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Ab initio and relativistic DFT study of spin–rotation and NMR shielding constants in XF₆ molecules, X = S, Se, Te, Mo, and W

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We present an analysis of the spin–rotation and absolute shielding constants of XF₆ molecules (X = S, Se, Te, Mo, W) based on *ab initio* coupled cluster and four-component relativistic density-functional theory (DFT) calculations. The results show that the relativistic contributions to the spin–rotation and shielding constants are large both for the heavy elements as well as for the fluorine nuclei. In most cases, incorporating the computed relativistic corrections significantly improves the agreement between our results and the well-established experimental values for the isotropic spin–rotation constants and their anisotropic components. This suggests that also for the other molecules, for which accurate and reliable experimental data are not available, reliable values of spin–rotation and absolute shielding constants were determined combining *ab initio* and relativistic DFT calculations. For the heavy nuclei, the breakdown of the relationship between the spin–rotation constant and the paramagnetic contribution to the shielding constant, due to relativistic effects, causes a significant error in the total absolute shielding constants. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4875696>]

I. INTRODUCTION

In the standard analysis of a nuclear magnetic resonance (NMR) spectrum, the shielding of a nucleus by the electrons is described in terms of the chemical shift defined with respect to a reference molecule. For each nuclear species active in NMR there is a separate, arbitrarily chosen scale. In contrast, theoretical calculations provide the (so-called) absolute shielding constants—values computed with respect to bare nuclei which, consistent with the definition of the effect, should be used to fix the scale for the shielding. However, NMR experiments for bare nuclei are not feasible, and the approach used to determine these constants from molecular data faces both methodological and practical problems, leading in many cases to unavoidable loss of accuracy.

The experimental determination of absolute shielding constants is usually based on Flygare's nonrelativistic relation between C^{el}(K), the electronic contribution to the nuclear spin–rotation constant of nucleus K, and σ^{para}(K), the paramagnetic contribution to the absolute shielding constant.^{1–3} In this approach, for nucleus K

$$\sigma^{\text{para}}(\text{K}) = \frac{1}{2} \frac{m_p}{m_e} \frac{C^{\text{el}}(\text{K})}{B} \frac{1}{g(\text{K})}, \quad (1)$$

where m_p and m_e are the proton and electron masses, B is the molecular rotational constant, and $g(\text{K})$ is the nuclear g factor. Recently, an alternative technique for the determination of absolute shielding constants directly from NMR spectra has been developed,⁴ avoiding the dependency on this relation between the spin–rotation and shielding constants. How-

ever, this approach requires the knowledge of accurate nuclear magnetic dipole moments, which are often unavailable, in particular for heavy nuclei.

Once the paramagnetic contribution is determined, the diamagnetic contribution is calculated using a theoretical method, and they are summed to obtain the total absolute shielding constant (at the nonrelativistic level, calculations of the diamagnetic contribution, an expectation value, are much more accurate than those of the paramagnetic one). However, because of the role of the relativistic corrections in the paramagnetic and diamagnetic contributions, as well as in the spin–rotation constants, this commonly used approach fails and gives incorrect values for the absolute shielding constants when molecules including relatively heavy atoms are considered. This has been confirmed recently by the calculations of nuclear spin–rotation constants based on new relativistic theory, first introduced by Aucar *et al.*⁵ and later developed in a more rigorous formulation by Xiao and Liu.^{6,7} For example, the results obtained by Malkin *et al.*⁸ using Aucar's approach showed that the values obtained using Flygare's relation for the absolute shielding constant of ¹¹⁹Sn are far from the chemical accuracy (being off by 1000 ppm, which amounts to 26% of the absolute shielding constants for SnH₄, 31% for Sn(CH₃)₄, and 29% for SnCl₄).

