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# Communication: The absolute shielding scales of oxygen and sulfur revisited

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We present an updated semi-experimental absolute shielding scale for the $^{17}$O and $^{33}$S nuclei. These new shielding scales are based on accurate rotational microwave data for the spin–rotation constants of H$_2^{17}$O [Puzzarini *et al.*, J. Chem. Phys. **131**, 234304 (2009)], C$^{17}$O [Cazzoli *et al.*, Phys. Chem. Chem. Phys. **4**, 3575 (2002)], and H$_2^{33}$S [Helgaker *et al.*, J. Chem. Phys. **139**, 244308 (2013)] corrected both for vibrational and temperature effects estimated at the CCSD(T) level of theory as well as for the relativistic corrections to the relation between the spin–rotation constant and the absolute shielding constant. Our best estimate for the oxygen shielding constants of H$_2^{17}$O is 328.4(3) ppm and for C$^{17}$O −59.05(59) ppm. The relativistic correction for the sulfur shielding of H$_2^{33}$S amounts to 3.3%, and the new sulfur shielding constant for this molecule is 742.9(4.6) ppm. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4913634]

## I. INTRODUCTION

The absolute chemical shielding constant of a nucleus provides a measure of the local magnetic field created around a nucleus by the surrounding electrons when the molecule is exposed to an external magnetic field.[1–3] If the nucleus has a permanent magnetic moment, the sum of the external magnetic field and the local magnetic field induced by the motion of the electrons can interact with the nuclear magnetic moment. As such, knowing the external magnetic field and the nuclear magnetic moment, detailed insight into the electronic structure of a molecule in the presence of an external magnetic field can be obtained. The difference of this interaction compared to that of a bare nuclear magnetic moment (no electrons) defines the absolute shielding constant of the nucleus. Due to the difficulty in determining the magnitude of an external magnetic field, and to some extent also the nuclear magnetic moments, in practical nuclear magnetic resonance (NMR) spectroscopy experiments, the change in the absolute shielding constant relative to a reference nucleus—*the chemical shift*—is instead reported. Nevertheless, the absolute shielding constant is important as a benchmark for quantum-chemical methods for calculating NMR parameters[4–8] as well as for the determination of nuclear magnetic moments.[9,10]

The magnetic moment of a nucleus may also interact with the magnetic moment induced by the molecular rotation arising from the small decoupling of the rotation of the electrons from the rotation of the nuclear framework.[11] This interaction is observable as the hyperfine structure in high-resolution rotational microwave spectra and is described by the nuclear spin–rotation tensor. Naively, it is tempting to assume a close relation between the nuclear spin–rotation

and the absolute shielding constant when considering that the induced magnetic moment arising from the molecular rotation is in the non-relativistic limit proportional to the magnetic moment induced by an external magnetic field.[11] Indeed, Flygare showed that within the non-relativistic framework the paramagnetic contribution to the absolute shielding tensor ($\sigma^{\text{para}}$) could be expressed in terms of the electronic contribution to the spin–rotation tensor ($\mathbf{C}^{\text{el}}$)[11,12]

$$\sigma_K^{\text{para}} = \frac{2\pi}{\hbar} \frac{m_p}{m_e} \frac{10^9}{g_K} \mathbf{C}_K^{\text{el}} \mathbf{I} = \sigma_K^{\text{SR}} - \frac{2\pi}{\hbar} \frac{m_p}{m_e} \frac{10^9}{g_K} \mathbf{C}_K^{\text{nuc}} \mathbf{I}, \quad (1)$$

where $m_p$ is the proton mass, $m_e$ is the electron mass, $g_K$ is the nuclear g-value of the nucleus K, $\hbar$ is the reduced Planck constant, $\mathbf{I}$ is the moment of inertia tensor, and $\sigma_K^{\text{SR}}$ refers to the nuclear spin-rotation tensor in ppm, while $\mathbf{C}_K^{\text{nuc}}$ is its nuclear contribution in kHz.

