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# Electric field effects on nuclear magnetic shielding of the 1:1 and 2:1 (homo and heterochiral) complexes of XOOX' (X, X' = H, CH<sub>3</sub>) with lithium cation and their chiral discrimination

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The set of 1:1 and 2:1 complexes of XOOX' (X, X' = H, CH<sub>3</sub>) with lithium cation has been studied to determine if they are suitable candidates for chiral discrimination in an isotropic medium via nuclear magnetic resonance spectroscopy. Conventional nuclear magnetic resonance is unable to distinguish between enantiomers in the absence of a chiral solvent. The criterion for experimental detection is valuated by the isotropic part of nuclear shielding polarisability tensors, related to a pseudoscalar of opposite sign for two enantiomers. The study includes calculations at coupled Hartree-Fock and density functional theory schemes for <sup>17</sup>O nucleus in each compound. Additional calculations for <sup>1</sup>H are also included for some compounds. A huge static homogeneous electric field, perpendicular to the magnetic field of the spectrometer, as big as  $\approx 1.7 \times 10^8$  V m<sup>-1</sup> should be applied to observe a shift of  $\approx 1$  ppm for <sup>17</sup>O magnetic shielding in the proposed set of complexes. © 2011 American Institute of Physics. [doi:10.1063/1.3632086]

## I. INTRODUCTION

An electric field leads to changes of chemical shift in nuclear magnetic resonance (NMR) spectroscopy. The phenomena have been rationalized by Buckingham<sup>1,2</sup> via a molecular response property called *electric dipole polarisability of nuclear magnetic shielding* or *nuclear magnetic shielding polarisability*. A big number of theoretical calculations, at different levels of approximation, have been reviewed by several authors, Raynes,<sup>3</sup> Augspurger *et al.*,<sup>4</sup> and Jameson and de Dios,<sup>5-7</sup> are between them.

Buckingham and Buckingham and Fischer showed how “chiral blindness” may be removed from the NMR by application of an external electric field, perpendicular to the magnetic field.<sup>8,9</sup> Harris and Jameson<sup>10</sup> proved the same derivation employing symmetry arguments for nuclear magnetic shieldings and spin-spin coupling constants, and related their proofs to the simulated creation of diastereoisomers proposed by Sears *et al.*<sup>11</sup> In principle, any chiral potential would break the “chiral blindness”.<sup>10</sup> Parity non-conserving effects are too small,  $\approx 10^{-10}$  ppm, to discriminate enantiomers.<sup>12</sup>

Higher order polarisabilities can be defined via the Buckingham approach.<sup>1,13</sup> They are small in magnitude, and surely difficult to be measured.

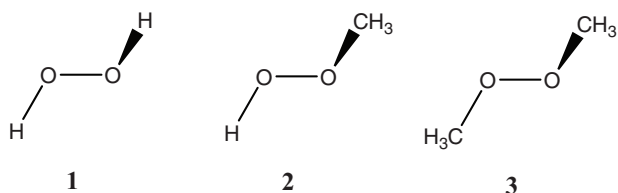
The third rank-tensor  $\sigma_{\alpha\beta\gamma}^I$ , usually referred to as *electric dipole polarisability of nuclear magnetic shielding*, or *nuclear magnetic shielding polarisability* of nucleus *I*,<sup>2</sup> has different sign for the two enantiomers (mirror images of chi-

ral molecule). The static  $\sigma_{\alpha\beta\gamma}^I$  is invariant in a change of a coordinate system only for the exact eigenstates of a model Hamiltonian.<sup>14,15</sup> The use of London orbitals guarantees the required invariance,<sup>16</sup> and although the faster convergence of GIAO calculations,<sup>17</sup> continuous transformation of the origin of the current density schemes is easier to implement at any level of accuracy, and becomes competitive, provided proper basis sets are employed.<sup>18</sup> There exists a pseudoscalar component of nuclear magnetic shielding arising from parity non-conservation (PV), with the same magnitude but opposite sign for the two enantiomeric forms.<sup>19,20</sup> According to current estimates for optimal magnetic resonance (NMR) resolution,<sup>21</sup> the predicted PV effects are several orders of magnitude below the detection limit for sulfur chemical shifts,<sup>20</sup> and by 1%–10% in relevant nuclei in CHFClBr.<sup>22</sup> The zero-point vibrational corrections are found to be of the order of less than 10% with respect to the PV contributions calculated at the equilibrium geometry.

So far, most of the studies concerning chiral distinction (or chiral recognition) with metal involved have been based on experimental approach. Some of us have published several computational studies on the chiral distinction where charged metallic atoms were present. Thus, lithium complexes of bis(*5H*-pyrroles), bis(oxazolines),<sup>23</sup> difuranes,<sup>24</sup> and 1-azahelicenes<sup>25</sup> as well as the complexes formed by hydrazine and metal atoms of the group 10 have been examined.<sup>26-28</sup> In addition, the chiral distinction of chromium (0) complexes, where hydrogen bond interactions were possible, have been considered.<sup>29</sup>

Hydrogen peroxide and its derivatives have been widely used as models to study chiral properties due to their small

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SCHEME 1. Hydrogen peroxide and its methyl derivatives.

size, which make them very suitable for theoretical studies. Recently, we have studied the geometric and energetic properties of the 1:1 and 2:1 complexes formed by three derivatives of hydrogen peroxide (Scheme 1) and lithium cation by means of *ab initio* computational methods up to MP2/aug-cc-pVTZ level.<sup>30</sup> That study includes the calculation of the optical rotatory power, NMR parameters, and the racemization barriers within the complex. In the present article, the effect of the electric fields on the NMR chemical shifts of the same complexes has been considered to test if their chiral discrimination in an isotropic medium might also be detected via nuclear magnetic resonance spectroscopy.

The present article is organized as follows: (i) Sec. II reviews some definitions to compute *nuclear magnetic shielding polarisability*, within the common origin (CO) formulation, and the formal annihilation of the diamagnetic contributions to quantum mechanical electron current density, via continuous transformation of its origin (CTOCD-DZ); (ii) Sec. III describes the chiral pseudoscalar of the *nuclear magnetic shielding polarisabilities* to be measured in an isotropic media; and (iii) Sec. IV reports and discusses calculations for <sup>17</sup>O nucleus magnetic shielding pseudoscalar in the set of 1:1 and 2:1 complexes of XOOX' (X, X' = H, CH<sub>3</sub>) with lithium cation, and for <sup>1</sup>H nucleus shielding pseudoscalar of XOOX' (X, X' = H, CH<sub>3</sub>) at coupled Hartree-Fock (CHF) and density functional theory (DFT) levels of theory.

