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An SCF-MO-INDO Study of Isotropic and Anisotropic Hyperfine Coupling Constants for Sigma Radicals

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A knowledge of theoretically calculated hyperfine coupling constants (hfc) for a radical is helpful in interpreting its electronic structure and explaining the magnitudes and signs of the observed values. In the calculation of the isotropic hfc, the spin-polarization effect should be included.[1] The one-center dipolar interaction integrals mainly contribute to anisotropic hfc.[2] With these two factors taken into consideration, an improved SCF-MO function has been constructed and the isotropic and anisotropic hfc have been calculated.

The ground electron-configuration (Ψ_g) for a radical was obtained in terms of the approximate open-shell MO's of Longuet-Higgins and Pople using INDO approximation.[3] There are four types of one-electron-excited electron-configurations which are eigen functions (doublet) of S_z and S^2. When SCF-MO's are used, however, only one of them (Ψ_{ik}(II))[4] interacts with Ψ_g and the wave function Ψ_g can be improved by use of the first order perturbation: $\Psi=\Psi_g+\sum\lambda_{ik}\Psi_{ik}$ (II). The i, j components ($i, j=X, Y, Z$) of the anisotropic hfc, A_{ij}^{N}, and the isotropic hfc, a^{N}, for a nucleus N are:

$$A_{ij}^{\mathrm{N}} = \mathrm{g}\beta\hbar\gamma_{\mathrm{N}}tr(\rho P),\ P_{rs} = \langle \chi_r | r_{\mathrm{N}}{}^{-5}(3r_{\mathrm{N}i}r_{\mathrm{N}j}-r_{\mathrm{N}}{}^2\delta_{ij}) | \chi_s \rangle, \tag{1}$$

$$a^{\mathrm{N}} = (8\pi/3)\mathrm{g}\beta\hbar\gamma_{\mathrm{N}}tr(\rho Q),\quad Q_{rs} = \langle \chi_r | \delta(r_{\mathrm{N}}) | \chi_s \rangle, \tag{2}$$

$$\rho_{rs} = C_{rm}C_{sm} + \sum_{i,k}(C_{ri}C_{sk}+C_{si}C_{rk})(mi|mk)/\Delta E_{ik}, \tag{3}$$

where C_{ri} are the LCAO coefficients ($\phi_i=\sum\chi_r C_{ri}$), ΔE_{ik} the energy differences between Ψ_{ik} (II) and Ψ_g, ρ_{rs} an element of the AO spin density matrix, and the other notations have their usual meaning. The second term in ρ_{rs} is what appears by spin-polarizarion. If AO's χ_r and χ_s belong to different atoms, dipolar interaction integrals P_{rs} are evaluated over the Slater type AO's[2] and one-center P_{rs} over the SCF-AO's expanded by Löwdin.[5] Q_{rs} are also evaluated over the Löwdin's SCF-AO's, only if both χ_r and χ_s are centered on the atom N.

The hfc of HCO, CO_2^-, $CH_2{=}CH$, HCN^-, and $CH{\equiv}C$ were calculated. The results for HCO, a typical σ-radical, are described in some detail. The electronic structure of this radical has been reported.[3]

Table 1. Contribution of electron-configurations to hfc (MHz) of ^{1}HCO in the principal axes

Configuration	a	A_{xx}	A_{xy}	A_{yy}	A_{zz}
Ψ_g	243	23.2	−3.3	−6.3	−16.9
$1\sigma\to6\sigma$	1	−0.1	0.2	0.0	0.1
$2\sigma\to6\sigma$	31	−3.3	2.1	1.3	2.0
$2\sigma\to7\sigma$	5	−1.0	−0.4	0.6	0.4
$3\sigma\to6\sigma$	9	−1.1	0.9	0.4	0.7
$3\sigma\to7\sigma$	2	−0.4	0.1	0.3	0.2
$1\pi\to2\pi$	0	0.6	−0.1	−0.6	0.0
$4\sigma\to7\sigma$	−3	0.8	0.5	−0.5	−0.4
Sum of $i\to k$	45	−4.6	3.3	1.5	3.1
Total	288	18.7	0.0	−4.8	−13.9

Table 2. Contribution of each atom to the anisotropic hfc (MHz) of H^{13}CO in the principal axes

