Internuclear distance dependence of the spin–orbit coupling contributions to proton NMR chemical shifts

Boris Minaev a, Juha Vaara b,1, Kenneth Ruud c, Olav Vahtras a, Hans Ågren a

a Department of Physics and Measurement Technology, Linköping University, S-58 183 Linköping, Sweden
b NMR Research Group, Department of Physical Sciences, University of Oulu, P.O. Box 333, FIN-90571 Oulu, Finland
c Department of Chemistry, University of Oslo, Blindern, P.O. Box 1033, N-0315 Oslo, Norway

Received 24 June 1998; in final form 1 September 1998

Abstract

The internuclear distance dependence of the electronic spin–orbit coupling contribution to nuclear magnetic resonance shielding constants – which causes the internal heavy-atom chemical shift of the proton shielding – is investigated using quadratic response theory. Calculations using a complete active space self-consistent field wavefunction on hydrogen iodide at different internuclear distances show a strong dependence of the spin–orbit coupling correction to the $^1$H shielding constant on internuclear separation. These results, combined with comparative calculations on HCl and HBr, indicate that the conformational dependence of the shielding constant is qualitatively changed when relativistic spin–orbit coupling corrections are important. This change is observed for HI and HBr, but not for HCl. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Heavy-atom (HA) effects are well known in molecular spectroscopy of the triplet state [1–3] in spin catalysis [4,5] and in nuclear magnetic resonance (NMR) spectroscopy [6–14]. The nature of the HA effects has been shown to be an enhancement of the spin–orbit coupling (SOC) [1,2,6,7,10]. The SOC depends strongly on the electron distribution close to the heavy nuclei where the electrons have a higher velocity than in the valence region. At the same time, the behaviour of the valence electrons in the rest of the system is important for an efficient SOC effect. For example, for the HA effect in phosphorescence, the valence electrons must provide an electric dipole transition moment [3] and, in spin catalysis, the valence-shell electrons must make bond cleavage easier by triplet $\sigma\pi^*$-type excitations [4,5]. For the SOC effect in NMR chemical shifts, the valence electrons must provide a magnetic dipole (orbital angular momentum) transition moment and allow for an efficient coupling with the Fermi-contact or the weaker spin–dipole interaction [10].

These requirements are fulfilled for the hydrogen halides of which, in particular, hydrogen iodide (HI) has a large SOC effect caused by the halogen. The importance of the SOC effect in HA effects on $^1$H NMR chemical shifts [7], in the $T_1 \leftrightarrow S_0$ photoabsorption and photodissociation [15], and in lowering the dissociation energy of the H–I bond [10] connects all these phenomena in HI. Semi-empirical calculations – accounting for SOC – along the disso-
cation reaction coordinate have illustrated the strong dependence of the \( T_1 \) \( \rightarrow \) \( S_0 \) transition matrix elements and the \( ^1H \) chemical shift on the H–I internuclear distance [10]. This distance dependence implies a substantial effect on the isotope and temperature dependence of the NMR shielding constants in this molecule [10].

There has been considerable interest in perturbation-theory calculations of the SOC contributions to the nuclear shieldings, using semi-empirical [7–10], unrestricted Hartree–Fock (UHF) [12], and density-functional theory (DFT) [13] approaches. Recently, a correlated ab initio method employing analytical quadratic response functions with self-consistent field (SCF) and multiconfigurational self-consistent field (MC-SCF) reference states was presented [16].

Studies of isotope and temperature effects on NMR shielding illustrates the importance of bond lengths and other structural parameters [17–19]. The present paper describes the first ab initio calculations of the internuclear distance dependence of the SOC contributions to the nuclear shielding tensor, using the HI molecule as an example. We consider the distance dependence of the shielding constant in the vicinity of the equilibrium geometry (\( r \leq 2 \text{ Å} \)) – far from the dissociation limit – for which the use of perturbation theory is valid. The conclusions are verified by corresponding calculations for HCl and HBr.