## II. NUCLEAR MAGNETIC SHIELDING IN THE PRESENCE OF AN ELECTRIC FIELD

In the presence of two external perturbations, i.e., the spatially uniform time-independent electric and magnetic fields  $\mathbf{E}$  and  $\mathbf{B}$ , a permanent dipole moment  $\boldsymbol{\mu}_I$ , and a nuclear magnetic dipole  $\mathbf{m}_I$ , on nucleus  $I$ , the energy of the molecule, evaluated in the singlet electronic state  $|\Psi_0\rangle \equiv |a\rangle$  is, employing Buckingham notation<sup>1,31</sup> to denote molecular tensors,

$$W_a = W_a^{(0)} - \boldsymbol{\mu}_\alpha \mathbf{E}_\alpha - \frac{1}{2} \alpha_{\alpha\beta} \mathbf{E}_\alpha \mathbf{E}_\beta + \dots + \sigma_{\alpha\beta}^I m_{I\alpha} \mathbf{B}_\beta + \sigma_{\alpha\beta,\gamma}^I m_{I\alpha} \mathbf{B}_\beta \mathbf{E}_\gamma + \frac{1}{2} \sigma_{\alpha\beta,\gamma\delta}^I m_{I\alpha} \mathbf{B}_\beta \mathbf{E}_\gamma \mathbf{E}_\delta. \quad (1)$$

The magnetic shielding at nucleus  $I$ , in the presence of an external, weak, homogeneous, electric field  $\mathbf{E}$  may be expanded as<sup>2,32</sup>

$$\sigma_{\alpha\beta}^I(\mathbf{E}) = \sigma_{\alpha\beta}^I + \sigma_{\alpha\beta\gamma}^I \mathbf{E}_\gamma + \frac{1}{2} \sigma_{\alpha\beta\gamma\delta}^I \mathbf{E}_\gamma \mathbf{E}_\delta. \quad (2)$$

The tensors  $\sigma_{\alpha\beta\gamma}^I$  and  $\sigma_{\alpha\beta\gamma\delta}^I$  are the nonlinear response of the electron cloud to first and second orders in  $\mathbf{E}$ . They are colloquially referred to as dipole shielding polarisabilities and first hypershielding polarisabilities.<sup>33,34</sup> From considerations of the energy (Eq. (1)),  $\sigma_{\alpha\beta\gamma}^I \equiv -\xi_{\alpha\beta\gamma}^I$  and  $\sigma_{\alpha\beta\gamma\delta}^I \equiv -\xi_{\alpha\beta\gamma\delta}^I$  from Ref. 9.

The total nuclear magnetic shielding at nucleus  $I$ ,

$$\sigma_{\alpha\beta}^I = \sigma_{\alpha\beta}^{dI} + \sigma_{\alpha\beta}^{pI}, \quad (3)$$

contains diamagnetic and paramagnetic contributions, to  $\sigma_{\alpha\beta}^I$ , within the CO Ramsey formulation,<sup>35,36</sup> that change in a transformation of the gauge of the vector potential in such a way that their sum stays the same for exact eigenstates to a model Hamiltonian.<sup>37</sup>

The auxiliary Hermitian operator,

$$\hat{T}_{I\alpha\beta}^n(r') = \frac{1}{2} \sum_{i=1}^n [(r_{i\alpha} - r'_\alpha) \hat{M}_{I\beta}^i + \hat{M}_{I\beta}^i (r_{i\alpha} - r'_\alpha)], \quad (4)$$

is used to define the CTOCD-DZ approach.<sup>38,39</sup> Within this approach, the diamagnetic contribution is replaced by the  $\Delta$  contribution,

$$\sigma_{\alpha\beta}^{\Delta I} = -\frac{e^2}{2m_e^2} \varepsilon_{\alpha\lambda\mu} \{ \hat{P}_\lambda, \hat{T}_{I\mu\alpha}^n \}_{-1}. \quad (5)$$

Thus, the total CTOCD-DZ magnetic shielding becomes

$$\sigma_{\alpha\beta}^I = \sigma_{\alpha\beta}^{\Delta I} + \sigma_{\alpha\beta}^{pI}. \quad (6)$$

The higher rank tensor  $\sigma_{\alpha\beta\gamma}^I$ , dipole shielding polarisability, is the sum of diamagnetic and paramagnetic contributions, via the Rayleigh-Schrödinger perturbation theory,<sup>1</sup>

$$\sigma_{\alpha\beta\gamma}^I = \sigma_{\alpha\beta\gamma}^{dI} + \sigma_{\alpha\beta\gamma}^{pI}, \quad (7)$$

$$\sigma_{\alpha\beta\gamma}^{dI} = \{ \hat{\sigma}_{\alpha\beta}^{dI}, \hat{\mu}_\gamma \}_{-1}, \quad (8)$$

$$\sigma_{\alpha\beta\gamma}^{pI} = \{ \hat{\sigma}_{\alpha\beta}^{pI}, \hat{\mu}_\gamma \}_{-1}. \quad (9)$$

The CTOCD-DZ approach provides another expression for the diamagnetic,  $\Delta$  contribution,<sup>40</sup>

$$\sigma_{\alpha\beta\lambda}^{\Delta I} = -\frac{e^3}{2m_e^2} \varepsilon_{\beta\lambda\mu} \{ \hat{P}_\lambda, R_\gamma, \hat{T}_{I\mu\alpha}^n \}_{-2}, \quad (10)$$

to the total CTOCD-DZ magnetic shielding polarisability,

$$\sigma_{\alpha\beta\gamma}^I = \sigma_{\alpha\beta\gamma}^{\Delta I} + \sigma_{\alpha\beta\gamma}^{pI}. \quad (11)$$

The CTOCD-DZ expressions (6) and (11) reduce to the conventional  $\sigma_{\alpha\beta}^I$  and  $\sigma_{\alpha\beta\gamma}^I$ , respectively, only if the hypervirial relationship,

$$\langle a | P_\alpha | j \rangle = -im_e \omega_{ja} \langle a | R_\alpha | j \rangle, \quad (12)$$

holds, that is, for exact eigenfunctions to any model Hamiltonian.<sup>41</sup> Within the exact CHF method, CO and CTOCD-DZ nuclear magnetic shielding and shielding polarisabilities are invariant in a coordinate transformation. In actual calculations, employing the algebraic approximation, condition (12) is only partially met, depending on the quality of the basis set, but CTOCD-DZ values remain invariant in

a coordinate transformation.<sup>40</sup> This result cannot be overemphasized, since the quality of the CHF calculations depends on the quality of the basis set.<sup>18</sup>

### III. THE CHIRAL PSEUDOSCALAR AND ITS APPLICATION TO THE PRESENCE OF ELECTRIC FIELD IN NMR SHIELDINGS

In an optically active liquid,  $\sigma_{\alpha\beta\gamma}^I$  has an isotropic part,  $\bar{\sigma}^I \varepsilon_{\alpha\beta\gamma}$  and the corresponding pseudoscalar is

$$\overline{\sigma^{(1)'}} = \frac{1}{6} \varepsilon_{\alpha\beta\gamma} \sigma_{\alpha\beta\gamma}^I, \quad (13)$$

allowing to Einstein summation convention and using the third-rank Levi-Civita skew-symmetric unit tensor,<sup>9,42</sup> non-zero for a chiral molecule. The pseudoscalar (13) is the basic quantity with opposite sign for two mirror image molecules in liquid or gas phase.