Equation (1) has provided a route for determining experimental absolute shielding scales by combining experimental spin–rotation constants with either approximate atomic contributions (applicable under the assumption that the change in the dissociation energy with a change in the nuclear charge is negligible)[13] or through the use of highly accurate *ab initio* theoretical data for the diamagnetic contribution to the absolute shielding constant.[14,15]

Recently, new and accurate experimental absolute shielding scales for $^{17}$O and $^{33}$S were determined by Puzzarini and coworkers[16,17] based on accurate experimental studies of the hyperfine structure in the microwave spectra of H$_2^{17}$O and H$_2^{33}$S, respectively. To this experimental data were added accurate theoretical results for the diamagnetic term, calculated at the coupled-cluster level of theory, including contributions arising from zero-point vibrational corrections and temperature effects. An absolute shielding constant

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of 325.3(3) ppm was obtained for $^{17}O$ in $H_2^{17}O$,[16] and 716.4(5) ppm for $^{33}S$ in $H_2^{33}S$.[17] Based on accurate and reliable experimental values for the $^{17}O$ spin–rotation constants for $C^{17}O$,[18] Wasylishen and Bryce derived in a similar manner an absolute shielding constant of −62.7(6) ppm for CO.[19]

The approach adopted in Refs. 16, 17, and 19 defines highly accurate *non-relativistic* absolute shielding scales for the considered nuclei. For use in comparing chemical shifts obtained experimentally with those obtained using non-relativistic chemical shielding calculations, this represents a consistent procedure. However, if we, for instance, want to determine the nuclear magnetic moment of a nucleus,[10] such an approach is not appropriate, as it neglects the fact that Eq. (1) is not valid when a full relativistic description of the spin–rotation and nuclear magnetic shielding constants is considered.[20,21] Indeed, Aucar *et al.* showed that at the four-component relativistic framework, there is no direct relationship between the absolute shielding constant and the nuclear spin–rotation constant,[20] and this finding was further substantiated by a detailed analysis of Xiao and Liu.[22] Through a perturbation analysis, Aucar *et al.* showed that whereas the relativistic spin–orbit corrections are common to both the spin–rotation and the nuclear magnetic shielding constants, relativistic operators probing the electron density close to the nucleus are unique to the shielding constants and do not appear for the spin–rotation constants.[20] As such, one would expect relativistic effects to be of equal importance for shielding and spin–rotation constants for nuclei in the vicinity of heavy elements, for which spin–orbit effects dominate and occur for both properties, whereas only shielding constants will display significant relativistic effects for the heavy element itself as spin–orbit effects no longer dominate and the shielding-specific scalar relativistic contributions give rise to the largest relativistic effects.

Malkin *et al.* showed that the currently best approach for obtaining quasi-experimental absolute shielding constants is to combine experimental spin–rotation data with the relativistic difference between nuclear spin–rotation data and the nuclear magnetic shielding constant.[21] We note that a similar result was later derived in the framework of density-functional theory by Xiao, Zhang, and Liu.[23] In the case of the $^{119}Sn$ nucleus, Malkin *et al.* showed that the relativistic correction between the shielding constant and the nuclear spin–rotation constant is highly transferable and large, about 1000 ppm, which amounts to about 25%-30% of the absolute chemical shielding for this fairly light nucleus.[21] In view of this fact and considering the accuracy of the available experimental and theoretical data for $H_2^{17}O$ and $H_2^{33}S$,[16,17] we believe that relativistic effects should be taken into account even for as light systems as water and hydrogen sulfide in order to provide the most accurate absolute shielding scales.

## II. COMPUTATIONAL DETAILS

All calculations of the relativistic corrections have been done with a development version of the ReSpect program,[24] calculating both the spin–rotation constants and nuclear magnetic shielding constants at the relativistic four-component Kohn-Sham density functional level of theory using the Dirac-Coulomb Hamiltonian (DKS). For the spin–rotation constants, the molecular center of mass along with a restricted kinetic balance approach applied at the integral level was chosen,[25] whereas for the shielding constant calculations, we apply the restricted magnetic balance condition and Gauge-Including Atomic Orbitals (GIAO) to improve basis set convergence and ensure gauge origin-independent results.[26,27] We have used the uncontracted core-valence quadruple zeta basis set of Dyall (dyall-cvqz),[28] in combination with the Perdew–Becke–Ernzerhof (PBE) functional.[29] In all cases, we have used the same geometries as in earlier work.[16,17] All coupled-cluster and experimental data have been collected from the literature (see Tables I and II for details and references).