2. Theory

The method we employ was discussed in detail in Ref. [16], and we here limit ourselves to a brief recapitulation. The NMR spectral line positions are described in the effective spin Hamiltonian by the nuclear shielding tensor \( \boldsymbol{\sigma}_K \), which couples the applied external magnetic field \( B_0 \) with the spin \( I_K \) of nucleus \( K \). The Cartesian \( \sigma \)-component of the shielding tensor can be written as

\[
\sigma_{K,\sigma} = \sigma_{K,\sigma}^d + \sigma_{K,\sigma}^p + \sigma_{K,\sigma}^{SO}
\]

where \( \sigma_{K,\sigma}^d \) and \( \sigma_{K,\sigma}^p \) are the diamagnetic and paramagnetic shielding tensors arising from second-order perturbation theory. These contributions are evaluated as a ground-state expectation value \( \langle \sigma_{K,\sigma}^p \rangle \) and as a linear response function \( \langle \sigma_{K,\sigma} \rangle \), respectively. There are four contributions to \( \sigma_{K,\sigma}^{SO} \):

\[
\sigma_{K,\sigma}^{SO} = \sigma_{K,\sigma}^{FC(1)} + \sigma_{K,\sigma}^{FC(2)} + \sigma_{K,\sigma}^{SD(1)} + \sigma_{K,\sigma}^{SD(2)}
\]

arising from the coupling of the SOC Hamiltonian [20]

\[
H_{SO} = \frac{e^2 \hbar}{4m_e^2} \frac{\mu_0}{4\pi} \times g_e \left[ \sum_L L \sum_i s_i \cdot 1_{L,i} - \sum_j (s_j + 2s_j) \cdot 1_{i,j} \right]
\]

\[
\equiv H_{SO(1)} + H_{SO(2)}
\]

with the Fermi-contact Hamiltonian

\[
H_{K,FC} = \frac{4\pi}{3} \frac{e\hbar^2}{m_e} \mu_0 \sum_K g_K \sum_i \delta(r_{ik}) I_K \cdot s_i
\]

and the spin–dipole Hamiltonian

\[
H_{K,SD} = \frac{e\hbar^2}{2m_e} \mu_0 \sum_K g_K \sum_i \frac{3r_{ik}r_{ik} - 1}{r_{ik}^3} I_K \cdot s_i.
\]

In the above equations, \( g_e \) is the electron g-factor, \( s_i \) the spin vector of the \( i \)-th electron, \( I_L \) the angular momentum of \( i \) with respect to nucleus \( L \), and \( r_{ik} \) the distance between \( i \) and \( L \). \( 1_{i,j} \) and \( 1_{i,j} \) are the corresponding quantities with respect to the position of electron \( j \).

The SOC contributions must be calculated from third-order perturbation theory [7] and can be expressed in terms of the quadratic response functions [16]

\[
\langle \langle H_{K,FC} : H_{SO(a)} \rangle \rangle \rangle_0 \]

for the \( \sigma_{K,\sigma}^{FC(a)} \) contributions, and

\[
\langle \langle H_{K,SD} : H_{SO(a)} \rangle \rangle \rangle_0 \]

for the \( \sigma_{K,\sigma}^{SD(a)} \) contributions. In both Eqs. (6) and (7), the operator \( H_{SO(a)} \) couples the external magnetic field with the electronic angular momentum \( L_{0} \) with respect to the gauge origin \( O \)

\[
H_{SO(a)} = \frac{e}{2m_e} \sum_L I_{L,0} \cdot B_0.
\]

When considering the shielding corrections due to zero-point motion, we also need to take into account
the second-order energy contribution from the spin–orbit operator to the ground-state potential-energy curve in order to be consistent with the present perturbative treatment of the SOC effects on $\sigma$. This energy correction is obtained as a linear response function at zero frequency [21]

$$E^{(2)} = \sum_n \frac{\langle 0 | H_{\text{SO}} | n \rangle \langle n | H_{\text{SO}} | 0 \rangle}{E_0 - E_n}$$

$$= \frac{1}{2} \langle\langle H_{\text{SO}}; H_{\text{SO}} \rangle \rangle_{\omega=0}. \quad (9)$$

The triplet quadratic response functions and all one- and two-electron SOC integrals have been implemented in the DALTON program [22], following the procedure described in Refs. [23,24].