Several other works verified numerically the breakdown of Flygare's relation, for instance in the studies of hydrogen halides^{9,10} and for ¹H and ^{35/37}Cl in HCl.¹¹ These previously reported results (as well as the present study, *vide infra*) show that relativistic corrections to the spin–rotation and shielding constants are of great significance for the heavy-atom centers as well as for light atoms located near heavy elements. A perturbation analysis of the relativistic effects to the nuclear

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magnetic shielding and spin–rotation constants shows that the spin–orbit effects are similar for the two properties, but not the scalar relativistic effects, the latter being much more important for the shielding constants in the heavy elements.^{5,12} Relativistically corrected shielding and spin–rotation constants are thus needed in high-quality quantum-chemical benchmark calculations. Because absolute chemical shielding constants are needed in the analysis of nuclear magnetic moments,¹³ the accuracy of their determination—in particular for heavy nuclei—is also of high importance.

Another problem arising for most of the molecules studied in this work is that the available experimental values for the spin–rotation constants were determined from NMR relaxation time measurements. There are many factors which affect the NMR relaxation time, and the spin–rotation constants obtained in this way are thus less reliable and less accurate than those determined from other spectroscopies. The SF₆ results, determined in a saturation absorption spectroscopy experiment, are presumably more reliable than experimental data obtained for the other molecules.

In this work we extend our studies of the relationship between NMR shielding and spin–rotation constants to hexafluorides of sulfur, selenium, tellurium, molybdenum, and tungsten. For these molecules (all of them of octahedral symmetry), there are some experimental spin–rotation constants available, and for ⁷⁷Se in SeF₆ and ¹²⁵Te in TeF₆ these data have been used to determine the absolute shielding scales.¹⁴ We estimate the accuracy of the literature *ab initio* and experimental data, focusing on the role of the relativistic corrections to the computed properties.

II. COMPUTATIONAL ASPECTS

Experimental equilibrium bond distances were used for SF₆, SeF₆, TeF₆, and WF₆, with $r(\text{S-F}) = 1.5560 \text{ \AA}$,¹⁵ $r(\text{Se-F}) = 1.678 \text{ \AA}$,¹⁶ $r(\text{Te-F}) = 1.811 \text{ \AA}$,¹⁴ and $r(\text{W-F}) = 1.833 \text{ \AA}$,¹⁷ respectively, whereas for MoF₆ we used a structure optimised at the SO-ZORA/BP86/TZ2P level with $r(\text{Mo-F}) = 1.847 \text{ \AA}$. The internuclear distances used correspond to available experimental data and/or values previously used in similar studies of spin–rotation and shielding constants. The same geometries were used both in the nonrelativistic and relativistic calculations. The use of experimental geometries implicitly includes the leading-order anharmonic contribution to the vibrational corrections to the molecular properties.¹⁸ The nuclear *g*-factors used in the calculations are $g(^{19}\text{F}) = 5.257736$, $g(^{33}\text{S}) = 0.429214$, $g(^{77}\text{Se}) = 1.070084$, $g(^{125}\text{Te}) = -1.77701$, $g(^{95}\text{Mo}) = -0.36568$, and $g(^{183}\text{W}) = 0.23557$, all taken from Ref. 19.

A. Nonrelativistic *ab initio* calculations

The nonrelativistic calculations were performed using the coupled cluster analytic linear response method.^{20,21} For SF₆, the CCSD(T) (coupled-cluster singles-and-doubles with a noniterative perturbative triples correction) approach was the highest level of approximation. For the larger molecules, the properties were computed at the CCSD level. The CFOUR program²² (locally modified to include the *g*-factors for the heavy nuclei) was used in all the nonrelativistic calculations.

In the nonrelativistic SF₆ and SeF₆ calculations we employed two of Dunning's augmented correlation-consistent sets,^{23–25} aug-cc-pCVTZ and aug-cc-pCVQZ. For Te we used Sadlej's pVTZ basis set,²⁶ an uncontracted completeness-optimised²⁷ basis previously employed in a study of TeH₂²⁸ and an uncontracted ANO-RCC basis set.²⁹ For molybdenum and tungsten, the uncontracted relativistic cvqz basis sets of Dyal^{30,31} combined with Dunning's uncontracted fluorine cc-pCVQZ basis were used in both the nonrelativistic and relativistic calculations. In all the nonrelativistic Hartree–Fock (HF) and coupled-cluster calculations, we used gauge-including atomic orbitals (GIAOs^{32,33}).