Therefore, the magnetic field induced at nucleus  $I$  by a laser polarized in a plane perpendicular to uniform magnetic field  $\mathbf{B}$  of the spectrometer gives rise to a chiral chemical shift,

$$\Delta \langle \mathbf{B}_I^n \rangle = -\overline{\sigma^{(1)'}} \mathbf{B} \times \mathbf{E}, \quad (14)$$

where  $\mathbf{E}$  and  $\mathbf{B}$  are, respectively, the electric and magnetic fields of the laser and the spectrometer.

The electric dipole moment,

$$\Delta \langle \boldsymbol{\mu} \rangle = -\overline{\sigma^{(1)'}} \mathbf{m}_I \times \mathbf{B}, \quad (15)$$

is induced in the electron cloud by the permanent magnetic dipole  $\mathbf{m}_I$  at nucleus  $I$ . In similar form, the orbital magnetic dipole moment of the electrons, induced by the electric field and the intrinsic magnetic dipole at nucleus  $I$ , is

$$\Delta \langle \mathbf{m} \rangle = -\overline{\sigma^{(1)'}} \mathbf{E} \times \mathbf{m}_I, \quad (16)$$

the isotropic component of the nuclear magnetic shielding polarisability. Here,  $\overline{\sigma^{(1)'}}$  gives rise to the chiral NMR shielding effects considered in this article.

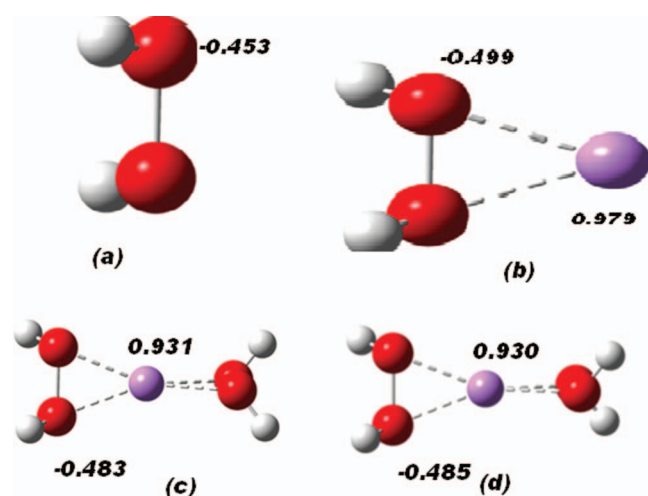


FIG. 1. Natural charges and structures of HOOH-Li<sup>+</sup> complexes, at the B3LYP/aug-cc-pVTZ level of theory: (a) HOOH; (b) HOOH:Li<sup>+</sup>; (c) HOOH:Li<sup>+</sup>:HOOH ( $D_2$ ); and (d) HOOH:Li<sup>+</sup>:HOOH ( $S_4$ ).

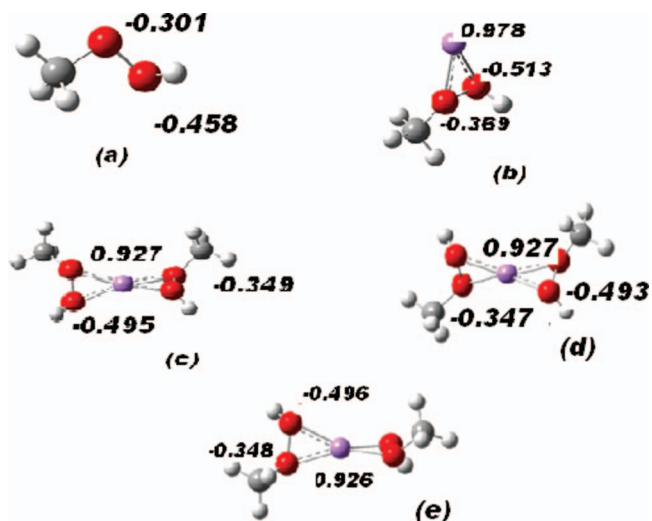


FIG. 2. Natural charges and structures of CH<sub>3</sub>OOH-Li<sup>+</sup> complexes, at the B3LYP/aug-cc-pVTZ level of theory: (a) CH<sub>3</sub>OOH; (b) CH<sub>3</sub>OOH:Li<sup>+</sup>; (c) CH<sub>3</sub>OOH:Li<sup>+</sup>:CH<sub>3</sub>OOH ( $C_2$ -A); (d) CH<sub>3</sub>OOH:Li<sup>+</sup>:CH<sub>3</sub>OOH ( $C_2$ -B); (e) CH<sub>3</sub>OOH:Li<sup>+</sup>:CH<sub>3</sub>OOH ( $C_1$ ) conformations for CH<sub>3</sub>OOH:Li<sup>+</sup>:CH<sub>3</sub>OOH.

