

## Nuclear Magnetoelectric Shieldings for Chiral Discrimination in NMR Spectroscopy. Theoretical Study of (*R<sub>a</sub>*)-1,3-Dimethylallene, (2*R*)-2-Methyloxirane, and (2*R*)-*N*-Methyloxaziridine Molecules

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**Abstract:** Dynamic magnetoelectric shieldings at the nuclei, having the same magnitude but opposite sign in D and L enantiomers, have been evaluated at the random-phase approximation level of accuracy for three chiral molecules of medium size. For frequencies normally operated in nuclear magnetic resonance spectroscopy, calculated values are probably too small to be detectable in disordered phase. Within the same experimental conditions, the isotropic part of nuclear magnetic shielding polarizability and a related pseudoscalar provide contributions 3 orders of magnitude bigger than the average magnetoelectric shieldings to (i) the magnetic field induced at a resonant nucleus and (ii) the induced electric dipole of electrons rotating at the Larmor frequency; therefore, nuclear magnetic shielding polarizabilities are probably more suitable than nuclear magnetoelectric shieldings for chiral discrimination in nuclear magnetic resonance spectroscopy.

### 1. Introduction

There has been interest in the possible applications of optical techniques in nuclear magnetic resonance (NMR)<sup>1–7</sup> and in electron spin resonance (ESR)<sup>8,9</sup> spectroscopies. Evans had argued that a circularly polarized laser beam could shift NMR frequencies to gigahertz values,<sup>10–12</sup> but his point was questioned by Barron via group-theoretical considerations.<sup>13</sup> Experimental evidence for the resonance shift of  $\approx 1$  Hz in an NMR spectrum, operating at 270 MHz, by optical irradiation at transparent wavelengths, was reported by Warren et al.<sup>14,15</sup> This estimate was revised in a successive paper, taking heating effects into account.<sup>5</sup>

Buckingham and Parlett<sup>3,4</sup> discussed mechanisms producing induced magnetic moment via the inverse Faraday ef-

fect<sup>16</sup> and magnetic field at a resonant nucleus (and consequent resonance shift) for a sample irradiated by circularly polarized light. The shifts so determined are small, but they are reversed by a change of the handedness of light.<sup>3</sup> For circularly polarized radiation, Harris and Tinoco<sup>1,2</sup> found negligible effects of light intensities on chemical shifts. The achiral fractional shift change due to a single proton absorption at resonance is estimated as big as 0.1 Hz. Chiral contributions would be 3 orders of magnitude too small to be observed.<sup>17</sup>

The molecular property emphasized by Buckingham and Parlett<sup>4</sup> is the antisymmetric polarizability induced by a nuclear magnetic moment interacting with the optical field. A different intrinsic response property—the nuclear magnetoelectric shielding (axial) tensor—has been considered to rationalize magnetic effects at the nuclei of a molecule in the presence of an electromagnetic field.<sup>18–20</sup>

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All the (nonvanishing) components (and the trace) of the magnetoelectric shielding at the nuclei could in principle be measured for a system in an ordered medium, e.g., in a crystal or in a liquid crystal matrix, although theoretical predictions for some molecules are extremely small.<sup>18,21,22</sup> The components (and the trace) of the shielding tensor have the identical absolute value but change sign for the same atom in two enantiomeric molecules.<sup>23</sup> Such a property could be useful for practical applications, according to recent studies. Buckingham<sup>24</sup> and Buckingham and Fischer<sup>25</sup> speculated on the possibility of chiral discrimination by applying an additional electric field to conventional NMR spectrometers. They showed that in chiral liquids there is an additional signal—an electric polarization—that is generated only by chiral centers and that precesses at the resonance frequency of that nucleus. Observation of the polarization would lift the chiral blindness of NMR.

The present paper sets out to evaluate the magnitude of average nuclear magnetoelectric shieldings in three optically active molecules, (*R<sub>a</sub>*)-1,3-dimethylallene, (2*R*)-2-methyloxirane, and (2*R*)-*N*-methyloxaziridine. A theoretical overview is given in section 2, and calculated values at the random-phase approximation<sup>26</sup> (RPA) level, equivalent to the coupled Hartree–Fock (CHF) approach,<sup>27</sup> are reported in section 3.

## 2. Response Tensors for Chiral Discrimination

For a molecule with  $n$  electrons and  $N$  nuclei, charge, mass, position with respect to an arbitrary origin, canonical, and angular momentum of the  $i$ th electron are indicated by  $-e$ ,  $m_e$ ,  $\mathbf{r}_i$ ,  $\mathbf{p}_i$ ,  $\mathbf{l}_i = \mathbf{r}_i \times \mathbf{p}_i$ ,  $i = 1, 2, \dots, n$ . Analogous quantities for nucleus  $I$  are  $Z_I e$ ,  $M_I$ ,  $\mathbf{R}_I$ , etc. Capital letters are used for global electronic operators, e.g.,  $\hat{\mathbf{R}} = \sum_{i=1}^n \mathbf{r}_i$ ,  $\hat{\mathbf{P}} = \sum_{i=1}^n \mathbf{p}_i$ , etc. The Einstein convention of implicit summation over two repeated Greek subscripts is in force, and  $\epsilon_{\alpha\beta\gamma}$  denotes the Levi-Civita unit pseudotensor. The electronic reference state  $|a\rangle \equiv |\Psi_a^{(0)}\rangle$  and the excited states  $|j\rangle \equiv |\Psi_j^{(0)}\rangle$  of the molecule are eigenfunctions of the unperturbed time-independent Hamiltonian  $H^{(0)}$ , i.e.,  $H^{(0)}|\Psi_j^{(0)}\rangle = E_j^{(0)}|\Psi_j^{(0)}\rangle$ . The natural transition frequencies are indicated by  $\omega_{ja} = \hbar^{-1}(E_j^{(0)} - E_a^{(0)})$ . SI units are employed.

