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Relationes

SCF MO INDO Calculation of g-Tensors of Some σ-Type Radicals

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The Longuet-Higgins and Pople type SCF MO theory was applied to the all-valence-electron systems of several σ-type radicals and their g-tensors were theoretically calculated with the Stone's equation. Principal values or diagonalyzed g-tensors were obtained and compared with experimental values in ESR spectra.

Many theoretical studies on the spin distribution in a free radical have been performed in connection with its ESR spectrum. However, there have been few discussions on the g-value, another ESR parameter. In previous papers [1], we applied the approximate open shell SCF MO method of Longuet-Higgins and Pople [2] to the all-valence-electron system of a simple nitric oxide radical (π-radical) and calculated the isotropic hyperfine coupling constants and the g-value with the CNDO/2 approximation [3]. The g-values of some σ-type radicals have been recently reported, while there have been very few theoretical studies on g-tensors. The theoretical estimation of the g-tensor of a σ-type radical is required in connection with its electronic structure and with the analysis of its complex *ESR* spectrum in solid solution. In this report, g-tensors of several σ-type radicals calculated with the INDO approximation [4] are presented.

The g-tensor of a σ-type radical was calculated by the following equation [5]:

$$\begin{aligned} g_{\alpha\beta} &= 2.00232(\delta_{\alpha\beta} + \Delta g_{\alpha\beta}), \\ \Delta g_{\alpha\beta} &= \sum_{i=1}^{m-1} \frac{\left(\phi_m \middle| \sum_t L_\alpha^t \middle| \phi_i\right)\left(\phi_i \middle| \sum_t \zeta_t L_\beta^t \middle| \phi_m\right)}{E_{i\to m} - E_g} \\ &\quad - \sum_{j=m+1}^{n} \frac{\left(\phi_m \middle| \sum_t L_\alpha^t \middle| \phi_j\right)\left(\phi_j \middle| \sum_t \zeta_t L_\beta^t \middle| \phi_m\right)}{E_{m\to j} - E_g} \end{aligned} \qquad (1)$$

where L_α^t is the angular momentum about the t'th nucleus, ζ_t, the spin-orbit coupling constant for the t'th atom, and m, i, j, and n refer to the singly occupied, doubly occupied, vacant, and the highest vacant MO's in the ground state electron configuration, respectively. E_g, $E_{i\to m}$, and $E_{m\to j}$ are the energies of the following antisymmetrized wave functions:

$$\begin{aligned}\Psi_g &= |\phi_1\bar{\phi}_1 \cdots \phi_i\bar{\phi}_i \cdots \phi_{m-1}\bar{\phi}_{m-1}\phi_m| \\ \Psi_{i\to m} &= |\phi_1\bar{\phi}_1 \cdots \phi_i\bar{\phi}_m \cdots \phi_{m-1}\bar{\phi}_{m-1}\phi_m| \\ \Psi_{m\to j} &= |\phi_1\bar{\phi}_1 \cdots \phi_i\bar{\phi}_i \cdots \phi_{m-1}\bar{\phi}_{m-1}\phi_j|\end{aligned} \tag{2}$$

then the energy differences in Eq. (1) were computed by the following equations:

$$\begin{aligned}E_{i\to m} - E_g &= \varepsilon_m - \varepsilon_i - (mm|ii) + \tfrac{1}{2}(mm|mm) + \tfrac{1}{2}(mi|im) \\ E_{m\to j} - E_g &= \varepsilon_j - \varepsilon_m - (mm|jj) + \tfrac{1}{2}(mm|mm) + \tfrac{1}{2}(mj|jm)\,.\end{aligned} \tag{3}$$

LCAO MO's, $\phi_i = \Sigma C_{ri}\chi_r$, and their orbital energies, ε_i, were evaluated by the SCF INDO matrix elements:

$$\begin{aligned}F_{rr} &= U_{rr} + \sum_{B\neq A}(P_{BB} - Z_B)\gamma_{AB} + \sum_t^A P_{tt}\{(rr|tt) - \tfrac{1}{2}(rt|tr)\} && (r \text{ on A}) \\ F_{rs} &= \tfrac{1}{2}(\beta_A + \beta_B)S_{rs} - \tfrac{1}{2}P_{rs}\gamma_{AB} && (r \text{ on A}, s \text{ on B}) \\ F_{rs} &= \tfrac{1}{2}P_{rs}\{3(rs|sr) - (rr|ss)\} && (r, s \text{ on A})\end{aligned} \tag{4}$$

where bond order P_{rs} is defined in Ref. [1] and all other notations are the same as those given by Pople *et al.* [4]. Evaluation of the matrix elements was based on them [4].

