Parity violation in nuclear magnetic resonance frequencies of chiral tetrahedral tungsten complexes NWXYZ (X, Y, Z = H, F, Cl, Br or I)

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Density functional theory within the two-component quasi-relativistic zeroth-order regular approximation (ZORA) is used to predict parity violation shifts in nuclei nuclear magnetic resonance shielding tensors of chiral, tetrahedrally bonded tungsten complexes of the form NWXYZ (X, Y, Z = H, F, Cl, Br or I). The calculations reveal that sub-mHz accuracy is required to detect such tiny effects in this class of compounds, and that parity violation effects are very sensitive to the choice of ligands.

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I. INTRODUCTION

Electro-weak currents violate parity symmetry, thus lifting the energetic degeneracy of enantiomers which leads to tiny differences in molecular properties of non-identical mirror-image molecules. Proposed experimental schemes to detect PV shifts in properties of chiral molecules range from Mössbauer spectroscopy, to vibrational spectroscopy, electron paramagnetic resonance (EPR) spectroscopy, rotational spectroscopy, nuclear magnetic resonance (NMR) spectroscopy including nuclear spin-spin couplings, quantum beats in optical rotation, and finally tunneling dynamics of chiral molecules. Despite some great efforts to measure such tiny PV effects in chiral molecules, which are expected to lie in the µHz to Hz region, all experiments have to be considered unsuccessful or unconvincing so far, despite occasional claims to the contrary (for a details discussion see Ref.31). The current status on experimental and theoretical attempts to search for suitable chiral molecules and subsequent PV measurements has been reviewed several times.

Experimental detection of nuclear magnetic resonance (NMR) frequency shifts is considered to be a feasible route towards a first observation of PV in chiral molecules. In contrast to nuclear spin-independent molecular PV effects aimed for in high-resolution vibrational spectroscopy, which may face difficulties in achieving an accuracy superior to high-precision atomic experiments on heavy elements such as cesium, a successful measurement of nuclear spin-dependent PV effects promises to give insight into hadronic weak interactions inside the nucleus. The reason for this is that for most nuclei the dominant contribution to the nuclear spin-dependent weak interaction between electrons and nuclei comes from the nuclear anapole moment, which is caused by parity violating interactions within the nucleus and which has only been measured once before in $^{133}$Cs.

The special electronic situation in open-shell diatomic molecules offers in principle unmasked access to nuclear spin-dependent PV interactions in a limited set of nuclei and promising candidate systems such as RaF have been proposed for this research line. Due to the near degeneracy of levels opposite parity in conventionally chiral molecules, the leading PV contribution (nuclear spin-independent or nuclear spin-independent) can conveniently be selected by the type of spectroscopy (NMR, MW, IR, UV). Furthermore, one can draw in principle from a wealth of NMR active nuclei to form chiral molecules, for which PV effects would be observable as parity violating frequency differences between enantiomers.
In this paper we compare PV effects in NMR shielding constants obtained from two-component quasi-relativistic density functional calculations for a whole range of chiral tetrahedral NWXYZ molecules as shown in Figure 1 for the S-enantiomer NWBrFI, with X, Y and Z representing hydrogen or the halogens F, Cl, Br and I. These chiral molecules contain heavy elements and serve as model compounds to estimate nuclear spin-dependent PV effects. However, we point out that only the non-chiral species NWH₃ and NWF₃ have been identified in the gas phase by Wang et al.⁵⁵,⁵⁶ so far. Gas-phase syntheses of the chiral derivatives with subsequent mass selection and isolation could open up the way for high-resolution gas-phase NMR spectroscopy. We mention that nuclear spin-independent PV effects in vibrational spectra of these chiral tungsten derivatives have been studied theoretically before.⁵⁷,⁵⁸