### IV. RESULTS AND DISCUSSION

A set of 1:1 and 2:1 complexes of XOOX' (X, X' = H, CH<sub>3</sub>) with lithium cation has been considered in the present study. All the systems have been optimized at the MP2/6-31+G(d,p) computational level<sup>43,44</sup> and frequency calculations have been carried out at the same computational level to confirm that the structures obtained correspond to energetic minima or true transition state (TS). All these calculations have been performed with the GAUSSIAN-03 package.<sup>45</sup>

The different complexes formed by the hydrogen peroxide derivatives with lithium cation (molecule 1) are displayed in Fig. 1, while Fig. 2 shows those derived from XOOX'

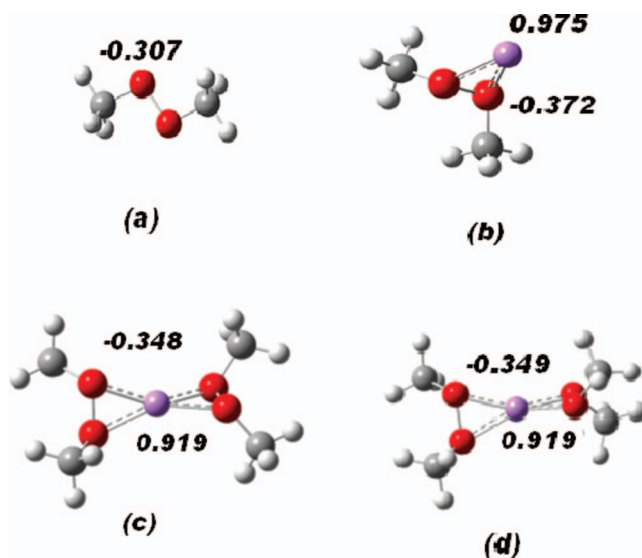


FIG. 3. Natural charges and structures of CH<sub>3</sub>OOCH<sub>3</sub>-Li<sup>+</sup> complexes, at the B3LYP/aug-cc-pVTZ level of theory: (a) CH<sub>3</sub>OOCH<sub>3</sub>; (b) CH<sub>3</sub>OOCH<sub>3</sub>:Li<sup>+</sup>; (c) CH<sub>3</sub>OOCH<sub>3</sub>:Li<sup>+</sup>:CH<sub>3</sub>OOCH<sub>3</sub> ( $D_2$ ); (d) CH<sub>3</sub>OOCH<sub>3</sub>:Li<sup>+</sup>:CH<sub>3</sub>OOCH<sub>3</sub> ( $S_4$ ).

TABLE I. Contraction of different basis sets employed to evaluate nuclear magnetic shielding for HOOH molecule.

Basis set <sup>a</sup>	# <sup>b</sup>	2 row elements	Hydrogen	SCF energy (a.u.)
I	136	[12s6p4d]	[9s3p]	-150.834265
II	124	[14s6p4d]→(9s5p4d)	[10s4p]→(6s4p)	-150.834272
III	148	[14s6p4d]	[10s4p]	-150.834314
IV	136	[14s9p4d]→(8s7p4d)	[11s4p]→(7s4p)	-150.835539
V	164	[12s8p4d]	[8s6p]	-150.843841
VI	166	[13s9p4d]	[8s6p]	-150.844991
VII	168	[14s9p4d]	[11s4p]	-150.847085
VIII	174	[14s9p4d]	[8s6p]	-150.847136

<sup>a</sup>See the text for description of the eight basis sets.<sup>b</sup>Number of contracted atomic functions.

X = H, X' = CH<sub>3</sub> (molecule **2**), and Fig. 3 corresponds to XOOX complexes with X = CH<sub>3</sub> (molecule **3**).

Zero order molecular orbitals were expanded over atomic basis functions. Eight basis sets have been employed to describe the CO and CTOCD-DZ shielding and shielding polarisabilities on the oxygen atom in HOOH. The basis sets are (I) 136 Gaussian functions corresponding to basis set from Ref. 46, uncontracted and removing the two most diffuse *s* functions for the heavy atoms and the most diffuse *s* function for the hydrogen; (II) 124 Gaussian functions,<sup>46</sup> (III) 148 Gaussian functions corresponding to basis set (II) uncontracted; (IV) 136 Gaussian functions for 2nd row elements taken from Ref. 47 and hydrogen functions taken from Ref. 48; (V) basis set (IV) removing the two most diffuse *s* functions and the most diffuse *p* functions; (VI) basis set (IV) removing the most diffuse *s* and *p* functions; (VII) taken from Ref. 49; and (VIII) basis set (VII) uncontracted. Table I reports the contraction of each basis set and the corresponding SCF energies for HOOH.

The dependence of the average magnetic shielding,  $\sigma^O = (1/3) \sum (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$ , and the invariant  $\overline{\sigma^{(1)O}}$  pseudoscalar (Eq. (13)) on basis set's quality was preliminary tested for HOOH using the eight basis sets in the CHF approach for CO and CTOCD-DZ procedures. This comparison, reported in Table II, shows that: (i) CTOCD-DZ calculations are near CO ones for basis sets I and V. (ii) CO calculations for two gauge origins: the center of mass (cm)

and the oxygen nucleus (O) are approximately identical for basis set V. The other basis sets do not seem flexible enough to guarantee reliable results. Basis set V is at the *Hartree-Fock limit* for HOOH magnetic shielding. Although the comparison between CO and CTOCD-DZ results shows that basis set VII has the best performance, the calculations are considerably more expensive than those from basis set V. The relative percentage difference between CO results provided by basis sets V and VII is in the order of 3%. Making a balance between cost and quality of the results and considering that the CTOCD-DZ calculations are very expensive for the set of 1:1 and 2:1 complexes of XOOX', we chose basis set V in the CO approximation and gauge origin in the nucleus whose shielding is being calculated to evaluate the nuclear magnetic shielding and the invariant pseudoscalar for each complex. We also performed the calculations for basis set I in order to compare the dependence of the results in the size of the basis set.

Electron correlation effects on shielding polarisabilities are known to be quite large,<sup>50-52</sup> but hopefully not so large to change magnitude and sign of individual components. Buckingham and Fischer found that MP2 calculations overemphasize the components of nuclear shielding polarisabilities in HOOH.<sup>9</sup> In this article, we employ the B3LYP (Refs. 53-56) and KT3 (Refs. 57 and 58) functionals of density functional theory (DFT) implemented in DALTON code,<sup>59</sup> in order to include correlation effects at low computational cost. The DFT calculations, also performed in the CO approximation, are compared with the CHF evaluations.

The SCF energies (in a.u.) for the 1:1 and 2:1 (homo and heterochiral) complexes of XOOX' (X, X' = H, CH<sub>3</sub>) with lithium cation for basis sets I and V are reported in Table III. The 2:1 complexes are anticooperative with respect to the 1:1 ones.<sup>30</sup> The heterochiral complexes are always more stable than the corresponding homochiral one but the energetic differences are always smaller than 10<sup>-3</sup> a.u. (~2.5 kJ mol<sup>-1</sup>).

Table IV reports the CHF nuclear magnetic shielding (in ppm) and pseudoscalar shielding polarisabilities (in ppm-a.u.) results for non-equivalent oxygen atoms in the complexes of molecules labeled **1**, **2**, and **3**. The calculations for the experimental geometries of HOOH and CH<sub>3</sub>OCH<sub>3</sub>,<sup>60,61</sup> are also included. The calculations on O<sub>1</sub> and cm gauge

TABLE II. Comparison of <sup>17</sup>O magnetic shielding (ppm) and pseudoscalar magnetic shielding polarisability (ppm-a.u.) of HOOH at the CHF level for different basis sets.