## III. RESULTS

Let us first consider the results for the spin–rotation constants of $H_2^{17}O$ and $H_2^{33}S$, for which a direct comparison with experiment is possible. Available literature data and our results are collected in Table I. Our results for the relativistic correction to the spin–rotation constant have been calculated as the difference between the PBE/dyall-cvqz results obtained at the four-component relativistic level and the non-relativistic results obtained with the same basis set and exchange–correlation functional. As expected for such light systems as water and hydrogen sulfide and the perturbational analysis of the relativistic effects on the spin–rotation constants[20] discussed in the introduction, the relativistic corrections are in general small, and most significant in the case of the hydrogen nuclei, as those are most influenced by the relativistic spin–orbit corrections occurring both for the shielding and the spin–rotation constants. For the water molecule, the relativistic correction is at most 0.8%, occurring for the $C_{aa}$ component of the hydrogen nucleus. Although the spin–rotation constants obtained at the DFT level differ, in some cases also substantially, from those obtained at the coupled–cluster levels,[16] these differences are due to limitations in the quality of the exchange–correlation functional rather than due to the relativistic effects, as those are overall small as seen from Table I. Even if these errors in the exchange–correlation functional also can lead to errors in the relativistic corrections, we believe these errors to be smaller because of a large degree of error cancellation between the relativistic and non-relativistic density-functional theory (DFT) calculations. Although in general small, when added to the coupled–cluster (CC) results, the relativistic corrections improve agreement with experiment in most cases, the $C_{bb}$ component of hydrogen being a notable exception.

For $H_2S$, the relativistic corrections are larger, now being as large 9% in the case of the $C_{bb}$ component of hydrogen. Even for one of the $^{33}S$ components, $C_{bb}$, there is a sizeable relativistic correction of almost 1%, improving the agreement with experiment though slightly overshooting the correction needed for the coupled–cluster result. Unfortunately, no experimental data are available for the proton spin–rotation constant, which could otherwise provide strong support for our results considering the magnitude of the relativistic corrections to the spin–rotation constant for this nucleus in hydrogen sulfide.

TABLE I. Calculated and experimental spin-rotation constants for $H_2^{17}O$ and $H_2^{33}S$ (in kHz).[a]

| Molecule | Tensor element | Nucleus | DKS[b] | CC[c] | ΔRel[d] | CC+ΔRel | Expt. |
|---|---|---|---|---|---|---|---|
| $H_2O$ | $C_{aa}$ | $^{17}O$ | −28.12 | −28.61 | 0.06 | −28.55 | −28.477(88)[e] |
|  | $C_{bb}$ | $^{17}O$ | −28.73 | −27.99 | −0.10 | −28.09 | −28.504(71)[e] |
|  | $C_{cc}$ | $^{17}O$ | −20.78 | −18.49 | 0.00 | −18.49 | −18.382(47)[e] |
|  | $C_{aa}$ | $^1H$ | −36.93 | −34.21 | −0.28 | −34.49 | −34.45(19)[e] |
|  | $C_{bb}$ | $^1H$ | −32.96 | −31.16 | −0.21 | −31.37 | −31.03(19)[e] |
|  | $C_{cc}$ | $^1H$ | −35.13 | −32.47 | −0.15 | −32.62 | −32.91(10)[e] |
| $H_2S$ | $C_{aa}$ | $^{33}S$ | 21.64 | 21.42 | 0.06 | 21.48 | 22.08(27)[f] |
|  | $C_{bb}$ | $^{33}S$ | 60.55 | 58.75 | 0.56 | 59.31 | 59.05(26)[f] |
|  | $C_{cc}$ | $^{33}S$ | 26.94 | 24.15 | 0.05 | 24.20 | 24.30(77)[f] |
|  | $C_{aa}$ | $^1H$ | −18.68 |  | −0.66 |  |  |
|  | $C_{bb}$ | $^1H$ | −15.32 |  | −1.35 |  |  |
|  | $C_{cc}$ | $^1H$ | −17.83 |  | −0.41 |  |  |