II. METHODOLOGY

The main contributions to the PV operator $\hat{H}_{PV}$ for electron-nucleus interaction consists of a nuclear spin independent $\hat{H}_{PV}^{(1)}$ and dependent $\hat{H}_{PV}^{(2)}$ part,

$$\hat{H}_{PV} = \hat{H}_{PV}^{(1)} + \hat{H}_{PV}^{(2)} = \frac{G_F}{2\sqrt{2}} \sum_i \left( \sum_{A=1}^{N_{nuc}} Q_W(A) \gamma_i^A \varrho_A (\vec{r}_i) + \sum_{A=1}^{N_{nuc}} \kappa_A \varrho_A (\vec{r}_i) \vec{\alpha}_i \cdot \vec{I}_A \right),$$

where $G_F = (2.22254 \times 10^{-14})E_h \alpha_0^3$ is Fermi’s weak coupling constant, and the sum runs over all $N_{nuc}$ nuclei in the system. $Q_W(A) \approx (1 - 4 \sin^2 \theta_W) Z_A - N_A$ is the electroweak charge of nucleus $A$ with proton number $Z_A$ and neutron number $N_A$. In the present work, the value for the Weinberg angle is set to $\sin^2 \theta_W = 0.2319$ as used in previous calculations. A recent
value determined at energies comparable to those considered here is $\sin^2 \theta_W = 0.2397 (18)^{50}$

We mention that radiative corrections alter the weak charge and one approximately obtains $Q_W \approx -0.9857 N_A + 0.0675 Z_A^{60,61} \rho_A(\vec{r})$ and $\vec{I}_A$ are the normalised nucleon density and the nuclear spin, respectively, $\gamma^5$ is the Dirac pseudoscalar (chirality operator), $\vec{\alpha}_i$ is a vector comprised of the Dirac matrices in standard form, $\vec{r}_e$ is the electron position vector and $\kappa_A$ is a nuclear state dependent parameter. We note here that different choices for the constant related to the nuclear spin-dependent parameter can be found in the literature, for instance $\kappa_A^{62}, k_{A,A}^{53}, g_{2A}^{P,15,51}, k_{NSD,A}^{63}$ and $(-\lambda)(1 - 4 \sin^2 \theta_W)^{16,18,22,64-66}$ which are simply related by

$$\frac{\kappa_A}{2} = k_{A,A} = g_{2A}^P = 2k_{NSD,A} = -\left(1 - 4 \sin^2 \theta_W\right) \lambda_A,$$

where $\lambda_A$ is a nuclear state (spin) dependent parameter. There are two contributions to these parameters. The first contribution comes from the electroweak neutral coupling between electron vector and nucleon axial-vector currents $(\vec{V}_e \vec{A}_N)^{67}$ and the second comes from the nuclear anapole moment. The nuclear anapole moment scales with $\kappa_A \sim A^{2/3}$ and becomes the dominant contribution for heavy nuclei (see Refs. 38, 52, 63, 68, and 69 for details).

The first part $\hat{H}_{PV}^{(1)}$ of the PV operator comprises the dominant contribution from the first-order neutral current interaction between electrons and nuclei. When nuclear spin-independent molecular properties, such as vibrational frequencies or electronic energies are considered, this is usually the only part of the operator taken under consideration in calculations.\cite{28,70-80}. For explicitly nuclear spin-dependent properties such as NMR frequencies or hyperfine splittings, however, the second part of the operator, $\hat{H}_{PV}^{(2)}$, is estimated to yield the dominant PV contribution in most cases.\cite{15} It should be kept in mind, however, that under certain conditions the nuclear spin independent operator can contribute to the interaction with similar strength.\cite{81} Furthermore, because of the approximate $Z^2$-scaling of $\hat{H}_{PV}^{(2)}$ operator, it is important to study nuclear spin-dependent PV effects in chiral molecules containing heavy elements.\cite{22,64,66,82}