B. Relativistic density-functional theory calculations

The relativistic effects were estimated based on four-component relativistic DFT calculations using the program package ReSpect,³⁴ in particular the module using the restricted magnetic balance scheme for the NMR shielding constant calculations^{35,36} and the restricted kinetic balance scheme in the case of the spin–rotation constant calculations.³⁷ The four-component values obtained at this level were compared with the corresponding nonrelativistic values. We have used the PBE³⁸ and BP86^{39,40} functionals in both the relativistic and nonrelativistic DFT calculations. In each case, the differences between PBE and BP86 values are below 1% for the spin–rotation constants, as well as for the dia- and paramagnetic contributions to the shielding, therefore we shall report only the PBE results (even though the differences are, in percentage terms, somewhat larger for the total shielding constants).

In the analysis of the relativistic effects, we used the uncontracted pc-3 basis set^{41,42} for fluorine and the uncontracted cc-pVQZ²⁴ basis set for sulfur. Dyal's relativistic cvqz basis sets were used in uncontracted form for selenium,⁴³ tellurium,⁴³ molybdenum,³⁰ and tungsten.³¹ To ensure overall consistency of the results, the spin–rotation and shielding constants were systematically computed using the common gauge origin approach.

III. RESULTS AND DISCUSSION

A. Nonrelativistic results

The nonrelativistic results for the shielding and spin–rotation constants determined using Hartree–Fock and coupled-cluster wave functions are listed in Table I.

A comparison of the aug-cc-pCVTZ and aug-cc-pCVQZ results for SF₆ shows that the basis set dependence of the absolute shielding constants for both ³³S and ¹⁹F is weak, about 2.0% at the CCSD level, and even smaller at the HF level. On the other hand, electron correlation effects are significant. For example, the HF values of $\sigma(^{33}\text{S})$ are approximately 12% larger than the coupled cluster ones for the same basis set. The basis set dependence of both spin–rotation constants is similar ($\sim 2.0\%$), the correlation effect is somewhat smaller for the isotropic spin–rotation constants of both nuclei (below 10%) and very small for $C_{\text{anis}}(\text{F})$ (following Ref. 44 we define $C_{\text{anis}} = C_{\perp} - C_{\parallel}$, where the directions refer to the X–F bond). For comparison with Ref. 44, we also performed test calculations

TABLE I. Nonrelativistic shielding constants (in ppm) and spin-rotation constants (in kHz) for XF_6 , ($X = {}^{33}\text{S}$, ${}^{77}\text{Se}$, ${}^{125}\text{Te}$, ${}^{95}\text{Mo}$, ${}^{183}\text{W}$).

Basis	Method	$\sigma(\text{S})$	$\sigma(\text{F})$	$\sigma_{\text{anis}}(\text{F})$	C(S)	C(F)	$C_{\text{anis}}(\text{F})$
S							
aug-cc-pCVTZ	HF	408.59	180.32	307.51	-0.814	-4.565	-4.210
aug-cc-pCVQZ	HF	403.18	177.26	311.88	-0.821	-4.615	-4.280
aug-cc-pCVTZ	CCSD	367.79	167.20	305.45	-0.867	-4.773	-4.188
aug-cc-pCVQZ	CCSD	360.33	163.43	310.41	-0.877	-4.834	-4.268
aug-cc-pCVTZ	CCSD(T)	357.47	161.54	307.87	-0.881	-4.861	-4.227
Basis	Method	$\sigma(\text{Se})$	$\sigma(\text{F})$	$\sigma_{\text{anis}}(\text{F})$	C(Se)	C(F)	$C_{\text{anis}}(\text{F})$
Se							
aug-cc-pCVTZ	HF	1384.78	215.32	286.16	-4.425	-3.453	-3.290
aug-cc-pCVQZ	HF	1375.82	213.63	288.83	-4.450	-3.477	-3.327
aug-cc-pCVTZ	CCSD	1264.50	192.02	299.60	-4.756	-3.768	-3.479
aug-cc-pCVQZ	CCSD	1247.37	188.65	304.45	-4.804	-3.816	-3.547
Basis	Method	$\sigma(\text{Te})$	$\sigma(\text{F})$	$\sigma_{\text{anis}}(\text{F})$	C(Te)	C(F)	$C_{\text{anis}}(\text{F})$
Te							
Sadlej	HF	2968.51	331.89	158.81	9.374	-1.613	-1.286
c-o-CV3Z	HF	2911.12	326.15	159.16	9.602	-1.680	-1.302
ANO-RCC	HF	2931.41	329.98	150.81	9.522	-1.637	-1.207
Sadlej	CCSD	2763.94	302.65	178.33	10.177	-1.943	-1.519
c-o-CV3Z	CCSD	2697.62	305.12	174.11	10.442	-1.925	-1.481
ANO-RCC	CCSD	2702.05	306.44	166.87	10.424	-1.910	-1.399
Basis	Method	$\sigma(\text{Mo})$	$\sigma(\text{F})$	$\sigma_{\text{anis}}(\text{F})$	C(Mo)	C(F)	$C_{\text{anis}}(\text{F})$
Mo							
Dyall	HF	198.21	-101.81	617.19	2.947	-6.393	-6.447
Dyall	CCSD	-259.25	-114.93	487.39	3.304	-6.541	-5.015
Basis	Method	$\sigma(\text{W})$	$\sigma(\text{F})$	$\sigma_{\text{anis}}(\text{F})$	C(W)	C(F)	$C_{\text{anis}}(\text{F})$
W							
Dyall	HF	3002.53	11.18	477.18	-2.909	-5.212	-4.879
Dyall	CCSD	2206.40	-7.01	395.69	-3.314	-5.419	-3.969

