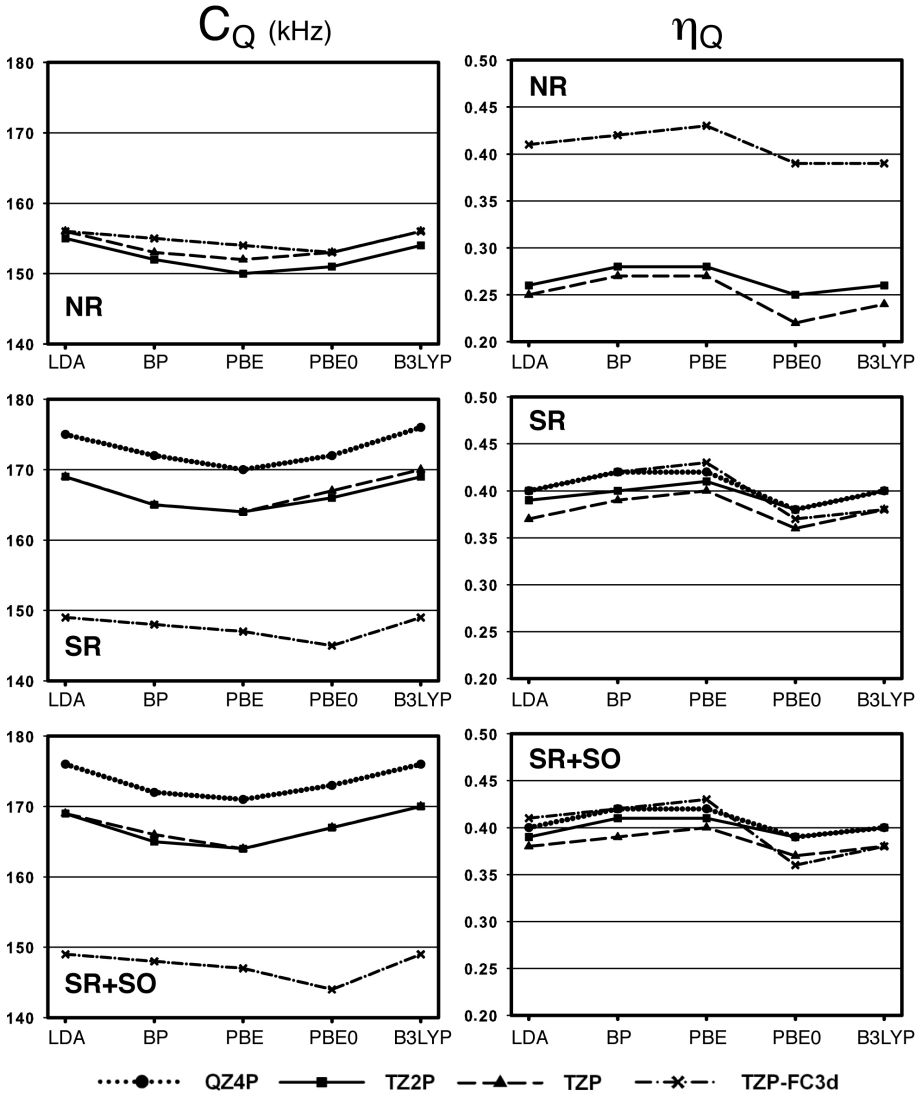

Figure 1: ^{95}Mo C_Q and η_Q computed for $Mo(CO)_6$ "benchmark" optimized geometry obtained within non-relativistic (NR), scalar relativistic (SR) and scalar relativistic including spin-orbit (SR+SO) approaches.

