

ANISOTROPY OF THE INDIRECT NUCLEAR SPIN-SPIN
COUPLING CONSTANT

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Various contributions to the anisotropy of the indirect nuclear spin-spin coupling constant in nuclear magnetic resonance are examined and order-of-magnitude calculations are reported for hydrocarbons and for methyl fluoride.

1. INTRODUCTION

Recently, Krugh and Bernheim [1] reported the existence of very large anisotropy of the indirect nuclear spin-spin coupling constants of methyl fluoride dissolved in a nematic solvent. Their results show that the anisotropy is especially large for the coupling constants between directly bonded nuclei (C-F and C-H). In the present paper, the origin of the anisotropy in the indirect nuclear spin-spin coupling constant is examined and the orders of magnitude of various contributions are calculated for hydrocarbons and for methyl fluoride with rather crude approximations.

2. ORIGIN OF ANISOTROPY

The Hamiltonian for the indirect nuclear spin-spin coupling in nuclear magnetic resonance spectra is given by the sum of the following four terms [2]:

i) Terms due to the magnetic shielding of the direct interaction of the nuclear spins by electron orbital motion.

$$\mathcal{H}_1^{(a)} = (e\hbar\beta/c) \sum_{A,B,k} \gamma_A \gamma_B r_{kA}^{-3} r_{kB}^{-3} [(I_A \cdot I_B)(r_{kA} \cdot r_{kB}) - (I_A \cdot r_{kB})(I_B \cdot r_{kA})], \quad (1)$$

$$\mathcal{H}_1^{(b)} = (2\beta\hbar/i) \sum_{A,k} \gamma_A r_{kA}^{-3} I_A \cdot (r_{kA} \times \nabla_k). \quad (2)$$

ii) (Electron-spin)-(nuclear-spin) dipolar interaction term.

$$\mathcal{H}_2 = 2\beta\hbar \sum_{A,k} \gamma_A [3(S_k \cdot r_{kA})(I_A \cdot r_{kA}) r_{kA}^{-5} - S_k \cdot I_A r_{kA}^{-3}]. \quad (3)$$

iii) Term due to the Fermi interaction between electron-spins and nuclear-spins.

$$\mathcal{H}_3 = (16\pi\beta\hbar/3) \sum_{A,k} \gamma_A \delta(r_{kA}) S_k \cdot I_A. \quad (4)$$

In the above equations, A and B denote nuclei and k refers to an electron. Since the indirect nuclear spin-spin interaction is a second-order property with respect to the Hamiltonians $\mathcal{H}_1^{(b)}$, \mathcal{H}_2 and \mathcal{H}_3 , the various contributions to the anisotropy may be summarized as shown in table 1. Among these contributions, the Fermi-spin dipolar cross term is expected to be an important source for the anisotropy of the coupling constant between light nuclei, although this contribution is averaged out to zero when the

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Table 1
Origin of the anisotropy of the electron-coupled nuclear spin-spin coupling constant

Interaction	Fermi \mathcal{H}_3	Spin dipolar \mathcal{H}_2	$\mathcal{H}_1^{(a)}$	Orbital $\mathcal{H}_1^{(b)}$
Fermi \mathcal{H}_3	isotropic	anisotropic	0	0
Spin dipolar \mathcal{H}_2		isotropic and anisotropic	0	0
Orbital $\mathcal{H}_1^{(a)}$			isotropic and anisotropic	---
				isotropic and anisotropic

molecule is rotating randomly. Moreover, table 1 suggests that the anisotropy of the H-H coupling constant should be very small.

Now, it may be useful to develop these contributions in terms of molecular orbital theory, along similar lines to the treatment of Pople and Santry [3]. By resorting to rather crude approximations ((i) use of a single determinant wavefunction, (ii) LCAO MO approximation and (iii) retaining only one-center integrals), the Fermi-spin dipolar cross term is written as

$$\begin{aligned}
 (K_{AB}^{(2,3)})_{\alpha\alpha} = & \\
 = & -(64\pi\beta^2/15)[(s_A | \delta(\mathbf{r}_A) | s_A) \langle r^{-3} \rangle_B \sum_i^{\text{occ}} \sum_j^{\text{unocc}} ({}^3\Delta E_{i \rightarrow j})^{-1} C_{i s_A} C_{j s_A} (2C_{i p_{\alpha B}} C_{j p_{\alpha B}} - \sum_{\beta} C_{i p_{\beta B}} C_{j p_{\beta B}}) + \\
 & + (s_B | \delta(\mathbf{r}_B) | s_B) \langle r^{-3} \rangle_A \sum_i^{\text{occ}} \sum_j^{\text{unocc}} ({}^3\Delta E_{i \rightarrow j})^{-1} C_{i s_B} C_{j s_B} (2C_{i p_{\alpha A}} C_{j p_{\alpha A}} - \sum_{\beta} C_{i p_{\beta A}} C_{j p_{\beta A}})], \quad (5)
 \end{aligned}$$