Using a formalism previously established,<sup>18–20,23</sup> the electric dipole operator is written

$$\hat{\mu} = -e\hat{\mathbf{R}} \quad (1)$$

and the operator for the magnetic field of  $n$  electrons on nucleus  $I$ , carrying an intrinsic magnetic dipole  $\mathbf{m}_I$ , is

$$\hat{\mathbf{B}}_I^n = -\frac{\mu_0}{4\pi} \frac{e}{m_e} \sum_{i=1}^n \frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3} \times \mathbf{p}_i \quad (2)$$

The expressions for first-order perturbing Hamiltonians used within the time-dependent perturbation scheme<sup>28</sup> are

$$\hat{H}^E = -\hat{\mu}_\alpha E_\alpha \quad (3)$$

$$\hat{H}^{\mathbf{m}_I} = -\hat{\mathbf{B}}_{I\alpha}^n m_{I\alpha} \quad (4)$$

The operator for the electric field acted on nucleus  $I$  by electron  $i$  is

$$\hat{\mathbf{E}}_I^i = \frac{1}{4\pi\epsilon_0} e \frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3} \quad (5)$$

and

$$\hat{\mathbf{E}}_I^n = \sum_{i=1}^n \hat{\mathbf{E}}_I^i \quad (6)$$

is the operator for the total field of  $n$  electrons. The force of the  $N$  nuclei on the  $n$  electrons is

$$\hat{\mathbf{F}}_n^N = -e \sum_{I=1}^N \sum_{i=1}^n Z_I \hat{\mathbf{E}}_I^i \quad (7)$$

Adopting the notation used by Orr and Ward<sup>29</sup> and Bishop<sup>30</sup> (OWB), the polarization propagator<sup>31</sup> for two operators  $\hat{A}$  and  $\hat{B}$  is defined

$$\langle\langle \hat{A}; \hat{B} \rangle\rangle_\omega = - \sum_P \sum_{j \neq a} \frac{\langle a | \hat{A} | j \rangle \langle j | \hat{B} | a \rangle}{E_j^{(0)} - E_a^{(0)} - \hbar\omega_\sigma} \quad (8)$$

where  $\sum_P$  indicates the sum over permutations of the pairs  $(\hat{A}/-\omega_\sigma)$  and  $(\hat{B}/\omega_1)$ , and  $\omega_\sigma = \omega_1 \equiv \omega$ . The electric dipole magnetoelectric shielding at nucleus  $I$ <sup>18,19,21–23</sup> is obtained by the real and imaginary contributions to the propagator  $\langle\langle \hat{B}_{I\alpha}^n; \hat{\mu}_\beta \rangle\rangle_\omega$

$$\lambda_{\alpha\beta}^I(-\omega; \omega) = -\mathcal{R}\langle\langle \hat{B}_{I\alpha}^n; \hat{\mu}_\beta \rangle\rangle_\omega = \frac{1}{\hbar} \sum_{j \neq a} \frac{2\omega_{ja}}{\omega_{ja}^2 - \omega^2} \mathcal{R}(\langle a | \hat{B}_{I\alpha}^n | j \rangle \langle j | \hat{\mu}_\beta | a \rangle) \quad (9)$$

$$\lambda_{\alpha\beta}^{\prime I}(-\omega; \omega) = \mathcal{F}\langle\langle \hat{B}_{I\alpha}^n; \hat{\mu}_\beta \rangle\rangle_\omega = -\frac{1}{\hbar} \sum_{j \neq a} \frac{2\omega}{\omega_{ja}^2 - \omega^2} \mathcal{F}(\langle a | \hat{B}_{I\alpha}^n | j \rangle \langle j | \hat{\mu}_\beta | a \rangle) \quad (10)$$

Equations 9 and 10 hold within the dipole length formalism.<sup>19,23</sup> Alternative definitions for the magnetoelectric shielding (10) are found in the dipole velocity gauge

$$\lambda_{\alpha\beta}^{\prime\prime I}(-\omega; \omega) = -\frac{e}{m_e \hbar} \sum_{j \neq a} \frac{2\omega}{\omega_{ja}(\omega_{ja}^2 - \omega^2)} \mathcal{R}(\langle a | \hat{B}_{I\alpha}^n | j \rangle \langle j | \hat{P}_\beta | a \rangle) \quad (11)$$

and in the dipole acceleration gauge

$$\lambda_{\alpha\beta}^{\prime\prime\prime I}(-\omega; \omega) = -\frac{e}{m_e \hbar} \sum_{j \neq a} \frac{2\omega}{\omega_{ja}^2(\omega_{ja}^2 - \omega^2)} \mathcal{F}(\langle a | \hat{B}_{I\alpha}^n | j \rangle \langle j | \hat{F}_{n\beta}^N | a \rangle) \quad (12)$$

allowing for the off-diagonal hypervirial relationships

$$\begin{aligned} \langle a | \hat{R}_\alpha | j \rangle &= \frac{i}{m_e} \omega_{ja}^{-1} \langle a | \hat{P}_\alpha | j \rangle = -\frac{1}{m_e} \omega_{ja}^{-2} \langle a | \hat{F}_{n\alpha}^N | j \rangle \\ &= \frac{e}{m_e} \omega_{ja}^{-2} \sum_{I=1}^N Z_I \langle a | \hat{E}_{I\alpha}^n | j \rangle \end{aligned} \quad (13)$$

Equations 13 for the matrix elements of the electric dipole operator are exactly satisfied by optimal variational wavefunctions.<sup>32</sup> In this ideal case, the quantum mechanical definitions 10–12 are theoretically and computationally equivalent.

Within the algebraic approximation, molecular orbitals (MO) are expressed as a linear combination of atomic orbitals (LCAO). In the limit of a complete set of expansion, the same numerical results would be obtained via (10)–(12). Therefore, closeness of the numerical results from different gauges (10)–(12) provides a measure of basis set quality and completeness.

The magnetoelectric shieldings 9 and 10–12 are equivalent to the polarizabilities introduced by Buckingham<sup>24</sup>

$$\lambda_{\alpha\beta}^I \equiv -\xi_{\beta\alpha}^I, \quad \lambda_{\alpha\beta}'^I \equiv -\xi_{\beta\alpha}'^I$$

**2.1. Magnetic Field Induced at a Nucleus by an Electric Field.** In NMR spectroscopy a strong static magnetic field with flux density  $\mathbf{B}^{(0)}$  produces a torque on a nuclear magnetic dipole  $\mathbf{m}_I$ , inducing Larmor precession with angular frequency  $\omega$ . If we take  $\mathbf{B}^{(0)}$  parallel to the  $z$  axis, the magnetization precesses around this axis. A magnetic field  $\mathbf{B}^{(1)}$  perpendicular to  $\mathbf{B}^{(0)}$ , formally required to be circularly polarized and synchronized with the precession of  $\mathbf{m}_I$  about  $\mathbf{B}^{(0)}$ , so that there is a coherence in the phase of the precessing nuclei, rotates the bulk magnetization of the precessing nuclei from the  $z$  direction to the  $xy$  plane.<sup>33,34</sup>

However, a linearly polarized field is adequate, as it can be thought of as the superimposition of two circularly polarized fields rotating in opposite directions. Only the component having the same sense as the precession synchronizes with the nuclear magnetic dipole; the other component is far from the resonance condition and has no effect.<sup>33,34</sup> In practice, a radiowave of frequency  $\omega$  is put in by passing a current through a coil at right angles to  $\mathbf{B}^{(0)}$  so as to induce an oscillating magnetic field  $\mathbf{B}^{(1)}$  along the coil axis, say in the  $x$  direction. If  $\omega$  coincides with the resonance frequency  $\omega_I$ , for nucleus  $I$  in a given molecular domain, the magnetic dipole will absorb energy from the coil, causing the macroscopic magnetization to rotate toward the  $xy$  plane and an emf to be induced in a receiver coil in the  $y$  direction.<sup>34</sup>

In modern NMR spectrometers, a  $\pi/2$  pulse rotates the equilibrium magnetization from the  $z$  direction of the magnetic field into the  $xy$  plane. Its free induction decay is recorded by the receiver coil. The NMR spectrum is obtained through Fourier transformation of the signal.

