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Relativistic study of nuclear magnetic shielding constants: tungsten hexahalides and tetraoxide

M. Hada, H. Kaneko, H. Nakatsuji *,1

Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

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Abstract

Relativistic ab initio calculations of the ^{183}W magnetic shielding constant and the chemical shift of WX_6 (X = F and Cl) and WO_4^{2-} are presented. The computational method is a combination of the relativistic spin-free no-pair theory and the spin–orbit unrestricted Hartree–Fock method, which has been applied previously to ^{199}Hg magnetic shielding constants. The spin-free relativistic (SFR) terms, involving the mass velocity and Darwin terms, are shown to be important for ^{183}W shielding constants. The spin–orbit interaction, which is smaller than the SFR term, works differently on WCl_6 and WO_4^{2-}. The effects of relaxing the inner s and p orbitals of W are investigated.

1. Introduction

Theoretical investigations on the magnetic shielding constants of heavy elements, especially the fifth-row elements such as Hg, Pt and W, have been limited, despite the wealth of experimental data [1,2], since the calculations must include relativistic effects. We have recently proposed a relativistic ab initio computational method for the magnetic shielding constant by combining the relativistic spin-free no-pair theory of Sucher [3] and Hess [4,5] and the spin–orbit unrestricted Hartree–Fock (SO-UHF) method developed in our laboratory, and applied it to calculations of the proton and ^{199}Hg magnetic shielding constants of the HX [6] and HgX_2 [7] (X = F, Cl, Br and I) molecules, respectively.

Our studies on NMR chemical shifts [8,9] have shown that the major mechanism of the magnetic shielding is an intrinsic property of the element itself, and therefore, related with the position of the nucleus in the periodic table [9]. For the relativistic effects, the following points have become clear [6,7,10–14]. When the resonant nucleus is not heavy but is bonded to a heavy element, the spin–orbit (SO) interaction of the heavy element has much influence on the chemical shift of the resonant nucleus. We have shown that the experimental trends in the NMR chemical shifts of the halogen complexes of ^{1}H, ^{13}C [10], ^{71}Ga, ^{115}In [11], ^{29}Si [12], ^{27}Al [13] and ^{119}Sn [14] can be reproduced only when the SO effects of the ligands are included. For compounds having heavy resonant nuclei, relativistic calculations have been made only for HgX_2 (X = Cl, Br, I) [7] and shown that the spin-free relativistic (SFR) effect of Hg is large and also that the coupling between the SO and SFR terms is significant. A further study is certainly necessary to understand the roles of the

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[*] Corresponding author.

[1] Also at the Institute for Fundamental Chemistry, 34-4 Takano Nishi-Hiraki-cho, Sakyo-ku, Kyoto 606, Japan.

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relativistic effects in the magnetic shielding constants and chemical shifts for compounds having heavy resonant nuclei. In this Letter we present ab initio relativistic calculations for the ^{183}W magnetic shielding constants of WO_4^{2-} and WX_6 (X = F and Cl), where the relativistic effects originate only from the resonant nucleus W.

2. Method and analysis

The spin-free relativistic (SFR) no-pair Hamiltonian defined with the external-field projectors [5] is used as a zeroth-order Hamiltonian. For comparison, we also use the non-relativistic Hamiltonian. The spin–orbit (SO) interaction is included using the conventional spin–orbit operator in the Breit–Pauli form and limited only to the one-electron term. We add the SO operator to the SFR Hamiltonian in the framework of the SO-UHF method [10]. The effects of the uniform external magnetic field and the magnetic field produced by the nuclear spin moment are also considered in the framework of the SO-UHF/finite perturbation method [10]. These magnetic operators are again in the conventional Breit–Pauli form. The wavefunctions are calculated at the Hartree–Fock level of approximation. The details of the calculations have been given in Refs. [6,7].