where $p_{\alpha A}$ denote the $2p_{\alpha}$ atomic orbital (α is x , y or z) of the A atom. \sum_{β} means the sum over the directions x , y and z except α . The other notations are the same as Pople and Santry's [3]. Further, if the average excitation energy approximation and the assumption of the orthogonality of the basic atomic orbitals are made, one obtains

$$\begin{aligned}
 (K_{AB}^{(2,3)})_{\alpha\alpha} = & (16\pi\beta^2/15)[(s_A | \delta(\mathbf{r}_A) | s_A) \langle r^{-3} \rangle_B ({}^3\Delta E)^{-1} (2P_{s_A p_{\alpha B}}^2 - \sum_{\beta} P_{s_A p_{\beta B}}^2) + \\
 & + (s_B | \delta(\mathbf{r}_B) | s_B) \langle r^{-3} \rangle_A ({}^3\Delta E)^{-1} (2P_{s_B p_{\alpha A}}^2 - \sum_{\beta} P_{s_B p_{\beta A}}^2)], \quad (6)
 \end{aligned}$$

where

$$P_{s_A p_{\alpha B}} = \sum_i^{\text{occ}} 2C_{i s_A} C_{i p_{\alpha B}}. \quad (7)$$

The other contributions shown in table 1 can also be formulated as above, but they are not given here for want of space. From the above equations and table 1, the Fermi-spin dipolar cross term is expected to make the dominant contribution to the anisotropy of the X-H coupling constant, where X is a nucleus other than a proton.

3. APPLICATIONS

Now it may be necessary to estimate the order of magnitude of each contribution shown in table 1. Although the anisotropies of coupling constants of hydrocarbons are not yet known, these are of basic

Table 2
Results of K_{AB} ($\text{cm}^{-3} \times 10^{20}$) for hydrocarbons (directly bonded) a, b)

Bond	Isotropic, $(K_{AB})_{\text{iso}}$ ^{c)}				Exptl.	Anisotropic, $(K_{\parallel} - K_{\perp})_{AB}$			
	Calc.					Calc.			
	Fermi	Spin dipolar	Orbital	Total		Fermi-spin dipolar	Spin dipolar	Orbital	Total
—C—H	44	0.0	0.0	44	41.8	11	0.0	0.0	11
=C—H	58	0.0	0.0	58	52.3	10	0.0	0.0	10
≡C—H	87	0.0	0.0	87	83.1	7.6	0.0	0.0	7.6
C—C	55	1.3	0.0	56	45.6	29	1.9	0.0	31
C=C	97	1.0	-12.4	86	89.0	34	-1.9	18.7	51
C≡C	219	5.0	0.0	224	225.9	38	-10.1	84.0	112

a) The molecular axis is parallel with the bond.

b) The values of ΔE are 15 eV for Fermi and Fermi-spin dipolar cross terms and 10 eV for the other contributions (see ref. [3]).

c) See ref. [3].

interest from a theoretical standpoint. Some approximate calculations of these are summarized in table 2. In these, we assumed i) homopolar bond, ii) localized sp^3 , sp^2 and sp hybrids respectively for carbon in single, double and triple bonds, iii) zero overlap integrals and iv) average excitation energy approximation (eq. (6)). The values of the average excitation energies, ΔE are 15 eV for the excitations concerning s-AO (Fermi and Fermi-spin dipolar cross terms), and 10 eV for the other excitations concerning only 2p-AO's [3]. The one-center integral values are summarized in table 3.

Table 3
One-center integrals (au) ^{a)}

Nucleus	$\langle s_A \delta(\mathbf{r}_A) s_A \rangle$	$\langle r^{-3} \rangle_A$
H	0.550 ^{b)}	0.0
C	2.767	1.692
F	11.966	7.546

a) Ref. [5].

b) Slater orbital with $Z = 1.2$.

Table 2 shows that the Fermi-spin dipolar cross term is a very important source for the anisotropy of the coupling constant, although the orbital contribution becomes important for the coupling between triply-bonded carbons. Furthermore, the anisotropies of the C—H couplings are expected to be small compared to the isotropic couplings, while those of the (singly, doubly, and triply bonded) C—C couplings are comparable in magnitude to their isotropic couplings.