Through the factor $\lambda_A$, $\hat{H}_{PV}^{(2)}$ contains also higher-order nuclear weak interaction effects. Because of the uncertainty for this factor (as it is of nuclear structure origin) we set $\lambda_A = -1$ in all our calculations and therefore values reported herein for NMR shielding constants and frequency splittings are effective in the sense that they have to be scaled by the negative of the actual value of $\lambda_A$, in order to obtain an estimate of measurable physical values. For
heavy nuclei, it is expected to lie between 1 and 10.83,84

All parity violation (PV) calculations were performed within the framework of the two-component quasi-relativistic zeroth-order regular approximation (ZORA)85–88 which was applied by Berger et al.89,90 to the calculation of PV energy differences between enantiomers and later62 to first-order PV contributions to NMR shielding tensors. Within this approach, the perturbed Hamiltonian including external magnetic field effects and PV contributions up to first order is given by (for simplicity we omit summation over electrons)

\[
\hat{h}_{\text{ZORA}} = \vec{\sigma} \cdot \vec{p} \tilde{\omega} \vec{\sigma} \cdot \vec{p} + V - q \left\{ \vec{\sigma} \cdot \vec{p}, \tilde{\omega} \vec{\sigma} \cdot \vec{A} \right\} + q^2 \left\{ \vec{\sigma} \cdot \vec{A}, \tilde{\omega} \vec{\sigma} \cdot \vec{A} \right\} + \frac{1}{c} \left\{ \vec{\sigma} \cdot \vec{\pi}, \tilde{\omega} \hat{f}_{\text{PV}} \right\},
\]

(3)

with \( \{x, y\} = xy + yx \) being the anticommutator. Here, \( \vec{p} \) is the linear momentum of the electron, \( \vec{\pi} = \vec{p} - q \vec{A} \) the conjugate momentum operator inside a magnetic field with vector potential \( \vec{A} \), and \( q = -e \) the charge of the electron. \( c \) is the speed of light in vacuum and \( \vec{\sigma} \) is the vector containing the three Pauli matrices. The nuclear spin-dependent PV operator \( \hat{f}^{(2)}_{\text{PV}} \) in the two-component form enters the Dirac \((2 \times 2)\) matrix equation in the off-diagonal and can be written as,

\[
\hat{f}^{(2)}_{\text{PV}} = \lambda_{\text{PV}} \sum_{A=1}^{N_{\text{nuc}}} \frac{\kappa_A}{h \gamma_A} \varrho_A(\vec{r}) \vec{\sigma} \cdot \vec{\mu}_A,
\]

(4)

where we introduced \( \lambda_{\text{PV}} \) as a formal perturbation parameter, \( h = \hbar /2\pi \) is the reduced Planck constant, and \( \gamma_A \) and \( \vec{\mu}_A = h \gamma_A \vec{I}_A \) are the gyromagnetic ratio and magnetic moment of nucleus \( A \) respectively.

Within the density-functional theory (DFT) approximation pursued here, the potential \( V \) is given by \( V = V_H + V_{XC} + V_N \) with the Hartree potential \( V_H \), the exchange-correlation potential \( V_{XC} \) and the electron-nucleus attraction potential \( V_N \). The ZORA factor \( \tilde{\omega} \) is given by,

\[
\tilde{\omega} = \frac{1}{2m_e - V/c^2},
\]

(5)

and computed using van Wülffen’s model potential \( \tilde{V} \) with additional damping instead of the actual potential \( V \) in order to circumvent a direct dependence of \( \tilde{\omega} \) on the electron orbitals and to alleviate the gauge dependence of the ZORA approach91,95. The model potential \( \tilde{V} \) used in the calculation of the ZORA factor \( \tilde{\omega} \) of Eq. 5 is described in detail in Ref. 91. Model potentials are calculated using the local density approximation exchange–correlation functional and superpositions of atomic model densities \( \rho_A^{\text{mod}} \). These model densities are
expanded in terms of Gaussian functions as described in Ref. 91. Exponents $\alpha_i^{\text{mod}}$ and coefficients $c_i^{\text{mod}}$ used in this work were determined by Christoph van Wülken$^91$ and are listed in Table S1.