using $r(\text{S-F}) = 1.56050 \text{ \AA}$, the results (HF and CCSD) differ from those shown in Table I by 1%–2%.

For SeF_6 and TeF_6 , the effects of electron correlation are similar to those observed for SF_6 . The CCSD shielding constants become approximately 10% smaller than the HF values (for the heavy atom and for the fluorines), while the spin-rotation constants increase by about 10%. There are more significant differences between the CCSD and HF shielding constants for MoF_6 and WF_6 . The total shielding constants of molybdenum in MoF_6 and fluorine in WF_6 become negative at the CCSD level, and the correlation effects on the tungsten shielding exceed 25%. On the other hand, the correlation effects on the spin-rotation constants in MoF_6 and WF_6 are similar to those in the other molecules.

B. Relativistic DFT calculations

The relativistic and nonrelativistic DFT results for the spin-rotation constants of the central atoms and fluorine are listed in Table II. The diamagnetic and paramagnetic contributions as well as total absolute shielding constants are listed in Table III. As expected, for the spin-rotation constants of the central nuclei, the relativistic effects increase from ${}^{33}\text{S}$ to ${}^{125}\text{Te}$. The relative role of the effect becomes significant for ${}^{125}\text{Te}$, being more than 10% of the total value. It is much smaller for ${}^{95}\text{Mo}$, while for ${}^{183}\text{W}$ it also contributes about 6%.

The overall comparisons indicate that for the spin-rotation constants of ${}^{19}\text{F}$ in all the molecules except TeF_6 , the relativistic effects are larger than for the central atoms. Similarly to the heavy atoms, the relativistic contribution to the fluorine isotropic spin-rotation constant increases from SF_6 to TeF_6 , becoming as large as 15.5% of the total value in TeF_6 . In MoF_6 , unlike for ${}^{95}\text{Mo}$, the isotropic spin-rotation constant of ${}^{19}\text{F}$ is noticeably affected by relativistic effects (4.7%). In the case of the anisotropic spin-rotation constants of ${}^{19}\text{F}$, those of the studied group 16 molecules increase similarly to the isotropic ones, with the effects being much more pronounced for ${}^{19}\text{F}$ in SeF_6 and TeF_6 .

