

*Supporting Information for:*

Towards Relatively General and Accurate Quantum Chemical  
Predictions of Solid-State  $^{17}\text{O}$  NMR Chemical Shifts in Various  
Biologically Relevant Oxygen-containing Compounds

By

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**Methodological study for Compound 6**

This compound was found to be challenging in the previous work,<sup>1</sup> with errors in  $\delta_{\text{iso}}$  of 202-218 ppm (28%-30% of the experimental shift). With the X-ray structure, we first tried a few different metal bases in the NMR calculation to see how this factor affects the prediction accuracy. As shown in Table S1, both the pure DFT method OP86 and the hybrid DFT method B3LYP were used, along with a locally dense basis set scheme using a large 6-311++G(2d,2p) basis for atoms in the metal first coordination shell and 6-31G(d) for other atoms. The metal bases studied are the effective core potential type bases in the Gaussian 09 software: CEP-121G, LanL2DZ, and SDD. This is similar to the approach used in the previous calculations of  $^{15}\text{N}$  NMR chemical shifts in metal- and NO-containing systems.<sup>2</sup> Results in Table S1 indicate that although the errors of 171-192 ppm are slightly better than the previous work, they are still significant, 24-27% of the experimental shift.

**Table S1.** Calculated  $^{17}\text{O}$  NMR Isotropic Chemical Shift

Method	Metal basis	First coordination shell basis	Other atoms' basis	$\delta_{\text{iso}}$ (ppm)
Expt.				717

B3LYP	CEP-121G	6-311++G(2d,2p)	6-31G(d)	896
OP86	CEP-121G	6-311++G(2d,2p)	6-31G(d)	907
B3LYP	LanL2DZ	6-311++G(2d,2p)	6-31G(d)	888
OP86	LanL2DZ	6-311++G(2d,2p)	6-31G(d)	899
B3LYP	SDD	6-311++G(2d,2p)	6-31G(d)	897
OP86	SDD	6-311++G(2d,2p)	6-31G(d)	909

Then, we worked on geometry-optimized structures of **6** with hydrogen positions being optimized. We first wanted to evaluate the effects of metal basis on both geometry optimization and NMR calculation. The basis for non-metal atoms is 6-311G(d) in the geometry optimization, which is relatively larger than 6-31G(d) used in the Text for organic molecule **1**, because **6** is a metal-containing system. The basis for non-metal atoms in the NMR calculation is 6-311++G(d,p), based on its good performance in the studies of organic molecules **1-4**. The method for NMR calculation here was OP86, since 1) it was found to yield excellent predictions for non-metal systems **1-4**, 2) its error listed in Table S1 is similar to that for B3LYP (~11 ppm difference, 1.5% of the experimental shift), 3) a more detailed study of NMR calculation method was to be discussed later. The partial geometry optimization method chosen here is B3LYP, with a more detailed study of geometry optimization method to be discussed later. As shown in Table S2, the effects of metal basis are actually very significant. For instance, with the same QZVP metal basis in optimization, the predicted isotropic shifts vary as much as 277 ppm among the different metal basis used in NMR calculations. The best metal basis for NMR calculation was found to be LanL2DZ. With the same LanL2DZ basis in NMR calculation, the use of different metal basis in geometry optimization also results in 139 ppm differences, with QZVP yielding the best prediction with an error of 71 ppm, which is more than half smaller than errors in Tables S1. These studies clearly indicate the selection of metal basis is critical for the accuracy in  $^{17}\text{O}$  NMR chemical shift predictions.

**Table S2.** Partial Optimization with B3LYP and NMR Calculation with OP86

Optimization Basis for Sn	NMR Calculation basis for Sn	$\delta_{\text{iso}}$ (ppm)	$\delta_{11}$ (ppm)	$\delta_{22}$ (ppm)	$\delta_{33}$ (ppm)
Expt.	Expt.	717	1450	600	100
QZVP	QZVP	1065	2416	657	122
QZVP	DGDZVP	794	1720	621	39
QZVP	cc-pwCVDZ-PP <sup>a)</sup>	893	1857	651	172
QZVP	LanL2DZ	788	1701	623	41
SDD	SDD	938	2078	672	65
SDD	DGDZVP	934	2072	665	64
SDD	cc-pwCVDZ-PP <sup>a)</sup>	1029	2195	701	192
LanL2DZ	LanL2DZ	927	2049	667	65
CEP-121G	LanL2DZ	927	2050	667	64

a) This is from EMSL basis set exchange website: <https://bse.pnl.gov/bse/portal>, while all other bases are from Gaussian 09 program.