The calculated magnetic shielding constant is partitioned into the diamagnetic, σ^{dia}, paramagnetic, σ^{para}, spin-dipolar, $\sigma^{\text{SO}}(\text{SD})$, and Fermi contact, $\sigma^{\text{SO}}(\text{FC})$ terms, as defined previously [6,10]. To understand the roles of the individual relativistic terms and the coupling thereof, we calculate at four levels of approximations which are summarized in Scheme (1) given as

level I: non-relativistic Hamiltonian,
level II: non-relativistic Hamiltonian plus SO term,
level III: relativistic spin-free no-pair Hamiltonian,
level IV: relativistic spin-free no-pair Hamiltonian plus SO term. (1)

The differences between the different levels of calculations have the meanings summarized in Scheme (2) given below:

level IV–level I: full relativistic effect,
level II–level I: SO effect in the non-relativistic environment,
level IV–level III: SO effect in the presence of the SFR terms,
level III–level I: SFR effects in the absence of the SO term,
level IV–level II: SFR effects in the presence of the SO term. (2)

3. Basis sets and geometries

The basis sets for the tungsten compounds presented are the Gaussian functions optimized by the non-relativistic calculations by Huzinaga et al. [15]. For W, we use three different contractions of the (15s12p9d3f) primitive set; set A the [7s6p4d1f] contraction in which the valence 6s and 6p orbitals are double-zeta but the core orbitals are minimal, set B the [10s6p4d1f] contraction in which the 1s orbital is uncontracted and composed of the primitive Gaussians and set C the [10s9p4d1f] contraction in which both 1s and 2p orbitals are uncontracted. The last two basis sets are designed to investigate the effects of relaxation of the inner core orbitals due to the relativistic effects. For the ligand atoms we use (10s7p)/[3s2p] for O, (10s7p)/[3s2p] for F and (11s8p)/[4s3p] for Cl, all taken from Ref. [15].

The geometries of WX_6 (X = F, Cl) and WO_4^{2-} are octahedral and tetrahedral, respectively, and the W–X distances are assumed to be 1.78, 1.83 and 2.26 Å for X = O, F and Cl, respectively [16]. The calculated magnetic shielding constants are gauge-origin independent in these molecular symmetries. We have not added the FOBFs (first-order higher angular momentum functions), which are effective in decreasing the gauge-origin dependence [17].

4. ^{183}W magnetic shielding constants

Fig. 1 shows the correlation between theory and experiment for ^{183}W chemical shifts in different levels of approximations. The reference compound is taken as WF_6. This figure shows that the SFR effects are important for the ^{183}W chemical shifts. The

Table 1
^{183}W magnetic shielding constants (ppm) and their analyses calculated with set A

Compound	Without SO				With SO							δ^{exp}
	σ^{dia}	σ^{para}	σ^{tot}	δ^{cal}	σ^{dia}	σ^{para}	σ^{SO}			σ^{tot}	δ^{cal}	
							SD	FC	total			
non-relativistic Hamiltonian												
	level I				level II							
WF_6	8982.71	−4694.13	4288.58	0	8982.54	−4737.30	6.22	23.59	29.81	4275.05	0	0
WO_4^{2-}	8887.16	−6363.33	2523.83	1764.75	8886.96	−6374.09	−92.24	223.60	131.36	2644.23	1630.82	1118
WCl_6	9135.68	−9378.18	−242.50	4531.08	9135.52	−9562.56	34.66	−89.61	−54.95	−481.98	4757.03	3302
spin-free relativistic Hamiltonian (external field)												
	level III				level IV							
WF_6	9087.64	−4215.08	4872.56	0	9087.53	−4240.88	−1.15	41.11	39.96	4886.61	0	0
WO_4^{2-}	8992.21	−5812.75	3179.46	1693.10	8992.10	−5832.19	−59.79	289.91	230.12	3390.03	1496.58	1118
WCl_6	9240.35	−8276.95	963.40	3909.16	9240.25	−8381.43	−3.67	−37.44	−41.11	817.72	4068.89	3302

chemical shifts calculated by the SFR Hamiltonian shown by filled circles and boxes are always closer to the experimental values than those calculated by the non-relativistic Hamiltonian shown by open circles and boxes. The SO effects, which are estimated by the differences between levels II and I and between levels IV and III, are different between WCl_6 and WO_4^{2-}; in WCl_6 it causes a higher field shift but in WO_4^{2-} it causes a lower field shift. For WCl_6, the SO effect makes the calculated chemical shift distant from the experimental value, and this is opposite to the case of HgX_2 (X = Cl, Br, I) [7].

The effect of uncontracting of the inner core orbitals of W is small but important. The basis set is improved in the order of sets A, B and C. The agreement with experiments is improved in this order at both the non-relativistic and relativistic levels. Further, the improvement is more significant at the relativistic levels (levels III and IV) than in the non-relativistic levels (levels I and II), as expected.