In ZORA SCF calculations and for the parity violating interaction, we used a Gaussian nuclear model$^92$ with exponent coefficients

$$\alpha_{\text{nuc}} = \frac{3}{2r_{\text{nuc}}(A)^2},$$

and

$$r_{\text{nuc}}(A) = (0.836A^{1/3} + 0.570) \text{ fm},$$

$A$ being the atomic mass number of the isotope with charge $Z$. For terms arising due to the vector potential $\vec{A}_\mu$, however, a point-like distribution of the nucleus’ magnetic moment has been assumed. All calculations reported herein were performed with a modified version of the TURBOMOLE program.$^93,94$

The parity-conserving NMR shielding tensor for a given nucleus $Q$ is defined as the second derivative of the total energy $E$ with respect to the nuclear magnetic moment $\vec{\mu}_Q$ of the nucleus under study and the externally applied magnetic field $\vec{B}$ taken for vanishing perturbations,

$$\sigma_{kl}(Q) := \left. \frac{d^2E}{dB_k d\mu_{Ql}} \right|_{\vec{T}=\vec{0}},$$

where $\vec{T}$ is the vector containing all perturbation parameters: $\vec{T}^T = (\vec{B}_T, \vec{\mu}_1, \ldots, \vec{\mu}_{N_{\text{nuc}}}, \lambda_{\text{PV}})$. Accordingly, the parity non-conserving NMR shielding tensor can be defined as a third-order derivative of $E$ with respect to $\vec{\mu}_Q$, $\vec{B}$ and the PV perturbation parameter $\lambda_{\text{PV}},$

$$\sigma_{kl}^{\text{PV}}(Q) := \left. \frac{d^3E}{dB_k d\mu_{Ql} d\lambda_{\text{PV}}} \right|_{\vec{T}=\vec{0}}.$$

After taking derivatives and neglecting contributions due to the nuclear spin-independent PV contribution $\hat{f}_{\text{PV}}^{(t)}$, one arrives at the following expression for the PV NMR shielding tensor,$^62$

$$\sigma_{kl}^{\text{PV}}(Q) = \sigma_{d,kl}^{\text{PV}}(Q) + \sigma_{p,kl}^{\text{PV}}(Q) + \sigma_{\text{so},kl}^{\text{PV}}(Q).$$

Subscripts d, p, so refer to diamagnetic, paramagnetic and spin-orbit coupling contributions according to their conventional meaning,$^96$ except for $\sigma_{p}^{\text{PV}}$ and $\sigma_{\text{so}}^{\text{PV}}$, where contributions
were grouped together according to their scaling behavior with respect to the nuclear charge (see Ref. 62 for details and explicit expressions).

Results will be reported in terms of NMR frequency splittings \( \Delta \nu^{PV} \) between left \((S)\)- and right \((R)\)-handed enantiomers inside a static homogeneous magnetic field of flux density \( B \):

\[
\Delta \nu^{PV} (Q) = \nu^S (Q) - \nu^R (Q) = B \gamma_Q \sigma^{PV} (Q) / \pi, \tag{11}
\]

with the isotropic shielding constant \( \sigma^{PV} = \frac{1}{3} \text{Tr} [\sigma^{PV}] \), to which the traceless diamagnetic PV shielding tensor \( \sigma^{PV}_{d,kt} (Q) \) does not contribute. For certain choices of density functionals, the remaining two linear response type terms can be computed within an uncoupled Kohn–Sham framework as the corresponding response equations can be decoupled due to time-reversal symmetry.