The total effective field acting upon  $\mathbf{m}_I$  is the vector sum  $\mathbf{B}(\omega) = \mathbf{B}^{(0)} + \mathbf{B}^{(1)}(\omega)$ . The response property involved is  $\sigma_{\alpha\beta}^I$ , the magnetic shielding of nucleus  $I$ , so that the magnetic field induced at the probe nucleus is<sup>19,20</sup>  $\Delta\langle B_{I\alpha}'^I \rangle = -\sigma_{\alpha\beta}^I B_\beta$ . In an isotropic medium we take the average  $\sigma_{av} = (1/3)\sigma_{\alpha\alpha}^I$ .

In principle, a time-dependent electric field  $\mathbf{E}(\omega)$  can be used to induce a magnetic field at nucleus  $I$ .<sup>18–20,23</sup> Time-dependent perturbation theory (TDPT)<sup>28,29,35,36</sup> can be applied to discuss the phenomenology. The expectation value of the magnetic field induced at the position of nucleus  $I$  by the  $n$ -electron cloud of a molecule responding to an external

electric field, described as a monochromatic wave with pulsation  $\omega$ , is given by the expression

$$\Delta\langle \hat{B}_{I\alpha}^n(\omega) \rangle = \lambda_{\alpha\beta}^I(-\omega; \omega) E_\beta(\mathbf{0}, \omega t) + \lambda_{\alpha\beta}'^I(-\omega; \omega) \dot{E}_\beta(\mathbf{0}, \omega t) \omega^{-1} \quad (14)$$

where  $E_\alpha(\mathbf{0}, \omega t)$  is the time-varying electric field at the origin of the coordinate system. A dot denotes partial time derivative.

The terms on the rhs of expression 14 have been obtained assuming spatially uniform electric field<sup>37</sup> over the molecular domain, within the Goeppert-Mayer dipole approximation.<sup>38,39</sup> One can also regard the magnetic field evaluated by eq 14 as the contribution provided by a Fourier component of the perturbing electric field. According to an obvious interpretation of eq 14, the second-rank tensors  $\lambda_{\alpha\beta}^I(-\omega; \omega)$  and  $\lambda_{\alpha\beta}'^I(-\omega; \omega)$  have been called magnetoelectric nuclear shieldings.<sup>18–20,23</sup>

Within the assumption of harmonic fields, the electric field at the origin of the coordinate system is  $E_\alpha = E_\alpha^{(0)} \cos(\omega t)$ , and its partial time derivative in the second addendum on the rhs of eq 14 can be replaced by an out-of-phase field allowing for the identity

$$\dot{E}_\alpha \omega^{-1} = -E_\alpha^{(0)} \sin(\omega t) = E_\alpha^{(0)} \cos(\omega t + \pi/2) \quad (15)$$

Therefore the magnetic field induced at the nucleus becomes

$$\Delta\langle \hat{B}_{I\alpha}^n(\omega) \rangle = \lambda_{\alpha\beta}^I(-\omega; \omega) E_\beta(\mathbf{0}, \omega t) + \lambda_{\alpha\beta}'^I(-\omega; \omega) E_\beta(\mathbf{0}, \omega t + \pi/2) \quad (16)$$

In an isotropic phase, the magnetic field, induced by linear response in the direction of the perturbing electric field at nucleus  $I$  of a (time-even) diamagnetic molecule, is evaluated via the second term of the rhs of eq 16

$$\Delta\langle \hat{B}_{I\beta}^n(\omega) \rangle = \frac{1}{3} \lambda_{\alpha\alpha}'^I(-\omega; \omega) E_\beta(\mathbf{0}, \omega t + \pi/2) \quad (17)$$

Within the model<sup>34</sup> quoted above, an alternating current is passed through a coil (mounted perpendicularly to  $\mathbf{B}^{(0)}$ ), which in turn gives rise to a linearly polarized electromagnetic field. The oscillating magnetic (electric) field is polarized along the  $x$  ( $y$ ) direction. Relationship 17 implies that a magnetic field  $\mathbf{B}^{(1)}$  linearly polarized along the  $y$  direction (regarded as the vector sum of two circularly polarized fields on the  $xy$  plane) can be generated by an out-of-phase, time-varying electric field linearly polarized in the same direction. Then the effect of the magnetic field described by eqs 16 and 17, induced by the electric field, could, if large enough, be detected by a receiver coil as a  $\pi/2$  out-of-phase signal.

**2.2. Electric Dipole Induced by a Nuclear Magnetic Dipole.** Allowing for the perturbing Hamiltonian 4 within the TDPT, an expression is obtained for the electric dipole induced by the precession of a permanent magnetic dipole at nucleus  $I$ .<sup>20,24,25</sup>

$$\Delta\langle \mu_\alpha(\omega) \rangle = -\lambda_{\beta\alpha}^I(-\omega; \omega) m_{I\beta} - \lambda_{\beta\alpha}'^I(-\omega; \omega) \dot{m}_{I\beta} \omega^{-1} \quad (18)$$

Relationship 18 can be rearranged, expressing the contribution of the second addendum on the rhs to the induced electric dipole as an out-of-phase term, as for relation 16.

**Table 1.** Nonvanishing Components of the Axial Tensor  $\lambda_{\alpha\beta}^I$  for Various Nuclear Site Symmetries

nuclear site symmetry	number of nonvanishing components		nonvanishing components
	total	unique	
$C_i, C_{2h}, D_{2h}, C_{4h}, D_{4h}, S_6, D_{3d}, C_{3h}, C_{6h}, D_{3h}, D_{6h}, D_{\infty h}, T_h, T_d, O_h$	0	0	
$C_1$	9	9	$xx, yy, zz, xy, yx, xz, zx, yz, zy$
$C_2$	5	5	$xx, yy, zz, xy, yx$
$C_s$	4	4	$xz, yz, zx, zy$
$D_2$	3	3	$xx, yy, zz$
$C_{2v}$	2	2	$xy, yx$
$C_4, C_3, C_6$	5	3	$xx = yy, zz, xy = -yx$
$S_4$	4	2	$xx = -yy, xy = yx$
$D_4, D_3, D_6$	3	2	$xx = yy, zz$
$C_{4v}, C_{3v}, C_{6v}, C_{\infty v}$	2	1	$xy = -yx$
$D_{2d}$	2	1	$xx = -yy$
$T, O$	3	1	$xx = yy = zz$

The induced magnetic field  $\Delta\langle\hat{B}_{I\alpha}^n(\omega)\rangle$  and electric dipole  $\Delta\langle\hat{\mu}_\alpha(\omega)\rangle$  are invariant in a translation of coordinate system,<sup>19,40</sup> as the magnetoelectric shieldings  $\lambda_{\alpha\beta}^I$  and  $\lambda_{\alpha\beta}^{I'}$  are origin independent.