Results and Discussion

The g-tensors of HCO, CH_3CO, NH_2CO, HCN^-, CO_2^-, NO_2, $CH_2=CH$ and the phenyl redical were calculated. The results on the HCO radical, ESR data of which are well known, are described in some detail. The geometry of this radical used is that obtained in its gas phase [6] and are shown in Fig. 1. The ground state electron configuration of HCO is:

$$(1\sigma)^2\,(2\sigma)^2\,(3\sigma)^2\,(1\pi)^2\,(4\sigma)^2\,(5\sigma)^1$$

excluding K-shell electrons of C and O, and vacant orbitals are 2π, 6σ and 7σ. The odd orbital 5σ consists of $2p_Y(O)$ and the carbon hybrid orbital along the axis bisecting the H–C–O angle. The 2π is the C–O π-antibonding orbital and the 4σ is mainly constructed by $2p_X(C)$, $2p_X(O)$ and $2p_Y(O)$. These orbitals play an important role in large deviations of g-tensors from the free spin value. The contribution of excited configurations to the g-tensor of HCO are listed in Table 1. The configurations $4\sigma\to5\sigma$ and $5\sigma\to2\pi$ make a most important contribution to Δg_{ZZ} and Δg_{XX}, respectively.

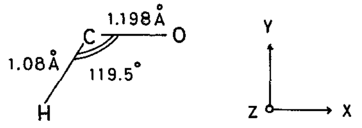


Fig. 1. Geometry of the formyl radical [6]

Table 1. *Contribution of excited configurations to g-tensor of the formyl radical in Fig. 1*

Excited configuration	ΔE(eV)	Δg_{XX}	Δg_{YX}	Δg_{YY}	$\Delta g_{ZZ}(\times 10^5)$
$1\sigma \rightarrow 5\sigma$	34.45	0	0	0	5
$2\sigma \rightarrow 5\sigma$	17.04	0	0	0	2
$3\sigma \rightarrow 5\sigma$	10.70	0	0	0	32
$1\pi \rightarrow 5\sigma$	8.28	30	−5	−1	0
$4\sigma \rightarrow 5\sigma$	7.30	0	0	0	121
$5\sigma \rightarrow 2\pi$	2.58	−408	−170	−55	0
$5\sigma \rightarrow 6\sigma$	7.90	0	0	0	−22
$5\sigma \rightarrow 7\sigma$	10.51	0	0	0	9
Total		−378	−175	−56	147

The diagonalyzed tensor, of which the principal axes are denoted by x, y and z, is shown in Table 2. For g_{yy}, g_{zz} and $g_{\mathrm{av.}}$, the agreement between calculated and observed values is satisfactory. The calculated g_{xx}, however, is different to some extent from Holmberg's experimental value observed in the single crystal of formic acid. From the direction cosines obtained (Table 3), the orientation of the principal axes of g-tensor with respect to the molecular coordinates was found. The rotation angle was about 24° (see Table 3). Molecular structures of many σ-type radicals have not been obtained and the calculations of σ-type radicals are often carried out with the assumed molecular structures. The molecular structure of HCO used in the present calculations is not one in the solid state

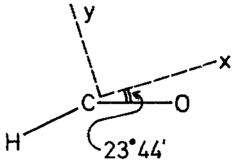
Table 2. *Calculated principal values of g-tensor of the formyl radical*

Principal values[a]	Calc.	Exp.[b]	Exp.[c]
g_{xx}	1.9978	1.9960	1.9948
g_{yy}	2.0025	2.0027	2.0023
g_{zz}	2.0038	2.0041	2.0037
$g_{\mathrm{av.}}$[d]	2.0014	2.0009	2.0003

[a] See Table 3 about the principal axes.
[b] Adrian, F. J., Cochran, E. L., Bowers, V. A.: J. chem. Physics **36**, 1661 (1962).
[c] Holmberg, R. W.: J. chem. Physics **51**, 3255 (1969).
[d] $g_{\mathrm{av.}} = (g_{xx} + g_{yy} + g_{zz})/3$.