### III. COMPUTATIONAL DETAILS

Gaussian basis sets used in calculating the PV NMR shielding tensors for the NWXYZ series of molecules discussed herein were all uncontracted and were constructed as described in the following. For hydrogen, the aug-cc-pVDZ basis set of Refs. 97 and 98 was employed (in uncontracted form). Exponent coefficients \( \alpha_i^{orb} \) of the uncontracted spherical Gaussian basis sets for all other atoms were taken from an even tempered list generated according to \( \alpha_i^{orb} = \gamma \beta^{N-i} \) with \( i = 1, 2, \ldots, N \) and \( N = 26 \). Herein we chose the largest exponent coefficient as \( \alpha_1^{orb} = 500000000 \ a_0^{-2} \) and the smallest as \( \alpha_{26}^{orb} = \gamma = (2/100) \ a_0^{-2} \). The set of exponents taken from this list are \((1-25s,2-26p,20-24d,22-23f)\) for N, \((1-25s,2-26p,15-25d,22-23f)\) for F, \((1-25s,2-26p,15-25d,22-23f)\) for Cl, \((1-25s,2-26p,15-25d,20-24f)\) for Br, \((1-25s,2-26p,12-25d,15-25f)\) for W, and \((1-25s,2-26p,15-25d,20-24f)\) for I.

For the PV calculations the gradient corrected Becke-Lee-Yang-Parr functional (B-LYP) was used. The structural parameters for the compounds studied were obtained through energy minimization using the B3LYP hybrid functional together with aug-cc-pVTZ basis sets, in connection with scalar relativistic pseudopotentials for W, Br and I, described in detail in Refs. 57 and 58. Parity violating NMR shielding tensors were obtained for the \(^{183}W\) isotope (natural abundance 14.31%), which has nuclear spin \( I = 1/2 \) and a gyromagnetic ratio of \( 1.1282406 \times 10^7 \) rad T\(^{-1}\) s\(^{-1}\). A common gauge origin placed at the position of the tungsten nucleus was employed in this study. We note that extension of the basis
set used leads to minor changes. For example, extending the f-set for N to (20-24f) and for Cl to (20-24f) changes $\Delta \nu_{PV}$ for $^{183}\text{W}$ by only $-0.02 \mu\text{Hz}$ for NWBrClIF compared to the smaller basis set. This is negligible compared to the effect different functionals would have on PV frequency shifts. For example, using the local density approximation\(^{102}\) we obtain (B-LYP values are given in parentheses) $-419 (-363) \mu\text{Hz}$ for NWHF1, $-106 (-88) \mu\text{Hz}$ for NWHClF, and $-106 (-94) \mu\text{Hz}$ for NWHBrCl for the $^{183}\text{W}$ NMR PV shift. The dependence of predictions for parity violation effects on the chosen density functional in vibrational spectra of these compounds has been discussed in detail before\(^{58}\).

IV. RESULTS AND DISCUSSION

In order to facilitate the selection of a chiral compound especially well suited for the investigation of PV NMR effects, it is important to assess the effect of different nuclei surrounding the nucleus under study. PV NMR frequency splittings $\Delta \nu_{PV}$ for the $^{183}\text{W}$ isotope and energy differences $\Delta E_{PV}$ between enantiomers for a series of chiral molecules of the general structure NWXYZ with X,Y,Z = H,F,Cl,Br or I have therefore been investigated and the results are listed in Table I. The compounds studied herein are derived by substitution from the NWH\(_3\) and NWF\(_3\) molecules synthesized by Wang et al.\(^{55,56}\) In the group of molecules from 1 to 4 shown in Table I all three hydrogen atoms have been substituted by halogens with respect to NWH\(_3\), in the group from 5 to 10 only two hydrogen atoms have been substituted. Figure 1 shows, for example, the structure of the S-enantiomer of NWBrFI.