$\lambda_{\alpha\beta}^I$  is odd under time reversal  $\hat{T}$  and inversion  $\hat{P}$ , and it vanishes for a closed-shell molecule in the absence of magnetic field.<sup>19,20,24,25</sup> However, it has a linear dependence on an applied magnetic field.<sup>20,24,25</sup> This case is best treated by taking into account quadratic response in terms of a third-rank tensor  $\sigma_{\alpha\beta\gamma}^I$ , referred to as polarizability of nuclear magnetic shielding.<sup>41</sup> The first term of eqs 14 and 18 suggests that, in the presence of an external magnetic field, we could replace the  $\lambda_{\beta\alpha}^I$  magnetoelectric shielding by the shielding polarizability via the scheme<sup>24,25</sup>

$$\lambda_{\beta\alpha}^I \rightarrow \sigma_{\beta\gamma\alpha}^I B_\gamma \quad (19)$$

so that, for instance, its contribution to the induced electric dipole becomes

$$\Delta\langle\mu_\alpha\rangle = -\sigma_{\beta\gamma\alpha}^I m_{I\beta} B_\gamma \quad (20)$$

The isotropic part  $\overline{\sigma^{(1)I}}_{\alpha\beta\gamma}$  and the pseudoscalar  $\overline{\sigma^{(1)I}} = (1/6)\epsilon_{\alpha\beta\gamma}\sigma_{\alpha\beta\gamma}^I$  have the same magnitude but opposite sign for enantiomeric molecules.<sup>24,25</sup> They are origin independent in the static case. The transformation law of dynamic polarizability of nuclear magnetic shielding in a gauge translation of the vector potential has been studied.<sup>40</sup>

**2.3. Magnetoelectric Shielding and Site Symmetry.**  $\lambda_{\alpha\beta}^{I'}$  is even under  $\hat{T}$  and odd under  $\hat{P}$ , and it is equal and opposite for the  $I$ th nucleus of D and L enantiomers, see the discussion after eq 921 of ref 23.

The number of unique parameters needed to describe this tensor, reported in Table 1, is obtained via group-theoretical methods,<sup>42</sup> taking into account the site symmetry. As the nuclear magnetoelectric shielding transforms like the optical rotatory power under symmetry operations, this number is the same as in the next-to-last column of Table 1 of ref 35.

**Table 2.** RPA Magnetoelectric Shieldings<sup>a</sup> of the (*R*<sub>a</sub>)-1,3-Dimethylallene Molecule via Dipole Length (*R*), Velocity (*P*), and Acceleration (*F*) Formalisms, for  $\omega = 10^{-7}$  au<sup>49</sup>

atom	form.	$xx \times 10^8$	$yy \times 10^8$	$zz \times 10^8$	$av \times 10^8$
C <sub>1</sub>	<i>R</i>	8.111	-1.863	-6.427	-0.05952
	<i>P</i>	8.165	-1.873	-6.459	-0.05577
	<i>F</i>	8.239	-1.828	-6.562	-0.05018
C <sub>3</sub>	<i>R</i>	-11.27	2.012	9.692	0.1442
	<i>P</i>	-11.23	2.077	9.594	0.1452
	<i>F</i>	-11.76	1.986	10.17	0.1325
C <sub>5</sub>	<i>R</i>	0.2200	-0.1096	-0.3274	-0.07232
	<i>P</i>	-0.01894	-0.02162	-0.2214	-0.08733
	<i>F</i>	0.6061	0.9649	-1.764	-0.06420
H <sub>1</sub>	<i>R</i>	-2.371	4.294	-0.9102	0.3377
	<i>P</i>	-2.383	4.308	-0.9161	0.3363
	<i>F</i>	-2.613	4.343	-0.8347	0.2986
H <sub>3</sub>	<i>R</i>	2.512	-5.446	1.729	-0.4015
	<i>P</i>	2.521	-5.453	1.728	-0.4012
	<i>F</i>	2.687	-5.478	1.722	-0.3563
H <sub>5</sub>	<i>R</i>	1.919	2.828	-1.525	1.074
	<i>P</i>	1.926	2.828	-1.528	1.075
	<i>F</i>	2.017	2.791	-1.487	1.107
H <sub>7</sub>	<i>R</i>	-0.07287	-3.047	-0.1551	-1.092
	<i>P</i>	-0.06639	-3.050	-0.1607	-1.092
	<i>F</i>	-0.1514	-3.014	-0.1581	-1.108

<sup>a</sup> The magnetoelectric shieldings in SI atomic units are obtained from the values in the table multiplying by  $\alpha^2 = 5.325 \dots \times 10^{-5}$ , see section 4. The conversion factor from SI au to SI units is  $1/\alpha c = 4.571 \dots \times 10^{-7} \text{ m}^{-1} \text{ s}$ .

The trace  $\lambda_{\alpha\alpha}^{I'}$  vanishes for achiral molecules, but, depending on site symmetry, diagonal and off-diagonal tensor components can be different from zero,<sup>18,21,22</sup> see Table 1. Therefore, measurements of the average value  $(1/3)\lambda_{\alpha\alpha}^{I'}$  may, in principle, serve for chiral discrimination in an isotropic phase.<sup>24,25</sup> However, the estimated magnitude is small, e.g.,  $|B_z \epsilon_{\alpha\beta\gamma} \lambda_{\alpha\beta}^I / 2\lambda_{\gamma\gamma}^{I'}| \approx 10^4$  in a field  $B_z \approx 10 \text{ T}$  for  $\text{CH}_3\text{CH}(\text{OH})\text{C}_6\text{H}_5$ .<sup>24</sup>

### 3. Theoretical Estimates of Average Magnetoelectric Shieldings

In the present study, a computational scheme<sup>18,21,22</sup> based on the random-phase approximation<sup>26,27</sup> was applied. Values of diagonal components of the  $\lambda_{\alpha\beta}^{I'}$  tensor were calculated by the SYSMO package<sup>43</sup> for three chiral systems, (*R*<sub>a</sub>)-1,3-dimethylallene, (*2R*)-2-methyloxirane, and (*2R*)-*N*-methyloxaziridine.