3. Computational details

The computational procedure used here is similar to that used in Ref. [16]. We use the basis set denoted as HIVu3 in Ref. [16]. This basis set is for iodine based on the compilation of Ref. [25], whereas the basis set of Huzinaga is used for hydrogen [26]. Three sets of tight functions are added to all shells that are occupied in the free atoms – that is, s-functions for hydrogen, and s-, p-, and d-functions for iodine. The exponents of the tight functions are given by the factor of three. The total basis set, which is uncontracted, is then (23s19p18d2f) for iodine and (9s3p1d) for hydrogen.

The calculations have been carried out using a complete active space SCF (CAS-SCF) wavefunction. All inner-shell orbitals of iodine were kept inactive. The active orbital space includes four valence orbitals doubly occupied in the electronic ground state, $(12\sigma^2(13\sigma)^2(6\pi^*)^2(6\pi)^2)$, plus four empty $\sigma$ MOs, two empty $\pi$ shells and one $d_z^2$ function. In the notation of Ref. [16], this is the $11\text{:}352\text{\:}\text{CAS}\text{\:}6331$ wavefunction. The number of determinants in the wavefunction is 128283.

The non-relativistic shielding tensors ($\sigma^d$ and $\sigma^p$) were calculated using gauge-including atomic orbitals (GIAO) as described in Ref. [27]. The partitioning of the diamagnetic and paramagnetic contributions has been done using the natural connection [28], which gives the correct origin dependence of the two individual contributions. The calculations of the SOC contributions to the shielding Eq. (2) were carried out using a common gauge origin placed on the iodine atom.

The zero-point vibrationally averaged shielding constant was calculated as the averaged Taylor series expansion [29]

$$\sigma = \sigma_e + \sigma_p^\omega \langle r - r_e \rangle^0 + \frac{1}{2} \sigma_{p',p} \langle (r - r_e)^2 \rangle^0, \quad (10)$$

where the subscript ‘e’ denotes quantities at the equilibrium geometry, and $\sigma_e$ and $\sigma_p^\omega$ are the first and second derivatives of the shielding constant with respect to bond length extension, taken at $r_e$. These parameters were obtained by fitting a fourth-order polynomial to the shielding constants calculated in the bond-length interval 1.4–1.8 Å, with points separated by 0.05 Å. The averages of the bond length extension and its square were calculated as described in Ref. [30], using the cubic and harmonic force constants, $f_{rr'}$ and $f_{r'r}$, respectively, obtained by fitting a fourth-order polynomial to the total SOC corrected energies.

4. Results and discussion

The CAS calculation at the equilibrium geometry predicts a vertical excitation energy of 5.3 eV for the $^3\Pi \leftarrow X^1\Sigma^+$ transition, and 5.9 eV for the $^1\Pi \leftarrow X^1\Sigma^+$ transition, in good agreement with the maximum of the continuous absorption observed at 46000 cm$^{-1}$ (5.7 eV) [15]. Both these lowest valence excited states $^3\Pi$ in HI are repulsive, and the vertical excitation to the singlet state corresponds approximately to the observed maximum. Accounting for SOC leads to a small red-shift of this absorption [10].

The non-relativistic $^1\text{H}$ shielding constants and the SOC corrections calculated at different internuclear distances are listed in Table 1 and illustrated in Fig. 1.

The present and previous [12,13,16] calculations of $\sigma_{1\text{H}}$ in HI are compared to experiment in Table 2. A very strong dependence of the SOC correction FC(1) on the internuclear distance is observed. The non-relativistic diamagnetic shielding $\sigma^d$ also depends strongly on the bond length, but with an opposite sign of the slope, diminishing rather fast in
Table 1
Calculated $^1$H nuclear shielding constants (in ppm) in the HI molecule as a function of internuclear distance $r$ (in Å). The ground-state potential energies $E$ corrected for the second-order spin–orbit interaction are also shown (in a.u.)