Property		$\sigma^O$	$\overline{\sigma^{(1)O}}$	$\sigma^O$	$\overline{\sigma^{(1)O}}$	$\sigma^O$	$\overline{\sigma^{(1)O}}$	$\sigma^O$	$\overline{\sigma^{(1)O}}$
Method	Basis set	I		II		III		IV	
	Gauge origin								
CHF-CO	cm	140.7	-3.4	139.5	-3.6	140.7	-3.7	134.1	-5.2
	O	140.9	-4.4	140.8	-4.4	140.9	-4.4	135.0	-6.4
CHF-CTOCD-DZ		103.7	-4.1	51.7	-4.4	103.8	-4.4	76.0	-6.4
Method	Basis set	V		VI		VII		VIII	
	Gauge origin								
CHF-CO	cm	139.4	-4.3	139.4	-4.3	135.4	-5.6	135.5	-4.4
	O	139.3	-4.9	139.3	-4.9	135.0	-6.3	135.1	-5.0
CHF-CTOCD-DZ		113.3	-4.9	113.3	-4.9	127.8	-6.4	127.9	-5.1



TABLE III. SCF energies (in a.u.) for the 1:1 and 2:1 (homo and heterochiral) complexes of XOOX' (X,X' = H, CH<sub>3</sub>) with lithium cation for basis sets I and V.

	Number of CGTO	ESCF(I)	Number of CGTO	ESCF(V)
<b>1</b>				
HOOH ( <i>C</i> <sub>2</sub> )	136	-150.834265	164	-150.843841
HOOH:Li <sup>+</sup> ( <i>C</i> <sub>2</sub> )	183	-158.124966	220	-158.134780
HOOH:Li <sup>+</sup> :HOOH ( <i>D</i> <sub>2</sub> )	319	-309.004028	384	-309.023122
HOOH:Li <sup>+</sup> :HOOH ( <i>S</i> <sub>4</sub> )	319	-309.004285	384	-309.023381
<b>2</b>				
CH <sub>3</sub> OOH ( <i>C</i> <sub>1</sub> )	222	-189.873624	272	-189.884265
CH <sub>3</sub> OOH:Li <sup>+</sup> ( <i>C</i> <sub>1</sub> )	269	-197.171344	328	-197.182248
CH <sub>3</sub> OOH:Li <sup>+</sup> : CH <sub>3</sub> OOH ( <i>C</i> <sub>2</sub> -A)	491	-387.093456	600	-387.114630
CH <sub>3</sub> OOH:Li <sup>+</sup> : CH <sub>3</sub> OOH ( <i>C</i> <sub>2</sub> -B)	491	-387.093468	600	-387.114653
CH <sub>3</sub> OOH:Li <sup>+</sup> : CH <sub>3</sub> OOH ( <i>C</i> <sub>1</sub> )	491	-387.093740	600	-387.114916
<b>3</b>				
CH <sub>3</sub> OOCH <sub>3</sub> ( <i>C</i> <sub>2</sub> )	308	-228.912607	380	-228.924311
CH <sub>3</sub> OOCH <sub>3</sub> :Li <sup>+</sup> ( <i>C</i> <sub>2</sub> )	355	-236.214865	436	-236.226939
CH <sub>3</sub> OOCH <sub>3</sub> :Li <sup>+</sup> : CH <sub>3</sub> OOCH <sub>3</sub> ( <i>D</i> <sub>2</sub> )	663	-465.177787	816	-465.201243
CH <sub>3</sub> OOCH <sub>3</sub> :Li <sup>+</sup> : CH <sub>3</sub> OOCH <sub>3</sub> ( <i>S</i> <sub>4</sub> )	663	-465.178173	816	-465.201598

origins are close enough to assure the good quality of both basis sets. The magnitude of the pseudoscalar for XOOX:Li<sup>+</sup> and XOOH:Li<sup>+</sup>, with *C*<sub>2</sub> symmetry, is the largest for each set of molecules. The conclusion is that lithiation affects the shielding polarisability more than complexation. It is also notable that the pseudoscalar is positive only for CH<sub>3</sub>OOH and CH<sub>3</sub>OOCH<sub>3</sub> (experimental geometry) for both basis sets and both gauge origins, and very small in CH<sub>3</sub>OOCH<sub>3</sub> (*C*<sub>2</sub> geometry). The lithiation produces a very similar effect on  $\overline{\sigma}^{(1)}_1$  for **1**, **2**, and **3** molecules, i.e., -23.4, -29.5, and -29.8 ppm-a.u., respectively. This is an important result because it is in-

dependent of the X group and might be a probe lithiation in a reaction path.

In order to take into account the correlation effects, we chose to employ the DFT scheme because our experience proves that it is suitable for the purpose.<sup>62,63</sup> We report in Tables V-VII the <sup>17</sup>O nuclear magnetic shielding and pseudoscalar shielding polarisabilities for basis sets I and V, taking the gauge origin in the nucleus whose shielding is reported. Table V reports the results for HOOH (molecule **1** and its corresponding experimental geometry<sup>60</sup>) and its lithium cation complexes. Results for both basis sets are very

TABLE IV. Comparison of <sup>17</sup>O<sub>1</sub> magnetic shielding (ppm) and pseudoscalar magnetic shielding polarisability (ppm-a.u.) in the complexes of **1**, **2**, and **3** molecules at the CHF level for basis sets I and V.

