

Supporting information for

Calculation of Chemical-Shift Tensors of Heavy Nuclei:

A DFT/ZORA Investigation of ^{199}Hg Chemical-Shift Tensors in Solids, and the Effects of Cluster Size and Electronic-State Approximations

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Table S1. Calculated NMR Chemical Shieldings for Small and Large Model Clusters of ^{199}Hg Solids.

Model clusters	σ_{11} (ppm)	σ_{22} (ppm)	σ_{33} (ppm)
Hg(SCN)₂			
Small Cluster	7505	8998	12511
Large Cluster	7847	8540	11677
Hg(CN)₂			
Small Cluster	7954	7958	13301
Large Cluster	7992	8046	12092
Hg(SeCN)₂			
Small Cluster	8465	9020	12418
Large Cluster	8542	9371	11450
Hg(Acetate)₂			
Small Cluster	9596	9890	12505
Large Cluster	9975	10102	11653
HgF₂			
Small Cluster	11578	11578	11578
Large Cluster	10887	10888	10888
HgCl₂			
Small Cluster	7987	7987	13181
Large Cluster	8284	8340	12319
HgBr₂			
Small Cluster	9964	9965	13142
Large Cluster	9926	9957	11398
HgI₂			
Small Cluster	11444	12293	12348
Large Cluster	10710	10750	11296
Hg₂Cl₂			
Small Cluster <u>Hg(1)</u>	7683	7683	13203
Small Cluster <u>Hg(2)</u>	7683	7683	13203
Large Cluster <u>Hg(1)</u>	8031	8031	11612
Large Cluster <u>Hg(2)</u>	8002	8002	11612

K[Hg(SCN)₃]			
Small Cluster	8021	8557	10208
Large Cluster	7883	8243	9837
Hg₂(H₂O)·2NO₃			
Small Cluster <u>Hg(1)</u>	9455	9516	13027
Small Cluster <u>Hg(2)</u>	9392	9497	13027
Large Cluster <u>Hg(1)</u>	9024	9113	12069
Large Cluster <u>Hg(2)</u>	8849	9126	12066

Table S2. Frozen Inner Shells in FCA(TZP)/AE and FCA(DZ)/AE Basis Sets for the Elements in Large Clusters.

Elements	Frozen Core Orbitals*
Hg	[...]4f
S, Cl	[...]2p
C, N, O, F	[...]1s
Se, Br	[...]3p
I	[...]4p

*Frozen inner shells are up to and including the listed orbitals for the given elements.

Table S3. Calculated NMR Chemical Shieldings of Large Clusters with FCA/TZP and FCA/DZ level of basis sets.

Model clusters	σ_{11} (ppm)	σ_{22} (ppm)	σ_{33} (ppm)
Hg(SCN)₂			
FCA(TZP)/AE	7860	8554	11670
FCA(DZ)/AE	7880	8640	11646
Hg(CN)₂			
FCA(TZP)/AE	8003	8044	12102
FCA(DZ)/AE	8058	8100	12127
Hg(SeCN)₂			
FCA(TZP)/AE	8535	9377	11464
FCA(DZ)/AE	8599	9333	11574
Hg(Acetate)₂			
FCA(TZP)/AE	9975	10100	11656
FCA(DZ)/AE	9980	10101	11749
HgF₂			
FCA(TZP)/AE	10831	10832	10832
FCA(DZ)/AE	10901	10902	10902
HgCl₂			
FCA(TZP)/AE	8286	8362	12326
FCA(DZ)/AE	8334	8400	12355
HgBr₂			
FCA(TZP)/AE	9935	9962	11353
FCA(DZ)/AE	9939	9967	11455
HgI₂			
FCA(TZP)/AE	10709	10753	11197
FCA(DZ)/AE	10637	10677	11088
Hg₂Cl₂			
FCA(TZP)/AE <u>Hg(1)</u>	8058	8058	11609
FCA(TZP)/AE <u>Hg(2)</u>	8028	8028	11609
FCA(DZ)/AE <u>Hg(1)</u>	8108	8108	11744
FCA(DZ)/AE <u>Hg(2)</u>	8092	8092	11744
K[Hg(SCN)₃]			
FCA(TZP)/AE	7893	8263	9848
FCA(DZ)/AE	7875	8306	9845
Hg₂(H₂O)·2NO₃			
FCA(TZP)/AE <u>Hg(1)</u>	9041	9116	12093
FCA(TZP)/AE <u>Hg(2)</u>	8869	9137	12089
FCA(DZ)/AE <u>Hg(1)</u>	9069	9093	12101
FCA(DZ)/AE <u>Hg(2)</u>	8901	9163	12102

Table S4. Calculated NMR Chemical Shieldings of Large Clusters with ZORA/Scalar and Nonrelativistic level of theory.

Model clusters	σ_{11} (ppm)	σ_{22} (ppm)	σ_{33} (ppm)
Hg(SCN)₂			
ZORA/Scalar	6162	6172	8607
Nonrelativistic	6366	6535	8702
Hg(CN)₂			
ZORA/Scalar	5643	5666	8914
Nonrelativistic	6190	6221	8971
Hg(SeCN)₂			
ZORA/Scalar	6049	6224	8507
Nonrelativistic	6115	6455	8707
Hg(Acetate)₂			
ZORA/Scalar	6723	6959	8741
Nonrelativistic	7366	7439	8880
HgF₂			
ZORA/Scalar	7821	7821	7822
Nonrelativistic	8158	8159	8159
HgCl₂			
ZORA/Scalar	6499	6500	8676
Nonrelativistic	6593	6593	8820
HgBr₂			
ZORA/Scalar	6356	6358	8380
Nonrelativistic	6411	6413	8563
HgI₂			
ZORA/Scalar	5810	5814	5863
Nonrelativistic	6298	6300	6378
Hg₂Cl₂			
ZORA/Scalar <u>Hg(1)</u>	6499	6500	8676
ZORA/Scalar <u>Hg(2)</u>	6496	6497	8676
Nonrelativistic <u>Hg(1)</u>	6593	6593	8820
Nonrelativistic <u>Hg(2)</u>	6593	6593	8821
K[Hg(SCN)₃]			
FCA/TZP	5687	5781	7047
FCA/DZ	6088	6276	7454
Hg₂(H₂O)·2NO₃			
ZORA/Scalar <u>Hg(1)</u>	7151	7165	9061
ZORA/Scalar <u>Hg(2)</u>	7086	7181	9063
Nonrelativistic <u>Hg(1)</u>	7028	7145	9084
Nonrelativistic <u>Hg(2)</u>	7027	7145	9083