Molecular geometries have been optimized at the HF/6-31G level using GAUSSIAN03,<sup>44</sup> as described in previous calculations of shielding polarizabilities<sup>45</sup> related to  $\lambda_{\alpha\beta}^I$ , see section 2.2. Other data needed to reproduce our results are available in that paper.<sup>45</sup> The same basis sets were tested to check convergence of calculated  $\lambda_{\alpha\beta}^{I'}$ . The best results obtained via the basis sets developed in refs 18, 21, and 22 are shown in Tables 2–4.

As a rule, reliable estimates are obtained via basis sets containing diffuse Gaussian functions, which provide accurate representation of the electric dipole, eq 1, rather than the magnetic field operator, eq 2. Therefore, Sadlej basis



**Table 3.** RPA Magnetoelectric Shieldings<sup>a</sup> of the (2*R*)-2-Methyloxirane Molecule via Three Formalisms, for  $\omega = 10^{-7}$  au<sup>49</sup>

atom	form.	xx × 10 <sup>8</sup>	yy × 10 <sup>8</sup>	zz × 10 <sup>8</sup>	av × 10 <sup>8</sup>
C <sub>1</sub>	<i>R</i>	−5.533	2.683	0.4494	−0.8001
	<i>P</i>	−5.444	2.678	0.3844	−0.7939
	<i>F</i>	−4.557	1.917	0.2985	−0.7804
C <sub>2</sub>	<i>R</i>	−8.867	−1.486	7.655	−0.8994
	<i>P</i>	−8.813	−1.535	7.704	−0.8813
	<i>F</i>	6.886	−1.418	6.002	−0.7638
C <sub>3</sub>	<i>R</i>	−0.9702	0.5765	−0.3359	−0.2432
	<i>P</i>	−0.9461	0.5818	−0.3194	−0.2279
	<i>F</i>	−1.017	0.4915	−0.2989	−0.2749
O <sub>1</sub>	<i>R</i>	65.88	−3.932	−46.88	5.023
	<i>P</i>	65.31	−3.597	−46.37	5.112
	<i>F</i>	50.79	−2.109	−34.68	4.667
H <sub>1</sub>	<i>R</i>	0.9140	−1.042	0.2766	0.04961
	<i>P</i>	0.9168	−1.045	0.2807	0.05075
	<i>F</i>	0.8967	−1.006	0.1087	0.0
H <sub>2</sub>	<i>R</i>	−1.836	3.382	−0.8728	0.2243
	<i>P</i>	−1.840	3.386	−0.8790	0.2221
	<i>F</i>	−1.827	3.211	−0.9490	0.1448
H <sub>3</sub>	<i>R</i>	1.603	−2.686	0.7583	−0.1080
	<i>P</i>	1.613	−2.689	0.7574	−0.1062
	<i>F</i>	1.503	−2.587	0.9580	−0.04198
H <sub>4</sub>	<i>R</i>	1.065	0.1711	−0.1803	0.3518
	<i>P</i>	1.067	0.1698	−0.1789	0.3526
	<i>F</i>	1.066	0.1377	−0.09872	0.3683
H <sub>5</sub>	<i>R</i>	−1.030	0.1972	−0.4732	−0.4353
	<i>P</i>	−1.031	0.1973	−0.4751	−0.4361
	<i>F</i>	−0.9853	0.2025	−0.5056	−0.4295
H <sub>6</sub>	<i>R</i>	−0.5083	0.9850	−0.1978	0.09295
	<i>P</i>	−0.5096	0.9857	−0.1977	0.09278
	<i>F</i>	−0.5314	0.9932	−0.1671	0.09826

<sup>a</sup> See footnote a to Table 2.

sets<sup>46</sup> are well suited to calculate magnetoelectric shieldings within dipole length and velocity formalisms. They provide results close to those from the bigger aug-cc-pVTZ basis sets.<sup>47,48</sup>

The  $\omega$  frequency assumed in the calculation is  $10^{-7}$  au, close to the value of the <sup>1</sup>H resonant frequency in a field of 14.1 T, see section 4. By comparison with the natural frequencies  $\omega_{ja}$ , it is seen that this value of  $\omega$  can be neglected in the denominator of eq 10. Therefore the magnitude of  $\lambda_{\alpha\beta}^I$  for a given optical  $\bar{\omega}$ , up to  $\approx 10^{-3}$  au, can approximately be estimated<sup>49</sup> multiplying the values of Tables 2–4 by  $\bar{\omega} \times 10^7$ .

According to previous experience, within the acceleration formalism, Gaussian functions are not suitable to describe accurately the electron charge density in the vicinity of a nucleus heavier than hydrogen.<sup>18,21,22</sup> Actually, the *F*-values obtained for the magnetoelectric shielding of oxygen and nitrogen nuclei are very poor in most cases. Strong discrepancies in magnitude and sign with *R*- and *P*-predictions can be observed in Tables 3 and 4.

Only for the (*R<sub>a</sub>*)-1,3-dimethylallene molecule are the *F*-estimates for hydrogen and carbon quite close to *R*- and *P*-, see Table 2. However, the ability of Gaussian functions to represent the force operator can be improved by ad hoc

**Table 4.** RPA Magnetoelectric Shieldings<sup>a</sup> of the (2*R*)-*N*-Methyloxaziridine Molecule via Three Formalisms, for  $\omega = 10^{-7}$  au<sup>49</sup>