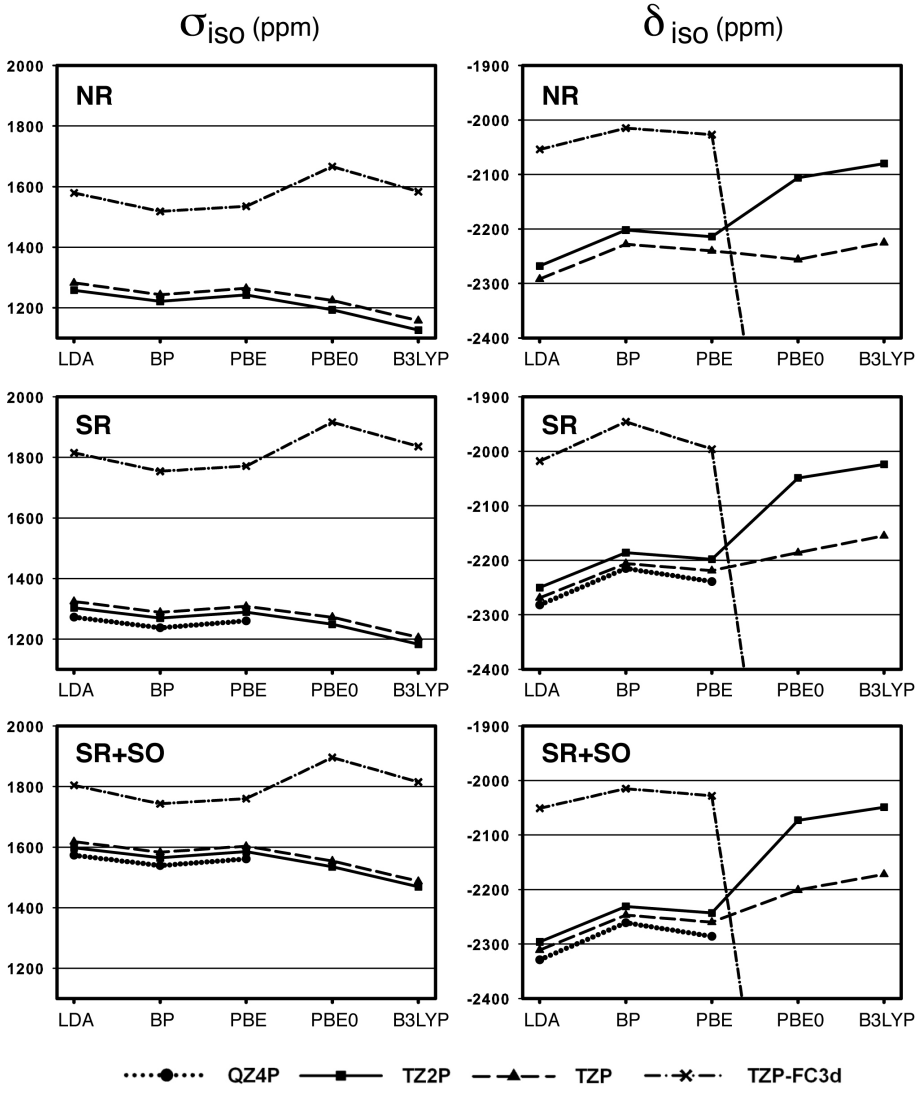

Figure 2: ^{95}Mo σ_{iso} and δ_{iso} computed for $Mo(CO)_6$ "benchmark" optimized geometry obtained within non-relativistic (NR), scalar relativistic (SR) and scalar relativistic including spin-orbit (SR+SO) approaches. Isotropic chemical shielding computed using TZP-FC3d basis set and hybrids are missing because they range between -3025 and -3118 ppm