<table>
<thead>
<tr>
<th>$r$</th>
<th>$E$</th>
<th>$\sigma^d$</th>
<th>$\sigma^p$</th>
<th>$\sigma^{\text{FC}(1)}$</th>
<th>$\sigma^{\text{FC}(2)}$</th>
<th>$\sigma^{\text{SD}(1)}$</th>
<th>$\sigma^{\text{SD}(2)}$</th>
<th>$\sigma^{\text{SO}}$</th>
<th>$\sigma^{\text{tot}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.30</td>
<td>0.069939</td>
<td>31.465</td>
<td>10.158</td>
<td>41.623</td>
<td>5.218</td>
<td>-0.402</td>
<td>0.310</td>
<td>-0.026</td>
<td>5.100</td>
</tr>
<tr>
<td>1.40</td>
<td>0.028887</td>
<td>26.565</td>
<td>11.084</td>
<td>37.649</td>
<td>6.768</td>
<td>-0.489</td>
<td>0.330</td>
<td>-0.026</td>
<td>6.583</td>
</tr>
<tr>
<td>1.45</td>
<td>0.016408</td>
<td>24.543</td>
<td>11.387</td>
<td>35.930</td>
<td>7.792</td>
<td>-0.549</td>
<td>0.342</td>
<td>-0.026</td>
<td>7.559</td>
</tr>
<tr>
<td>1.50</td>
<td>0.007952</td>
<td>22.771</td>
<td>11.601</td>
<td>34.372</td>
<td>9.028</td>
<td>-0.624</td>
<td>0.357</td>
<td>-0.027</td>
<td>8.735</td>
</tr>
<tr>
<td>1.55</td>
<td>0.002740</td>
<td>21.222</td>
<td>11.741</td>
<td>32.963</td>
<td>10.521</td>
<td>-0.715</td>
<td>0.374</td>
<td>-0.027</td>
<td>10.154</td>
</tr>
<tr>
<td>1.60</td>
<td>0.000000</td>
<td>19.758</td>
<td>11.281</td>
<td>31.579</td>
<td>12.510</td>
<td>-0.837</td>
<td>0.396</td>
<td>-0.028</td>
<td>12.041</td>
</tr>
<tr>
<td>1.65</td>
<td>-0.000410</td>
<td>18.703</td>
<td>11.838</td>
<td>30.541</td>
<td>14.514</td>
<td>-0.961</td>
<td>0.418</td>
<td>-0.029</td>
<td>13.942</td>
</tr>
<tr>
<td>1.70</td>
<td>0.000692</td>
<td>17.693</td>
<td>11.813</td>
<td>29.507</td>
<td>17.167</td>
<td>-1.126</td>
<td>0.446</td>
<td>-0.031</td>
<td>16.456</td>
</tr>
<tr>
<td>1.75</td>
<td>0.003075</td>
<td>16.829</td>
<td>11.749</td>
<td>28.577</td>
<td>20.393</td>
<td>-1.328</td>
<td>0.478</td>
<td>-0.032</td>
<td>19.511</td>
</tr>
<tr>
<td>1.80</td>
<td>0.006445</td>
<td>16.093</td>
<td>11.651</td>
<td>27.744</td>
<td>24.329</td>
<td>-1.574</td>
<td>0.514</td>
<td>-0.034</td>
<td>23.236</td>
</tr>
<tr>
<td>2.00</td>
<td>0.025488</td>
<td>14.210</td>
<td>11.024</td>
<td>25.234</td>
<td>51.315</td>
<td>-3.269</td>
<td>0.727</td>
<td>-0.047</td>
<td>48.726</td>
</tr>
</tbody>
</table>

Fig. 1. Calculated internuclear distance dependence of of different contributions to the $^1$H shielding constants of HI molecule (in ppm). (1) $\sigma^d$, (2) $\sigma^p$, (3) $\sigma^{\text{FC}(1)}$, (4) $\sigma^{\text{FC}(2)}$, (5) $\sigma^{\text{SD}(1)}$, (6) $\sigma^{\text{SD}(2)}$, (7) $\sigma^{\text{SO}}$, (8) $\sigma^{\text{tot}}$.