The absolute shielding constants as well as their dia- and paramagnetic contributions are listed in Table III and show that relativistic correction for the ${}^{33}\text{S}$ total absolute shielding is 42.6 ppm, increasing to 265.4 and 852.0 ppm, respectively, for ${}^{77}\text{Se}$ and ${}^{125}\text{Te}$. Relativistic effects of similar magnitude have been reported in DFT studies of SeH_2 and TeH_2 ,²⁸ 246.36 ppm for ${}^{77}\text{Se}$ and 1006.07 ppm for ${}^{125}\text{Te}$ (see also other values discussed in Ref. 28). In addition, the SeH_2 – SeF_6 chemical shift obtained comparing the computed absolute shielding constants, 935 ppm, is in good agreement with the experimental value, 957 ppm.¹⁴

For ${}^{95}\text{Mo}$, the relativistic correction is 593.6 ppm and causes a sign change of the total shielding constant (see below). The largest relativistic contributions are observed in WF_6 : for ${}^{183}\text{W}$ it is 4014.6 ppm, and for ${}^{19}\text{F}$ this effect is

TABLE II. Relativistic and nonrelativistic (NR) spin-rotation constants for XF_6 ($X = {}^{33}\text{S}$, ${}^{77}\text{Se}$, ${}^{125}\text{Te}$, ${}^{95}\text{Mo}$, ${}^{183}\text{W}$), calculated at the four-component level of theory using the PBE functional (in kHz).^a

	C(X)			C(F)			C _{anis} (F)		
	Relativistic	NR	Δ	Relativistic	NR	Δ	Relativistic	NR	Δ
SF ₆									
PBE	-0.95	-0.97	0.02	-5.91	-5.85	-0.06	-5.20	-5.09	-0.11
CC		-0.88			-4.86			-4.23	
SeF ₆									
PBE	-5.55	-5.47	-0.08	-5.50	-5.09	-0.41	-5.51	-4.84	-0.67
CC		-4.80			-3.82			-3.55	
TeF ₆									
PBE	13.27	11.86	1.41	-3.15	-2.66	-0.49	-2.92	-2.10	-0.82
CC		10.42			-1.91			-1.40	
MoF ₆									
PBE	3.72	3.72	-0.01	-6.98	-7.31	0.33	-3.53	-3.55	0.02
CC		3.30			-6.54			-5.02	
WF ₆									
PBE	-4.17	-3.88	-0.29	-5.49	-6.21	0.72	-2.98	-3.18	0.20
CC		-3.31			-5.42			-3.97	

^a Δ is the difference between the relativistic and NR value. The nonrelativistic values were calculated by increasing the speed of light by a factor of 100. For comparison, our best coupled-cluster (CC) results are also tabulated.

67.7 ppm. The computed tungsten shielding constants can be compared to the results of Hada *et al.*,⁴⁵ who obtained 4358.07 ppm in the nonrelativistic calculation and 5750.69 ppm in the relativistic approach (using relativistic spin-free no-pair theory and the spin-orbit unrestricted Hartree-Fock method).

As shown in Table III, relativistic effects cause a considerable error in determining the paramagnetic contribution to the absolute shielding constant, when it is obtained from the electronic contribution to the spin-rotation constant using Eq. (1) (denoted as σ^{SR}). This is in line with previous findings.⁸⁻¹¹

It has been established that the paramagnetic contribution is usually overestimated in DFT.⁴⁶⁻⁴⁸ Comparing the nonrelativistic CCSD and DFT results we find that this contribution is $\approx 10\%$ too large for all the central nuclei at the DFT level, and 65–100 ppm too large for the fluorine nuclei. However, we only use the DFT results to estimate the relativistic correction,

which should not be significantly affected by these overestimations as the same basis set and functional are always used in the relativistic and nonrelativistic approach. Furthermore, the DFT paramagnetic terms are of similar magnitude in the relativistic and nonrelativistic approach (with the exception of $\sigma^{\text{para}}({}^{183}\text{W})$), and we may assume that the overestimation of the results is also similar and thus should cancel in the estimated relativistic correction.

IV. COMPARISON WITH EXPERIMENTAL DATA

To obtain the best theoretical estimate for the spin-rotation and nuclear magnetic shielding constants, we assume that the different contributions to the computed properties are additive. Hence, for comparison with available experimental data, we use the sum of the best nonrelativistic result (CCSD value obtained with the largest basis set) and the DFT relativistic correction. For SF₆, we include as an additive

TABLE III. Relativistic and nonrelativistic isotropic shielding constants for XF_6 ($X = {}^{33}\text{S}$, ${}^{77}\text{Se}$, ${}^{125}\text{Te}$, ${}^{95}\text{Mo}$, ${}^{183}\text{W}$), calculated at the four-component level of theory using the PBE functional (in ppm).^a