Tables 1–3 show the ^{183}W magnetic shielding constants and their partitioning into σ^{dia}, σ^{para}, $\sigma^{SO}(SD)$ and $\sigma^{SO}(FC)$ in the calculational levels I–IV defined in Scheme (1). Table 4 shows the

Table 2
^{183}W magnetic shielding constants (ppm) and their analyses calculated with set B

Compound	Without SO				With SO							δ^{exp}
	σ^{dia}	σ^{para}	σ^{tot}	δ^{cal}	σ^{dia}	σ^{para}	σ^{SO}			σ^{tot}	δ^{cal}	
							SD	FC	total			
non-relativistic Hamiltonian												
	level I				level II							
WF_6	8891.53	−4690.58	4300.95	0	8991.36	−4733.74	6.30	27.61	33.91	4291.52	0	0
WO_4^{2-}	8895.98	−6358.10	2537.88	1763.07	8895.78	−6368.65	−92.07	204.66	112.59	2639.73	1651.79	1118
WCl_6	9144.50	−9372.58	−228.08	4529.03	9144.34	−9556.96	34.86	−105.65	−70.79	−483.41	4774.93	3302
spin-free relativistic Hamiltonian (external field)												
	level III				level IV							
WF_6	9670.97	−4138.31	5532.66	0	9970.86	−4164.23	0.26	165.03	165.29	5671.92	0	0
WO_4^{2-}	9575.85	−5725.66	3850.19	1682.47	9575.73	−5745.59	−57.17	846.63	785.46	4615.61	1056.31	1118
WCl_6	9823.22	−8136.64	1686.58	3846.08	9823.12	−8240.90	0.75	−18.18	−17.43	1564.80	4107.12	3302

Table 3
^{183}W magnetic shielding constants (ppm) and their analyses calculated with set C

Compound	Without SO				With SO							δ^{exp}
	σ^{dia}	σ^{para}	σ^{tot}	δ^{cal}	σ^{dia}	σ^{para}	σ^{SO}			σ^{tot}	δ^{cal}	
							SD	FC	total			
non-relativistic Hamiltonian												
	level I				level II							
WF_6	8990.31	−4632.24	4358.07	0	8995.87	−4638.12	−21.42	27.29	5.87	4363.61	0	0
WO_4^{2-}	8894.61	−6331.92	2562.69	1795.38	8900.16	−6340.60	−103.53	198.21	94.68	2654.25	1709.36	1118
WCl_6	9143.16	−8846.81	296.35	4061.72	9148.73	−8872.94	−47.08	−101.08	−148.16	127.62	4235.99	3302
spin-free relativistic Hamiltonian (external field)												
	level III				level IV							
WF_6	9800.14	−4217.32	5582.82	0	9812.69	−4223.76	−21.52	183.47	161.95	5750.69	0	0
WO_4^{2-}	9705.02	−5788.21	3916.82	1666.00	9717.58	−5800.79	−94.52	793.28	698.76	4615.55	1135.14	1118
WCl_6	9951.94	−8018.13	1933.81	3649.01	9964.49	−8024.71	−35.25	25.38	−9.87	1929.91	3820.78	3302

analysis defined by Scheme (2) for the magnetic shielding constants and for the chemical shift.

The magnetic shielding constants are essentially determined by the paramagnetic term σ^{para} at all levels of approximations. The Fermi contact term is small in the non-relativistic Hamiltonian, while it is significant in the relativistic Hamiltonian, showing that the coupling between the SFR and SO Hamiltonians is important. The absolute values of the magnetic shielding constants based on the relativistic and non-relativistic calculations are very different, while the differences in the chemical shifts are small, showing that the relativistic effects due to W are partially cancelled in the chemical shifts. This is in marked contrast to the case of HgX_2 (X = Cl, Br, I) [7], where the ligands are also heavy.

5. Analysis

We next investigate the relativistic effect in more detail using the analysis defined by Scheme (2) shown in Table 4. We first examine the effect on the shielding constant. We note that the relativistic effects in WO_4^{2-} have a trend similar to those in $HgCl_2$ [7]. As seen from the last two rows of Table 4, the most important relativistic effect is due to the SFR term of tungsten, and in sets B and C the SO effect also becomes important through coupling with the SFR term.

In WX_6 (X = F, Cl), the importance and the role of the SFR term are similar to those in WO_4^{2-}, but in WCl_6 the SFR term due mainly to the W atom is larger than that in WF_6. When the relativistic reorganization of the inner core orbitals of W is included, the SFR effect increases. Further, the SO effects in WCl_6 have a sign different from those in WO_4^{2-}.