the vicinity of equilibrium. The SOC correction increases, and the geometry dependences of the two contributions almost cancel at short bond lengths ($r \leq 1.7$ Å). The lowest rovibrational level of the ground state of HI has a large wavefunction amplitude in the region $1.6 \pm 0.1$ Å. Zero-point vibrational averaging, with $f_{zz} = 2.99 \text{ aJ/Å}^2$ and $f_{rr} = -14.68 \text{ aJ/Å}^3$, leads to a slightly reduced value of the total non-relativistic shielding $\sigma^{nr}$ – as observed previously for non-metallic main group compounds see for instance Ref. [33] – whereas the SOC correction increases (Table 2). The total vibrationally averaged $^1$H shielding constant for HI is slightly increased compared to the value calculated at the equilibrium distance $r_c = 1.605$ Å (Table 2). Thus, SOC induced by the heavy atom reverses the sign of the vibrational contribution to the $^1$H shielding. As it is caused by a decreasing triplet excitation energy with bond length extension, the effect is similar to that observed in the internuclear distance dependence of the $J_{\text{HD}}$ spin–spin coupling constant in HD reported by Bacskay [34].

Calculations without relativistic corrections predict a negative temperature dependence of the $^1$H shielding constant in HI, whereas taking the SOC into account leads to a weak positive temperature dependence at room temperature. At $T \geq 600$ K – where the excited vibrational energy levels become significantly populated – we predict an even stronger positive temperature dependence of the $^1$H shielding constant.

Considering the importance of the different contributions to the total SOC-induced $^1$H shielding constant, we observe that the positive FC(1) term is strongly increasing at longer distances and becomes dominating. In absolute values, the ordering of the
Table 2

Comparison of theoretical and experimental $^1$H shielding constants of the HI molecule $^a$

<table>
<thead>
<tr>
<th>Theory</th>
<th>$\sigma_{\text{nr}}$</th>
<th>$\sigma_{\text{FC(1)}}$</th>
<th>$\sigma_{\text{FC(2)}}$</th>
<th>$\sigma_{\text{SD(1)}}$</th>
<th>$\sigma_{\text{SD(2)}}$</th>
<th>$\sigma_{\text{SO}}$</th>
<th>$\sigma_{\text{1st}}$</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHF$^b$</td>
<td>30.44</td>
<td>15.61</td>
<td>0.40</td>
<td>16.01</td>
<td>46.45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DFT$^c$</td>
<td>31.65</td>
<td>13.00</td>
<td></td>
<td>13.00</td>
<td>44.65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAS$^d$</td>
<td>31.58</td>
<td>12.510</td>
<td>$-0.837$</td>
<td>0.396</td>
<td>$-0.028$</td>
<td>12.04</td>
<td>43.62</td>
<td></td>
</tr>
<tr>
<td>CAS$^e$</td>
<td>31.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.29</td>
<td>44.61</td>
<td>43.86$^f$</td>
</tr>
</tbody>
</table>

$^a$ Values in ppm.

$^b$ Ref. [12].

$^c$ Ref. [13]. The non-relativistic shielding constants (from Table 3 of Ref. [13]) are calculated with the BII basis. The SO-corrections (from Table 2 of Ref. [13]) are calculated with the large UP basis set, E128 integration grid and the finite perturbation parameter $\lambda = 0.0001$.

$^d$ Ref. [16]. CAS/HIVu3 results at $r_e = 1.605$ Å.

$^e$ CAS/HIVu3 in this work with zero-point vibrational averaging.

$^f$ Ref. [31]. Gas-phase NMR chemical shift with respect to CH converted into absolute shielding using $\sigma_{\text{HCH}} = 30.61$ ppm [32].

other SOC terms is $|\text{FC}(2)\rangle \langle \text{SD}(1)| \langle \text{SD}(2)|$, with the two-electron contributions always being negative. Although the FC(2) and SD(1) contributions increase in absolute value with increasing internuclear distance, their magnitude still never becomes more than 7% of the FC(1) value. At short internuclear distances ($r = 1.3$ Å), FC(2) and SD(1) almost cancel. At longer distances, the FC(2) contribution increases in magnitude faster than SD(1), and the contribution from these two terms become increasingly more negative. The total SOC contribution becomes more important in comparison with the non-relativistic value for longer bond lengths. The overall magnitude of the SOC contributions may be appreciated by considering the ratio $\sigma_{\text{SO}}/\sigma_{\text{nr}}$ which is 0.17, 0.38, 0.84, and 1.93 at the internuclear distances 1.4, 1.605, 1.8 and 2 Å, respectively. At still longer bond lengths, the SOC contribution grows by orders of magnitude and gives a vibrational correction which is unphysical since the perturbation treatment breaks down. Therefore, the vibrational averaging is restricted to the range (1.4–1.8 Å) mentioned above.