	Relativistic, PBE					Nonrelativistic, PBE			CC
	σ^{dia}	σ^{SR}	σ^{para}	$\sigma^{\text{dia+SR}}$	$\sigma^{\text{dia+para}}$	σ^{dia}	σ^{para}	$\sigma^{\text{dia+para}}$	$\sigma^{\text{dia+para}}$
³³ S	1371.6	-1066.0	-1040.6	305.6	331.1	1370.2	-1081.7	288.5	357.5
⁷⁷ Se	3314.2	-2319.7	-2047.9	994.5	1266.2	3295.7	-2290.9	1000.8	1247.4
¹²⁵ Te	5716.7	-3660.4	-2528.5	2056.3	3188.2	5639.0	-3302.7	2336.2	2702.1
⁹⁵ Mo	4309.9	-5060.3	-4515.5	-750.4	-205.6	4272.4	-5071.6	-799.2	-259.3
¹⁸³ W	9264.8	-8477.3	-4153.0	787.5	5111.9	9008.8	-7911.5	1097.3	2206.4
σ (F) in									
SF ₆	561.7	-466.2	-461.9	95.5	99.7	561.5	-462.3	99.2	161.5
SeF ₆	555.1	-490.4	-486.0	64.7	69.1	554.9	-460.2	94.7	188.7
TeF ₆	549.1	-349.0	-344.7	200.1	204.4	548.9	-307.1	241.8	306.4
MoF ₆	547.3	-701.6	-697.4	-154.3	-150.1	547.2	-731.0	-183.8	-114.9
WF ₆	548.1	-560.8	-557.3	-12.7	-9.3	548.1	-625.1	-77.0	-7.0

^aThe nonrelativistic values were calculated by increasing the speed of light by a factor of 100. For comparison, our best coupled-cluster (CC) results are also tabulated.

TABLE IV. Spin-rotation constants (in kHz).^{a,b}

	C(X)			Experiment	C(F)			
	Nonrelativistic	Δ	Total		Nonrelativistic	Δ	Total	Experiment
³³ S	-0.89	0.02	-0.87					
⁷⁷ Se	-4.80	-0.08	-4.88	-5.086 ± 0.175^{14}				
¹²⁵ Te	10.42	1.41	11.83	10.53 ± 0.49^{14}				
⁹⁵ Mo	3.30	-0.01	3.29					
¹⁸³ W	-3.31	-0.29	-3.60					
					C(F)		C _{anis} (F)	
	Nonrelativistic	Δ	Total	Experiment	Nonrelativistic	Δ	Total	Experiment
SF ₆	-4.92	-0.06	-4.98	-5.140 ± 0.010^{49}	-4.31	-0.11	-4.42	-4.600 ± 0.010^{50}
SeF ₆	-3.82	-0.41	-4.23	-4.46 ± 0.10^{51}	-3.55	-0.67	-4.22	-4.47 ± 0.23^{51}
TeF ₆	-1.91	-0.49	-2.40	-2.44 ± 0.07^{51}	-1.40	-0.82	-2.22	-2.07 ± 0.17^{51}
MoF ₆ ^c	-6.54	0.33	-6.21	$3.23(-4.54)^{52}$	-5.02	0.02	-5.00	$-1.58(-2.22)^{52}$
WF ₆ ^c	-5.42	0.72	-4.70	$3.01(-4.23)^{52}$	-3.97	0.20	-3.77	$-2.63(-3.69)^{52}$

^aFor SF₆, the CCSD(T)-CCSD differences are included in the nonrelativistic values as additive corrections. Δ is the relativistic correction.

^bIn Refs. 14 and 52, only C_{iso}^2 and C_{anis}^2 were determined; in Refs. 51 and 52, $C_{\text{anis}} = C_{\parallel} - C_{\perp}$.

^cRescaled experimental values in parentheses, see the text.

correction also the difference between the CCSD(T) and CCSD results (aug-cc-pCVTZ results, see Table I).