atom	form.	xx × 10 <sup>8</sup>	yy × 10 <sup>8</sup>	zz × 10 <sup>8</sup>	av × 10 <sup>8</sup>
C <sub>1</sub>	<i>R</i>	1.666	−4.467	−1.765	−1.522
	<i>P</i>	1.713	−4.496	−1.809	−1.531
	<i>F</i>	3.500	−5.590	−2.195	−1.428
C <sub>2</sub>	<i>R</i>	3.427	−2.511	0.7644	0.5602
	<i>P</i>	3.422	−2.495	0.7569	0.5610
	<i>F</i>	4.372	−3.448	1.285	0.7362
N <sub>1</sub>	<i>R</i>	−12.40	−37.93	30.73	−6.534
	<i>P</i>	−12.20	−38.57	30.73	−6.681
	<i>F</i>	51.83	−81.83	29.90	−0.03377
O <sub>1</sub>	<i>R</i>	3.656	70.92	−33.24	13.78
	<i>P</i>	3.133	73.89	−32.90	14.71
	<i>F</i>	−65.43	174.2	−20.88	29.31
H <sub>1</sub>	<i>R</i>	−0.8194	2.425	−0.8505	0.2516
	<i>P</i>	−0.8217	2.421	−0.8490	0.2502
	<i>F</i>	−0.5015	2.266	−0.8754	0.2963
H <sub>2</sub>	<i>R</i>	2.886	−1.970	0.2514	0.3892
	<i>P</i>	2.889	−1.968	0.2596	0.3934
	<i>F</i>	3.112	−1.726	0.1230	0.5031
H <sub>3</sub>	<i>R</i>	1.794	−0.5595	0.6338	0.6229
	<i>P</i>	1.792	−0.5639	0.6333	0.6203
	<i>F</i>	2.106	−0.9393	0.9611	0.7094
H <sub>4</sub>	<i>R</i>	−1.120	0.1689	−0.6674	−0.5396
	<i>P</i>	−1.115	0.1720	−0.6724	−0.5386
	<i>F</i>	−0.8996	0.2889	−0.6002	−0.4036
H <sub>5</sub>	<i>R</i>	0.1827	0.4023	−0.2735	0.1038
	<i>P</i>	0.1816	0.4120	−0.2752	0.1061
	<i>F</i>	0.1921	0.3414	−0.05236	0.1604

<sup>a</sup> See footnote a to Table 2.

procedures for “polarized” basis sets, providing a better description of the charge distribution near the nuclei.<sup>50</sup>

A preliminary attempt has been made in the present work, developing a “semipolarized” basis set from the Sadlej basis sets<sup>46</sup> for the (2*R*)-*N*-methyloxaziridine molecule. To keep the basis size as small as possible, the set of hydrogen functions was left unchanged, as it is large enough to provide almost the same results within different gauges in Tables 2–4. The basis sets of C, N, and O were polarized via the recipe of ref 50. The predictions obtained in the *F*-formalism, see Table 2 of the Supporting Information, are significantly improved compared to Table 4. The results from *R*- and *P*-approaches also agree quite nicely.

Other procedures based on R12 basis sets<sup>51</sup> can be applied according to previous investigations<sup>52</sup> to improve predictions within the acceleration formalism. The *F*-results obtained for the water molecule, reported in Table 1 of the Supporting Information, are close to convergence, i.e., fairly similar to those from *R*- and *P*-formalisms. They show that the problem can, at least in principle, be solved.

Therefore, the accuracy of the present calculation was assessed via closeness of results within dipole length and dipole velocity gauges from the basis sets employed<sup>18,21,22</sup> (We recall that they should be the same for complete basis sets.). It can reasonably be assumed that calculated *R*- and *P*-values for the molecules examined here are close to the limit for the RPA scheme.

#### 4. Units and Magnitude of Observable Properties

The calculations were carried out setting to 1 the base units<sup>53</sup> of mass  $m_e = 9.109\,381\,88 \times 10^{-31}$  Kg, charge  $e = 1.602\,176\,462 \times 10^{-19}$  C, action  $\hbar = 1.054\,571\,596 \times 10^{-34}$  J s, permittivity  $\kappa_0 = 4\pi\epsilon_0$ , with  $\epsilon_0 = 8.854\,187\,817 \dots \times 10^{-12}$  F m<sup>-1</sup>, and speed of light  $c = 299\,792\,458$  m s<sup>-1</sup>.

Derived units, e.g., the bohr  $a_0 = 0.529\,177\,2083 \times 10^{-10}$  m and the hartree  $E_h = m_e e^4 / \kappa_0^2 \hbar^2 = e^2 / \kappa_0 a_0 = 4.359\,743\,81 \times 10^{-18}$  J, are accordingly set to 1. The magnetic constant is  $\mu_0 = 1/\epsilon_0 c^2$  and  $\mu_0/4\pi = 1 \times 10^{-7}$  N A<sup>-2</sup>. The CODATA recommended values for the base and derived units are taken from ref 54.

The magnetoelectric shieldings 10 in (SI) atomic units are obtained from the values in the tables by expressing  $\mu_0/4\pi = \alpha\hbar/e^2c$  in the same units via the fine structure constant  $\alpha = e^2/\kappa_0\hbar c = 7.297\,352\,533 \times 10^{-3}$ . The conversion factor is  $\alpha^2 = 5.325\,135\,399 \times 10^{-5}$ . Within the SI system of units, the magnetoelectric shielding has dimension T V<sup>-1</sup> m  $\equiv$  m<sup>-1</sup> s, i.e., inverse velocity, see eq 14. Therefore the conversion factor from SI au to SI units is  $1/\alpha c = 4.571\,028\,927 \times 10^{-7}$  m<sup>-1</sup> s.

Within the cgs system of units, the magnetoelectric shielding is dimensionless. Its definition contains  $c$  in the denominator, instead of  $\mu_0/4\pi$ , see, for instance, eq 33 of ref 18. Then the value in the cgs system is obtained multiplying by  $\alpha$  the results in the tables. If the electric field is expressed in statV cm<sup>-1</sup>, with  $1 \text{ V m}^{-1} = 10^4/c \text{ statV cm}^{-1}$ , the induced magnetic field is obtained in gauss (1 G =  $10^{-4}$  T).

The largest value obtained for the average magnetoelectric shielding of <sup>17</sup>O in (2R)-N-methyloxaziridine is  $\approx 14 \times 10^{-8}$  in the units of Table 4, corresponding to  $7.5 \times 10^{-12}$  au, that is,  $3.4 \times 10^{-18}$  T mV<sup>-1</sup>, for a pulsation  $\omega \approx 1 \times 10^{-7}$  au of the order typically available in proton magnetic resonance experiments<sup>49</sup> (e.g., for <sup>1</sup>H, in a magnetic field  $B = 14.1$  T, resonance occurs at 600 MHz, equivalent to  $9.12 \times 10^{-8}$  au). However, the magnetic field density  $\approx 114$  T, needed for <sup>17</sup>O resonance at  $\omega = 1 \times 10^{-7}$  au, is unrealistic. Therefore, we take a scaled  $\lambda_{av}'^O \approx 4.6 \times 10^{-19}$  T V<sup>-1</sup> m for the resonance frequency  $\nu = 89.23$  MHz of <sup>17</sup>O in a field of 15.45 T.<sup>49</sup>

This value is used to estimate the magnetic field induced at the oxygen nucleus by an electric field and to make a comparison with a corresponding estimate of magnetic field induced via the isotropic part  $\sigma^{(1)O} \epsilon_{\alpha\beta\gamma}$  of the magnetic hypershielding at the oxygen nucleus in the same molecule.<sup>45</sup> Equations 16 and 19 show that an electric field can be applied to observe an induced magnetic field at <sup>17</sup>O. A calculated value<sup>45</sup> for the pseudoscalar<sup>25</sup>  $\sigma^{(1)O}$  is  $\approx 7.8 \times 10^{-17}$  mV<sup>-1</sup>, and then the electric field should be as big as  $\approx 1.3 \times 10^8$  V m<sup>-1</sup> to induce a magnetic field corresponding to 0.01 ppm,<sup>45</sup> normal to the strong magnetic field of an NMR spectrometer, that is  $1.545 \times 10^{-7}$  T, if we assume to operate at 15.45 T.<sup>49</sup> The same electric field would induce a magnetic field of magnitude  $6.0 \times 10^{-11}$  T at <sup>17</sup>O in (2R)-N-methyloxaziridine, allowing for the second term in eq 16. The ratio of the first term to the second in this relationship is  $\approx 2.6 \times 10^3$ .