Gauge origin	CHF-(I)				CHF-(V)			
	O <sub>1</sub>		CM		O <sub>1</sub>		CM	
	$\sigma^{O_1}$	$\overline{\sigma}^{(1)}_1$	$\sigma^{O_1}$	$\overline{\sigma}^{(1)}_1$	$\sigma^{O_1}$	$\overline{\sigma}^{(1)}_1$	$\sigma^{O_1}$	$\overline{\sigma}^{(1)}_1$
<b>1</b>								
HOOH (exp-geometry)	138.8	-9.8	111.7	-9.8	137.3	-10.7	137.1	-9.8
HOOH ( <i>C</i> <sub>2</sub> )	140.9	-4.3	140.7	-3.4	135.5	-5.0	135.5	-4.4
HOOH:Li <sup>+</sup> ( <i>C</i> <sub>2</sub> )	149.6	-23.4	149.6	-23.2	148.2	-23.4	148.3	-23.5
HOOH:Li <sup>+</sup> :HOOH ( <i>D</i> <sub>2</sub> )	149.6	-15.8	150.4	-15.1	147.8	-16.0	148.3	-15.2
HOOH:Li <sup>+</sup> :HOOH ( <i>S</i> <sub>4</sub> )	149.8	-16.6	150.5	-15.7	147.9	-16.7	148.5	-15.9
<b>2</b>								
CH <sub>3</sub> OOH ( <i>C</i> <sub>1</sub> )	127.8	11.8	126.1	9.56	126.5	12.5	125.0	10.41
CH <sub>3</sub> OOH:Li <sup>+</sup> ( <i>C</i> <sub>1</sub> )	104.0	-29.2	103.9	-29.1	102.3	-29.5	102.2	-29.5
CH <sub>3</sub> OOH:Li <sup>+</sup> : CH <sub>3</sub> OOH ( <i>C</i> <sub>2</sub> -A)	111.5	-16.0	112.2	-14.6	109.4	-15.6	109.6	-13.4
CH <sub>3</sub> OOH:Li <sup>+</sup> : CH <sub>3</sub> OOH ( <i>C</i> <sub>2</sub> -B)	111.2	-16.5	111.7	-15.8	109.1	-15.7	109.4	-14.6
CH <sub>3</sub> OOH:Li <sup>+</sup> : CH <sub>3</sub> OOH ( <i>C</i> <sub>1</sub> )	111.1	-15.9	111.4	-15.0	109.0	-15.9	109.1	-13.9
<b>3</b>								
CH <sub>3</sub> OOCH <sub>3</sub> (exp-geometry)	89.8	11.6	89.4	9.87	87.5	10.80	87.4	9.61
CH <sub>3</sub> OOCH <sub>3</sub> ( <i>C</i> <sub>2</sub> )	92.4	0.03	92.8	0.8	90.1	0.02	90.75	0.7
CH <sub>3</sub> OOCH <sub>3</sub> :Li <sup>+</sup> ( <i>C</i> <sub>2</sub> )	84.5	-29.1	84.1	-29.5	82.3	-29.4	82.3	-29.8
CH <sub>3</sub> OOCH <sub>3</sub> :Li <sup>+</sup> : CH <sub>3</sub> OOCH <sub>3</sub> ( <i>D</i> <sub>2</sub> )	88.6	-13.5	89.4	-12.0	86.0	-13.5	86.6	-11.7
CH <sub>3</sub> OOCH <sub>3</sub> :Li <sup>+</sup> : CH <sub>3</sub> OOCH <sub>3</sub> ( <i>S</i> <sub>4</sub> )	88.4	-14.7	89.2	-12.6	86.0	-14.0	86.4	-12.4

TABLE V. Comparison of  $^{17}\text{O}_1$  magnetic shielding (ppm) and pseudoscalar magnetic shielding polarisability (ppm-a.u.) in the complexes of molecule **1** at the B3LYP level for basis sets I and V.

Gauge origin	$\text{O}_1$			
	B3LYP-(I)		B3LYP-(V)	
	$\sigma_{\text{O}_1}^{\text{O}}$	$\overline{\sigma}_{\text{O}_1}^{\text{O}}$	$\sigma_{\text{O}_1}^{\text{O}}$	$\overline{\sigma}_{\text{O}_1}^{\text{O}}$
Compound				
<b>1</b>				
HOOH (exp-geometry)	102.0	21.3	100.3	19.3
HOOH ( $C_2$ )	103.9	22.9	102.1	20.6
HOOH:Li <sup>+</sup> ( $C_2$ )	112.6	-37.4	110.9	-37.6
HOOH:Li <sup>+</sup> :HOOH ( $D_2$ )	112.8	-26.6	110.7	-27.0
HOOH:Li <sup>+</sup> :HOOH ( $S_4$ )	113.0	-28.8	111.0	-29.2

similar, but different from the CHF calculations reported in Table IV: (a) The correlation diminishes the nuclear shielding,  $\sigma_{\text{O}_1}^{\text{O}}$ , (b) changes the sign of the pseudoscalar,  $\overline{\sigma}_{\text{O}_1}^{\text{O}}$  for HOOH, and increases its value, and (c) HOOH:Li<sup>+</sup> also shows the greatest pseudoscalar value. The results for the experimental HOOH geometry are very similar to those corresponding to the optimized structure. Table VI corresponds to CH<sub>3</sub>OOH (molecule **2**) and its complexes. For this case, there are two non-equivalent oxygen atoms,  $^{17}\text{O}_1$  and  $^{17}\text{O}_2$ . The comparison with the CHF results from Table IV shows: (a) The correlation diminishes both nuclear magnetic shieldings, (b) pseudoscalar shielding polarisabilities are negative for both nuclei, and  $\overline{\sigma}_{\text{O}_1}^{\text{O}}$  is greater than  $\overline{\sigma}_{\text{O}_2}^{\text{O}}$  in an order of magnitude, and (c) CH<sub>3</sub>OOH:Li<sup>+</sup> also shows the greatest pseudoscalar value for both non-equivalent oxygen atoms. Table VII reports B3LYP  $^{17}\text{O}_1$  results for CH<sub>3</sub>OOCH<sub>3</sub> (molecule **2**, and its corresponding experimental geometry<sup>61</sup>) and its complexes.

The sensitivity of the calculated pseudoscalar to the specific DFT functional was studied in Table VIII for both basis sets. KT3 oxygen magnetic shielding is greater than B3LYP result for both basis sets, but the pseudoscalar corrections are similar for both DFT functionals. Table IX compares KT3 and B3LYP proton magnetic shielding and  $\overline{\sigma}_{\text{O}_1}^{\text{H}}$  arrived at in HOOH and CH<sub>3</sub>OOCH<sub>3</sub>:Li<sup>+</sup>:CH<sub>3</sub>OOCH<sub>3</sub>. The compari-

TABLE VI. Comparison of  $^{17}\text{O}_1$  and  $^{17}\text{O}_2$  magnetic shielding (ppm) and pseudoscalar magnetic shielding polarisability (ppm-a.u.) in the complexes of molecule **2** at the B3LYP level for basis sets I and V.