Atom		A_{xx}	A_{xy}	A_{yy}	A_{zz}
C	$2p_x{}^2$	−4.3	0	2.2	2.2
	$2p_y{}^2$	−27.4	0	54.8	−27.4
	$2p_z{}^2$	−1.5	0	−1.5	2.9
	Others	0	−0.1	0	0
	Total of C	−33.2	−0.1	55.5	−22.3
H		3.1	2.9	−0.8	−2.3
O		4.6	−2.8	−1.3	−3.3
	H+O	7.7	0.1	−2.1	−5.6
Total		−25.5	0	53.4	−28.0

The contribution of each electron-configuration to hfc for the proton is shown in Table 1. We see that the most important contribution is C–H $\sigma\to\sigma^*$ ($2\sigma\to6\sigma$). Spin-polarization should be included in the calculation of anisotropic hfc as for the isotropic hfc.

Each atom of HCO contributes to hfc of ^{13}C (Table 2). Holmberg[6] resolved the experimentally observed hfc (MHz) of ^{13}C into two axial parts: $(A_{xx}, A_{yy}, A_{zz})=(-48, 72, -24)=(-40, 80, -40)_{2py}+(-8, -8, 16)_{2pz}$. The second term shows the contribution of the carbon $2p_z$ orbital normal to the molecular plane. Table 2 suggests that the effect of neighbouring atoms is larger than that of C($2p_z$), and that the observed values can be resolved into those of $2p_x$ and $2p_y$. Direction cosines obtained show that the principal axis y of ^{1}H, ^{13}C, and ^{17}O rotate by 75°, 33°, and 16° from the C–O bond, respectively. The results for HCO are compared with available experimental data in Table 3. Satisfactory agreement was found for both

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[2] T. Morikawa, O. Kikuchi, and K. Someno, *Theoret. chim. Acta*, **24**, 393 (1972).

[3] T. Morikawa, O. Kikuchi, K. Someno, *ibid.*, **22**, 224 (1971).

[4] O. Kikuchi and K. Someno, This Bulletin, **40**, 2972 (1967).

[5] P.-O. Löwdin, *Phys. Rev.*, **90**, 120 (1953).

[6] R. W. Holmberg, *J. Chem. Phys.*, **51**, 3255 (1969).

Table 3. Calculated results for σ-radicals (MHz)
(Data in the parentheses are experimental.)

Radical	Nucleus	a	A_{xx}	A_{yy}	A_{zz}	Ref.
HCO	^{1}H	288	19	−5	−14	
		(354)	(25)	(−8)	(−17)	6
		(381)	(15)	(−2)	(−14)	7
	^{13}C	550	−25	53	−28	
		(365)	(−48)	(72)	(−24)	6
		(378)	(−39)	(50)	(−12)	7
	^{17}O	−22	47	−100	54	
		(—)	(—)	(—)	(—)	
CO_2^-	^{13}C	610	−21	54	−33	
		(467)	(−47)	(79)	(−33)	8
	^{17}O	−29	38	−75	38	
		(−90)	(25)	(−53)	(28)	8
HCN^-	^{1}H	356	19	−8	−11	
		(384)	(—)	(—)	(—)	9
	^{13}C	550	−21	35	−14	
		(207)	(—)	(—)	(—)	9
	^{14}N	10	43	−20	−23	
		(18)	(—)	(—)	(—)	9
Vinyl	$^{1}H_{\alpha}$	56	36	−9	−27	
		(45)	(38)	(−11)	(−27)	10, 11
	$^{1}H_{trans}$	251	8	−6	−2	
		(190)	(—)	(—)	(—)	10
	$^{1}H_{cis}$	118	10	−5	−5	
		(95)	(—)	(—)	(—)	10
	$^{13}C_{\alpha}$	388	−58	110	−51	
		(301)	(—)	(—)	(—)	12
	$^{13}C_{\beta}$	−27	13	−4	−9	
		(−24)	(—)	(—)	(—)	12
Ethynyl	^{1}H	151	4	−2	−2	
		(45)	(—)	(—)	(—)	10
	$^{13}C_{\alpha}$	978	87	−44	−44	
		(—)	(—)	(—)	(—)	
	$^{13}C_{\beta}$	54	27	−13	−13	
		(—)	(—)	(—)	(—)	

the isotropic and the anisotropic hfc. The present results are slightly better than the previous ones,[2] *e. g.*, for the anisotropic hfc (MHz) of ^{13}C, from (−17, 47, −30) to (−25, 53, −28). The isotropic and anisotropic hfc of other σ-radicals calculated by the present method, some of which are given in Table 3, are useful for the analysis of complicated ESR spectra in solid solution.

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