[a]Here $C_{aa}$, $C_{bb}$, and $C_{cc}$ are the diagonal elements of the spin–rotation tensor when calculated in the principal axes of the moment of inertia tensor of the studied system.
[b]Four-component DFT (PBE/dyall-cvqz) calculations (this work).
[c]$H_2S$: Equilibrium best-estimate value (see Ref. 17) augmented by vibrational corrections obtained at the CCSD(T)/aug-cc-pCVQZ level. $H_2O$: Equilibrium value obtained at the CCSD(T)/aug-cc-pCV6Z level augmented by vibrational corrections obtained at the CCSD(T)/aug-cc-pCV5Z level by means of the DVR-QAK approach (see Ref. 16).
[d]Relativistic contribution to the spin–rotation tensor obtained as the difference between four-component Dirac–Kohn–Sham and non-relativistic Kohn–Sham DFT calculations. For computational details, see text.
[e]Reference 16.
[f]Reference 17.

Let us now turn to the determination of the new, semi-experimental absolute shielding scale for oxygen and sulfur. Available literature data and our results are collected in Table II. For all the non-relativistic results, we report the results of Refs. 16 and 17, and we refer to these works for more details of the results and the approach used to derive the absolute shielding scales.

We first subtract the vibrational corrections from the experimental spin–rotation constants to obtain an equilibrium geometry experimental spin–rotation constant, and then subtract the relativistic correction from the spin–rotation constant given in Table I in order to derive a truly non-relativistic value for the spin–rotation constant at the equilibrium geometry. This semi-experimental non-relativistic spin–rotation constant is then converted to the paramagnetic shielding constant following Eq. (1), to which we then add a non-relativistic diamagnetic contribution, zero-point vibrational corrections, and temperature effects (all calculated non-relativistically at the CCSD(T) level of theory) before finally adding the difference between the four-component relativistic and the one-component non-relativistic shielding constant, both calculated at the PBE/dyall-cvqz level of theory. This gives, in the final row, the semi-experimental absolute shielding constants of 328.4(3) ppm for $^{17}O$ in $H_2O$, 742.9(4.6) ppm for $^{33}S$ in $H_2^{33}S$. A similar procedure yields in the case of CO a value of −59.05(59) ppm for the $^{17}O$ shielding.

The first thing to note from the results in Table II is that for the shielding constants, relativistic corrections are larger than for the spin–rotation constants, being as large as 3% of the total absolute shielding constant of oxygen in CO, and 3.3% in the case of the sulfur shielding in $H_2S$, and very sizeable in terms of the absolute values, and thus these effects cannot be ignored when accurate absolute shielding constants are to be determined, even for as light an element as oxygen.

Another important thing to note is that the relativistic effects differ for the same nucleus in different molecules, being 3.0 ppm for water and 1.8 ppm for CO, and thus also the chemical shift of the oxygen atom will be affected by relativistic effects. The chemical shift can be determined very accurately using NMR spectroscopy, and the chemical shift of $^{17}O$ in water relative to CO is experimentally found to be 386.2 ppm.[30,31] With existing absolute shielding scales,[16,19] this chemical shift is found to be overestimated by 1.8 ppm, 388.0 ppm. Our currently proposed experimental absolute shielding scales

TABLE II. Semi-experimental isotropic oxygen and sulfur shielding constants for $H_2^{17}O$, $H_2^{33}S$, and $C^{17}O$.