Gauge origin	$\text{O}_1$			
	B3LYP-(I)		B3LYP-(V)	
	$\sigma_{\text{O}_1}^{\text{O}}$	$\overline{\sigma}_{\text{O}_1}^{\text{O}}$	$\sigma_{\text{O}_1}^{\text{O}}$	$\overline{\sigma}_{\text{O}_1}^{\text{O}}$
Compound				
<b>2</b>				
CH <sub>3</sub> OOH ( $C_1$ )	74.5	-10.6	72.3	-9.5
CH <sub>3</sub> OOH:Li <sup>+</sup> ( $C_1$ )	49.7	-45.6	47.5	-45.6
CH <sub>3</sub> OOH:Li <sup>+</sup> :CH <sub>3</sub> OOH ( $C_2$ -A)	58.0	-24.7	55.4	-24.7
CH <sub>3</sub> OOH:Li <sup>+</sup> :CH <sub>3</sub> OOH ( $C_2$ -B)	57.6	-26.0	54.9	-24.7
CH <sub>3</sub> OOH:Li <sup>+</sup> :CH <sub>3</sub> OOH ( $C_1$ )	57.5	-26.5	54.9	-26.5

TABLE VII. Comparison of  $^{17}\text{O}_1$  magnetic shielding (ppm) and pseudoscalar magnetic shielding polarisability (ppm-a.u.) in the complexes of molecule **3** at the B3LYP level for basis sets I and V.

Gauge origin	$\text{O}_1$			
	B3LYP (basis set)			
	(I)	(V)	(I)	(V)
Compound	$\sigma_{\text{O}_1}^{\text{O}}$	$\overline{\sigma}_{\text{O}_1}^{\text{O}}$	$\sigma_{\text{O}_1}^{\text{O}}$	$\overline{\sigma}_{\text{O}_1}^{\text{O}}$
<b>3</b>				
CH <sub>3</sub> OOCH <sub>3</sub> (exp-geometry)	30.41	1.44	27.62	0.42
CH <sub>3</sub> OOCH <sub>3</sub> ( $C_2$ )	34.05	0.01	31.32	0.01
CH <sub>3</sub> OOCH <sub>3</sub> :Li <sup>+</sup> ( $C_2$ )	21.34	-37.6	18.66	-37.7
CH <sub>3</sub> OOCH <sub>3</sub> :Li <sup>+</sup> :CH <sub>3</sub> OOCH <sub>3</sub> ( $D_2$ )	26.98	-11.8	23.80	-11.9
CH <sub>3</sub> OOCH <sub>3</sub> :Li <sup>+</sup> :CH <sub>3</sub> OOCH <sub>3</sub> ( $S_4$ )	26.80	-13.6	23.60	-13.6

son with proton calculations for HOOH molecule, reported in Ref. 9, is very successful for both functionals.

All the calculations have been done for a static external electric field. It is known that HOOH is a floppy molecule where the PV contribution mentioned in Sec. I varies significantly near the equilibrium geometry as a function of the dihedral angle.<sup>20,22,64,65</sup> This compound has a torsional mode around the OO bond, giving rise to a double minimum potential. The property of interest may depend on nuclear geometry, and it needs to be averaged over the vibrational ground state, giving rise to the zero-point vibrational averages (ZPVA) correction. We consider that lithiation, and also the following complexation, prevents from vibration around the equilibrium geometry of the resulting molecules, and taking into account that the ZPVA corrections for electric polarisabilities and hyperpolarisabilities in hydrogen peroxide represent only 1% and 2% of the respective electronic quantities,<sup>66</sup> we did not evaluate the corresponding ZPVA correction for  $\overline{\sigma}_{\text{O}_1}^{\text{O}}$ , after computing the magnitude of observed effect.

In order to estimate the possibility of observing a change in the magnitude of the nuclear shielding due to the presence of an external electric field, we take 1 ppm-a.u. = 1.944667 × 10<sup>-18</sup> m/V from Ref. 42. The greatest  $|\overline{\sigma}_{\text{O}_1}^{\text{O}}|$  are in the order of 30 ppm-a.u. for CHF, and from 37 to 45 ppm-a.u. for B3LYP approximations. Therefore, a huge static homogeneous electric field, perpendicular to the strong magnetic field **B** in a NMR spectrometer, and as big as ≈ 1.7 × 10<sup>8</sup> V m<sup>-1</sup>, or from 1.2 × 10<sup>8</sup> V m<sup>-1</sup> to 1.4 × 10<sup>8</sup> V m<sup>-1</sup> should be applied to observe a change corresponding to ≈ 1 ppm, for  $^{17}\text{O}$  magnetic shielding. Such an experiment in the chiral molecules considered in this article is far beyond the present capabilities for a laboratory.

We found that absolute value of the calculated pseudoscalar,  $|\overline{\sigma}_{\text{O}_1}^{\text{O}}|$ , is generally much smaller than the six individual components of the magnetic shielding polarisability from which it was obtained by contraction with the Levi-Civita antisymmetric tensor [see Eq. (28)]. For instance, the components of the contributions to  $|\overline{\sigma}_{\text{O}_1}^{\text{O}_1}|$  in CH<sub>3</sub>OOH:Li<sup>+</sup> ( $C_1$ ), are (in ppm-a.u.): xyz = -124.5, xzy = 50.7, yzx = -1219.6, yxz = 18.4, zxy = 85.2, zyx = -1054.167, for the B3LYP approximation. This behavior shows that chiral discrimination would preferably be attempted by NMR in

TABLE VIII. Comparison of B3LYP and KT3 level oxygen magnetic shielding (ppm) and pseudoscalar magnetic shielding polarisability (ppm-a.u.) in the complexes of **3** molecules at the B3LYP and KT3 level for basis sets I and V.

Gauge origin	$O_1$							
	B3LYP-(I)		KT3-(I)		B3LYP-(V)		KT3-(V)	
	$\sigma^{O_1}$	$\overline{\sigma^{(I)}_1^O}$	$\sigma^{O_1}$	$\overline{\sigma^{(I)}_1^O}$	$\sigma^{O_1}$	$\overline{\sigma^{(I)}_1^O}$	$\sigma^{O_1}$	$\overline{\sigma^{(I)}_1^O}$
<b>3</b>								
CH <sub>3</sub> OOCH <sub>3</sub> (exp-geometry)	30.41	1.44	37.31	-1.43	27.62	0.42	34.70	-1.83
CH <sub>3</sub> OOCH <sub>3</sub> (C <sub>2</sub> )	34.05	0.01	41.36	-0.01	31.32	0.01	38.85	-0.00
CH <sub>3</sub> OOCH <sub>3</sub> :Li <sup>+</sup> (C <sub>2</sub> )	21.34	-37.6	30.23	-39.3	18.66	-37.7	27.81	-38.9
CH <sub>3</sub> OOCH <sub>3</sub> :Li <sup>+</sup> :CH <sub>3</sub> OOCH <sub>3</sub> (D <sub>2</sub> )	26.98	-11.8	35.83	-9.95	23.80	-11.9	32.94	-9.82
CH <sub>3</sub> OOCH <sub>3</sub> :Li <sup>+</sup> :CH <sub>3</sub> OOCH <sub>3</sub> (S <sub>4</sub> )	26.8	-13.6	35.62	-12.5	23.6	-13.6	32.74	-12.4

ordered, or partially ordered phase, since an external field of  $4.8 \times 10^6 \text{ V m}^{-1}$ , Eq. (29), perpendicular to the strong magnetic field  $\mathbf{B}$  in the NMR spectrometer, should be enough to observe yzx or zyx magnetic shielding components, producing a shift of  $\approx 1 \text{ ppm}$ , for  $^{17}\text{O}$ .