Table 3. *Direction cosines between principal axes x, y and z of g-tensor and molecular axes X, Y and Z of the formyl radical*

	x	y	z
X	0.9154	−0.4025	0.0
Y	0.4025	0.9154	0.0
Z	0.0	0.0	1.0



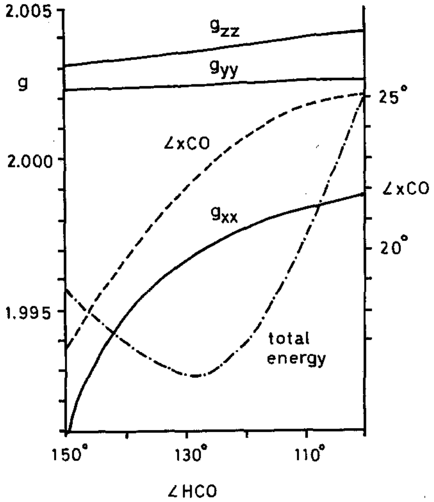


Fig. 2. Dependence of the *g*-tensor, the principal axes of the *g*-tensor and the total energy of the formyl radical on its bond angle H–C–O

Table 4. *Calculated principal values of some σ-type radicals*[a] *(Data in brackets are experimental)*

	g_{xx}	g_{yy}	g_{zz}	$g_{av.}$
CH_3CO	1.9983 (1.9964)	2.0022 (2.0019)	2.0035 (2.0040)	2.0013 (2.0008)[b]
HCN^-	1.9996 (–)	2.0026 (–)	2.0030 (–)	2.0017 (2.0022)[c]
NH_2CO	2.0001 (–)	2.0023 (–)	2.0038 (–)	2.0021 (2.0017)[d]
CO_2^-	1.9966 (1.9973)	2.0024 (2.0016)	2.0048 (2.0032)	2.0013 (2.0007)[e]
NO_2	1.9908 (1.9910)	2.0024 (2.0020)	2.0067 (2.0062)	1.9999 (1.9997)[f]
$CH_2=CH$	2.0021 (–)	2.0023 (–)	2.0023 (–)	2.0022 (2.0022)[g]
Phenyl	2.0020 (2.0014)	2.0023 (2.0023)	2.0024 (2.0034)	2.0023 (2.0024)[h]

[a] References on molecular geometries; Pople, J. A., Gordon, M.: J. Amer. chem. Soc. **89**, 4253 (1967), Claesson, S., Donohue, J., Schomaker, V.: J. Amer. chem. Soc. **16**, 207 (1948), etc.

[b] Data of $(COOH)CH_2CO$. McCalley, R. C., Kwiram, A. L.: J. Amer. chem. Soc. **92**, 1441 (1970).

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where ESR of HCO was observed. Therefore, the dependence of calculated g-tensors on their molecular structures should be examined in the present theoretical study. Thus, the relation between the g-tensor of HCO and the angle H–C–O was examined. Results are shown in Fig. 2. Total energy of the system and the direction of the principal axis x are also presented in Fig. 2.

The calculated value of g_{xx} depends considerably on the H–C–O angle: 1.9989 (100°) – 1.9909 (150°). On the other hand, the angular dependence of g_{yy} and g_{zz} is small. The principal values at energy minimum angle, $\sphericalangle$ HCO = 130°, were; $g_{xx} = 1.9967$, $g_{yy} = 2.0025$, $g_{zz} = 2.0035$ and $g_{av.} = 2.0009$. The best agreement of calculated g-tensor with observed one was obtained from the molecular structure with $\sphericalangle$ HCO = 140°: $g_{xx} = 1.9949$, $g_{yy} = 2.0024$, $g_{zz} = 2.0033$ and $g_{av.} = 2.0002$.

The results on the other radicals are listed in Table 4. The very good agreement between calculated and observed g-tensor of the NO_2 radical is noteworthy. Because, in the present study, NO_2 is the only radical of which both ESR data and molecular structure have been observed in the same condition, in its gas phase. It is concluded from the present study that the method described here is applicable to other radicals and the g-tensors calculated are useful in connection with the electronic structures of σ-type radicals and with the analysis of complicated ESR spectra in solid solution.

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