The magnitude of the electric dipole induced by the precession of <sup>17</sup>O nuclear magnetic dipole,  $\approx 1.132 \times 10^{-26}$  JT<sup>-1</sup>, is analogously estimated via eq 18. In a magnetic field of 15.45 T, the contribution from the first term on the rhs of this relationship, allowing for scheme 19, is<sup>45</sup>  $\approx 1.4 \times 10^{-41}$  Cm. The second term contributes  $\approx 5.2 \times 10^{-45}$  Cm.<sup>55</sup> The ratio is  $\approx 2.6 \times 10^3$ . Therefore, the contribution arising from the magnetoelectric shielding  $\lambda_{av}'^O \approx 4.6 \times 10^{-19}$  T mV<sup>-1</sup> is negligible, compared with that from  $\sigma^{(1)O} \approx 7.8 \times 10^{-17}$  mV<sup>-1</sup> in magnetic fields normally available in NMR,<sup>49</sup> unless higher  $\omega$  values were used via experimental techniques that cannot be foreseen at the present time.

It can be asked if any effect could be detected in other spectral regions, e.g., for a molecule absorbing infrared radiation. Equation 18 would imply that the vibration of a nucleus carrying a permanent magnetic dipole moment also induces an electric dipole in the electrons, oscillating with the same frequency as that of the nuclear motion. The average electric dipole vanishes in isotropic phase. However, if a strong magnetic field  $B_z$  is applied, there is a magnetization along the  $z$  axis, which arises from magnetic moments of nuclei precessing at the Larmor frequency. The macroscopic magnetization should oscillate, following the nuclear vibration. The frequency  $\omega$  of the oscillating induced electric dipole would be  $\approx 10^4$ – $10^6$  times bigger than the Larmor frequency, of the order  $10^8$  Hz in NMR experiments. As the vibrational frequency  $\omega$  in the denominator of eq 10 is negligible compared to the natural transition frequencies  $\omega_{ja}$ , the magnetoelectric shieldings in Tables 1–3 would therefore increase by a factor of  $\approx 10^5$  due to  $\omega$  in the numerator. The magnitude of the induced dipole 18 would increase to the same extent.

#### 5. Concluding Remarks

The magnetic field induced at the nuclei of a molecule by a time-varying electric field and the rotating electric dipole induced by the precession of nuclear magnetic dipoles have the same magnitude but different sign for D and L enantiomers. The dynamic magnetoelectric shieldings at the nuclei of three molecules, (*R<sub>a</sub>*)-1,3-dimethylallene, (2R)-2-methyloxirane, and (2R)-N-methyloxaziridine, have been calculated for a frequency  $\omega = 10^{-7}$  au, close to the <sup>1</sup>H resonant frequency in a field of 14.1 T, at the random-phase approximation level via extended basis sets.

The accuracy of the theoretical predictions was established via closeness of corresponding results within dipole-length and dipole-velocity gauges. The average values, defined as one-third the trace of the tensor, are usually much smaller than the diagonal tensor components. The latter are characterized by a different sign, so that partial cancellation occurs—the situation is analogous to that observed for the optical rotatory power tensor.

The calculations show that, for the molecules considered, the order of magnitude of the frequency dependent average magnetoelectric shielding, in the most favorable case, i.e., for oxygen shielding in (2R)-N-methyloxaziridine, is approximately  $4.6 \times 10^{-19}$  T m V<sup>-1</sup> at the resonance frequency 89.23 MHz in a magnetic field of 15.45 T. Therefore, in the

disordered phase, the contributions from the average magnetoelectric shielding to the magnetic field induced at  $^{17}\text{O}$  and to the rotating orbital electric dipole are negligible compared with those arising from the isotropic part of the nuclear magnetic shielding polarizability in magnetic fields operated in NMR spectroscopy.