All calculations that include the SOC corrections reproduce qualitatively the relativistic increase of the $^1$H shielding in the series HF, HCl, HBr, HI [16]. A similar increase in the internuclear distance dependence of $\sigma_{\text{nr}}$ in the two heavier members of the series can be expected on grounds of the present calculations. We performed the corresponding zero-point vibrational averaging calculation for H$^{35}$Cl and H$^{79}$Br as well (the parameters $\sigma_{r}, \sigma_{\text{eff}}, f_{rr}$ and $f_{rrr}$, obtained from CAS$^{6331}$/HIVu3 calculations [16]) for all the three molecules, are available from the authors). In the case of HBr, the equilibrium and zero-point averaged $\sigma_{\text{nr}}$ are 31.03 and 30.76 ppm, respectively, while after the SOC correction the corresponding values are 34.98 and 35.15 ppm. The behaviour is thus fully analogous to HI, except that the increase of the SOC effect is not as dramatic. For the lighter HCl molecule, $\sigma_{\text{nr}}$ is changed from its equilibrium value 30.82 to 30.53 ppm, whereas the corresponding change of the SOC corrected results is from 31.51 to 31.30 ppm. Here the SOC effect merely reduces the magnitude of the zero-point vibrational correction, not altering its direction.

We note that the deviation from experiment in the CAS calculations of Ref. [16] can partly be attributed to zero-point vibrational effects, but that our vibrationally corrected results overshoot the experimental values by 0.8, 0.6 and 1.7% for HCl, HBr and HI, respectively. A more complete treatment of dynamical correlation effects than that obtained with the CAS$^{6331}$ wavefunction is most likely needed in order to obtain quantitative agreement with experiment.

5. Conclusions

We have presented quadratic response calculations of the corrections to the nuclear shielding tensor induced by electronic spin–orbit coupling as a function of internuclear distance in HI. The one- and two-electron spin–orbit interactions with both the
Fermi contact and spin–dipole operators have been taken into account.

The SOC contribution increases monotonically, becoming about 8 times larger when the internuclear distance increases from 1.4 to 2.0 Å. At the internuclear separation of 2.0 Å, the SOC contribution is twice as large as the non-relativistic shielding constant. The non-relativistic diamagnetic contribution $\sigma^d$ also shows strong dependence on the bond length, and decreases with increasing bond length in the vicinity of the equilibrium. At short bond lengths ($r \leq 1.7$ Å), the geometry dependencies of $\sigma^{SO}$ and $\sigma^d$ almost cancel. The total zero-point vibrationally averaged, spin–orbit corrected $^1$H shielding constant in HI is slightly increased in comparison with the value calculated at $r_e$, opposite to what is obtained in a non-relativistic calculation. An analogous behaviour is observed for HBr but not for HCl, reflecting the relative importance of SOC in these systems.

The strong internuclear distance dependence of the SOC correction to the $^1$H shielding constant in HI obtained in this work gives support to the predictions of the external heavy-atom effect in NMR spectra [10]. Semi-empirical calculations of the $^1$H shielding constant in H$_2$Se and H$_2$Hg predict an increase of the SOC correction ($\sigma^{SO}(1)$) and of the total $\sigma_H$ value by an order of magnitude even for HBr but not for HCl, reflecting the relative importance of SOC in these systems. These predictions can now be tested at the ab initio level. It appears reasonable to assume that the interplay between NMR shielding constants and molecular conformation becomes more delicate when spin–orbit coupling contributions are important.

Acknowledgements

The authors acknowledge the computational resources provided by the Center for Scientific Computing (Espoo, Finland) and the Research Council of Norway (Program for Supercomputing).

References
