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SCF MO INDO Calculation of Anisotropic Hyperfine Coupling Tensors for σ-Type Radicals

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The anisotropic hyperfine coupling tensors for some σ-type radicals (HCO, FCO, NO_2, CO_2^-, CN, phenyl, vinyl) were calculated. The calculation was performed with an all-valence-electron approximate open-shell MO method using the INDO approximation and with the dipolar integrals evaluated over Slater-type AO's. The diagonalyzed tensors were in reasonable agreement with the available data of experiment.

There have been relatively few theoretical studies of the anisotropic hyperfine coupling constants. Some of the reasons for this may be: (a) the experimental data of anisotropic hyperfine structure are less abundant than those for isotropic cases, (b) the theoretical evaluation of anisotropic interaction requires the appropriate theoretical formula in addition to the spin density calculation. The anisotropic term of the hyperfine interaction gives valuable information about the electronic structure of the paramagnetic species, for it is possible from the anisotropic term to estimate both the p-character of the odd-orbital centered on the atom of which the nucleus interacts with an unpaired electon and the s- and p-character of the odd-orbitals on the neighbouring atoms. A theoretical study on this subject will be useful in predicting magnitudes and signs of hyperfine coupling constants, and in interpreting known hyperfine coupling constants in terms of the electronic structure of the species.

Table 1. Contribution of each atom to the hyperfine tensor for HCO (MHz)

Nucleus	Atom	A_{XX}	A_{XY}	A_{YY}	A_{ZZ}[a]
^1H	H	0.0	0.0	0.0	0.0
	C	− 7.1	6.6	20.8	−13.7
	O	4.2	3.5	− 1.0	− 3.2
	Total	− 2.8	10.1	19.8	−16.9
^{13}C	H	− 0.5	2.5	2.5	− 1.9
	C	− 8.3	−30.4	32.8	−24.4
	O	5.5	1.3	− 2.2	− 3.3
	Total	− 3.4	−26.6	33.1	−29.7
^{17}O	H	− 0.3	− 0.3	0.1	0.2
	C	− 2.3	1.1	0.8	1.6
	O	26.6	27.7	−66.0	36.8
	Total	29.3	28.5	−65.2	38.6

[a] The molecular axes X, Y, and Z are along the C—O bond and perpendicular to X and Z, and to the molecular plane, respectively. All A_{XZ} and A_{YZ} are equal to zero.

The anisotropic hyperfine coupling tensor for the nucleus N of a radical, $A_{ij}(\mathrm{N})$ $(i, j = X, Y, Z)$, may be derived from the expectation value $\langle \Psi_g | H | \Psi_g \rangle$, where Ψ_g is an all-antisymmetrized wave function [1], and H is the Hamiltonian of anisotropic hyperfine interaction. Molecular orbitals ϕ_i are expressed as linear combinations of atomic orbitals $\chi_\mu : \phi_i = \Sigma \chi_\mu C_{\mu i}$. Thus,

$$A_{ij}(\mathrm{N}) = -g\beta\hbar\gamma_{\mathrm{N}} \sum_{\mu,\nu} C_{\mu m} C_{\nu m} t_{ij}(\chi_\mu \chi_\nu)\,, \qquad (1)$$
$$t_{ij}(\chi_\mu \chi_\nu) = \langle \chi_\mu | r^{-5}(r^2 \delta_{ij} - 3r_i r_j) | \chi_\mu \rangle\,.$$

The dipolar integrals $t_{ij}(\chi_\mu \chi_\nu)$, were evaluated at the level of approximation corresponding to that employed in the INDO calculation of Ψ_g. Namely, all three-

Table 2. Calculated principal values (MHz) for some σ-radicals (data in parentheses are experimental)

Radical	Nucleus	A_{xx}	A_{yy}	A_{zz}	Ref.
HCO	^{1}H	24	− 7	− 17	
		(15)	(− 2)	(− 14)	[2]
		(25)	(− 8)	(− 17)	[3]
	^{13}C	− 17	47	− 30	
		(− 39)	(50)	(− 12)	[2]
		(− 48)	(72)	(− 24)	[3]
	^{17}O	35	− 73	39	
		—	—	—	
FCO	^{13}C	38	− 13	− 25	
	^{17}O	− 73	35	38	
		—	—	—	
	^{19}F	389	−191	−198	
		(534)	(−267)	(−267)	[2]
NO_2	^{14}N	− 8	22	− 14	
		(− 22)	(37)	(− 15)	[4]
	^{17}O	− 68	32	36	
		(− 97)	(52)	(45)	[4]
CO_2^-	^{13}C	− 12	44	− 32	
		(− 47)	(79)	(− 33)	[5]
	^{17}O	− 54	26	28	
		(− 53)	(25)	(28)	[5]
CN	^{13}C	− 36	72	− 36	
		(− 45)	(90)	(− 45)	[6]
	^{14}N	− 14	29	− 14	
		(− 15)	(31)	(− 15)	[6]
Phenyl	$^{13}C_1$	− 40	84	− 44	
		—	—	—	
	$^{13}C_2$	11	− 3	− 7	
		—	—	—	
	$^1H_2$	− 4	11	− 7	
		(− 6)	(13)	(− 7)	[7]
CH_2=CH	$^{13}C_1$	− 46	96	− 49	
		—	—	—	
	$^1H_1$	34	− 7	− 26	
		(38)	(− 11)	(− 27)	[8]

center integrals and all two-center integrals involving the product $\chi_\mu \chi_\nu$ in which μ and ν belong to different atoms were assumed to be negligible, and the remaining two-center and one-center integrals were analytically evaluated over Slater orbitals. An approximate open-shell SCF MO INDO method used for the calculation of spin density has been reported in elsewhere [1].

The hyperfine tensor for the magnetic nucleus is obtained from the total of contribution of each atom, according to Eq. (1). The calculated results of the formyl radical HCO shown in Table 1 indicate that to the tensor for the carbon-13 or oxygen-17 nucleus the orbitals centered on the same nucleus mainly contribute, and to the tensor for the proton the orbitals of oxygen atom do to some extent. The three tensors were diagonalyzed and the results compared with the available data of experiment in Table 2, where x, y, and z denote the principal axes. The agreement is satisfactory for the proton, but not quantitatively satisfactory for the carbon-13, especially for A_{xx}. The orientation of the principal axes with respect to the molecular frame can be estimated by the direction cosines obtained. The angle between x and C—H bond for ^{1}H or ^{13}C is 69° or 28°, respectively. The dependence of the principal values for HCO on H—C—O angle is not large, e.g., A_{xx}(H), A_{yy}(H), and A_{zz}(H) in MHz units are 27, -9, and -18 for 130°, 24, -7, and -17 for 120°, 20, -5, and -16 for 110°, respectively.

Calculated principal values for other σ-type radicals are shown in Table 2. No signs of anisotropic hyperfine splitting can be determined by ESR experiment. It may be noted that the signs of some observed data are assigned by the calculated results and listed in Table 2. The calculated tensors for nuclei which are one or more bonds away from the radical-center are in relatively satisfactory agreement with the observed values, e.g., for the proton of vinyl or phenyl, for the nitrogen-14 of CN.

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