| Molecule | $H_2O$ | $H_2S$ | CO |
|---|---|---|---|
| $(C_{exp}^0)^{a}$ (kHz) | −25.12(12)[b] | −35.14(49)[c] | −31.609(41)[d] |
| $\Delta C_{nr}^{vib}$ (kHz) | −3.38[b] | −1.68[c] | −0.100[e] |
| $(\Delta C_{rel}^{eq})^{f}$ (kHz) | −0.01 | −0.22 | −0.087 |
| $(C_{nr}^{eq})^{g}$ (kHz) | −21.73(12) | −33.24(49) | −31.474(41) |
| $(\sigma_{nr,p}^{eq})^{h}$ (ppm) | −78.9(3) | −326.7(4.6) | −499.88(59) |
| $(\sigma_{nr,d}^{eq})^{i}$ (ppm) | 416.4[b] | 1065.5[c] | 445.04[e] |
| $(\sigma_{nr}^{eq})^{j}$ (ppm) | 337.5(3) | 738.8(4.6) | −54.84(59) |
| $\Delta\sigma_{nr}^{vib}$ (ppm) | −11.7[b] | −19.7[c] | −5.73[e] |
| $\Delta\sigma_{nr}^{T}$ (ppm) | −0.4[b] | −0.8[c] | −0.35[e] |
| $(\Delta\sigma_{rel}^{eq})^{f}$ (ppm) | 3.0 | 24.6 | 1.87 |
| $\sigma^0$ ($T=300$ K) (ppm) | 328.4(3) | 742.9(4.6) | −59.05(59) |

[a]Experimental spin–rotation constant for the vibrational ground state.
[b]Reference 16.
[c]Reference 17.
[d]Reference 18.
[e]Reference 4.
[f]Four-component DFT-GIAO (PBE/dyall-cvqz) calculations (this work).
[g]$C_{nr}^{eq} = C_{exp}^0 - \Delta C_{nr}^{vib} - \Delta C_{rel}^{eq}$.
[h]Paramagnetic part of the isotropic shielding constant derived from $C_{nr}^{eq}$ using Flygare's relation Eq. (1).
[i]Non-relativistic diamagnetic contribution to the isotropic NMR shielding constant.
[j]$\sigma_{nr}^{eq} = \sigma_{nr,d}^{eq} + \sigma_{nr,p}^{eq}$.

yield better agreement with the experimental chemical shift, 387.5 ppm, though a difference of about 1.3 ppm remains.

Our results for $^{33}$S of 742.9(4.6) ppm differ as expected substantially from the non-relativistic absolute shielding scale recently proposed by Helgaker *et al.*[17] of 716.4(4.6) ppm. However, this original datum was based on converting the experimental spin–rotation constants using Eq. (1), whereas a truly non-relativistic value for the absolute $^{33}$S shielding of H$_2$$^{33}$S should be 718.3(4.6) ppm obtained by correcting the experimental data for the relativistic effects on the spin–rotation constant (see Table II). This truly non-relativistic absolute shielding constant is in much better agreement with the best quantum-chemical calculations at the CCSD(T) level that yield a value of 719.0 ppm at 300 K.[17] The small discrepancy between theory and experiment at the non-relativistic level for the $^{33}$S shielding constant in hydrogen sulfide is thus largely resolved, also lending support to the quality of the experimental data.

## IV. CONCLUDING REMARKS

Combining previously published high-quality experimental spin–rotation data and accurate coupled-cluster calculations with our own calculations of relativistic corrections to shielding and spin–rotation constants, we have revised the absolute shielding scales for the $^{17}$O and $^{33}$S nuclei, being for $^{17}$O in H$_2$$^{17}$O 328.4(3) ppm and −59.05(59) ppm in C$^{17}$O, and for $^{33}$S in H$_2$$^{33}$S it is 742.9(4.6) ppm, in very good agreement with an earlier prediction by Antušek and Jaszuński of 740.3(3.0) ppm.[32] These fully relativistic absolute shielding constants will be valuable when determining updated nuclear magnetic moments for these nuclei, or as benchmark results for different relativistic approximations for calculating nuclear magnetic shielding constants. For benchmarking approximate methods for calculating non-relativistic shielding constants, previously published results[16] for $^{17}$O still remain valid, whereas we propose a minor revision for $^{33}$S in order to remove the small relativistic corrections that are present in the experimental datum, the new non-relativistic absolute shielding scale being 718.3(4.6) ppm for this nucleus in H$_2$$^{33}$S.

## ACKNOWLEDGMENTS

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