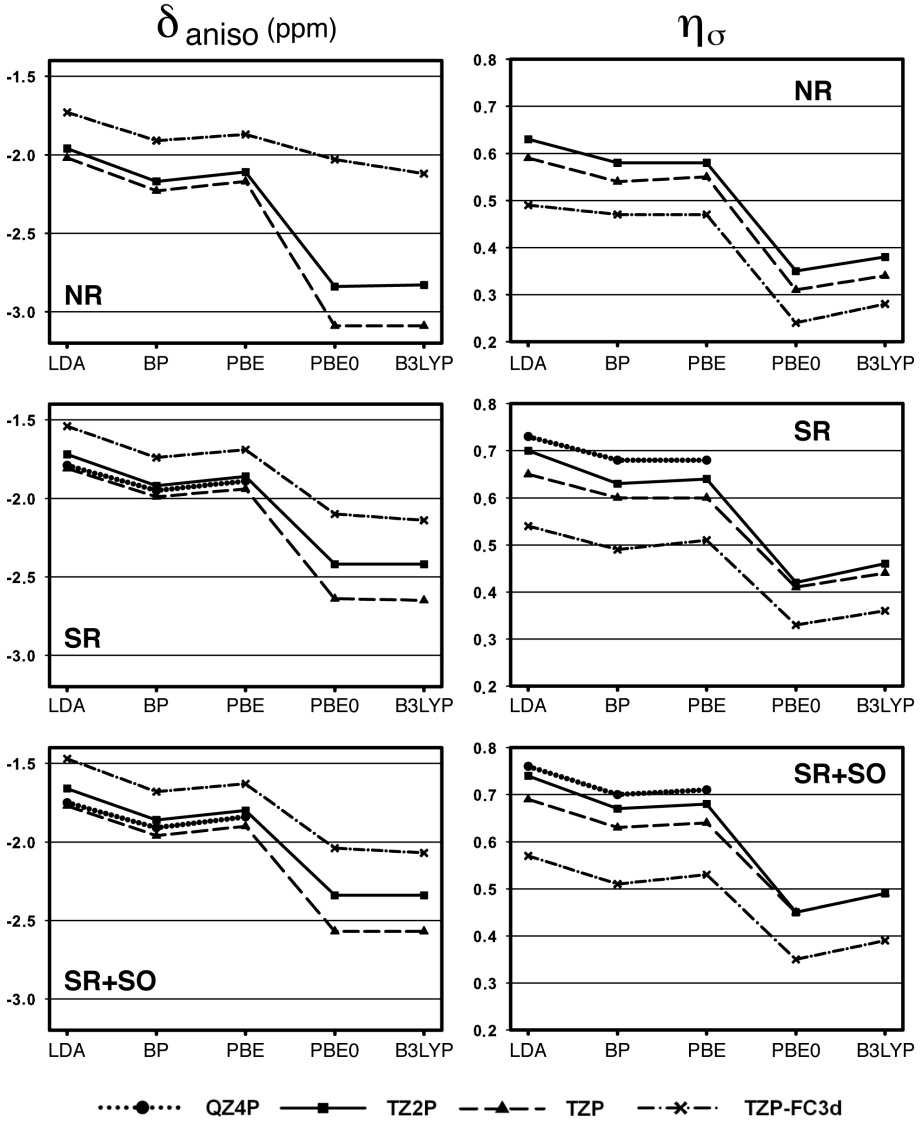

Figure 3: ^{95}Mo δ_{aniso} and η_σ computed for $Mo(CO)_6$ optimized geometries obtained within non-relativistic (NR), scalar relativistic (SR) and scalar relativistic including spin-orbit (SR+SO) approaches.

Table 1. ^{95}Mo C_Q (kHz) computed for $Mo(CO)_6$ using **(a)** its experimental structural parameters and **(b)** «benchmark» optimized geometry within non-relativistic (NR), scalar relativistic (SR) and scalar-relativistic including spin-orbit (SR+SO) approaches.

(a)

	NR			SR				SR+SO			
	TZP-FC3d	*TZP*	*TZ2P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*
LDA	486	469	466	462	508	507	527	462	510	507	529
BP	477	452	448	452	490	489	509	452	490	489	512
PBE	473	448	444	448	486	485	504	448	486	485	507
PBE0	462	434	428	433	476	476	495	433	476	476	498
B3LYP	477	448	442	448	490	489	510	447	490	490	512

(b)

	NR			SR				SR+SO			
	TZP-FC3d	*TZP*	*TZ2P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*
LDA	156	156	155	149	169	169	175	149	169	169	176
BP	155	153	152	148	165	165	172	148	166	165	172
PBE	154	152	150	147	164	164	170	147	164	164	171
PBE0	153	153	151	145	167	166	172	144	167	167	173
B3LYP	156	156	154	149	170	169	176	149	170	170	176

Table 2. ^{95}Mo η_Q computed for $Mo(CO)_6$ using **(a)** its experimental structural parameters and **(b)** «benchmark» optimized geometry within non-relativistic (NR), scalar relativistic (SR) and scalar-relativistic including spin-orbit (SR+SO) approaches.

(a)

	NR			SR				SR+SO			
	TZP-FC3d	*TZP*	*TZ2P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*
LDA	0.095	0.077	0.078	0.096	0.094	0.095	0.092	0.096	0.094	0.095	0.091
BP	0.094	0.077	0.078	0.096	0.095	0.095	0.094	0.096	0.095	0.095	0.092
PBE	0.096	0.079	0.079	0.097	0.096	0.096	0.094	0.097	0.096	0.096	0.093
PBE0	0.084	0.066	0.068	0.084	0.087	0.087	0.083	0.085	0.087	0.087	0.083
B3LYP	0.085	0.068	0.070	0.086	0.089	0.089	0.086	0.085	0.089	0.089	0.085

(b)