With the QZVP metal basis for optimization and LanL2DZ metal basis for NMR calculation from above calculations, we then performed a more detailed study of geometry optimization method to see if other methods could further improve the accuracy. Interestingly, even 20 different DFT methods were studied, the predicted isotropic shifts display a relatively much smaller range (762-790 ppm, see Table S3), compared to the effect of metal basis in geometry optimization in Table S2. In fact, the final two methods used in the Text for a broader range of systems also show that the method for geometry optimization is less critical. Here, the best method is mPWP86, with an error now reduced to 45 ppm (6.3% of the experimental isotropic shift). With this geometry optimization method, we further tested a few more metal bases as shown in Table S4. It is interesting to note that except for the all-electron basis set DGDZVP which produced the same results as with the all-electron basis QZVP, all other effective core potential bases yielded larger errors. Therefore, these calculations further support the use of QZVP as an excellent metal basis in geometry optimization. As a result, we used the mPW86 method with a QZVP metal basis and 6-311G(d) for non-metals in the geometry optimization part of subsequent calculations.

**Table S3.** Partial Optimization with Different Methods and NMR Calculation with OP86

Method	$\delta_{\text{iso}}$ (ppm)	$\delta_{11}$ (ppm)	$\delta_{22}$ (ppm)	$\delta_{33}$ (ppm)
Expt.	717	1450	600	100
PBEPBE	783	1635	673	40
M06	776	1668	618	40
M06L	780	1678	620	40
BP86	763	1635	615	39
BPBE	764	1639	615	39
BPW91	766	1642	616	39
BVWN5	789	1703	623	41
BVWN	790	1704	623	41
mPWB95	763	1636	615	39
mPWLYP	777	1671	619	40
mPWP86	762	1633	615	39
mPWPL	788	1700	623	41
mPWVWN	789	1703	623	41
B3LYP	788	1701	623	41
mPWPBE	764	1637	615	39
mPWVWN5	789	1701	623	41
BB95	763	1636	615	39
BLYP	777	1671	619	40
BTPSS	763	1636	615	39
mPWTPSS	763	1636	615	39

**Table S4.** Different Metal Bases with the mPWP86 Partial Optimization

Basis set in Popt	$\delta_{\text{iso}}$ (ppm)	$\delta_{11}$ (ppm)	$\delta_{22}$ (ppm)	$\delta_{33}$ (ppm)
CEP-4G	927	2049	667	64
CEP-31G	927	2049	667	64
CEP-121G	927	2049	667	64
DGDZVP	762	1633	615	39
LanL2DZ	926	2047	667	64
LanL2MB	927	2050	668	64
SDD	926	2046	667	65

We then performed a more detailed study of the NMR calculation method, with the LanL2DZ basis for metal and 6-311++G(d,p) for non-metal atoms based on the results discussed above (Table S2), in order to see if other methods could further improve the accuracy. Here, the 18 different DFT methods in the NMR calculation step yielded a range of 762-822 ppm, which is larger than the calculated range from using different geometry optimization methods. This indicates that the method of the NMR calculation is also important. But this range is still smaller than those from using different metal bases in both geometry optimization and NMR calculation.

Therefore, this methodological study suggests that the most important part for  $^{17}\text{O}$  NMR chemical shift predictions in metal-containing systems may be the metal bases in both the geometry optimization and NMR calculation steps, and the second most important factor is the NMR calculation method, while the geometry optimization method is less critical.

As shown in Table S5, the best NMR shift prediction method for compound **6** is still OP86. The next best predicted  $\delta_{\text{iso}}$ 's are around 780 ppm, from using several methods, including B3LYP. Since B3LYP predicted  $\delta_{\text{iso}}$  has only 2.8% larger error compared with the value from using OP86 and it was used widely in previous studies of many different systems,<sup>1, 3-7</sup> both OP86 and B3LYP methods were further evaluated in the  $^{17}\text{O}$  NMR chemical shift calculations of other systems discussed in the Text.

**Table S5.** Results from Using Different DFT methods in NMR Calculations. (Unit: ppm)

Methods	$\delta_{\text{iso}}$	$\delta_{11}$	$\delta_{22}$	$\delta_{33}$
Expt.	717	1450	600	100
BP86	780	1698	685	95
BPBE	787	1720	686	94
BPW91	788	1719	688	95
BVWN5	781	1683	697	100
BVWN	780	1683	696	100
mPWB95	822	1802	703	99
mPWLYP	782	1687	696	102
mPWP86	780	1696	686	96
mPWPL	781	1682	698	101
mPWVWN	780	1681	697	101
mPWPBE	787	1717	687	95
mPWVWN5	781	1681	697	101
BB95	822	1804	703	98
BLYP	782	1689	695	101

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B3LYP	782	1681	719	86
BTPSS	792	1732	687	95
mPWTPSS	792	1730	688	96
OP86	762	1679	661	85

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