We next examine the effect on the chemical shift, a relative quantity. From the last two rows of Table 4, we see that the importance of the SFR term decreases more extensively than those in the nuclear shielding constants; the SFR term is mainly due to the W atom, so that it cancels to some extent in the chemical shift. The SO effect becomes relatively important in the chemical shift, though it is again due essentially to the W atom; the SO effects of the O, F, and Cl atoms are insignificant. This result implies that the SFR effect is more local than the SO effect.

6. Conclusions

The relativistic calculations of the ^{183}W magnetic shielding constants in WX_6 (X = F and Cl) and WO_4^{2-} provide the following conclusions.

1. The relativistic effect is important for the ^{183}W magnetic shielding constant and chemical shift. The agreement with experiment is improved when the relativistic effect is included.

Table 4
Analysis of relativistic effects for the ^{183}W shielding constant and chemical shift (ppm)

Term	WF_6 shielding constant			WO_4^{2-} shielding constant			WCl_6 shielding constant			WO_4^{2-} − WF_6 chemical shift [a]			WCl_6 − WF_6 chemical shift [a]		
	Set A	Set B	Set C	Set A	Set B	Set C	Set A	Set B	Set C	Set A	Set B	Set C	Set A	Set B	Set C
level IV–level I	598	1371	1393	867	2078	2053	1060	1793	1634	269	708	661	462	422	242
level II–level I	−14	−9	6	121	102	92	−239	−255	−169	134	111	86	−226	−246	−175
level IV–level III	14	139	168	211	765	699	−146	−122	−4	197	626	592	−160	−261	−172
level III–level I	584	1232	1225	656	1313	1354	1206	1915	1637	73	82	130	622	683	413
level IV–level II	612	1380	1387	746	1976	1961	1300	2048	1802	135	596	574	688	668	415

[a] The sign of the chemical shift is just reversed from that of Tables 1–3.

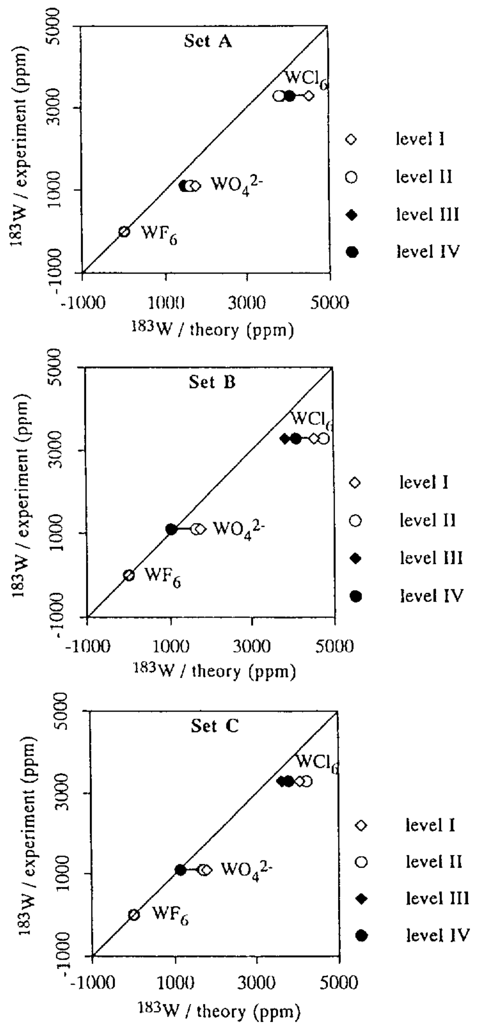

Fig. 1. Correlations between theory and experiment for ^{183}W chemical shifts in WX_6 (X = F and Cl) and WO_4^{2-}. The upper, middle and lower figures show the results calculated by sets A, B and C, respectively. Levels I–IV are defined by Scheme (1) of the text.

2. For molecules having no heavy ligands, the SFR term of heavy resonant nuclei is a major relativistic contribution to the shielding constant, while the SO term is secondary.

3. The coupling between the SFR and SO terms is large as in HgX_2.

4. A relaxation of the inner core 1s and 2p orbitals of W gives a better description of the relativistic effect.

Part of this study has been presented at the ESF Workshop on the calculation of NMR parameters held in Helsinki [18].

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