Beside the scaling of PV effects with nuclear charge, there is still no generally applicable simple model for PV effects available to design good ligands around a central chiral atom for future PV measurements\(^{103}\) and one has to rely on explicit quantum theoretical calculations. However, Figure 2 indicates that there is a correlation between the absolute values of $\Delta \nu_{PV}$ and $\Delta E_{PV}$, and they group together in certain sets of molecules, i.e. those which contain no hydrogen, those which contain fluorine and hydrogen and the remaining three containing hydrogen but no fluorine. We observe the strongest PV energy difference for NWHClI, but we mention here that the results could be quite sensitive to the DFT approximation applied.\(^{104}\) Nevertheless, the order of magnitude of the PV energy differences $\Delta E_{PV}$ is comparable to those reported for PbHBrClF,\(^{105}\) and as expected much larger compared to the
TABLE I. PV $^{183}$W NMR frequency splittings $\Delta \nu = \nu^S - \nu^R$ due to the isotropic parity violating NMR shielding constants and PV energy differences $\Delta E_{PV}$ between the $S$- and $R$-enantiomers within a series of compounds NWXYZ with XYZ= H, F, Cl, Br or I, calculated using the B-LYP functional. The NMR frequencies were obtained at a magnetic flux density of $B = 11.7$ T and are given here in $\mu$Hz. $\Delta E_{PV}/\hbar$ is given in Hz. The total PV frequency splitting $\Delta \nu_{PV}$ is defined in Eq. 10. $\Delta \nu_{PV,p}$ and $\Delta \nu_{PV,so}$ are related to the paramagnetic and spin-orbit coupling contributions to the isotropic part of the NMR shielding tensor. Results are given with three significant figures for $\Delta \nu_{PV}$, the individual contributions to $\Delta \nu_{PV}$ were rounded to the same accuracy as $\Delta \nu_{PV}$.

| Number | Molecule          | $\Delta \nu_{PV}/\mu$Hz | $\Delta \nu_{PV,p}/\mu$Hz | $\Delta \nu_{PV,so}/\mu$Hz | $\Delta E_{PV}/(\hbar$ Hz) |
|--------|-------------------|--------------------------|----------------------------|-----------------------------|----------------------------|
| 1      | NWBrClF           | -9.09                    | 1.15                       | -10.24                      | -27.9                      |
| 2      | NWClFI            | -25.9                    | 3.6                        | -29.6                       | -74.0                      |
| 3      | NWBrFI            | -16.7                    | 4.8                        | -21.4                       | -47.6                      |
| 4      | NWBrClI           | 0.398                    | 2.578                      | -2.179                      | -2.21                      |
| 5      | NWHBrCl           | -94.1                    | -43.4                      | -50.8                       | 83.4                       |
| 6      | NWHBrI            | -196                     | -96                        | -101                        | 134                        |
| 7      | NWHClII           | -293                     | -139                       | -154                        | 214$^a$                    |
| 8      | NWHClF            | -88.4                    | -41.8                      | -46.6                       | -8.24                      |
| 9      | NWHBrF            | -176                     | -74                        | -102                        | 36.6                       |
| 10     | NWHFI             | -363                     | -152                       | -210                        | 104                        |

$^a$) This value of $\Delta E_{PV}/\hbar$ compares to 138 Hz (242 Hz) of Ref. 58 obtained at the B3LYP (LDA) level of theory.

In the first series of compounds containing no hydrogen and showing rather small PV effects, the relative ordering of the absolute values of the PV frequency splittings $\Delta \nu_{PV}$ and energy differences $\Delta E_{PV}$ is the same, i.e. $4 < 1 < 3 < 2$. Here, the most significant effect seems to be an order of magnitude increase in $\Delta E_{PV}$ and an even stronger increase in $\Delta \nu_{PV}$ upon introducing fluorine as a ligand. The large impact of fluorine substitution is most probably due to its large electronegativity which seems to cause a stronger “chiral chiral polyhalomethanes (CHXYZ)$^{80,105}$ or polyhalocubanes$^{79}$ if one omits the hypothetical astatine derivative CHAtFI.
FIG. 2. (Color online) Plot of the PV $^{183}$W NMR frequency splitting $\Delta \nu_{PV}$ against the PV energy difference $\Delta E_{PV}$ (absolute values only)

field$^\dagger$ around the tungsten atom. For PV energy shifts this has been observed before.$^{106}$ The paramagnetic and spin-orbit coupling contributions to the frequency splitting, are of opposite sign, with the negative spin-orbit coupling contribution being larger by an order of magnitude with respect to the paramagnetic one in compounds 1, 3 and 2 and of roughly the same size in 4. The total frequency splitting is thus negative for compounds 1, 3 and 2 and positive for compound 4, where the spin-orbit coupling paramagnetic contributions almost cancel each other out.