The final spin-rotation constants are listed in Table IV. The relativistically corrected values of SF₆, SeF₆, and TeF₆ are in general in good agreement with the corresponding experimental data. As pointed out above, the relativistic corrections play a significant role in the calculation of the spin-rotation constants, more pronounced in case of ¹⁹F than for the central nucleus. More importantly, these corrections significantly improve agreement with experiment for all the isotropic and anisotropic constants in these three molecules, with the exception of C(¹²⁵Te). This exception is rather surprising considering that the large corrections to the isotropic and anisotropic *fluorine* constants in TeF₆ bring it into good agreement with experimental data.

The experimental value for ¹⁹F in SF₆, determined using saturation absorption spectroscopy technique, is -5.140 ± 0.010 kHz.⁴⁹ Our best estimate of the isotropic spin-rotation constant, -4.98 kHz, is much closer to the experimental value than a previously reported TZVP(DFT) result of -4.377 kHz⁴⁴ (the same is also true for the anisotropy, we find $C_{\text{anis}}(\text{F}) = -4.42$ kHz, to be compared with -4.095 kHz in Ref. 44).

In contrast, the ¹⁹F experimental constants for MoF₆ and WF₆ are much smaller than the calculated values. For instance, the computed value of C(F) in MoF₆ is -6.21 kHz, whereas the experimental value is (-3.23) kHz. However, as stated in Ref. 52, the method used to determine the spin-rotation constants was leading to significantly too small value of C(F) in SF₆, 3.66 kHz, and presumably the same applies to the similarly derived values of C(F) in MoF₆ and WF₆. We can define a rescaling factor by fitting C(F) in SF₆ to the best now available experimental value, -5.140 kHz, and multiply the corresponding results for MoF₆ and WF₆ by this factor. As shown in Table IV, rescaling the original experimental data yields results in much better agreement with the calculations, in particular for WF₆.

In order to provide an estimate for the errors in our calculated spin-rotation constants arising from the neglect of vibrational corrections, we have made a simple analysis of the dependence of the spin-rotation constants on the X-F bond distance. For the heavy element, the distance dependence is near linear, suggesting that the dominating vibrational correction arises from the anharmonic vibrational correction accounted for through our use of experimental geometries (with the exception of MoF₆). For the fluorines, however, a stronger quadratic distance dependence is observed, suggesting also non-negligible harmonic vibrational corrections.

Based on this rather crude analysis, we would estimate our errors in the spin-rotation constants due to the neglect of vibrational corrections to be 0.1–0.2 kHz for the heavy elements and about 0.2–0.4 kHz for the fluorines. The errors for MoF₆ can be expected to be larger due to the use of an optimised geometry in this case.

In Table V, the relativistically corrected values of the absolute shielding constants are listed together with available experimental values. As previously discussed, the experimental procedure for determining absolute shielding constants was based on Flygare's^{2,3} relation, in which the paramagnetic contribution was obtained from the electronic part of the spin-rotation constant and the diamagnetic contribution from the absolute shielding of a free atom and a nuclear contribution. The absolute shielding constants of ⁷⁷Se and ¹²⁵Te in SeF₆ and TeF₆ have been determined in this way,¹⁴ using free-atom shielding constants of 3298 ppm for ⁷⁷Se and 6580 ppm for ¹²⁵Te. These values included large relativistic corrections (300 and 1220 ppm, respectively), and the error bars did not include the uncertainty in these corrections. It appears that for both ⁷⁷Se and ¹²⁵Te, the correction has been overestimated (see Table V). For SeF₆, using smaller values for the relativistic correction would increase the discrepancy with our value by ~ 50 ppm, whereas for TeF₆ it would bring the value of Ref. 14 about 250 ppm closer to our result.

TABLE V. Shielding constants (in ppm).^{a,b}

	$\sigma(X)$				$\sigma(F)$			
	Nonrelativistic	Δ	Total	Experiment	Nonrelativistic	Δ	Total	Experiment
SF ₆	350.0	42.6	392.6	379.90 ⁵³	157.8	0.5	158.3	144 ± 6 ⁵¹
SeF ₆	1247.4	265.4	1512.8	1438 ± 64 ¹⁴	188.7	−25.6	163.1	140 ± 6 ⁵¹
TeF ₆	2702.1	852.0	3554.1	3790 ± 130 ¹⁴	306.4	−37.4	269.0	253 ± 6 ⁵¹
MoF ₆	−259.3	593.6	334.4		−114.9	33.7	−81.2	≈−95 ^{54,55}
WF ₆	2206.4	4014.6	6221.0		−7.0	67.7	60.7	≈27 ^{54,56}

^aFor SF₆, the CCSD(T)-CCSD differences are included in the nonrelativistic values as additive corrections. Δ is the relativistic correction.