	NR			SR				SR+SO			
	TZP-FC3d	*TZP*	*TZ2P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*
LDA	0.41	0.25	0.26	0.40	0.37	0.39	0.4	0.41	0.38	0.39	0.40
BP	0.42	0.27	0.28	0.42	0.39	0.40	0.42	0.42	0.39	0.41	0.42
PBE	0.43	0.27	0.28	0.43	0.40	0.41	0.42	0.43	0.40	0.41	0.42
PBE0	0.39	0.22	0.25	0.37	0.36	0.38	0.38	0.36	0.37	0.39	0.39
B3LYP	0.39	0.24	0.26	0.38	0.38	0.40	0.4	0.38	0.38	0.40	0.40

Table 3. ^{95}Mo σ_{iso} (ppm) computed for $Mo(CO)_6$ using **(a)** its experimental structural parameters, **(b)** optimized geometries (using a molecular approach) and **(c)** «benchmark» optimized geometry within non-relativistic (NR), scalar relativistic (SR) and scalar-relativistic including spin-orbit (SR+SO) approaches.

(a)

	NR			SR				SR+SO			
	TZP-FC3d	*TZP*	*TZ2P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*
LDA	1610	1317	1294	1846	1360	1339	1309	1835	1654	1634	1610
BP	1546	1275	1253	1782	1320	1301	1270	1770	1615	1597	1573
PBE	1563	1297	1274	1799	1340	1321	1293	1787	1635	1617	1595
PBE0	1691	1252	1222	1944	1302	1279		1924	1584	1565	
B3LYP	1607	1184	1155	1863	1234	1212		1842	1516	1498	

(b)

	NR			SR				SR+SO			
	TZP-FC3d	*TZP*	*TZ2P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*
LDA	1620	1324	1342	1893	1411	1424	1397	1882	1705	1720	1699
BP	1379	1064	1095	1670	1188	1213	1190	1659	1482	1509	1491
PBE	1414	1109	1138	1702	1228	1252	1229	1691	1522	1547	1531
PBE0	1524	1102	1127	1816	1241	1263		1805	1523	1550	
B3LYP	1299	839	872	1612	1011	1040		1599	1291	1325	

(c)

	NR			SR				SR+SO			
	TZP-FC3d	*TZP*	*TZ2P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*
LDA	1579	1282	1258	1815	1324	1303	1272	1804	1618	1598	1573
BP	1518	1243	1221	1754	1288	1269	1237	1743	1583	1565	1539
PBE	1535	1264	1242	1771	1308	1289	1260	1760	1603	1585	1561
PBE0	1666	1224	1193	1916	1272	1249		1896	1554	1535	
B3LYP	1583	1157	1126	1836	1205	1183		1815	1487	1469	

Table 4. ^{95}Mo δ_{iso} (ppm) computed for $Mo(CO)_6$ using **(a)** its experimental structural parameters, **(b)** optimized geometries (using a molecular approach) and **(c)** «benchmark» optimized geometry within non-relativistic (NR), scalar relativistic (SR) and scalar-relativistic including spin-orbit (SR+SO) approaches.

(a)

	NR			SR				SR+SO			
	TZP-FC3d	TZP	TZ2P	TZP-FC3d	TZP	TZ2P	QZ4P	TZP-FC3d	TZP	TZ2P	QZ4P
LDA	-2085	-2328	-2304	-2050	-2304	-2286	-2318	-2082	-2347	-2332	-2366
BP	-2042	-2259	-2234	-1974	-2238	-2218	-2249	-2042	-2279	-2263	-2294
PBE	-2054	-2273	-2246	-2024	-2251	-2230	-2272	-2056	-2292	-2275	-2320
PBE0	-3050	-2284	-2135	-3102	-2216	-2079		-3117	-2231	-2103	
B3LYP	-3075	-2253	-2109	-3129	-2184	-2053		-3145	-2201	-2078	

(b)

	NR			SR				SR+SO			
	TZP-FC3d	TZP	TZ2P	TZP-FC3d	TZP	TZ2P	QZ4P	TZP-FC3d	TZP	TZ2P	QZ4P
LDA	-2170	-2400	-2348	-2104	-2361	-2317	-2343	-2136	-2403	-2363	-2391
BP	-2072	-2259	-2199	-2039	-2252	-2277	-2175	-2071	-2292	-2242	-2258
PBE	-2094	-2288	-2226	-2060	-2277	-2222	-2220	-2092	-2317	-2266	-2267
PBE0	-2960	-2145	-2023	-2985	-2149	-1952		-3009	-2165	-1970	
B3LYP	-2920	-2077	-1845	-2980	-2057	-1883		-3003	-2063	-1908	