In the second and third set of compounds, molecules 5 to 10, which show large PV frequency splittings compared to the first set, the relative ordering of the absolute values of the PV NMR frequency splittings is $5 < 6 < 7$ and $8 < 9 < 10$. If we regard them as two distinct sets as shown in Figure 2 the same is true for the PV energy differences. For both properties, however, the three molecules containing iodine display larger absolute values than the other three, and NWHFI shows the largest absolute value with $\Delta \nu_{PV} = -363$ $\mu$Hz. This comes also from the fact that the paramagnetic and spin-orbit coupling contributions to the PV frequency splitting are of the same sign for molecules of the second and third set, which enhances the increase in frequency splittings. All of the predicted $^{183}$W PV NMR frequency splittings for members of the second and third series of molecules, 5 to 10, are
significantly larger than the values predicted for molecules 1 to 4, and substituting any of the halogens in the first series by hydrogen almost always leads to at least an order of magnitude increase in the PV NMR frequency splittings. The only exception to this is the substitution of iodine by hydrogen in NWClFI, where there is an increase by a factor 4 “only”. A possible reason for this trend is the larger asymmetry (chirality) of the electronic environment of the tungsten nucleus, introduced by substituting atoms of different size and electronegativity.

It is also possible to analyze the impact of atomic substitution with respect to the different electronegativities (χ) of the substituents, which is largest for fluorine and smallest for hydrogen: The relative sequence of electronegativities (χ) of the substituents is χ(F) > χ(Cl) > χ(Br) > χ(I) > χ(H) with χ(Cl) ≥ χ(N) ≥ χ(Br). As mentioned earlier, this could explain, why in the first series of molecules there is a pronounced increase in the absolute values of both ∆E_{PV} and ∆ν_{PV} upon fluorine substitution. It could also explain an increase in PV properties upon substitution of hydrogen for one of the three heavier halogens, but it is less clear, why there should be such a pronounced increase even when hydrogen is substituted for fluorine.

Regarding PV NMR frequency splittings, a comparison with ^{13}C NMR shielding tensors in CHBrClF and CHBrFI presented in Ref. 65 shows, that like the PV energy difference, the isotropic ^{183}W NMR shielding constants are of opposite sign in this series and the relative ordering of the resulting frequency splittings is also changed: In Ref. 65 the ^{13}C NMR shieldings in CHBrClF and CHBrFI are similar in size with the ordering depending on the choice of density functional. In the present study, the isotropic ^{183}W PV NMR shielding constant in NWBrFI is almost twice as large as that in NWBrClF. However, for the values of ∆E_{PV} reported in Refs. 80 and 105, the increase from CHBrClF to CHBrFI is even more pronounced than the one reported herein for the ^{183}W shieldings in NWBrClF and NWBrFI.

V. CONCLUSION

We have studied PV effects for the NMR shielding tensor in chiral tungsten compounds within the ZORA approach. We found that PV NMR frequency splittings seem to be even more sensitive to atomic substitution than PV energies, with an increase of ∆ν_{PV} by three orders of magnitude from NWBrClI to NWHFI! This sensitivity offers excellent prospects
for the design of thermodynamically stable compounds suited for a NMR experiment aiming at molecular PV, where it would seem prudent to surround a heavy, NMR active nucleus in the chiral center of a molecule with ligands providing a strongly heterogeneous electronic environment.

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