^bFor ¹⁹F in MoF₆ and WF₆, experimental values determined from the chemical shifts.

An analysis of the errors due to the neglect of vibrational corrections similar to that done for the spin–rotation constants suggests errors for the heavy elements of about 15 ppm for ³³S, 20 ppm for ⁷⁷Se and ¹²⁵Te, and around 100–150 ppm for ⁹⁵Mo and ¹⁸³W. For the fluorines, we estimate the errors to be about 20–30 ppm for all compounds.

In the case of ³³S, we note that a new experimental absolute shielding scale was recently presented by Helgaker *et al.*⁵⁷ This shielding scale is based on accurate experimental H₂³³S spin–rotation data obtained using gas-phase microwave spectroscopy. In deriving the new absolute shielding scale, Eq. (1) was used and it does therefore only provide a *nonrelativistic* absolute shielding scale. Unfortunately, there are no experimental data for gaseous H₂S. We can, however, combine the sulfur shielding constant in OCS, 781.2 ppm, derived using this new absolute shielding scale, with the gas phase chemical shifts reported in Ref. 53, to obtain 344.1 ppm for the absolute shielding of ³³S in SF₆, in good agreement with our nonrelativistic shielding constant in Table V.

V. CONCLUSIONS

We have investigated the spin–rotation and shielding constants of S, Se, Te, Mo, and W hexafluorides using a combination of *ab initio* calculations and relativistic four-component DFT calculations. The results indicate that the relativistic corrections are important for the comparison of computed spin–rotation constants with experiment, contributing for instance ≈15% to the ¹⁹F spin–rotation constant in TeF₆. We have determined new values of the spin–rotation constants of ⁹⁵Mo and ¹⁸³W in MoF₆ and WF₆. The previously determined isotropic and anisotropic spin–rotation constants of ¹⁹F in MoF₆ and WF₆ are in disagreement with our calculated values, raising doubts about the quality of the original experimental results. We rescaled these experimental constants using new experimental data for SF₆; the rescaled constants are in much better agreement with our results, suggesting that our values determined from the *ab initio* and four-component relativistic DFT calculations are a better estimate of these spin–rotation constants than the existing, unmodified, experimental data.

In all the investigated hexafluorides, the absolute shielding constants depend strongly on relativistic effects. As expected, the relativistic effect increases going from the comparably light nuclei to the heavier ones. For instance, it contributes 10% to $\sigma(^{33}\text{S})$ in SF₆, whereas it contributes as

much as 24% for ¹²⁵Te in TeF₆. The calculated nonrelativistic electronic contribution to the spin–rotation constant is proportional to the paramagnetic contribution to the shielding constant. However, at the relativistic level of theory they differ significantly, reflecting differences in the perturbation operators in the relativistic domain. Large differences between the paramagnetic shieldings computed directly and obtained from the spin–rotation constants confirm that for molecules having heavy nuclei, the determination of NMR shielding constants based on spin–rotation constant measurements is not sufficiently accurate. Therefore, in the hexafluorides studied here (similarly as observed previously^{8,10,11} in other molecules), applying Flygare’s relation between the electronic contribution to the spin–rotation constant and the paramagnetic contribution to the shielding causes significant errors for the heavy-atom nuclei as well as for the light atoms in the vicinity of the heavy atoms. The shielding constants for both the central nuclei as well as for fluorine are improved when the relativistic corrections are added to the values obtained from the nonrelativistic *ab initio* calculations.

To summarize, the calculated spin–rotation constants give results that are comparable with accurate experimental values. When reliable experimental data are not available, the values determined using accurate nonrelativistic *ab initio* methods together with the relativistic corrections from four-component DFT calculations may provide improved estimates of both spin–rotation and absolute NMR shielding constants.

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