At present, methyl fluoride is the only compound for which the anisotropy of the indirect nuclear spin-spin coupling has been observed [1]. Since the anisotropy in the indirect nuclear spin-spin coupling was obtained by subtracting the direct coupling from the observed total anisotropy, some uncertainty of the experimental value still remains owing to the uncertainty of the geometry and of the anharmonicity in vibration of the methyl fluoride [1]. Thus, an order-of-magnitude calculation of the anisotropy of the indirect nuclear spin-spin coupling constant may be useful. The various contributions to the anisotropy are calculated by using the MO's obtained by the CNDO/2 method [4], without making the average-excitation-energy approximation (eq. (5)). The results are summarized in table 4 with the isotropic coupling constants obtained by the same approximate method.

Table 4 shows that the Fermi-spin dipolar cross term is an important source for the anisotropy. For the C—F coupling constant, both the isotropic and anisotropic couplings are small if compared with experiment. (This is mainly due to the large value of the calculated ${}^3\Delta E_{i \rightarrow j}$.) The ratio of

Table 4
Results of K_{AB} ($\text{cm}^{-3} \times 10^{20}$) for the methyl fluoride with CNDO/2 method

A-B	Isotropic, $(K_{AB})_{\text{iso}}$				Anisotropic, $(K_{\parallel} - K_{\perp})_{AB}$ ^{a)}					Exptl. ^{b)}
	Calcd.				Calcd.					
	Fermi	Spin dipolar	Orbital	Total	Fermi-spin dipolar	Spin dipolar	Orbital	Total		
C-F	-20.6	3.5	-0.9	-18.0	-56.99	37.2	6.1	-1.1	42.2	246 ± 46
C-H	24.4	0.0	0.0	24.4	49.27	-3.6	0.0	0.0	-3.6	626 ± 43
H-F	0.79	0.0	0.0	0.79	4.10	-1.2	0.0	0.0	-1.2	-1.6 ± 4.8
H-H	0.37	0.0	0.0	0.37	-0.80	0.0	0.0	0.0	0.0	0.0

a) The direction of the molecular axis is parallel with the C-F bond.

b) Ref. [1].

$(K_{\parallel} - K_{\perp})_{\text{CF}}/(K_{\text{CF}})_{\text{iso}}$ is -2.3 for the calculated values and -4.3 ± 0.8 for the experimental ones. For the C-H coupling, the calculated anisotropy is too small to compare with experiment. Moreover, within the present approximations, it is expected to be minus in sign if the molecular axis is taken to be parallel to the C-F bond. Thus, at present, it seems necessary to examine more carefully both the approximations introduced in the present calculations (see the next section) and the experimental values. For the coupling constants between non-directly bonded nuclei, the calculated anisotropy is small as may be expected from eq. (6). The anisotropy of the H-H coupling constant is expected to be zero within the present approximations.

4. DISCUSSION

The large anisotropy of the C-H coupling constant of methyl fluoride reported by Krugh and Bernheim [1] cannot be interpreted from the present calculations. Of the previous approximations (section 2), the one-center integral approximation seems most drastic. Then we examined the effect of the two-center integrals of the type, $(2s(\text{C}) | \delta(\mathbf{r}_{\text{H}}) | s_{\text{H}})$, $(2p_{\sigma}(\text{C}) | \delta(\mathbf{r}_{\text{H}}) | s_{\text{H}})$ and $(2p_{\pi}(\text{C}) | \delta(\mathbf{r}_{\text{H}}) | s_{\text{H}})$. The correction due to these two-center integrals to the anisotropy of the C-H coupling is only 2% of the one-center contribution.

It should be emphasized that the figures given in table 4 are results which are very sensitive to the approximations introduced in the molecular orbital calculations and are therefore subject to considerable error. It seems necessary to use more reliable molecular orbitals, such as non-empirical molecular orbitals, and a more refined method. Further experimental study, especially for hydrocarbons, would be very valuable from the theoretical standpoint*.

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* Experimental values of the anisotropy of ^{13}C -H indirect spin coupling constants in some methyl derivatives have recently been obtained by the present authors. The manuscript is now in preparation.

REFERENCES

- [1] T. R. Krugh and R. A. Bernheim, J. Am. Chem. Soc. 91 (1969) 2385.
- [2] N. F. Ramsey, Phys. Rev. 91 (1953) 303.
- [3] J. A. Pople and D. P. Santry, Mol. Phys. 8 (1964) 1.
- [4] J. A. Pople and G. A. Segal, J. Chem. Phys. 44 (1966) 3289.
- [5] J. A. Morton, Chem. Rev. 64 (1964) 453.