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**Supporting Information Available:** Test of convergence of nuclear magnetoelectric shieldings in the acceleration formalism for the water molecule and estimates for the (2*R*)-*N*-methyloxaziridine molecule via a semipolarized Sadlej basis set. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Harris, R. A.; Tinoco, I., Jr. *Science, N. Y.* **1993**, *259*, 835–836.
- (2) Harris, R. A.; Tinoco, I., Jr. *J. Chem. Phys.* **1994**, *101*, 9289–9294.
- (3) Buckingham, A. D.; Parlett, L. C. *Science, N. Y.* **1994**, *264*, 1748–1750.
- (4) Buckingham, A. D.; Parlett, L. C. *Mol. Phys.* **1997**, *91*, 805–813.
- (5) Warren, W. S.; Goswami, D.; Mayr, S. *Mol. Phys.* **1993**, *93*, 371–375.
- (6) Li, L.; He, T.; Chen, D.; Wang, X.; Liu, F.-C. *J. Phys. Chem. A* **1998**, *102*, 10385–10390.
- (7) Jaszuński, M.; Rizzo, A. *Mol. Phys.* **1999**, *96*, 855–861.
- (8) Buckingham, A. D.; Parlett, L. C. *Chem. Phys. Lett.* **1995**, *243*, 15–21.
- (9) Li, L.; He, T.; Wang, X.; Liu, F.-C. *Chem. Phys. Lett.* **1998**, *268*, 549–556.
- (10) Evans, M. W. *J. Phys. Chem.* **1991**, *95*, 2256–2260.
- (11) Evans, M. W. *Physica B (Amsterdam)* **1992**, *182*, 227–236.
- (12) Evans, M. W. *Adv. Chem. Phys.* **1993**, *51*, 85.
- (13) Barron, L. D. *Physica B (Amsterdam)* **1992**, *190*, 307–309.
- (14) Warren, W. S.; Mayr, S.; Goswami, D.; West, A. P., Jr. *Science, N. Y.* **1992**, *255*, 1683–1685.
- (15) Warren, W. S.; Mayr, S.; Goswami, D.; West, A. P., Jr. *Science, N. Y.* **1993**, *259*, 836.
- (16) van der Ziel, J. P.; Pershan, P. S.; Malmstrom, L. D. *Phys. Rev. Lett.* **1965**, *15*, 190–193.
- (17) According to a private communication quoted in section IV of ref 2, W. S. Warren eventually agreed that chiral shifts are unobservable in the conditions discussed in previous references.<sup>14,15</sup>
- (18) Lazzeretti, P.; Zanasi, R. *Phys. Rev. A* **1986**, *33*, 3727–3741.
- (19) Lazzeretti, P. *Adv. Chem. Phys.* **1987**, *75*, 507–549.
- (20) Lazzeretti, P. *Chem. Phys.* **1989**, *134*, 269–278.
- (21) Lazzeretti, P.; Zanasi, R. *J. Chem. Phys.* **1987**, *87*, 472–480.
- (22) Lazzeretti, P.; Zanasi, R.; Bursi, R. *J. Chem. Phys.* **1988**, *89*, 987–996.
- (23) Lazzeretti, P. Electric and Magnetic Properties of Molecules. In *Handbook of Molecular Physics and Quantum Chemistry*; John Wiley & Sons, Ltd.: Chichester, 2003; Vol. 3, Part 1, Chapter 3.
- (24) Buckingham, A. D. *Chem. Phys. Lett.* **2004**, *398*, 1–5.
- (25) Buckingham, A. D.; Fischer, P. *Chem. Phys.* **2006**, *324*, 111–116.
- (26) Rowe, D. J. *Rev. Mod. Phys.* **1968**, *40*, 153–166.
- (27) Jørgensen, P.; Simons, J. *Second Quantization-Based Method in Quantum Chemistry*; Academic Press: New York, 1981; p 149.
- (28) Langhoff, P. W.; Epstein, S. T.; Karplus, M. *Rev. Mod. Phys.* **1972**, *44*, 602–644.
- (29) Orr, B. J.; Ward, J. F. *Mol. Phys.* **1971**, *20*, 513–526.
- (30) Bishop, D. M. *Rev. Mod. Phys.* **1990**, *62*, 343–374.
- (31) Olsen, J.; Jørgensen, P. *J. Chem. Phys.* **1985**, *82*, 3235–3264.
- (32) Epstein, S. T. *The Variation Method in Quantum Chemistry*; Academic Press: New York, 1974; pp 92–104.
- (33) Abragam, A. *Principles of Nuclear Magnetism*; Oxford University Press: Amen House, London, 1961; Chapter II, p 19.
- (34) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *High Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon Press: Oxford, 1967; pp 10–13.
- (35) Buckingham, A. D. *Adv. Chem. Phys.* **1967**, *12*, 107–142.
- (36) Bogaard, M. P.; Orr, B. J. Electric Dipole Polarizabilities of Atoms and Molecules. In *International Review of Science. Molecular Structure and Properties. Physical Chemistry Series Two*; Buckingham, A. D., Ed.; Butterworths: London, 1975; Vol. 2.
- (37) In the radiation gauge the scalar potential vanishes. Within the dipole approximation, the vector potential is assumed uniform over the molecular dimensions, and then the electric field is also spatially uniform.
- (38) Goeppert-Mayer, M. *Ann. Phys. (Leipzig)* **1931**, *9*, 273.
- (39) Cohen-Tannoudji, C.; Dupont-Roc, J.; Grynberg, G. *Photon & Atoms*; John Wiley & Sons: New York, 1989; p 269.
- (40) Lazzeretti, P.; Soncini, A.; Zanasi, R. *Theor. Chem. Acc.* in press. DOI:10.1007/s00214-006-0184-3.
- (41) Buckingham, A. D. *Can. J. Chem.* **1960**, *38*, 300–307.
- (42) McWeeny, R. *Symmetry*; Pergamon Press: Oxford, 1963; pp 211–218.
- (43) Lazzeretti, P.; Malagoli, M.; Zanasi, R. *Technical Report on Project "Sistemi Informatici e Calcolo Parallelo"*; Research Report 1/67; CNR: 1991.
- (44) Frisch, M. J.; Trucks, G. W.; et al. *Gaussian 2003, Revision B.05*; Gaussian, Inc.: Pittsburgh, PA, 2003.
- (45) Zanasi, R.; Pelloni, S.; Lazzeretti, P. *J. Comput. Chem.* **2007**, *28*, 2159–2163.
- (46) Sadlej, A. J. *Collect. Czech. Chem. Commun.* **1988**, *53*, 1995.
- (47) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007–1023.

- (48) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1995**, *103*, 4572–4585.
- (49) As 1 au of  $\omega$  is  $6.579\,683\,921 \times 10^{15}$  Hz from ref 54, and the resonance frequency of a nucleus with magnetogyric ratio  $\gamma_I$  is  $\nu_I = \gamma_I B / 2\pi$ , the magnetic field density  $B$  for proton resonance is  $\approx 15.45$  T for  $\omega = 1 \times 10^{-7}$  au. However, if one takes this value for a proton, then, allowing for the corresponding magnetogyric ratios,<sup>56</sup>  $\omega$  is only 0.2514 times this frequency for  $^{13}\text{C}$ , 0.1014 times for  $^{15}\text{N}$ , and 0.1356 times for  $^{17}\text{O}$  (for  $B = 15.45$  T). It is unrealistic to use  $\omega = 1 \times 10^{-7}$  au for these heavier nuclei; therefore, the magneto-electric shieldings of  $^{13}\text{C}$ ,  $^{15}\text{N}$ , and  $^{17}\text{O}$  in the tables should be scaled by the same factors.
- (50) Wolinski, K.; Roos, B. O.; Sadlej, A. J. *Theor. Chim. Acta* **1985**, *68*, 431–444.
- (51) Bakken, V.; Helgaker, T.; Klopper, W.; Ruud, K. *Mol. Phys.* **1999**, *96*, 653–671.
- (52) Soncini, A.; Lazzeretti, P.; Bakken, V.; Helgaker, T. *J. Chem. Phys.* **2004**, *120*, 3142–3151.
- (53) McWeeny, R. *Nature* **1973**, *243*, 196–198.
- (54) Mohr, P. J.; Taylor, B. N. *Rev. Mod. Phys.* **2000**, *72*, 351–495, Table XXVIII.
- (55) In the case of  $^{17}\text{O}$  with  $I = 5/2$  there are also nuclear electric quadrupole contributions that are not present on the  $I = 1/2$  nuclei. Therefore, the  $^{17}\text{O}$  nucleus, although displaying the largest isotropic magnetoelectric shielding in the compounds studied here, is most likely all but an ideal probe, due to low receptivity and unfavorable nuclear spin, which may cause undesirable lifetime broadening of signals.
- (56) [www.webelements.com](http://www.webelements.com).

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