(c)

	NR			SR				SR+SO			
	TZP-FC3d	TZP	TZ2P	TZP-FC3d	TZP	TZ2P	QZ4P	TZP-FC3d	TZP	TZ2P	QZ4P
LDA	-2054	-2292	-2268	-2018	-2269	-2250	-2282	-2051	-2311	-2296	-2329
BP	-2015	-2228	-2202	-1946	-2206	-2186	-2215	-2015	-2247	-2231	-2261
PBE	-2027	-2240	-2214	-1996	-2219	-2198	-2239	-2028	-2260	-2243	-2286
PBE0	-3025	-2256	-2106	-3074	-2186	-2049		-3089	-2201	-2073	
B3LYP	-3051	-2225	-2080	-3102	-2155	-2024		-3118	-2172	-2049	

Table 5. ^{95}Mo δ_{aniso} (ppm) computed for $Mo(CO)_6$ using **(a)** its experimental structural parameters and **(b)** «benchmark» optimized geometry within non-relativistic (NR), scalar relativistic (SR) and scalar-relativistic including spin-orbit (SR+SO) approaches.

(a)

	NR			SR				SR+SO			
	TZP-FC3d	*TZP*	*TZ2P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*
LDA	3.39	3.76	3.88	3.94	4.29	4.48	4.57	4.17	4.49	4.72	4.89
BP	2.25	2.28	2.38	2.79	2.90	3.09	3.30	3.00	3.07	3.30	3.59
PBE	2.54	2.66	2.74	3.08	3.26	3.42	3.72	3.28	3.42	3.64	4.01
PBE0	0.89	1.53	1.30	1.40	1.00	0.89		1.46	0.98	0.83	
B3LYP	0.89	1.37	1.25	1.33	0.98	0.86		1.40	0.94	0.93	

(b)

	NR			SR				SR+SO			
	TZP-FC3d	*TZP*	*TZ2P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*
LDA	-1.73	-2.02	-1.96	-1.54	-1.81	-1.72	-1.79	-1.47	-1.77	-1.66	-1.75
BP	-1.91	-2.23	-2.17	-1.74	-1.99	-1.92	-1.95	-1.68	-1.96	-1.86	-1.91
PBE	-1.87	-2.17	-2.11	-1.69	-1.94	-1.86	-1.89	-1.63	-1.90	-1.80	-1.84
PBE0	-2.03	-3.09	-2.84	-2.10	-2.64	-2.42		-2.04	-2.57	-2.34	
B3LYP	-2.12	-3.09	-2.83	-2.14	-2.65	-2.42		-2.07	-2.57	-2.34	

Table 6. ^{95}Mo η_σ computed for $Mo(CO)_6$ using **(a)** its experimental structural parameters and **(b)** «benchmark» optimized geometry within non-relativistic (NR), scalar relativistic (SR) and scalar-relativistic including spin-orbit (SR+SO) approaches.

(a)

	NR			SR				SR+SO			
	TZP-FC3d	*TZP*	*TZ2P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*
LDA	0.42	0.46	0.46	0.37	0.42	0.40	0.42	0.36	0.41	0.40	0.40
BP	0.61	0.71	0.71	0.50	0.58	0.56	0.56	0.48	0.58	0.54	0.52
PBE	0.55	0.62	0.62	0.46	0.52	0.51	0.49	0.45	0.52	0.49	0.47
PBE0	0.24	0.86	0.85	0.64	0.03	0.64		0.68	0.18	0.93	
B3LYP	0.24	0.98	0.64	0.72	0.28	0.98		0.75	0.46	0.71	

(b)

	NR			SR				SR+SO			
	TZP-FC3d	*TZP*	*TZ2P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*	*TZP-FC3d*	*TZP*	*TZ2P*	*QZ4P*
LDA	0.49	0.59	0.63	0.54	0.65	0.70	0.73	0.57	0.69	0.74	0.76
BP	0.47	0.54	0.58	0.49	0.60	0.63	0.68	0.51	0.63	0.67	0.70
PBE	0.47	0.55	0.58	0.51	0.60	0.64	0.68	0.53	0.64	0.68	0.71
PBE0	0.24	0.31	0.35	0.33	0.41	0.42		0.35	0.45	0.45	
B3LYP	0.28	0.34	0.38	0.36	0.44	0.46		0.39	0.49	0.49	