Buckingham also described the effect of a uniform electric field on the nuclear shielding, after averaging over all molecular orientations in the NMR external magnetic field, but keeping the electric field direction fixed on the molecule,<sup>2</sup>

$$\sigma_{Av}^I = -A_\gamma^I E_\gamma - B_{\gamma\delta}^I E_\gamma E_\delta, \quad (17)$$

where Einstein summation is implied on Eq. (17). The shielding polarisabilities are related to  $A_\gamma$  values by

$$A_\gamma^I = -\left(\frac{1}{3}\right) \sigma_{\alpha\alpha\gamma}^I. \quad (18)$$

Table X reports  $A_\gamma^{O_1}$  values for the complexes HOOH:Li<sup>+</sup>, CH<sub>3</sub>OOH:Li<sup>+</sup>, and CH<sub>3</sub>OOCH<sub>3</sub>:Li<sup>+</sup>, which have the largest numbers for the pseudoscalar, using B3LYP functional and basis set V. The value  $A_\gamma E_\gamma \approx 1 \text{ ppm}$  should be observed applying an external electric field of  $\approx 1.4 \times 10^6 \text{ V m}^{-1}$ , significantly lesser than  $\approx 1.7 \times 10^8 \text{ V m}^{-1}$  necessary to observe the invariant. An external electric field fixed in the  $x$  direction would be very suitable to observe the effect in an ordered or semi-ordered phase. These systems also

show the largest dipolar moment for each series of (**1**, **2**, **3**) molecule complexes: 4.1, 5.2, and 5.3 D, respectively, at the B3LYP/aug-cc-pVTZ approximation.

Figures 1–3 show the natural charges (in electrons) on oxygen and lithium atoms evaluated also at the B3LYP/aug-cc-pVTZ level of theory. Lithium atom has positive charge for all the systems, and oxygen atoms show negative charge values. XOOX':Li<sup>+</sup> complexes show the largest charge transfer between oxygen and lithium atoms for 1, 2, and 3 complexes. These are the same compounds that exhibit the largest pseudoscalar in Tables IV–VIII, and the largest  $A_\gamma$  values in Table X. The open question is on the existence of a relationship between the observed charge transfer and the increment in the absolute value of the pseudoscalar. A definitive answer requires of further researching in additional series of compounds.

## V. CONCLUSIONS

A theoretical study of the oxygen shielding polarisability on 1:1 and 2:1 complexes formed by hydrogen peroxide derivatives with lithium cation has been carried out by means of CHF and B3LYP (KT3) computational methods for 1, 2, and 3 XOOX' molecules (X, X' = H, CH<sub>3</sub>). For the three sets of complexes, the results confirmed that lithiation is more important than complexation. It is evident that correlation plays an important effect on these quantities. Chiral discriminations

TABLE IX. Comparison of proton magnetic shielding (ppm) and pseudoscalar magnetic shielding polarisability (ppm-a.u.) in two compounds of complexes belonging to **1** and **3** molecules at the B3LYP and KT3 level basis sets I and V.

Compound	Gauge origin H <sub>1</sub>							
	B3LYP-(I)		KT3-(I)		B3LYP-(V)		KT3-(V)	
	$\sigma^{H_1}$	$\overline{\sigma^{(I)}_1^{H_1}}$	$\sigma^{H_1}$	$\overline{\sigma^{(I)}_1^{H_1}}$	$\sigma^{H_1}$	$\overline{\sigma^{(I)}_1^{H_1}}$	$\sigma^{H_1}$	$\overline{\sigma^{(I)}_1^{H_1}}$
<b>1</b>								
HOOH (exp-geometry)	27.27	-5.75	27.04	-5.93	26.06	-6.06	27.48	-5.93
HOOH (C <sub>2</sub> )	27.46	-4.75	27.61	-5.14	26.31	-4.93	26.54	-5.27
<b>3</b>								
CH <sub>3</sub> OOCH <sub>3</sub> :Li <sup>+</sup> :CH <sub>3</sub> OOCH <sub>3</sub> (D <sub>2</sub> )	29.06	-0.01	29.02	0.01	28.10	-0.02	28.12	0.01



TABLE X.  $A_{\gamma}^{O_1}$  (ppm-a.u.) and  $\overline{\sigma^{(1)O_1}}$  for HOOH:Li<sup>+</sup>, CH<sub>3</sub>OOH:Li<sup>+</sup>, and CH<sub>3</sub>OOCH<sub>3</sub>:Li<sup>+</sup>, employing B3LYP functional and basis set V.

Complex	HOOH:Li <sup>+</sup>	CH <sub>3</sub> OOH:Li <sup>+</sup>	CH <sub>3</sub> OOCH <sub>3</sub> :Li <sup>+</sup>
$A_x^{O_1}$	-2391	3297	3329
$A_y^{O_1}$	-274.1	516.4	-875.6
$A_z^{O_1}$	108.8	-587.9	-161.4
$\overline{\sigma^{(1)O_1}}$	-37.6	-45.6	-37.7

by NMR oxygen chemical shifts in the presence of an electric uniform field requires of strengths in the order of  $\approx 1.7 \times 10^8$  V m<sup>-1</sup> in isotropic media, and  $\approx 1.4 \times 10^6$  V m<sup>-1</sup> in ordered or semi-ordered phase for our estimations, with the disadvantage of undesirable lifetime broadening of oxygen signals. This set of compounds provide an upper bound for the electric field required for this kind of complexes, which is useful for future experiments. The comparison between CO and CTOCD-DZ calculations for HOOH proves that the basis sets employed in our estimations have enough flexibility to guarantee that they are confident. Finally, the relationship between NBO charge transfer and increment of the shielding polarisabilities is interesting and it would be revisited in systems for which the presence of an alkaline metal define the charge accommodation and with a great ORP to benefit the observation of electric field effects.

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